

Microwave Spectroscopic and Quantum Chemical Investigations on Aromatic Five-membered Heterocycles with a Carbonyl Substituent

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vorgelegt von
Christina Dindić, M. Sc.

aus
Düsseldorf, Deutschland

Berichter: Assoc. Prof. Dr. rer. nat. Ha Vinh Lam Nguyen

Univ.-Prof. Dr. rer. nat. Arne Lüchow

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“Yes, of course duct tape works in a near-vacuum. Duct tape works anywhere.
Duct tape is magic and should be worshiped.”

The Martian by Andy Weir

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7.1 Naturwissenschaftlichen Journalen

7.1.1 **C. Dindić**, W. Stahl, H. V. L. Nguyen

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Mikrowellenspektroskopische und Quantenchemische Untersuchungen an
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7.3.2 Marc Kreutzer

Structures and internal dynamics of 2-Acetyl-3-Methylthiophene studied by
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Summary

In this dissertation a combination of molecular jet Fourier transform microwave spectroscopy and quantum chemical calculations was employed to analyse the structural characteristics and internal dynamics, in particular methyl internal rotation, of five thiophene and one furan derivative, all of them containing one substituent with a carbonyl group. The molecular targets are 2-propionylthiophene, 2-acetylthiophene, three isomers of 2-acetylmethylthiophene, and 2-acetylfuran.

For 2-propionylthiophene two conformers, *syn* and *anti*, were identified in the spectrum with torsional barriers of 807 cm^{-1} and 865 cm^{-1} for the *syn*- and the *anti*-conformer, respectively. The planarity of the molecule was controversial in calculations at different levels of theory. Therefore, three ^{13}C -isotopologues in the propionyl group and the ^{34}S -isotopologue in the ring were measured, enabling a partial r_s structure determination of the most stable *syn*-conformer. This structure determination confirmed that the molecule is not planar, as there is a small, but non-zero tilt angle between the ethyl group and the thiophene ring.

For 2-acetylthiophene two conformers were also identified in the spectrum, alongside the ^{34}S -isotopologue of both conformers, all ^{13}C -isotopologues of the energetically more stable *syn*-conformer, and some ^{13}C -isotopologues of the *anti*-conformer. The barriers of internal rotation were determined to be 330 cm^{-1} and 296 cm^{-1} for the *syn*- and the *anti*-conformer, respectively. They remained almost constant for all isotopologues of a conformer.

2-acetylfuran was investigated to study the effects of the heteroatom in the ring compared to 2-acetylthiophene. A *syn*- and an *anti*-conformer with barriers to internal rotation of 240 cm^{-1} and 320 cm^{-1} were identified in the spectrum alongside several isotopologues with essentially unchanged barriers. A comparison with the sulphur analogue, 2-acetylthiophene, showed, that the heteroatom in the ring significantly influences the conformational stability. Furans favour the *anti*-conformation, while in thiophenes the *syn* form is more stable due to the different electrostatic interactions between the heteroatom in the aromatic ring and the oxygen atom of the acetyl group.

While 2-propionylthiophene, 2-acetylthiophene and 2-acetylfuran are molecules featuring internal rotation of only one methyl rotor, the three isomers of 2-acetylmethylthiophene are two-top molecules. They were investigated to study effects of multiple rotors on the microwave spectra and the influence of a methyl group attached to the aromatic thiophene ring on the methyl internal rotation of 2-acetylthiophene. Results of the present thesis together with those of previous investigations on thiophene and furan derivatives have shown that the negative

mesomeric and inductive effects of the carbonyl moiety in the acetyl group cause a decrease of the torsional barrier of the methyl rotor attached to the ring (called the ring methyl top), while a methyl group causes an increase due to its positive inductive effect when substituted at the same position. Steric interactions can influence these effects. The conformation of the acetyl group barely influences the torsional barrier of the ring methyl top.

The acetyl methyl group possesses a unique sensitivity to the structure of the moiety attached at the other side of the carbonyl bond. From the results of the present thesis the so-called “thiophene class” was established, which collects all molecules featuring an acetyl group connected to a thiophene ring at the other side of the carbonyl bond. It was shown that the torsional barriers of the acetyl methyl group are always around 300 cm^{-1} , serving as a very reliable estimation for future investigations.

Zusammenfassung

In dieser Dissertation wurde eine Kombination aus Molekularstrahl-Fouriertransform-Mikrowellenspektroskopie und quantenchemischen Rechnungen eingesetzt, um die strukturellen Eigenschaften und interne Dynamik, im Besonderen die interne Rotation, von fünf Thiophen- und einem Furan-Derivat die alle einen Substituenten mit einer Carbonyl-Gruppe enthalten zu untersuchen. Bei den untersuchten Molekülen handelt es sich um 2-Propionylthiophen, 2-Acetylthiophen, drei Isomere von 2-Acetylmethylthiophen, und 2-Acetylfuran.

Für 2-Propionylthiophen wurden zwei Konformere, *syn* und *anti*, mit Rotationsbarrieren von jeweils 807 cm^{-1} und 865 cm^{-1} im Spektrum zugeordnet. Die Planarität des Moleküls wurde bei Rechnungen mit verschiedenen quantenchemischen Methoden unterschiedlich vorausgesagt. Daher wurden drei Isotopologe mit ^{13}C -Isotopen in der Propionylgruppe sowie das ^{34}S -Isotopolog im Ring gezielt gemessen. Dies ermöglichte eine partielle r_s Strukturbestimmung des stabileren *syn*-Konformeres. Die Strukturbestimmung bestätigte, dass das Molekül nicht planar ist, da es einen kleinen Neigungswinkel ungleich Null zwischen der Ethylgruppe und dem Thiophen Ring gibt.

Für 2-Acetylthiophen wurden auch zwei Konformere im Spektrum gefunden, ebenso wie die ^{34}S -Isotopologe beider Konformere, alle ^{13}C -Isotopologe der energetisch stabileren *syn*-Form, und ein paar ^{13}C -Isotopologe des *anti*-Konformeres. Die Barrieren der internen Rotation wurden für das *syn*- und *anti*-Konformer als 330 cm^{-1} und 296 cm^{-1} bestimmt. Diese Barrieren bleiben nahezu konstant für alle Isotopologe eines Konformeres.

2-Acetylfuran wurde untersucht, um die Effekte des Heteroatoms im Ring im Vergleich zu 2-Acetylthiophen zu erforschen. Sowohl ein *syn*- und ein *anti*-Konformer mit Rotationsbarrieren von 240 cm^{-1} und 320 cm^{-1} als auch mehrere Isotopologe mit nahezu unveränderten Barrieren wurden im Spektrum identifiziert. Ein Vergleich mit dem Schwefel Analogon 2-Acetylthiophen zeigte, dass das Heteroatom im Ring die Stabilität der Konformere signifikant beeinflusst. Furane bevorzugen die *anti*-Konformation, während für Thiophene die *syn* Form aufgrund von anderen elektrostatischen Interaktionen zwischen dem Heteroatom im aromatischen Ring und dem Sauerstoff Atom in der Acetylgruppe stabiler ist.

Während 2-Propionylthiophen, 2-Acetylthiophen und 2-Acetylfuran Moleküle sind, die eine Methylgruppe mit interner Rotation besitzen, haben die drei Isomere von 2-Acetylmethylthiophen jeweils zwei interne Rotoren. Sie wurden untersucht, um den Effekt mehrerer interner Rotoren auf die Mikrowellenspektren zu untersuchen, und um zu erforschen,

welchen Einfluss eine weitere Methylgruppe am aromatischen Thiophen Ring auf die interne Rotation von 2-Acetylthiophen hat.

Aus den in dieser Arbeit erhaltenen Ergebnissen, sowie im Vergleich mit denen aus vorangehenden Untersuchungen von Thiophenen und Furanen, konnte erkannt werden, dass der negative mesomere und induktive Effekt der Carbonylgruppe eine Erniedrigung der Rotationsbarriere des mit dem Ring verbundenen Methylrotors (der sogenannte Ring Methyl Top) verursacht. Eine Methylgruppe hingegen bewirkt aufgrund ihres positiven induktiven Effekts eine Erhöhung der Rotationsbarriere wenn sie an der gleichen Stelle substituiert wird. Sterische Interaktionen können diese Effekte beeinflussen. Die Konformation der Acetylgruppe hat kaum einen Einfluss auf die Barriere des Ring Methyl Top.

Die Acetylgruppe besitzt eine einzigartige Sensitivität gegenüber der Struktur, die mit der anderen Seite der Carbonyl Bindung verbunden ist. Mit den Ergebnissen dieser Arbeit wurde die sogenannte „Thiophen Klasse“ etabliert, welche Moleküle umfasst, die eine Acetylgruppe verbunden mit einem Thiophen Ring beinhalten. Es wurde gezeigt, dass die Rotationsbarriere einer Acetylmethylgruppe in diesem Fall immer bei etwa 300 cm^{-1} liegt. Dies erlaubt zuverlässige Einschätzungen für zukünftige Untersuchungen.

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I Introduction

Microwave spectroscopy has been well established for decades as one of the most reliable methods to accurately determine structural parameters. It allows the distinction of conformers, structure determination via isotopic substitution, and the study of internal dynamics such as large amplitude motions.

One kind of large amplitude motion, methyl internal rotation, has been of special interest beside the classical structural topics for a long time [6][7]. It causes splittings in the spectrum if the torsional barrier is finite and the investigation of internal rotations can be useful in order to study interactions occurring in the molecule. A group featuring internal rotation that has a known sensitivity to the structure of the molecular frame is the acetyl methyl group. *Andresen et al.* recently introduced a classification system linking the torsional barrier to the molecular structure at the other side of the carbonyl bond, establishing that C_1 conformers of methyl *n*-alkyl ketones exhibit barriers to methyl internal rotation of about 240 cm^{-1} , while for the C_s conformers the barriers are approximately 180 cm^{-1} [8][9][10][11]. *Herbers et al.* expanded this classification by the “phenyl class”, members of which possess barriers to internal rotation of approximately 600 cm^{-1} [12]. The study of different thiophene derivatives connected to an acetyl methyl group in this thesis was an effort to extend this class system by the “thiophene class”.

With the conjugated π -double bond system present in thiophene it is also possible to study the interactions between multiple rotors. The delocalized π -electron system connecting them allows the transfer of electronic effects through the entire π -system, which can influence the methyl torsion. Previous investigations on molecules containing multiple rotors and a π -electron system such as the three isomers of dimethylanisole [13][14][15], three isomers of dimethylbenzaldehyde [16], *o*- and *m*-xylene [17][18], two isomers of dimethylfluorobenzene [19][20], 4-methylacetophenone [12], as well as some five-membered aromatic rings like the 2,5-isomers of dimethylthiophene [21], dimethylfuran [22], and dimethylpyrrole [23] or 2-acetyl-5-methylfuran [24] and 4,5-dimethylthiazole [25] clearly showed these effects, but a full exploration of electrostatic interactions was not possible yet. Further information on several molecules possessing a heteroaromatic two-top system thus provides valuable data in exploring these interactions between internal rotors across a π -double bond system.

With a compound such as thiophene another aspect to consider is the influence of the heteroatom in the ring on both the molecular structure as well as the internal rotation. Several

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sulphur/oxygen analogues have already been investigated in the literature [21][22][26][27][28][29][30][31], all of them showing that the barriers to methyl internal rotation in oxygen containing molecules are higher than those in their sulphur analogues. As none of these previously investigated molecules contains an acetyl methyl group however, it is of interest to see if this trend would continue or be broken due to the properties of the carbonyl moiety.

This thesis is divided into several parts, with Part I, this Introduction, followed by Part II giving a summary of the necessary microwave spectroscopic theory, the experimental procedure employed in this work, as well as an overview for the basic foundations of the fitting programs in use. Part III covers the investigations on the three one-top molecules studied in this thesis: 2-acetylthiophene (Chapter 3), 2-propionylthiophene (Chapter 4) and 2-acetylfuran (Chapter 5), the results of which have already been published in Ref. [4], [1] and [2], respectively. Part IV details the investigations into the two-top molecules 2-acetyl-3-methylthiophene (Chapter 6), 2-acetyl-4-methylthiophene (Chapter 7) and 2-acetyl-5-methylthiophene (Chapter 8). The results for 2-acetyl-3-methylthiophene were already published in Ref. [3], those for 2-acetyl-4-methylthiophene in Ref. [5]. The Conclusion in Part V examines the results obtained for the molecules investigated in this thesis, comparing them to each other as well as to relevant examples from the literature, leading to the establishment of the “thiophene class”. Lastly, the Bibliography and Appendix are marked as Part VI and Part VII, respectively.

II Theoretical Background and Methods

1. Theoretical Background

This chapter focuses on the theoretical background of microwave spectroscopy based mainly on the descriptions by Gordy and Cook in Ref. [7]. Parts of this chapter have been adapted from my master's thesis (2018) [32].

The basis of all spectroscopic methods is the interaction between electromagnetic waves and atoms or molecules. Microwave spectroscopy utilizes electromagnetic waves with wavelengths ranging from approximately 30 cm to 0.3 mm, corresponding to frequencies from 1 GHz to 1 THz. In this thesis a frequency range from 2.0 to 26.5 GHz [33] is employed. This microwave frequency range corresponds to the energy differences between rotational transitions within a vibrational state. Thus microwave spectra are often referred to as rotational spectra.

The angular momentum $\vec{l}$ (Equation 1.1) describes rotational movement as the product of the moment of inertia I and the angular velocity $\vec{\omega}$.

$$\vec{l} = I\vec{\omega} \quad (1.1)$$

The moment of inertia I (Equation 1.2) consists of six components defined as I_{fg} with $f, g \in \{x, y, z\}$ in an arbitrary centre-of-mass and molecular-fixed three dimensional coordinate system.

$$I = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \quad (1.2)$$

The matrix elements are defined as follows, with N giving the number of nuclei in the molecule and m_i the mass of the atom i :

$$I_{xx} = \sum_{i=1}^N m_i (y_i^2 + z_i^2) \quad (1.3a)$$

$$I_{yy} = \sum_{i=1}^N m_i (z_i^2 + x_i^2) \quad (1.3b)$$

$$I_{zz} = \sum_{i=1}^N m_i (x_i^2 + y_i^2) \quad (1.3c)$$

$$I_{xy} = I_{yx} = - \sum_{i=1}^N m_i x_i y_i \quad (1.3d)$$

$$I_{zx} = I_{xz} = - \sum_{i=1}^N m_i x_i z_i \quad (1.3e)$$

$$I_{yz} = I_{zy} = - \sum_{i=1}^N m_i y_i z_i \quad (1.3f)$$

To simplify calculations however, the principal axis system, which is a molecular-fixed inertial axis system, is preferred over the arbitrary centre-of-mass system. It offers the advantage of a diagonalized inertia tensor I (Equation 1.4) where all off diagonal elements become zero. This inertia tensor can be calculated from the one given in Equation 1.2 through a principal axis transformation. The principal axes are denoted as a , b and c , making the principal moments of inertia become I_a , I_b and I_c (Equation 1.5). They follow the proportion $I_a \leq I_b \leq I_c$ by definition.

$$I = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix} \quad (1.4)$$

$$I_a = \sum_{i=1}^N m_i (b_i^2 + c_i^2) \quad (1.5a)$$

$$I_b = \sum_{i=1}^N m_i (a_i^2 + c_i^2) \quad (1.5b)$$

$$I_c = \sum_{i=1}^N m_i (a_i^2 + b_i^2) \quad (1.5c)$$

1.1. Rigid Rotor

A simple quantum mechanical model oftentimes used to describe rotating systems in the gas phase is the rigid rotor model, where the rotational energy is equal to the kinetic energy (Equation 1.6).

$$T = \frac{1}{2} \vec{\omega}^\dagger I \vec{\omega} \quad (1.6)$$

Additionally to the inertia tensor (Equation 1.4) the rotational energy is also dependent on the angular velocity vector $\vec{\omega}$ as well as the transposed angular velocity vector $\vec{\omega}^\dagger$, which are defined as follows:

$$\vec{\omega} = \begin{pmatrix} \omega_a \\ \omega_b \\ \omega_c \end{pmatrix} \quad \vec{\omega}^\dagger = (\omega_a \ \omega_b \ \omega_c) \quad (1.7)$$

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The expression for the kinetic energy is thus:

$$T = \frac{1}{2}(I_a\omega_a^2 + I_b\omega_b^2 + I_c\omega_c^2) \quad (1.8)$$

In accordance with Equation 1.1, the angular velocities can be replaced by the corresponding angular momenta $l_a = I_a\omega_a$, $l_b = I_b\omega_b$ and $l_c = I_c\omega_c$, which leads to the Hamilton function (Equation 1.9). By replacing the angular momenta with their operators the corresponding Hamilton operator (Equation 1.10) is obtained.

$$H = \frac{l_a^2}{2I_a} + \frac{l_b^2}{2I_b} + \frac{l_c^2}{2I_c} \quad (1.9)$$

$$\hat{H} = \frac{\hat{l}_a^2}{2I_a} + \frac{\hat{l}_b^2}{2I_b} + \frac{\hat{l}_c^2}{2I_c} \quad (1.10)$$

Based on their moments of inertia rigid rotors can be grouped into the categories of symmetric tops, where two moments of inertia are identical, and asymmetric tops, with three different moments of inertia.

prolate top	$I_a < I_b = I_c$	} symmetric tops
oblate top	$I_a = I_b < I_c$	
linear molecules	$I_a \simeq 0, I_b = I_c$	
spherical top	$I_a = I_b = I_c$	
asymmetric top	$I_a < I_b < I_c$	

There are multiple possibilities to assign the principal axes a , b and c to the axes x , y , and z of the arbitrary system. Therefore these differently assigned systems are distinguished as the *I*, *II* and *III*-representations, each of them referring to whether the quantization axis z becomes the a , b or c axis, respectively. Depending on the cyclic order of the remaining two axes, these representations can either be right hand cyclic (labeled with r as a superscript) or left hand cyclic (superscript l). The choice of representation is usually dependent on the rotor type; for prolate tops the *I*-representation is preferred, for oblate tops the *III*-representation [34].

1.1.1. Symmetric Top

With two identical moments of inertia, the Hamilton operator given in Equation 1.10 can be simplified. Equation 1.11 gives the example of a Hamilton operator for the case of an oblate top with $I_a = I_b$.

$$\hat{H} = \frac{\hat{l}_a^2 + \hat{l}_b^2}{2I_b} + \frac{\hat{l}_c^2}{2I_c} \quad (1.11)$$

To further simplify the expression, the correlation between the total angular momentum and its components (Equation 1.12) can be utilized to transform the Hamilton operator according to Equation 1.13.

$$\hat{l}^2 = \hat{l}_a^2 + \hat{l}_b^2 + \hat{l}_c^2 \quad (1.12)$$

$$\hat{H} = \frac{1}{2} \left(\frac{\hat{l}_a^2 + \hat{l}_b^2}{I_b} + \frac{\hat{l}_c^2}{I_c} \right) = \frac{\hat{l}^2}{2I_b} \left(\frac{1}{2I_c} - \frac{1}{2I_b} \right) \hat{l}_c^2 \quad (1.13)$$

The Hamilton operator and the angular momentum operators $\hat{l}^2$ as well as either $\hat{l}_a^2$, $\hat{l}_b^2$ or $\hat{l}_c^2$ commute, thus simultaneous eigenfunctions $\Psi_{J,K,M}$ exist. Ψ is hereby the wave function at a given energy level.

$$\hat{l}^2 \Psi_{J,K,M} = \hbar^2 J(J+1) \Psi_{J,K,M} \quad (1.14)$$

$$\hat{l}_c \Psi_{J,K,M} = \hbar K_c \Psi_{J,K,M} \quad (1.15)$$

$J = 0, 1, 2, \dots$ is the rotational quantum number, $K_c = 0, \pm 1, \pm 2, \dots \pm J$ the projection quantum number and h and $\hbar$ are the Planck constant and the reduced Planck constant, respectively.

To obtain the eigenfunctions as well as the corresponding eigenvalue $\tilde{E}_{J,K,M}$, the Hamilton operator is used in the Schrödinger equation (Equation 1.16). The eigenvalue E in the Schrödinger equation gives the energy of a rotational level.

$$\hat{H} \Psi = E \Psi \quad (1.16)$$

$$\frac{\hat{l}^2}{2I_b} \Psi_{J,K,M} + \left(\frac{1}{2I_c} - \frac{1}{2I_b} \right) \hat{l}_c^2 \Psi_{J,K,M} = \tilde{E}_{J,K,M} \Psi_{J,K,M} \quad (1.17)$$

$$\frac{\hbar^2}{2I_b} J(J+1) \Psi_{J,K,M} + \left(\frac{\hbar^2}{2I_c} - \frac{\hbar^2}{2I_b} \right) K_c^2 \Psi_{J,K,M} = \tilde{E}_{J,K,M} \Psi_{J,K,M} \quad (1.18)$$

$$\tilde{E}_{J,K,M} = \frac{\hbar^2}{2I_b} J(J+1) + \left(\frac{\hbar^2}{2I_c} - \frac{\hbar^2}{2I_b} \right) K_c^2 \quad (1.19)$$

The expression for the eigenvalue $\tilde{E}_{J,K,M}$ (Equation 1.19) can be further transformed by using the rotational constants A , B and C , which are defined as shown below. The resulting expression for the energy eigenvalues of a rotational level $E_{J,K,M}$ (Equation 1.20) of an oblate top is given in frequency units.

$$A = \frac{h}{8\pi^2 I_a} \quad B = \frac{h}{8\pi^2 I_b} \quad C = \frac{h}{8\pi^2 I_c}$$

$$\frac{\tilde{E}_{J,K,M}}{h} = E_{J,K,M} = B J(J+1) + (C - B) K_c^2 \quad (1.20)$$

For a prolate top with $I_a < I_b = I_c$ the eigenvalue is therefore:

$$\frac{\tilde{E}_{J,K,M}}{h} = E_{J,K,M} = B J(J+1) + (A - B) K_a^2 \quad (1.21)$$

For a transition between two rotational levels the transitions dipole moment μ_{nm} is defined according to Equation 1.22, with Ψ_n^* as the conjugated complex of the wave function of the lower level n , $\hat{\mu}$ the dipole moment operator, and Ψ_m the wave function of the upper level m .

$$\mu_{nm} = \int \Psi_n^* \hat{\mu} \Psi_m d\tau \neq 0 \quad (1.22)$$

Only transitions $J'_{K'} \leftarrow J_K$ where the transition dipole moment is unequal to zero are allowed, which yields the following selection rules for symmetric tops:

$$\begin{aligned} \Delta J &= \pm 1 \\ \Delta K &= 0 \quad \text{with } K \in \{K_a, K_c\} \\ \mu_{\text{permanent}} &\neq 0 \end{aligned}$$

1.1.2. Asymmetric Top

Asymmetric tops possess three inequivalent moments of inertia $I_a < I_b < I_c$ as mentioned before. Ray's asymmetry parameter κ indicates the degree of asymmetry [35].

$$\kappa = \frac{2B - A - C}{A - C} \quad (1.23)$$

The parameter κ is defined for values between -1 and $+1$. The borders mark the two symmetric tops, with the prolate top ($\kappa = -1$) at one end and the oblate top ($\kappa = +1$) at the other. Values of molecules that are not symmetric fall between -1 and $+1$, with the largest asymmetry at $\kappa = 0$. In cases where κ is close to either -1 or $+1$, the molecules are considered "near prolate" or "near oblate" tops.

The energy levels in asymmetric rotors are labelled J_{K_a, K_c} as they are located between the energy levels of prolate and oblate tops. While the levels corresponding to $-K$ and $+K$ are degenerate in symmetric tops, they are separated in an asymmetric one. Thus a symmetric rotor has only $J + 1$ sublevels for each rotational level J , while in an asymmetric rotor the rotational levels have $2J + 1$ sublevels. Following Equation 1.22 the selection rules for rotational transitions $J'_{K'_a, K'_c} \leftarrow J_{K_a, K_c}$ are thus:

<i>R</i> -branch	$\Delta J = +1$
<i>Q</i> -branch	$\Delta J = 0$
<i>P</i> -branch	$\Delta J = -1$

A further categorization of transitions according to the projected dipole vector on the principal axes is also possible, as they correspond with different patterns and branches occurring in the microwave spectrum. These different types of transitions are only allowed when a molecule possesses a non-zero dipole moment in the respective direction. The intensity of the observed transitions decreases with increasing ΔK .

<i>a</i> -type:	$\Delta K_a = 0, \pm 2, \pm 4 \dots$	$\Delta K_c = \pm 1, \pm 3, \pm 5 \dots$
<i>b</i> -type:	$\Delta K_a = \pm 1, \pm 3, \pm 5 \dots$	$\Delta K_c = \pm 1, \pm 3, \pm 5 \dots$
<i>c</i> -type:	$\Delta K_a = \pm 1, \pm 3, \pm 5 \dots$	$\Delta K_c = 0, \pm 2, \pm 4 \dots$

The inertial defect Δ_c (Equation 1.24) is a parameter used to evaluate the structure of a molecule, more specifically its planarity. It is calculated from the effective moments of inertia I_i^v . For a planar molecule in its equilibrium state the value of the inertial defect is zero (Equation 1.25).

$$\Delta_c = I_c^v - I_a^v - I_b^v \quad (1.24)$$

$$I_c^e - I_a^e - I_b^e = 0 \quad (1.25)$$

1.2. Centrifugal Distortion

Real molecules cannot be fully described by the rigid rotor model, as they are not rigid. To gain a better approximation, centrifugal forces that lead to distortions such as changes in bond lengths and angles have to be taken into consideration. To determine the centrifugal distortion either Watson's A or Watson's S reduction are typically used. Which method is chosen depends on the symmetry of the molecule, as Watson's A reduction is used for asymmetric molecules, Watson's S for (near) symmetric molecules. This Section will focus on Watson's A reduction.

In order to determine the centrifugal distortion constants the Hamilton operator has to be expanded. For an asymmetric top the Hamilton operator is thus the sum of the Hamilton operators of the rigid rotor ($\hat{H}_r$) and the quartic centrifugal distortion ($\hat{H}_{cd}^{(4)}$) (Equation 1.26) [7][36].

$$\hat{H}^{(A)} = \hat{H}_r + \hat{H}_{cd}^{(4)} \quad (1.26)$$

The Hamilton operator of the centrifugal distortion is defined in Equation 1.27, with $\tau_{\alpha\beta\gamma\delta}$ as distortion coefficients.

$$\hat{H}_{cd}^{(4)} = \frac{\hbar^4}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} \hat{l}_\alpha \hat{l}_\beta \hat{l}_\gamma \hat{l}_\delta \quad \text{with } (\alpha, \beta, \gamma, \delta) \in \{a, b, c\} \quad (1.27)$$

The operator used in the Watson's A reduction (Equation 1.28) can be gained through transformation. The five centrifugal distortion coefficients of the fourth order Δ_J , Δ_{JK} , Δ_K , δ_J and δ_K can be determined from experimental data. The effects of centrifugal distortion are more pronounced for higher J quantum numbers.

$$\hat{H}_{cd}^{(4)} = -\Delta_J \hat{l}^4 - \Delta_{JK} \hat{l}^2 \hat{l}_a^2 - \Delta_K \hat{l}_a^4 - 2\delta_J \hat{l}^2 (\hat{l}_b^2 - \hat{l}_c^2) - \delta_K [\hat{l}_a^2 (\hat{l}_b^2 - \hat{l}_c^2) + (\hat{l}_c^2 - \hat{l}_b^2) \hat{l}_a^2] \quad (1.28)$$

1.3. Internal Rotation

Additionally to the overall rotation of a molecule, two groups of the molecule connected by a single bond can also rotate respectively to each other in a so called internal rotation or large amplitude motion (LAM). The smaller group of the two is considered the rotor, the rest of the molecule the frame. The most extensively studied type of rotor and the one relevant for this thesis is the methyl group. Due to its C_3 -symmetry a methyl group can form three equivalent structures via rotations of 120° (see Figure 1.1).

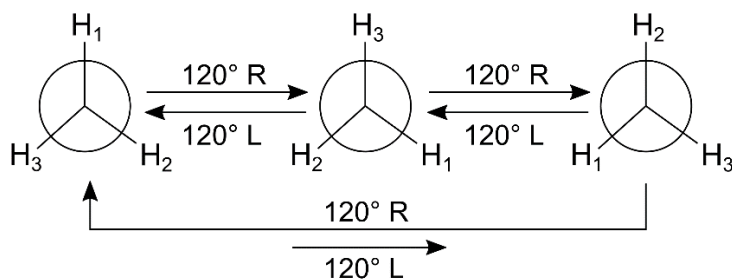


Figure 1.1: Internal rotation of a methyl group with three equivalent structures obtained for rotations of 120° to the right (R) or left (L).

As the potential of such an internal rotation is periodic, it can be described by a Fourier series expansion as given in Equation 1.29, with α as the angle of internal rotation or torsional angle and N the number of equivalent configurations.

$$V(\alpha) = a_0 + \sum_{k=1}^{\infty} a_k \cos kN\alpha \quad (1.29)$$

with

$$a_0 = - \sum_{k=1}^{\infty} a_k$$

For a methyl group with three equivalent configurations ($N = 3$), Equation 1.29 becomes Equation 1.30. Usually the first two terms of the expansion are sufficient to describe the rotation accurately; oftentimes even the V_6 -term can be neglected.

$$V(\alpha) = \frac{V_3}{2} (1 - \cos(3\alpha)) + \frac{V_6}{2} (1 - \cos(6\alpha)) + \dots \quad (1.30)$$

The resulting potential for an $N = 3$ internal rotor is depicted in Figure 1.2. The minima in the curve correspond with the three equivalent structures depicted in Figure 1.1. The maxima between them show the barrier necessary to overcome for the internal rotation. As such the V_3 value is often also called the barrier height.

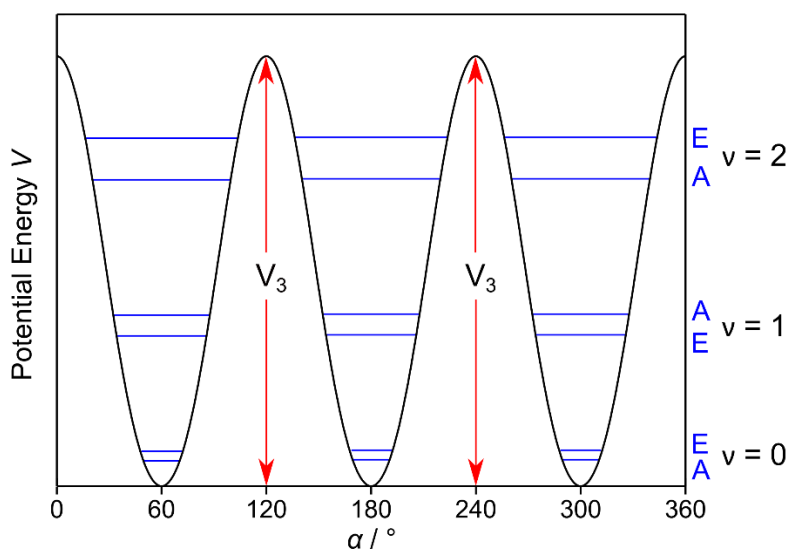


Figure 1.2: Schematic potential energy curve in dependence of the torsional angle α for an internal rotor with three equivalent configurations. The torsional barrier is marked as V_3 . The vibrational states are indicated by the quantum number v . The energy levels split into the A and E species due to internal rotation.

Internal rotation causes splittings of each vibrational state v into an A and a twofold degenerated E level as indicated in Figure 1.2. For microwave spectroscopy this is of importance as the A-E splitting can be visible in the spectrum, depending on the potential barrier V_3 hindering the internal rotation. Three cases of potential barriers are typically distinguished:

(1) If the barrier is infinitely high, the torsion of a methyl group can be described as three harmonic oscillators. No torsional splitting is observed in the spectrum as each vibrational level is three-fold degenerated. The molecule can simply be considered as a rigid rotor.

(2) A barrier of zero describes a free internal rotor where all energy levels except the first one are two-fold degenerated. It can be imagined that the rotation can be clockwise or counterclockwise. The levels are labeled with the quantum number $m = 0, \pm 1, \pm 2, \dots$

(3) If the barrier falls between those of a rigid rotor (1) and the free internal rotor (2) quantum mechanical tunnelling effects cause the threefold degeneracy of the vibrational levels to be lifted. Instead, they split into a nondegenerate level, the A species, and a two-fold degenerated level, the E species. These two-fold degenerated levels can be referred to with the $\sigma = \pm 1$ notation. The nondegenerate A species is referred to as $\sigma = 0$. Transitions are only allowed between the same species. Coriolis interactions cause the A and E rotational energy levels J to be slightly different, which means the energetic difference and thus transition frequencies

are different, leading to the so-called A-E splitting in the microwave spectrum. Equation 1.31 gives an expression for the energy $U_{v\sigma}(\alpha)$ of the split rotational energy levels. The symmetry of the torsional wave functions is given by σ , $A_k^{(v)}$ is a normalisation factor.

$$U_{v\sigma}(\alpha) = \sum_{k=-\infty}^{\infty} A_k^{(v)} e^{i(3k+\sigma)\alpha} \quad (1.31)$$

The initial Hamilton operator of the rigid rotor has to be expanded in order to calculate the energy of the rotational energy levels of each species (Equation 1.32). As such the Hamilton operator is then made up of three parts, which correspond to the overall rotation including centrifugal distortion effects ($\hat{H}_R$), the internal torsion ($\hat{H}_T$) and the interaction between the two ($\hat{H}_{RT}$)

$$\hat{H} = \hat{H}_R + \hat{H}_T + \hat{H}_{RT} \quad (1.32)$$

Following the publications by *Lin* and *Swalen* in Ref. [6] and *Dreizler* in Ref. [37], the angular momentum l (Equation 1.33) and the inertia tensor I (Equation 1.34) are extended by the angular momentum l_α and moment of inertia I_α of the internal rotor, respectively.

$$l = \begin{pmatrix} l_a \\ l_b \\ l_c \\ l_\alpha \end{pmatrix} \quad (1.33)$$

$$I = \begin{pmatrix} I_a & 0 & 0 & \lambda_a I_\alpha \\ 0 & I_b & 0 & \lambda_b I_\alpha \\ 0 & 0 & I_c & \lambda_c I_\alpha \\ \lambda_a I_\alpha & \lambda_b I_\alpha & \lambda_c I_\alpha & I_\alpha \end{pmatrix} \quad (1.34)$$

The factor λ_g expresses the angle between the internal rotor axis i and the principal axis $g = a, b, c$.

$$\lambda_g = \cos \angle(i, g) \quad (1.35)$$

Using Equations 1.33 and 1.34 the parts of the Hamilton operator from Equation 1.32 become:

$$\begin{aligned} \hat{H}_R = & \left(\frac{1}{2I_a} + Z_{aa} \right) \hat{l}_a^2 + \left(\frac{1}{2I_b} + Z_{bb} \right) \hat{l}_b^2 + \left(\frac{1}{2I_c} + Z_{cc} \right) \hat{l}_c^2 + \frac{1}{2} Z_{ab} (\hat{l}_a \hat{l}_b + \hat{l}_b \hat{l}_a) \\ & + \frac{1}{2} Z_{bc} (\hat{l}_b \hat{l}_c + \hat{l}_c \hat{l}_b) + \frac{1}{2} Z_{ac} (\hat{l}_a \hat{l}_c + \hat{l}_c \hat{l}_a) \end{aligned} \quad (1.36)$$

$$\hat{H}_T = F \hat{l}_\alpha^2 + V(\alpha) \quad (1.37)$$

$$\hat{H}_{RT} = -2Q_a \hat{l}_a \hat{l}_\alpha - 2Q_b \hat{l}_b \hat{l}_\alpha - 2Q_c \hat{l}_c \hat{l}_\alpha \quad (1.38)$$

The new parameters are defined as follows:

$$Z_{gg'} = F \rho_g \rho_{g'} \quad (1.39)$$

$$F = \frac{1}{2I_\alpha r} \quad (1.40)$$

$$\rho_g = \frac{\lambda_g I_\alpha}{I_g} \quad (1.41)$$

$$Q_g = F \rho_g \quad (1.42)$$

$$r = 1 - I_\alpha \left(\frac{\lambda_a}{I_a} + \frac{\lambda_b}{I_b} + \frac{\lambda_c}{I_c} \right) \quad (1.43)$$

For molecules with two internal rotors, referred to as 1 and 2 in the index, terms for the second rotor as well as terms to describe the interaction between the two rotors are added to the potential function. In Equation 1.44 the potential is once again given for two rotors with $N = 3$. Terms of V_6 and higher are neglected [37].

$$V(\alpha_1, \alpha_2) = \frac{V_{3,1}}{2}(1 - \cos(3\alpha_1)) + \frac{V_{3,2}}{2}(1 - \cos(3\alpha_2)) + V_{cc} \cos(3\alpha_1) \cos(3\alpha_2) + V_{ss} \sin(3\alpha_1) \sin(3\alpha_2) + \dots \quad (1.44)$$

Similarly the Hamilton operator is expanded by a term that reflects coupling interactions between the two rotors ($\hat{H}_{TT}$). In the two-rotor Hamiltonian, there are two terms for the internal torsion, $\hat{H}_{T1}$ and $\hat{H}_{T2}$, one for each rotor. They are calculated according to Equation 1.37.

$$\hat{H} = \hat{H}_R + \hat{H}_{T1} + \hat{H}_{T2} + \hat{H}_{RT} + \hat{H}_{TT} \quad (1.45)$$

$$\hat{H}_{TT} = F_{12}(\hat{l}_1 \hat{l}_2 + \hat{l}_2 \hat{l}_1) + V_{cc} \cos(3\alpha_1) \cos(3\alpha_2) + V_{ss} \sin(3\alpha_1) \sin(3\alpha_2) + \dots \quad (1.46)$$

Two internal rotors change the splittings of the energy levels and thus also the splittings in the microwave spectrum. As shown in Figure 1.3, a vibrational level that splits into an A and a two-fold degenerated E species for a single rotor, splits even further into five torsional components $(\sigma_1 \sigma_2) = (00), (01), (10), (11), \text{ and } (12)$ for a two-top molecule. σ_1 and σ_2 refer to the individual rotors and their state, (00) being the state where no internal rotation occurs. (01) and (10) can be illustrated as states where only one of the tops rotates. (11) and (12) refer to the state where both tops rotate, either in the same or in different directions [14][38].

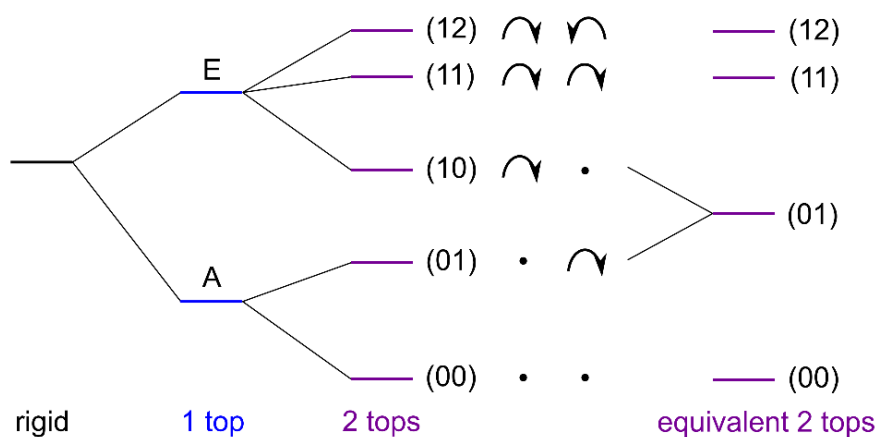


Figure 1.3: Schematic energy level diagram illustrating the splittings caused by internal rotation for (i) a rigid rotor (no torsional splitting), (ii) a molecule containing one methyl rotor (splitting into an A and an E species), and (iii) a molecule containing two inequivalent methyl rotors (splitting into five torsional species). A dot symbolizes the $\sigma = 0$ state, a clockwise arrow the $\sigma = +1$ and an anti-clockwise arrow the $\sigma = -1$ state. [38] (Figure modified from Ref. [3].)

1.4. Isotopologue Effect

Isotopes of chemical elements possess the same number of protons but a different number of neutrons. Accordingly they have different masses. This is relevant to microwave spectroscopy as the moment of inertia is dependent on the mass (see Equation 1.3 and 1.5). As shown in Section 1.1.1., the rotational constants of a molecule and thus also the energy eigenvalues depend on the moments of inertia. Consequently, rotational transitions and the microwave spectra of isotopologues are different.

A method developed by Kraitchman [39] uses these different spectra and their rotational constants to determine experimental atom positions in the molecule. For the structure determination it is assumed that bond lengths and angles are unchanged by the isotopic substitution. Thus the parent species, which is the isotopologue with the highest natural abundance, can be used as a basis for the calculations. In the principal axis system of the parent species (see Equation 1.4) the inertia tensor I' for an isotopologue where a single atom has been exchanged becomes:

$$I' = \begin{pmatrix} I'_{aa} & I'_{ab} & I'_{ac} \\ I'_{ba} & I'_{bb} & I'_{bc} \\ I'_{ca} & I'_{cb} & I'_{cc} \end{pmatrix} = \begin{pmatrix} I_a + \mu(b^2 + c^2) & -\mu \cdot a \cdot b & -\mu \cdot a \cdot c \\ -\mu \cdot b \cdot a & I_b + \mu(a^2 + c^2) & -\mu \cdot b \cdot c \\ -\mu \cdot c \cdot a & -\mu \cdot c \cdot b & I_c + \mu(a^2 + b^2) \end{pmatrix} \quad (1.47)$$

$$\mu = \frac{M \Delta m}{M + \Delta m}. \quad (1.48)$$

M is the mass of the original molecule, Δm the change in mass due to isotopic substitution.

The principal axes of the original molecule and the substituted molecule are generally not the same. However, it is assumed that the substituted atom and its parent species have the same atom position. If the moments of inertia and masses of both are known, the atom position can thus be determined according to the following equations:

$$\Delta I = I'_i - I_i \text{ with } i = a, b, c \quad (1.49)$$

$$\Delta P_a = \frac{1}{2}(\Delta I_b + \Delta I_c - \Delta I_a) \quad (1.50a)$$

$$\Delta P_b = \frac{1}{2}(\Delta I_a + \Delta I_c - \Delta I_b) \quad (1.50b)$$

$$\Delta P_c = \frac{1}{2}(\Delta I_a + \Delta I_b - \Delta I_c) \quad (1.50c)$$

$$|a| = \sqrt{\frac{\Delta P_a}{\mu} \left(1 + \frac{\Delta P_b}{I_b - I_a}\right) \left(1 + \frac{\Delta P_c}{I_c - I_a}\right)} \quad (1.51a)$$

$$|b| = \sqrt{\frac{\Delta P_b}{\mu} \left(1 + \frac{\Delta P_a}{I_a - I_b}\right) \left(1 + \frac{\Delta P_c}{I_c - I_b}\right)} \quad (1.51b)$$

$$|c| = \sqrt{\frac{\Delta P_c}{\mu} \left(1 + \frac{\Delta P_a}{I_a - I_c}\right) \left(1 + \frac{\Delta P_b}{I_b - I_c}\right)} \quad (1.51c)$$

If isotopologues of all atoms can be measured, a structure determination of the entire molecule becomes possible. The signs of the coordinates cannot be determined as the moment of inertia is dependent on squared coordinate values. They are thus often derived from quantum chemical calculations. [39]

2. Methods

The investigations of each molecule in this thesis followed the same basic approach.

First, quantum chemical calculations were carried out. Conformational analysis starting from different initial geometries were performed to find possible configurations of each molecule. The obtained geometries were checked for convergence with structure optimizations under full geometry relaxation, followed by harmonic frequency calculations carried out at the same level of theory as the previous conformational analysis and structure optimizations. This step was intended to ascertain whether the obtained conformers are true minima on the energy surface or merely saddle points. Potential energy curves for the internal rotor(s) of the predicted conformers were calculated next, giving an estimation of the barrier height.

Using the rotational constants of the optimized conformers, their microwave spectra over the entire frequency range covered by the spectrometer used in this thesis (see Section 2.2.) were predicted with the program *XIAM* [40].

Based on these predicted spectra a frequency range was chosen for the broadband scan, intending to scan a part of the spectra with intense transitions. For the molecules investigated in this thesis, usually transitions with quantum numbers between $J = 4$ and $J = 6$ with K_a and $K_c = 0$ or 1 were the most intense and thus the focus of the scan.

The broadband scan was measured with the molecular beam Fourier transform microwave (MB-FTMW) spectrometer described in Section 2.2. The predicted spectra were then used to assign the recorded spectrum. The energetically most stable conformer was searched for first, followed by the less stable conformers and/or isotopologues, if unassigned lines remained.

To assign and fit the spectra, the program *XIAM* [40] was mainly used. For several molecules the program *SFLAMS* (Separately Fitting of Large Amplitude Motion Species) [12] was additionally needed. The two fitting programs are explained in more detail in Section 2.3.

High resolution measurements were carried out once an initial fit based on the assignment from the broadband spectrum was successful.

2.1. Quantum Chemical Calculations

The *Gaussian 16* program package [41] was used for quantum chemical calculations. Multiple calculation methods such as MP2 [42], B3LYP [43][44], the *ab initio* CCSD method [45] as well as other density functional theory methods such as M06-2X [46] and ω B97X-D [47] were employed in combination with different basis sets. For initial calculations, the MP2/6-311++G(d,p) and B3LYP-D3BJ/6-311++G(d,p) levels of theory were usually chosen. The specific calculation methods used for each molecule are given in the respective chapter. Multiple methods and basis sets were later used in the systematic basis set variation intended for benchmarking purposes for all investigated molecules.

Simulations were performed with computing resources granted by RWTH Aachen University under project rwth0369.

2.2. Microwave Spectrometer

Here a short description of the spectrometer used in this thesis is given based on Ref. [33] and [48]. For more detail see Ref. [33]. Parts of this Section have been adapted from my master's thesis (2018) [32].

A simplified diagram of the MB-FTMW spectrometer operating in the frequency range from 2.0 to 26.5 GHz used to record the spectra of all molecules investigated in this thesis is shown in Figure 2.1.

The microwave frequency ν is generated in the microwave synthesizer. The signal is then converted up in a single sideband modulator to the frequency of $\nu + 160$ MHz before the pin diode switch cuts the signal into pulses that are used to polarize the molecules inside the Fabry-Perot resonator. Through adjustment of the resonator mirrors, a standing wave is created inside the chamber. The distance of the mirrors is dependent on the polarization frequency. Through the standing wave with a frequency of $\nu + 160$ MHz, the formerly independent rotation of the molecules inside the chamber becomes synchronized. The polarized rotating macroscopic object thus gets a measurable oscillation dipole moment. Once the microwave pulse ends, the molecules go back into their initial state and the synchronization decays, leading to a decay of the macroscopic dipole moment. An antenna collects the molecular signal with a frequency of $\nu + 160 + \delta$ MHz and transmits it through the pin diode switch into the first intermediate frequency (IF) mixer, where it is down converted with ν to $160 + \delta$ MHz. Following an amplification, the signal is down converted once again in the

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second IF mixer to $2.5 \text{ MHz} + \delta$ before being digitized in a transient recorder. Finally, a Fourier transformation is carried out in a computer and the signal can be analyzed.

The evacuated chamber was kept at a pressure of 10^{-7} mbar between two measurements, and 10^{-5} mbar during a measurement. Due to the rapid expansion of the gas upon entering the low pressure chamber, the temperature decreases almost to the absolute zero point because of the Joule-Thompson effect. The temperature of the molecular jet was approximately 1-2 K.

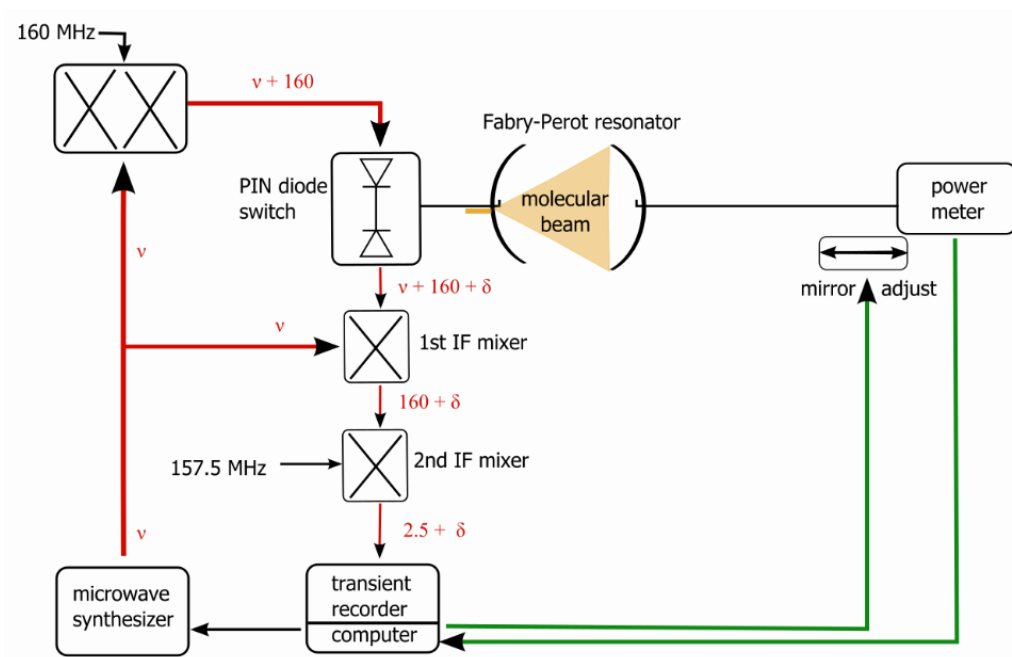


Figure 2.1: A simplified block diagram of the MB-FTMW spectrometer used in this thesis [48] (Figure modified from Ref. [32]).

2.3. Fitting Programs

2.3.1. XIAM

This explanation of the XIAM code is based on Ref. [40]. The XIAM program as well as more information are available on the PROSPE website [49].

The program XIAM can be used to predict and fit spectra of rigid rotor molecules and molecules with up to three internal rotors as well as one nucleus with quadrupole coupling. The basis for the code is the Combined Axis Method (CAM) first introduced by Woods [50][51], later modified by Vacherand *et. al.* [52]. The CAM method combines the principle inertial axis system (see Section 1.) with the rho axis system. The rho axis system is fixed to the molecular frame while choosing the main z axis in such a way that it aligns with the vector ρ of the internal rotor axis.

XIAM initially uses the principal axis system with a Hamiltonian analogous to the ones shown in Section 1.3., with $\hat{H}_r$ as the rotational part of the Hamiltonian, $\hat{H}_{cd}$ the centrifugal distortion term, and $\hat{H}_i$ the term for internal rotation with i denoting the number of internal rotors.

$$\hat{H} = \hat{H}_r + \hat{H}_{cd} + \hat{H}_i \quad (2.1)$$

Starting from the principal axis system, a transformation into the rho axis system via the Euler angles β and γ is performed. As each internal rotor is set up in its own rho axis system, this procedure must be carried out for each top successively if multiple rotors are considered.

$$\cos \beta = \frac{\rho_z}{\rho} = \frac{\rho_z}{\sqrt{\rho_x^2 + \rho_y^2 + \rho_z^2}} \quad (2.2)$$

$$\cos \gamma = \frac{\rho_x}{\sqrt{\rho_x^2 + \rho_y^2}} \quad (2.3)$$

The Hamiltonian is transformed using the rotation matrix $D(\beta, \gamma)$ and the corresponding operator $\hat{D}$. $\hat{H}'_i$ is the Hamiltonian of the internal rotor in the rho axis system.

$$D(\beta, \gamma) = \begin{pmatrix} \cos \beta & 0 & -\sin \beta \\ 0 & 1 & 0 \\ \sin \beta & 0 & \cos \beta \end{pmatrix} \begin{pmatrix} \cos \beta & \sin \beta & 0 \\ -\sin \beta & \cos \beta & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (2.4)$$

$$\hat{D} = \exp(-i\beta\hat{l}_y) \exp(-i\gamma\hat{l}_z) \quad (2.5)$$

$$\hat{H}_i = \left(\hat{D}(\beta, \gamma) \right)^{-1} \hat{H}'_i(\rho) \hat{D}(\beta, \gamma) \quad (2.6)$$

The Hamilton matrix in the rho axis system is diagonal in the rotational quantum number K , unlike the matrix in the principal axis system (see Section 1.3.). As such eigenvalues and eigenfunctions can be calculated much more conveniently.

The eigenvalue matrix obtained in the rho axis system is then transformed back into the principal axis system. The polar coordinates δ_i and ε_i are used to describe the position of the internal rotor axis in the principal axis system, analogous to β and γ referring to the vector ρ in the rho axis system.

$$\cos \delta_i = \cos \angle(z, i) = \lambda_{z,i} \quad (2.7)$$

$$\cos \varepsilon_i = \frac{|\lambda_{y,i}| \lambda_{x,i}}{\sqrt{\lambda_{x,i}^2 + \lambda_{y,i}^2}} \quad (2.8)$$

2.3.2. SFLAMS

The program *SFLAMS* [12] has the advantage that it can fit torsional species separately from each other. To achieve this, the rigid rotor Hamiltonian is extended by the term H_{op} , which uses odd power terms of the angular momentum components (Equation 2.10).

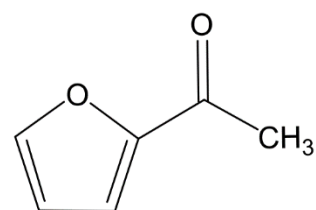
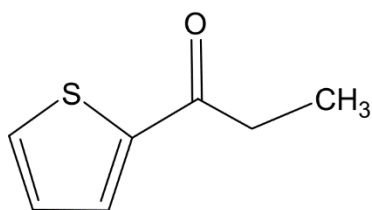
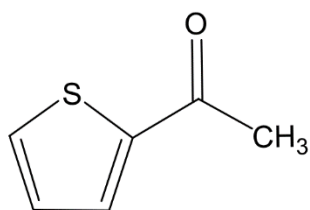
$$\hat{H} = \hat{H}_r + \hat{H}_{cd} + \hat{H}_{op} \quad (2.9)$$

$$\hat{H}_{op} = q \hat{l}_a + r \hat{l}_b + s \hat{l}_c \quad (2.10)$$

$$\hat{H}_{op}^{planar} = q \hat{l}_a + r \hat{l}_b \quad (2.11)$$

The added angular momentum components change sign under the time-reversal operation, making the Hamiltonian effective and different from the normal Hamiltonian. Coefficients that include the numerical expectation value of an odd power are thus included, which can describe the torsional angular momentum operator of the methyl group(s). Thus the added term is necessary to fit all torsional species except for the A or (00) species. Equation 2.11 gives the term for a planar rotor. Both $\hat{H}_{op}$ Hamiltonians can be supplemented by higher order terms such as $q_J \hat{l}_a^2 \hat{l}_a$, $q_K \hat{l}_a^3$, $r_J \hat{l}_b^2 \hat{l}_b$ or $r_K \hat{l}_b^3$ if necessary [12][53].

III One-Top Molecules



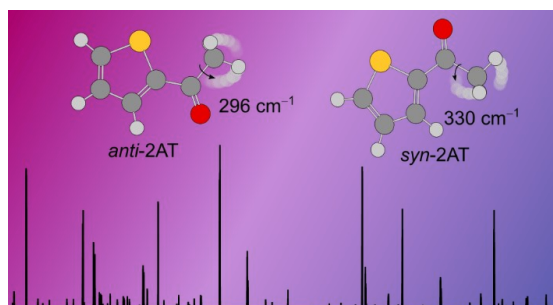
3. 2-Acetylthiophene

The main text passages of this chapter have already been published in Ref. [4]:

Christina Dindić, Jil Ludovicy, Vladimir Terzi, Arne Lüchow, Natalja Vogt, Jean Demaison and Ha Vinh Lam Nguyen

Determination of the semiexperimental equilibrium structure of 2-acetylthiophene in the presence of methyl internal rotation and substituent effects compared to thiophene

Phys. Chem. Chem. Phys. **2022**, 24, 3804-3815.



Parts of the publication are reproduced (and adapted) from *Phys. Chem. Chem. Phys.* 2022, 24, 3804-3815 with permission from PCCP Owner Societies. Christina Dindić performed measurements, quantum chemical calculations, spectral assignments and wrote the main part of the manuscript. Ha Vinh Lam Nguyen, Arne Lüchow, Natalja Vogt and Jean Demaison co-wrote the manuscript. The quantum chemical calculations and structure determination performed by Jil Ludovicy, Vladimir Terzi, Natalja Vogt and Jean Demaison featured in the publication have not been reproduced in this dissertation. Figures taken from Ref. [4] have been modified for consistent formatting in this dissertation.

3.1. Introduction

Over the history of microwave spectroscopy, methyl internal rotation has always been a subject of special interest alongside structural chemistry as the classic topic [54][53]. When the molecule contains a methyl rotor with a finite torsional barrier, torsional fine structures of all rotational transitions in form of A-E doublets are observed [38]. If the methyl group is attached to a system containing conjugated π -double bonds, the behaviour of the methyl internal rotation becomes unpredictable, because the delocalization of π -electrons can transfer electronic effects through the entire π -system. Acetyl methyl rotors are known to be sensitive to the structure of the moiety attached at the other side of the carbonyl bond, expressed through the torsional barrier. For example, the C_1 conformers of methyl n -alkyl ketones exhibit barriers to methyl internal rotation of about 240 cm^{-1} , while values found for the C_s conformers

are approximately 180 cm^{-1} [8][9][10][11]. The torsional barrier increases significantly to about 600 cm^{-1} in acetophenone derivatives where a phenyl ring is attached to the carbonyl group [12] or to 430 cm^{-1} for the *antiperiplanar* conformers and 350 cm^{-1} for the *synperiplanar* conformers of α,β -unsaturated ketones [55]. As such the investigation of 2-acetylthiophene (2AT) is an effort to further the knowledge about acetyl group containing ketones and the first data point as the prototype molecule towards establishing a possible “thiophene class”.

3.2. Quantum Chemical Calculations

3.2.1. Conformational Analysis

The only structural element determining the conformations of 2AT is the acetyl group, as the thiophene ring is known to be planar [56][57][58] and the rotation of the methyl group does not create new conformers. For the conformational analysis, the dihedral angle $\alpha = \angle(\text{S1}-\text{C2}-\text{C6}=\text{O7})$ (for atom numbering see Figure 3.1) was varied in steps of 10° and all other geometry parameters were optimized with the MP2 [42] and B3LYP [43][44] methods in combination with Pople’s basis set 6-311++G(d,p) [59] using the *Gaussian 16* program package [41]. The D3 model of Grimme [60] with Becke-Johnson (BJ) damping [61] was added to take into account the dispersion interactions. These two different methods were employed, since many previous investigations have reported method-dependent discrepancies between optimized structures [62][63]. The potential energy curves drawn in Figure 3.2 using coefficients from a Fourier expansion given in Table A.1 in the Appendix show that method-dependent discrepancies also occur for 2AT. Both the MP2 and B3LYP methods agree on one distinct minimum at $\alpha = 0^\circ$, corresponding to a *syn* orientation of the oxygen and the sulphur atoms of 2AT, but at $\alpha = 180^\circ$ the B3LYP-D3BJ curve possesses one minimum corresponding to a planar *anti*-conformation, contrasting with the double minimum obtained for the MP2 curve. The inset in Figure 3.2 illustrates energy data points obtained from calculations at the MP2/6-311++G(d,p) level around the 180° area with a finer step width of 1° to capture the double minimum clearly where the acetyl group is tilted out of the thiophene plane by about $\pm 6^\circ$ at the minimum configuration.

Subsequently, optimizations of the structures with the *syn* and *anti* S1–C2–C6=O7 fragments under full geometry relaxation including frequency calculations yielded the fully optimized structures (called *syn* and *anti*, respectively, see Figure 3.1). They were both confirmed to be stable. The nuclear coordinates of *syn*- and *anti*-2AT optimized at the B3LYP-D3BJ/6-311++G(d,p) and MP2/6-311++G(d,p) level of theory are given in Table A.2 in the Appendix. The calculated rotational constants, dipole moments, dihedral angles and energy differences obtained at both levels are listed in Table 3.1.

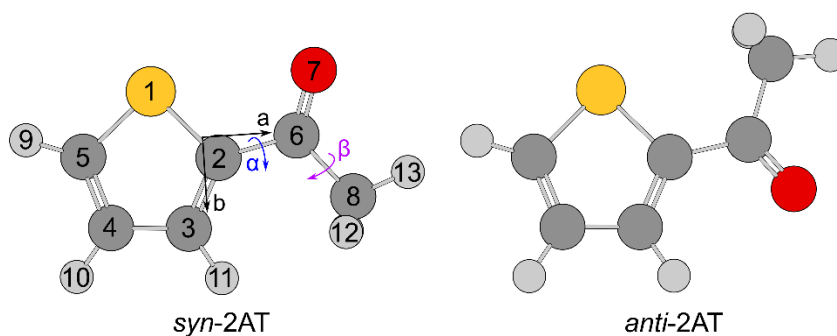


Figure 3.1: The two conformers of 2AT, *syn* and *anti*. Atom numbering, dihedral angles and principal axis are marked at *syn*-2AT. H14 lies behind H12. The sulphur atom is marked in yellow, oxygen atom in red, carbon atoms are in dark grey and hydrogen atoms in light grey. (Figure modified from Ref. [4].)

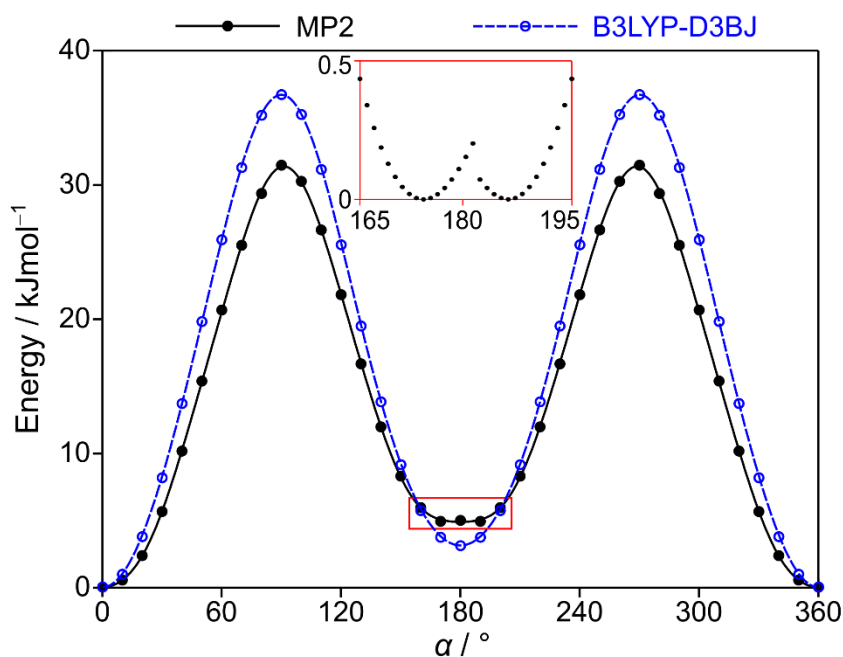


Figure 3.2: The potential energy curves of 2AT obtained by rotating the acetyl group about the C2–C6 bond (for atom numbering see Figure 3.1) by varying the dihedral angle α in a grid of 10° . Calculations were performed at the MP2/6-311++G(d,p) and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The relative energies are given in respect to the lowest energy conformation with $E_{\text{MP2}} = -704.3348246$ Hartree and $E_{\text{B3LYP-D3BJ}} = -705.7934819$ Hartree. The inset shows the data points of the region between 165° and 195° in a grid of 1° . (Figure modified from Ref. [4].)

Table 3.1: Calculated rotational constants, dipole moments, dihedral angles and relative energies for the two conformers of 2AT. For both MP2 and B3LYP-D3BJ methods, the 6-311++G(d,p) basis set was used.

Par.	Unit	MP2		B3LYP-D3BJ	
		<i>syn</i>	<i>anti</i>	<i>syn</i>	<i>anti</i>
A_e	MHz	3554.5554	3528.4064	3558.9758	3526.8413
B_e	MHz	1414.4817	1414.7173	1409.8986	1412.6037
C_e	MHz	1018.2769	1019.3106	1016.2252	1014.9726
μ_a	D	-2.03	2.75	-1.97	-2.59
μ_b	D	3.84	-1.95	3.30	-1.80
μ_c	D	0.00	-0.38	0.00	0.00
α	°	0.00	173.97	-0.02	180.00
ΔE^a	kJ/mol	0	5.73	0	2.58

^a Energy including zero-point corrections relative to that of the more stable conformer *syn*-2AT with $E_{\text{MP2}} = -704.231465$ Hartree and $E_{\text{B3LYP-D3BJ}} = -705.7934819$ Hartree.

3.2.2. Basis Set Variations

Due to the discrepancies between the MP2 and B3LYP methods used for the structure optimizations, as well as a benchmarking effort attempting to find a level of theory which allows for a cost-efficient yet reasonably accurate prediction of rotational constants to ease the assignment of microwave spectra of similar molecules, geometry optimizations were repeated using different methods and basis sets. In addition to the MP2 [42] and B3LYP [43][44] methods, the *ab initio* CCSD [45] method as well as other density functional theory methods M06-2X [46] and ω B97X-D [47] were employed. Furthermore, the B3LYP functional was used both with Grimme's dispersion correction including Becke-Johnson damping (D3BJ) [61] and without (D3) [64], but also in combination with the Coulomb-attenuating method (CAM-B3LYP) [65]. These methods were combined with a variety of basis sets, such as Pople's basis sets [59] (6-31G or 6-311G) with or without diffuse (+ or ++) functions. Polarization functions like (d,p), (df,dp), (2d,2p), (2df,2pd), (3df,3dp) are included in all cases. Polarized valence double- (cc-pVDZ) and triple-zeta (cc-pVTZ) Dunning's basis sets were also utilized [66], without or with diffuse functions included in the augmented basis sets known as aug-cc-pVDZ and aug-cc-pVTZ [67]. [3]

The rotational constants derived from all optimized structures are listed in Table A.3 in the Appendix and will be discussed later in Section 3.4. in relation to the experimentally determined values. At all levels of theory, the *syn*-conformer is energetically more favourable with an energy difference from about 2.1 to 6.2 kJ·mol⁻¹ (see Table A.3). Therefore, it was questionable whether both conformers could be observed in the microwave spectrum under the used molecular jet conditions where the rotational temperature is only about 1 – 2 K.

3.2.3. Methyl Internal Rotation

The barrier to internal rotation for the acetyl methyl group of 2AT was predicted by varying the dihedral angle $\beta = \angle(\text{C2-C6-C8-H12})$ in 10° steps between 0° and 360°. The resulting potential energy curves for both conformers calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory are shown in Figure 3.3. For the *syn*-conformer the potential exhibits the typical threefold symmetry expected for a methyl group. The predicted torsional barrier is 320.5 cm⁻¹ (MP2) or 220.8 cm⁻¹ (B3LYP-D3BJ). The corresponding values for the *anti*-conformer are 284.6 cm⁻¹ and 193.6 cm⁻¹. For *anti*-2AT, the MP2 potential exhibits a double minimum around 60°, 180° and 300° due to a switch between the two non-planar structures, whereas B3LYP-D3BJ predicts a threefold potential. The Fourier coefficients of the parameterised potentials are given in Table A.4 in the Appendix.

The barriers to internal rotation were furthermore calculated with all method/basis set combinations used in Section 3.2.2. for the structure optimization. The calculated values are listed in Table A.3 in the Appendix. It is noteworthy that for geometry optimizations attempts on extensive benchmarking exist, aiming at calculating rotational constants to guide the spectral assignment [68], but the same is not the case for methyl torsional barriers. The reason might be the challenge in accurate calculations of energies. While 1 kJ·mol⁻¹, corresponding to 84 cm⁻¹, already indicates highly accurate energy calculations, it does not satisfy the experimental requirements, considering that a change of one cm⁻¹ in the torsional barrier might lead to a shift of hundreds of MHz of the frequencies in the microwave spectrum [3].

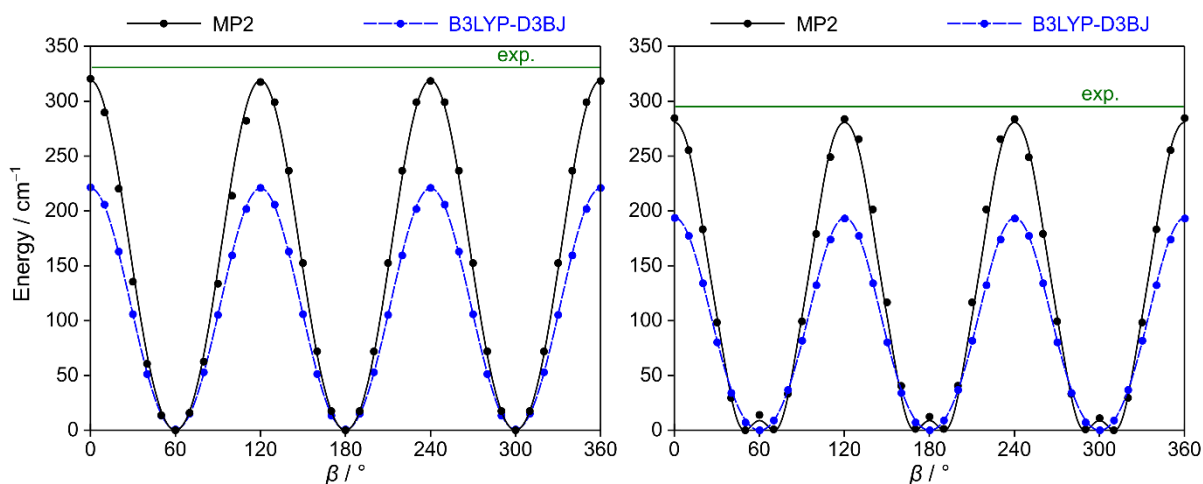


Figure 3.3: Potential energy curves of *syn*-2AT (left hand side) and *anti*-2AT (right hand side) obtained by rotating the acetyl methyl group about the C6–C8 bond in 10° steps. The MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory were used. The predicted torsional barriers are 320.5 cm⁻¹ and 220.8 cm⁻¹ for *syn*-2AT, as well as 284.6 cm⁻¹ and 193.6 cm⁻¹ for *anti*-2AT, respectively. The experimental values of 330.2 cm⁻¹ and 296.0 cm⁻¹ are shown by a horizontal line. (Figure modified from Ref. [4].)

3.3. Microwave Spectroscopy

3.3.1. Experimental Setup

The microwave spectrum was recorded using a molecular jet FTMW spectrometer operating in the frequency range from 2.0 to 26.5 GHz [33]. The substance was purchased from Sigma-Aldrich, Schnelldorf, Germany, with a stated purity of 98 % and used without any further purification. A scan from 9.0 to 15.4 GHz was recorded as a series of overlapping spectra with a step width of 0.25 MHz, which is the resolution of the scan frequencies. The substance was placed on a 5 cm piece of pipe cleaner and inserted upstream of the nozzle. Helium with a backing pressure of about 2 bar was flown over the sample and carried the substance into the cavity. A portion of the scan is illustrated in Figure 3.4. Each line of the scan was initially measured with 50 co-added free-induction decays and then subsequently remeasured at a higher resolution with an experimental accuracy of 2 kHz [69]. Measurements outside of the survey spectrum were carried out after the spectrum was assigned.

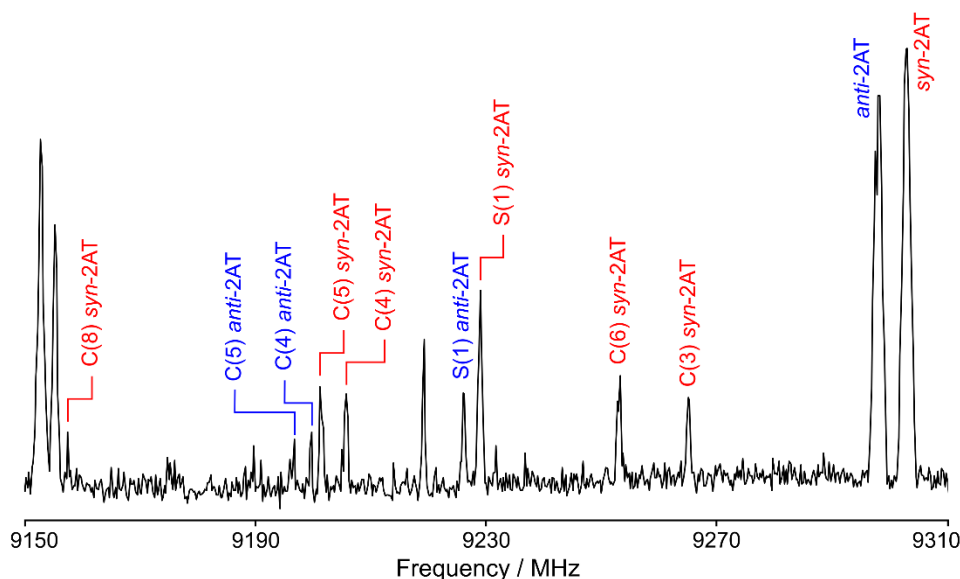


Figure 3.4: A portion of the scan of 2AT in the frequency range from 9150 to 9310 MHz recorded by overlapping spectra with 50 co-added decays per each spectrum. Lines belonging to the $4_{04} \leftarrow 3_{03}$ transition are labelled with the corresponding conformer, ^{34}S - or ^{13}C -isotopologue, as well as the atom position in parentheses. The intensities are given in a logarithmic scale in an arbitrary unit. The temperature of the molecular jet was approximately 1-2 K. (Figure modified from Ref. [4].)

3.3.2. Spectral Assignment

The assignment was started using the rotational constants calculated at the MP2/6-311++G(d,p) level of theory listed in Table 3.1. As the *syn*-conformer was predicted to be energetically more favourable, a rigid rotor spectrum was predicted first for this conformer and compared with the survey spectrum. From values of the calculated dipole moments (see Table 3.1), only *a*- and *b*-type transitions were expected.

The rigid rotor assignment was straightforward with the measurement accuracy of the scan (250 kHz) as the predicted rotational constants were adequately close to the experimental ones. However, when the high resolution measurements were analysed, the assignment became more difficult. The transition $3_{03} \leftarrow 2_{02}$ shown in Figure 3.5 exemplifies that the line frequencies of the *syn*- and *anti*-conformers are often very close to each other due to their similar rotational constants (see Table 3.1). Furthermore, splittings arising from the internal rotation of the methyl group are in the same order of magnitude, making the correct assignment of the conformational and torsional species even more challenging. Nevertheless, transitions of both conformers including their torsional splittings could be assigned. The resulting global

fits and molecular parameters obtained with the *XIAM* program [40] are summarised in Table 3.2; the assigned frequencies are listed in Tables A.5 and A.6 in the Appendix. In total, 138 A and 174 E species transitions were assigned for *syn*-2AT, as well as 117 and 128 transitions, respectively, for *anti*-2AT.

As expected, mostly *a*- and *b*-type transitions were found for both conformers, although a small number of E species *c*-type and *x*-type (ΔK_a and ΔK_c are both even) lines were also measured. For the E species, the quantum numbers K_a and K_c have lost their meaning and only indicate the order of energy in analogy to the asymmetric top energy level. The rotational constant of the methyl rotor F_0 could not be fitted for either of the conformers and was fixed to 158 GHz, a typical value for methyl groups. The estimated measurement accuracy, corresponding to $1/10^{\text{th}}$ of the average line width at half height, is 2.5 kHz.

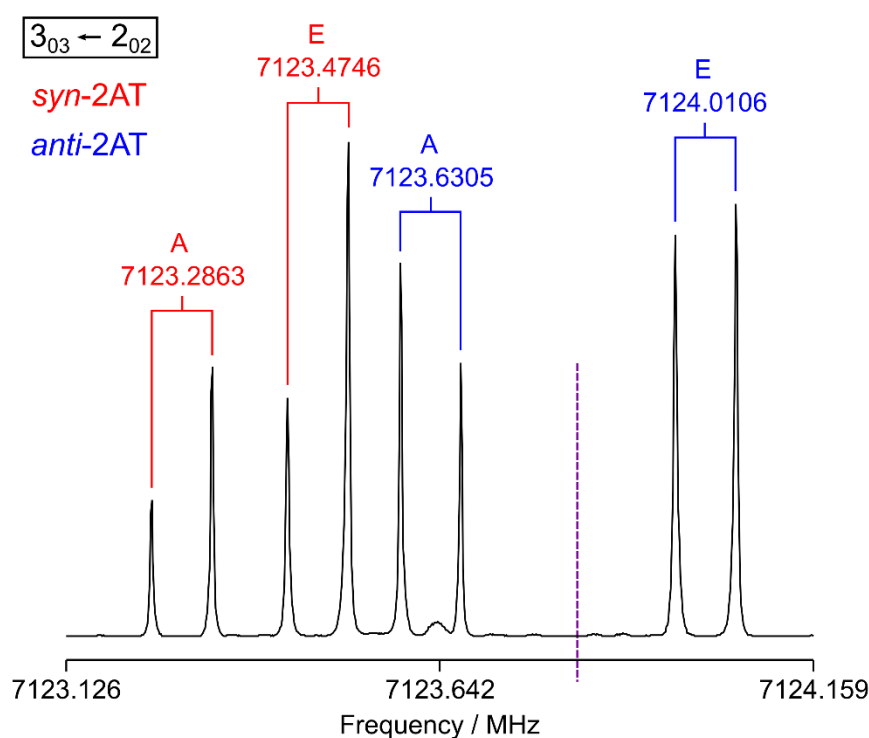


Figure 3.5: A high resolution measurement of the $3_{03} \leftarrow 2_{02}$ transition of 2AT recorded at 7123.83 MHz (shown as a dotted line). For this spectrum 153 decays were co-added. The splittings indicated by brackets are caused by the Doppler effect; the mean frequency is the transition frequency. The A-E torsional splitting is 188.3 kHz and 380.1 kHz for *syn*-2AT (red) and *anti*-2AT (blue), respectively. (Figure modified from Ref. [4].)

Table 3.2: Experimental spectroscopic parameters of the *anti*- and *syn*-conformers of 2AT obtained with the program *XIAM*.

Par. ^a	Unit	<i>syn</i>	<i>anti</i>
A_0	MHz	3588.05339(29)	3555.438(21)
B_0	MHz	1415.91822(11)	1418.7605(47)
C_0	MHz	1022.074502(72)	1020.7702(47)
D_J	kHz	0.05417(64)	0.05274(35)
D_{JK}	kHz	0.0470(51)	0.0755(39)
D_K	kHz	0.3743(89)	0.359(17)
d_1	kHz	−0.01724(41)	−0.01719(21)
d_2	kHz	−0.00223(25)	−0.002105(98)
V_3	cm ^{−1}	330.187(35)	295.957(17)
$D_{p_i^2 J}$	kHz		41.06(48)
$D_{p_i^2 K}$	MHz	−0.1311(53)	−0.1239(19)
$\angle(i,a)$	deg	47.937(23)	61.6587(72)
$\angle(i,b)$	deg	42.063(23)	28.3413(72)
$\angle(i,c)$	deg	90.0 ^b	90.0 ^b
Δ_c^c	uÅ ²	−3.313	−3.258
N_A/N_E^d	-	138/174	117/128
σ^e	kHz	5.1	2.4

^a All parameters refer to the principal axis system. Watson's S reduction and I' representation were used. ^b Fixed due to symmetry. ^c Pseudo inertial defect. ^d Number of A and E species transitions. ^e Standard deviation of the fit.

3.3.3. Isotopologues

After the assignment of *syn*- and *anti*-2AT a large number of lines still remained in the spectrum which were assumed to belong to the isotopologues. With a natural abundance of 4.25% [70], ³⁴S is the isotopologue with the highest possibility to be visible in the spectrum. The ³⁴S frequencies for the more stable *syn*-conformer were predicted first by using the following method, which was also published in Ref. [1].

The Cartesian coordinates of the optimized structure, given in Figure 3.1, were used, and the mass of the sulphur atom was adjusted to calculate the rotational constants of the isotopologue. The predicted ³⁴S- frequencies ν_{calc}^{iso} were corrected with the differences $\Delta\nu_{cal}$ between the frequencies predicted with the B_e rotational constants obtained at the MP2/6-311++G(d,p) level ν_{calc}^{parent} and the experimental frequencies ν_{obs}^{parent} of the main species, leading to successful assignments using the corrected frequencies ν_{iso} .

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$$\Delta\nu_{cal} = \nu_{obs}^{parent} - \nu_{calc}^{parent} \quad (3.1)$$

$$\nu_{iso} = \nu_{calc}^{iso} + \Delta\nu_{cal} \quad (3.2)$$

Straightforwardly, 51 A and 50 E species ^{34}S -*syn*-2AT transitions could be assigned, but the remaining unassigned lines were still numerous. Thus, the ^{13}C - and ^{18}O -isotopologue spectra were predicted following the same method. Rotational transitions of all six ^{13}C -isotopologues could be found and assigned, including A-E torsional splittings except for $^{13}\text{C}(2)$. Being close to the centre of mass of the molecule (see Figure 3.1), $^{13}\text{C}(2)$ transitions are close to those of the parent species and thus were often covered by the stronger main isotopologue transitions. Nevertheless, 15 transitions could be measured by exploiting that the separation between the parent species and the $^{13}\text{C}(2)$ lines increases with higher K_a quantum numbers. These transitions are weaker than those with lower K_a quantum numbers, and therefore, only A species lines could be measured, while the E species lines were too weak to be found. The ^{18}O -isotopologue spectrum was too weak to be observed even after intensive search. The obtained molecular parameters for all *syn*-2AT isotopologues are given in Table 3.3, and the assigned transitions of all isotopologues are listed in Table A.7 in the Appendix.

Since there were still unassigned lines remaining in the spectrum, it was first attempted to match them to the ^{33}S -isotopologue of *syn*-2AT with a natural abundance of 0.75%. However, the line intensities were weak due to the hyperfine splittings of the ^{33}S nucleus, and only a small number of possible transitions with which a reasonable fit was not achieved were found. The next step was then to consider the isotopologues of *anti*-2AT and the ^{34}S , $^{13}\text{C}(4)$ and $^{13}\text{C}(5)$ spectra of this conformer could be assigned (see Table 3.4 for the fits and Table A.8 in the Appendix for frequency lists), which were weak but still visible in the survey spectrum as shown in Figure 3.4. A small number of transitions could also be found for the other ^{13}C -isotopologues (see Table A.9), allowing initial fits by using three rotational constants for $^{13}\text{C}(3)$ and $^{13}\text{C}(6)$ as given in Table A.10. It seems highly likely that the assigned transitions belong to these isotopologues, but since further transitions were too weak to be observed and the assignment of the torsional species was uncertain, especially for the $^{13}\text{C}(3)$ isotopologue, satisfactorily accurate fits were not possible. Therefore, these isotopologues are not considered in the further analysis.

Based on the data of the assigned isotopologues a structure determination for *syn*-2AT was possible, which can be found in Ref. [4].

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Table 3.3: Molecular parameters of the ^{34}S - and ^{13}C -isotopologues of *syn*-2AT obtained with the program *XIAM*.

Par. ^a	Unit	$^{34}\text{S}(1)$	$^{13}\text{C}(2)$	$^{13}\text{C}(3)$	$^{13}\text{C}(4)$	$^{13}\text{C}(5)$	$^{13}\text{C}(6)$	$^{13}\text{C}(8)$
A_0	MHz	3526.99134(52)	3587.09861(14)	3538.0689(14)	3549.30592(91)	3588.0210(13)	3588.09149(79)	3556.6433(14)
B_0	MHz	1409.06281(21)	1415.90395(17)	1414.90446(51)	1401.38369(36)	1395.56772(42)	1405.83288(43)	1390.75940(41)
C_0	MHz	1013.51470(13)	1021.99301(19)	1017.45163(17)	1011.35655(22)	1011.42683(18)	1016.81168(28)	1006.40046(23)
D_J	kHz	0.0566(22)	0.054168 ^b	0.0476(66)	0.0565(21)	0.0584(40)	0.0528(55)	0.0550(39)
D_{JK}	kHz	0.046977 ^b	0.046977 ^b	0.046977 ^b	0.046977 ^b	0.092(30)	0.046977 ^b	0.046977 ^b
D_K	kHz	0.386(51)	0.374286 ^b	0.239(67)	0.314(73)	0.402(78)	0.482(78)	0.453(73)
d_1	kHz	-0.0180(13)	-0.017242 ^b	-0.0137(38)	-0.0173(17)	-0.0202(24)	-0.0207(29)	-0.0218(24)
d_2	kHz	-0.002231 ^b	-0.002231 ^b	-0.002231 ^b	-0.002231 ^b	-0.002231 ^b	-0.002231 ^b	-0.002231 ^b
V_3	cm^{-1}	330.069(64)	329.871494 ^b	333.48(46)	331.27(26)	329.80(13)	330.40(12)	331.52(42)
$D_{p_i^2 K}$	MHz	-0.131132 ^b	-0.131132 ^b	-0.131132 ^b	-0.131132 ^b	-0.307(49)	-0.131132 ^b	-0.131132 ^b
$\angle(i, a)$	deg	47.433(43)	52.9969 ^b	48.01(12)	48.480(72)	47.282(99)	47.918(72)	47.15(11)
$\angle(i, b)$	deg	42.567(43)	37.0031 ^b	41.99(12)	41.520(72)	42.718(99)	42.082(72)	42.85(11)
Δ_c^c	$\text{u}\text{\AA}^2$	-3.312	-3.315	-3.312	-3.313	-3.314	-3.313	-3.313
N_A/N_E^d	-	51/50	15/-	35/17	36/16	33/19	30/27	38/16
σ^e	kHz	4.4	2.3	3.5	3.7	3.6	5.3	4.2

^a All parameters refer to the principal axis system. Watson's S reduction and I' representation were used. $\angle(i, c)$ is fixed to 90° due to symmetry in all fits. F_0 is fixed to 158.0 GHz. ^b Values of the centrifugal distortion constants and the higher order parameter $D_{p_i^2 K}$ were fixed to those of the main isotopologue given in Table 3.2.

^c Pseudo inertial defect. ^d Number of A and E species transitions. ^e Standard deviation of the fit.

Table 3.4: Molecular parameters of the ^{34}S - and two ^{13}C -isotopologues of *anti*-2AT obtained with the program *XIAM*.

Par. ^a	Unit	$^{34}\text{S}(1)$	$^{13}\text{C}(4)$	$^{13}\text{C}(5)$
A_0	MHz	3491.23489(67)	3522.7755(17)	3554.00476(73)
B_0	MHz	1413.21114(38)	1403.58030(58)	1398.84537(48)
C_0	MHz	1012.82096(12)	1010.41239(14)	1010.49887(16)
D_J	kHz	0.0570(43)	0.05274 ^b	0.05274 ^b
D_{JK}	kHz	0.098(21)	0.0755 ^b	0.0755 ^b
D_K	kHz	0.274(54)	0.359 ^b	0.359 ^b
d_1	kHz	−0.0225(42)	−0.01719 ^b	−0.01719 ^b
d_2	kHz	−0.0064(32)	−0.002105 ^b	−0.002105 ^b
V_3	cm ^{−1}	295.606(88)	/	/
$D_{p_i^2 J}$	kHz	43.22(90)	/	/
$\angle(i,a)$	deg	62.319(42)	/	/
$\angle(i,b)$	deg	27.681(42)	/	/
Δ_c^c	uÅ ²	−3.385	−3.354	−3.355
N_A/N_E^d	-	42/21	10/−	11/−
σ^e	kHz	2.6	1.6	3.1

^a All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. $\angle(i,c)$ is fixed to 90° due to symmetry in all fits. F_0 is fixed to 158.0 GHz. ^b Values of the centrifugal distortion constants were fixed to those of the main isotopologue listed in Table 3.2. ^c Pseudo inertial defect. ^d Number of A and E species transitions. ^e Standard deviation of the fit.

3.4. Discussion

3.4.1. Conformational Stability

Quantum chemical calculations at different levels of theory consistently predict the *syn*-conformer of 2AT to be energetically more stable than the *anti*-conformer. However, the difference in energy varies strongly from about 2.1 to 6.2 kJ·mol^{−1} (see Table A.3 in the Appendix). The relative intensity observed in the experimental spectrum indicates that transitions of the *anti*-conformer are only slightly weaker than those of the *syn* form, as can be recognised exemplarily for the *a*-type transition $4_{04} \leftarrow 3_{03}$ in Figure 3.4 as well as the *b*-type transition $5_{05} \leftarrow 4_{14}$ in Figure A.1 in the Appendix, hinting at a rather small energy difference. Nevertheless, a quantitative statement on the conformational stability and intensity is not possible, due to the lack of dipole moment measurements, and because the intensity ratio obtained with the experimental setup in use is rather unreliable.

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The microwave spectra of another thiophene derivative related to 2AT, 2-thiophenecarboxaldehyde [71][72], has been reported in the literature. Both molecules exhibit two stable conformers with the S–C bond and the carbonyl group in *anti* or *syn* position, with the *syn*-conformer being more stable. The stability of these two forms stems from interactions between the aromatic ring and the carbonyl group. Planar forms are furthermore favoured due to the maximum overlap between π -orbitals they provide. [73] The higher stability of the *syn*-conformer can be explained based on a stabilisation from electrostatic interaction between the opposite charges on the oxygen and sulphur atoms, as visualised for 2AT in Figure 3.7 with the charge data obtained from NBO calculations [74] performed using the *Gaussian 16* program package [41].

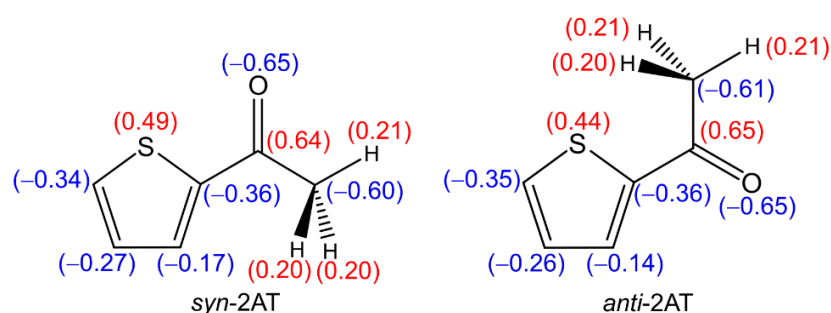


Figure 3.7: Charge distribution in *syn*- and *anti*-2AT obtained from NBO calculations at the MP2/6-311++G(d,p) level of theory. (Figure modified from Ref. [4].)

3.4.2. Quality of the Fits

As can be recognised in Table 3.2, using three rotational constants, five quartic centrifugal distortion constants, the angle between the internal rotor axis and the principal *a*-axis, as well as two higher order parameters $D_{p_i^2 J}$ and $D_{p_i^2 K}$ describing the centrifugal distortion of the methyl internal rotor, the standard deviation achieved for *anti*-2AT is 2.4 kHz. This value is in good keeping with the measurement accuracy. For *syn*-2AT, if the $D_{p_i^2 J}$ parameter is included, the standard deviation of the fit is 1.9 kHz, showing that the *XIAM* program performs well for both conformers of 2AT. However, the *A* rotational constant strongly correlates with $D_{p_i^2 J}$. By fitting $D_{p_i^2 J}$, it was found that for the main isotopologue of *syn*-2AT (i) the *A* rotational constant is by two orders of magnitude less well-determined and (ii) its value changes by 1.6 MHz, as summarised in Table 3.5. Interestingly, the fits of all isotopologues, except C(2) for which no E species lines are observable, are much less sensitive to D_{pi2J} , so that the two above mentioned problems do not occur. All *syn*-2AT isotopologue fits were therefore performed

without including $D_{p_i^2 J}$, and thus possess higher standard deviation (except for $^{13}\text{C}(2)$ with a much better deviation of 2.3 kHz due to the observation of only A species lines).

3.4.3. Molecular Parameters

For *syn*-2AT the values of equilibrium rotational constants calculated at different levels of theory, summarised in Tables A.3, are generally close to those deduced from the experiments for basis sets using the (ndf,npd) polarization functions ($n = 1-3$) in combination with the MP2 or B3LYP methods. For the M06-2X and ω B97XD methods, the 6-311G(d,p) basis set with or without diffuse functions performs well. In the case of *anti*-2AT, only the three levels M06-2X/6-311G(d,p), M06-2X/6-311+G(d,p) and M06-2X/6-311++G(d,p) seem suitable.

The inertial defects $\Delta_c = I_c - I_a - I_b$ of the *syn*- and *anti*-conformer are $-3.313 \text{ u}\text{\AA}^2$ and $-3.258 \text{ u}\text{\AA}^2$, respectively. The values for their isotopologues are mostly identical, with the exception of the ^{34}S -*anti*-2AT isotopologue, which has an inertial defect of $-3.285 \text{ u}\text{\AA}^2$. The inertial defect is a parameter that corresponds to the planarity of a molecule, which remains largely unchanged for each isotopologue. An in depth discussion on the structure of 2AT can be found in Ref. [4].

3.4.4. Methyl Internal Rotation

The torsional barrier of the acetyl methyl group could be well-determined in the fits of both conformers and most of the observed isotopologues. Only for C(2)-*syn*-2AT which lies almost at the centre of mass of the molecule, and the two ^{13}C isotopologues observable for *anti*-2AT, no E species transitions were measurable and therefore, the torsional barrier could not be deduced. For *syn*-2AT, a barrier height of about 329.9 cm^{-1} was found for the parent species, which remains almost constant for all isotopologues. A slightly lower, yet similar value of about 296 cm^{-1} was obtained for *anti*-2AT as well as for its ^{34}S isotopologue.

The initially predicted values for the torsional barriers (see Section 3.2.3.) were significantly closer to the experimentally determined ones at the MP2/6-311++G(d,p) level of theory than those calculated with the B3LYP-D3BJ method. The MP2 method performs better in calculating the V_3 barrier overall compared to B3LYP as can be seen in the benchmarking calculations listed in Table A.3 in the Appendix, although it is still not convincingly accurate with deviations largely around 20 to 30 cm^{-1} depending on the basis set in use. Similarly “low” deviations are achieved with the M06-2X method, although here there are large

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Table 3.5: Rotational constants, higher order $D_{p_i^2 J}$ and $D_{p_i^2 K}$ parameters, standard deviation σ and pseudo inertial defect Δ_c of *syn*- and *anti*-2AT obtained with the program *XIAM* using different sets of high order parameters.

<i>syn</i> -2AT						<i>anti</i> -2AT			
Par.	Unit	$D_{p_i^2 J} + D_{p_i^2 K}$	$D_{p_i^2 J}$	$D_{p_i^2 K}^a$	none	$D_{p_i^2 J} + D_{p_i^2 K}^b$	$D_{p_i^2 J}$	$D_{p_i^2 K}$	none
A	MHz	3589.676(26)	3588.04877(38)	3588.05339(29)	3588.04887(38)	3555.438(21)	3554.61453(75)	3554.6181(11)	3554.6155(11)
B	MHz	1415.7100(49)	1415.91824(20)	1415.91822(11)	1415.91833(19)	1418.7605(47)	1419.16713(28)	1419.16865(34)	1419.16879(36)
C	MHz	1021.8664(49)	1022.07432(14)	1022.074502(72)	1022.07440(13)	1020.7702(47)	1021.17627(20)	1021.17725(25)	1021.17724(26)
$D_{p_i^2 J}$	kHz	19.73(46)	2.9(19)	/	/	41.06(48)	28.7(19)	/	/
$D_{p_i^2 K}$	MHz	-0.1739(22)	/	-0.1311(53)	/	-0.1239(19)	/	-0.0580(99)	/
σ	kHz	1.9	8.8	5.1	8.8	2.4	10.5	13.9	14.9
Δ_c	uÅ ²	-3.201	-3.313	-3.313	-3.313	-3.258	-3.386	-3.386	-3.386

^a Fit chosen for structure determination as given in Table 3.2. ^b Fit given in Table 3.2.

differences depending on the basis set. No method or basis set stands out as best suited. As an example, for *syn*-2AT M06-2X/aug-cc-pVDZ (deviation of 2.2 cm⁻¹) calculates the value closest to the experimental barrier, but for *anti*-2AT the same calculation method is off by 51.4 cm⁻¹, while the MP2/6-311G(2df,2pd) level predicts the value closest to the experimental one (deviation of 0.6 cm⁻¹).

3.5. Conclusion

The *syn*- and *anti*-conformers of 2AT were assigned in the microwave spectrum as well as the ³⁴S-isotopologue of both conformers, all ¹³C-isotopologues of *syn*-2AT and some ¹³C-isotopologues of *anti*-2AT. Splittings caused by methyl internal rotation of the acetyl methyl group could be resolved for both conformers and the ³⁴S-isotopologues as well as all ¹³C-isotopologues of *syn*-2AT except for the one located too closely to the centre of mass of the molecule C(2). Analysing these splittings enables the determination of a torsional barrier of about 296 cm⁻¹ for *anti*-2AT and 330 cm⁻¹ for *syn*-2AT. The torsional barrier remains almost constant for all isotopologues of a conformer.

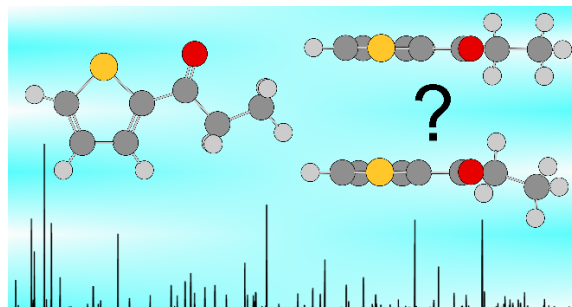
4. 2-Propionylthiophene

The main text passages of this chapter have already been published in Ref. [1]:

Christina Dindić, Wolfgang Stahl and Ha Vinh Lam Nguyen

2-Propionylthiophene: planar, or not planar, that is the question

Phys. Chem. Chem. Phys. **2020**, *22*, 19704-197012.



Parts of the publication are reproduced (and adapted) from *Phys. Chem. Chem. Phys.* 2020, 22, 19704-197012 with permission from PCCP Owner Societies. Christina Dindić performed measurements, quantum chemical calculations, spectral assignments and wrote the main part of the manuscript. Ha Vinh Lam Nguyen co-wrote the manuscript. Wolfgang Stahl discussed and corrected the contents of the manuscript. Hajar Bouzouma is gratefully acknowledged for her contribution to the measurements and assignments during her research project at the RWTH Aachen University. Figures taken from Ref. [1] have been modified for consistent formatting in this dissertation.

4.1. Introduction

Building on the previous investigation of 2AT (Chapter 3, [4]), 2-propionylthiophene (2PT) is investigated, where the alkyl group is lengthened from a methyl group to an ethyl group. Experimental insights into the orientation of the propionyl moiety were gained.

It is known that if an ethyl group is attached to a frame with C_s symmetry, in the case of 2PT the $(C_4H_3S)-C=O$ frame, it prefers two orientations: the C_s (or in-plane) conformer with the ethyl C–C bond also lying on the plane of the frame and the C_1 (*gauche* or out-of-plane) conformer with the methyl group tilted out of that plane. [75][76][77][78][79] For the carbonyl group, there are two possible orientations referring to the sulphur atom, *syn* and *anti*, as already established with 2AT. Therefore, it was almost obvious to assume that four stable conformers of 2PT would exist with two possible orientations of the ethyl group (C_s and C_1) and two of the carbonyl group (*syn* and *anti*). This assumption was to be validated in the investigation, and it was also of interest to find out which conformers are present in the experimental spectrum.

Furthermore, 2PT was investigated to shed light on the question “planar or not planar”, which had arisen in systematic investigations on structures of alkyl ketones like ethyl methyl ketone [80] and diethyl ketone [62], where discrepancies between the calculated structure and the experimentally determined one regarding the orientation of the alkyl chain were found. While quantum chemistry sometimes predicts that the alkyl group(s) should be tilted out of the C-(C=O)-C plane by a small angle, typically from 5° to 15°, a model for an effective planar molecule could be applied with success to reproduce the experimental spectra. Similar problems were encountered in investigations on aliphatic ketones with longer carbon chains such as pentan-2-one [8], hexan-2-one [9] and heptan-2-one [10], or even when the alkyl chain is branched as in the cases of pinacolone [81] and methyl neopentyl ketone [82]. A conclusive statement could not be drawn since the experimental data did not allow to confirm or deny a C_s structure, as no isotopic species could be measured. As a full structure determination was possible for 2AT due to the strong isotopologue signals, it was feasible that isotopologues would also be detectable for 2PT and thus help answer this question.

4.2. Quantum Chemical Calculations

4.2.1. Conformational Analysis

Similar to 2AT, the conformational landscape of 2PT is entirely determined by the orientation of the propionyl moiety, expressed by the dihedral angles $\alpha = \angle(\text{S1}, \text{C2}, \text{C6}, \text{O7})$ and $\beta = \angle(\text{C2}, \text{C6}, \text{C8}, \text{C9})$, as the thiophene ring is planar [56][57][58]. Varying α corresponds to a rotation of the thiophene ring about the C2–C6 bond, and varying β to the rotation of the ethyl group about the C6–C8 bond (for atom numbering see Figure 4.1).

Structure optimizations were carried out at the MP2/6-311++G(d,p) [42][59] level of theory using the *Gaussian 16* programme package [41], as this combination of method and basis set has yielded reliable starting values for the rotational constants of other molecules containing an ethyl group and an aromatic ring such as phenetole [83], or an ethyl group and a carbonyl bond such as ethyl acetate [84], methyl propionate [85], and *N,N*-diethylpropionamide [86]. Potential energy scans performed by varying the dihedral angle α at a starting value of 180° for β yielded two stable conformers where the oxygen atom is either in a *syn*-orientation at $\alpha = 0^\circ$ or in an *anti*-orientation at $\alpha = 180^\circ$ relative to the sulphur atom of the thiophene ring. Full geometry optimizations revealed that the *syn*-conformer is energetically more favourable by 4.89 kJ/mol, whereby zero-point energy corrections have been taken into account. This is a result of the orbital interactions, mainly due to electrostatic interaction between the oxygen

atom of the carbonyl group and the sulphur atom in the thiophene ring [73], as has been reviewed and extensively discussed in Ref. [71].

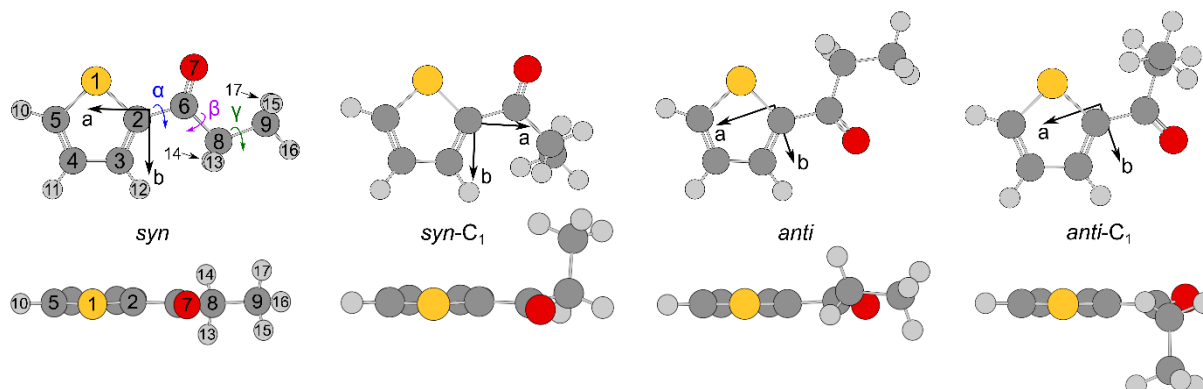


Figure 4.1: Molecular structures in front view (upper trace) and side view (lower trace) of four conformers of 2PT optimized at the MP2/6-311++G(d,p) level of theory under full relaxation in their principal axes of inertia. The *syn*- and *anti*-conformers were observed in the experimental spectrum. Each of the conformers *syn*-C₁ and *anti*-C₁ exists as an image and a mirror image structure. Atom numbering and definitions of the dihedral angles are given at the *syn*-conformer. (Figure modified from Ref. [1].)

Starting at either $\alpha = 0^\circ$ or 180° , the dihedral angle β was subsequently varied in 10° steps, while all other geometry parameters including α were optimised under full relaxation. The potential energy points obtained from scans at $\alpha = 0^\circ$ (*syn* conformations) were parameterized with a one-dimensional Fourier expansion. The potential curve was drawn using the obtained Fourier coefficients as illustrated in Figure 4.2. The Fourier coefficients are available in Table B.1 in the Appendix.

In total, four conformers were found on the potential energy surfaces, all of which were confirmed as true minima by frequency calculations. The so-called *syn*-conformer is energetically most stable with a *syn* orientation between the oxygen and the sulphur atoms and a nearly in-plane orientation of the propionyl chain. The entire propionyl group is tilted out of the thiophene plane by an angle of 2.6° , and the ethyl group is bent by 4.8° (see the values of α and β given in Table 4.1). In conformer *syn*-C₁ at $\beta \approx 80^\circ$ and its energetically equivalent mirror image *syn*-C₁* at $\beta \approx -80^\circ$, the methyl group is tilted out of the C-C=O-C plane by 78.7° . Two conformers with an *anti*-orientation between the two heteroatoms were also observed with similar positions of the ethyl group. The geometries of all conformers are illustrated in Figure 4.1; the atomic coordinates are given in Table B.2 in the Appendix.

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Table 4.1: Energy differences (in kJ/mol) including zero-point corrections between the four conformers of 2PT as well as the dihedral angles α and β (in degrees), rotational constants (in MHz) and dipole moments (in D).

	<i>syn</i>	<i>syn-C₁</i>	<i>anti</i>	<i>anti-C₁</i>
$\Delta E_{\text{MP2}}^{\text{a,b}}$	0.00	2.31	4.89	6.18
$\Delta E_{\text{B3LYP-D3BJ}}^{\text{a,b}}$	0.00	2.28	2.71	4.82
$\Delta E_{\text{M06-2X}}^{\text{a,b}}$	0.00	4.00	2.94	6.82
$\alpha_{\text{MP2}}^{\text{b}}$	−2.6	5.1	172.8	−170.8
$\beta_{\text{MP2}}^{\text{b}}$	175.2	78.7	172.5	83.4
$\alpha_{\text{B3LYP-D3BJ}}^{\text{b}}$	0.0	2.1	−180.0	−176.5
$\beta_{\text{B3LYP-D3BJ}}^{\text{b}}$	−180.0	83.4	180.0	86.1
$\alpha_{\text{M06-2X}}^{\text{b}}$	0.0	1.9	−180.0	−175.8
$\beta_{\text{M06-2X}}^{\text{b}}$	180.0	79.9	−180.0	82.8
A_e^{c}	3394.9	2617.5	3245.4	2547.6
B_e^{c}	877.0	1029.0	904.8	1059.3
C_e^{c}	703.1	800.9	716.0	826.0
A_0^{d}	3394.0	2597.4	3235.0	2535.0
B_0^{d}	866.0	1024.8	897.4	1055.4
C_0^{d}	695.3	795.6	709.7	817.8
μ_a^{e}	1.48	−1.07	−2.10	2.12
μ_b^{e}	3.86	4.18	−2.34	−2.57
μ_c^{e}	0.06	−0.09	−0.46	0.57

^a Relative to the most stable conformer *syn*-2PT with $E_{\text{MP2}} = -743.3985996$ Hartree, $E_{\text{B3LYP-D3BJ}} = -745.1229209$ Hartree and $E_{\text{M06-2X}} = -744.9051432$ Hartree. ^b Calculated with the basis set 6-311++G(d,p). ^c Equilibrium rotational constants obtained from geometry optimizations at the MP2/6-311++G(d,p) level of theory. ^d Vibrational ground state rotational constants obtained from anharmonic frequency calculations at the MP2/6-311++G(d,p) level of theory. ^e Calculated at the MP2/6-311++G(d,p) level of theory.

4.2.2. Basis Set Variations

The optimizations were repeated using different combinations of methods and basis sets (see Section 3.2.2.). The resulting rotational constants and dihedral angles α and β of the assigned conformers are given in Table B.3 in the Appendix. For these two conformers a notable difference was found in the optimized structures obtained at different levels of theory. Several MP2 levels predicted a small out-of-plane tilt angle for the propionyl and the ethyl groups with the dihedral angles α and β deviating by up to 8° from those of a planar structure, while all other methods yielded a perfect in-plane orientation of the entire propionyl group.

The energy difference between the conformers also depends on the method and basis set in use. An example is shown in Figure 4.2, where the difference between the *syn*- and *syn*-C₁-conformers is much higher in calculations with the B3LYP-D3BJ and M06-2X than with the MP2 method. While all levels of theory consistently predict the *syn*-conformer to be lowest and the *anti*-C₁ to be highest in energy, the energy order between *syn*-C₁ and *anti* is method-dependent, as shown in Table 4.1. Similar disagreement in energy calculations at different levels of theory were found in previous investigations [86][87].

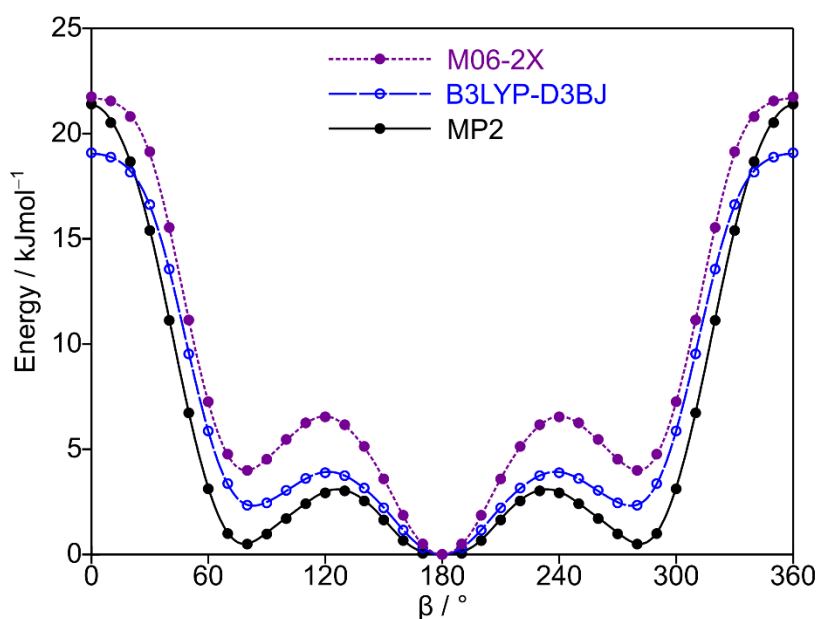


Figure 4.2: The potential energy curves of 2PT obtained by rotating the ethyl group about the C6–C8 bond in 10° steps calculated using the MP2, B3LYP-D3BJ and M06-2X methods in combination with the 6-311++G(d,p) basis set. All starting geometries possess a *syn*-orientation between the two heteroatoms of the molecule. The energies are given relative to the lowest energy conformation with $E_{\text{MP2}} = -743.5311916$ Hartree, $E_{\text{B3LYP-D3BJ}} = -745.1229207$ Hartree and $E_{\text{M06-2X}} = -744.9051433$ Hartree. The minimum at 180° corresponds to the *syn*-

conformer and the minima at about $\pm 80^\circ$ to conformer *syn*-C₁ and its mirror image. (Figure modified from Ref. [1].)

4.2.3. Methyl Internal Rotation

To determine the barrier to internal rotation of the methyl group, geometry optimisations were carried out by varying the dihedral angle $\gamma = \angle(\text{C6}, \text{C8}, \text{C9}, \text{H15})$ in steps of 10° . The threefold potentials of the most stable *syn*-conformer calculated at the MP2/6-311++G(d,p), B3LYP-D3BJ/6-311++G(d,p) and M06-2X/6-311++G(d,p) levels of theory are shown in Figure 4.3. The value of the barrier height predicted with different methods varies significantly, ranging from 764.5 to 929.3 cm^{-1} for the *syn*-conformer. Similar values are found for all other conformers. Therefore, torsional splittings in the microwave spectrum were expected to be small, but resolvable with the resolution of the spectrometer used in this investigation.

The barriers to internal rotation of *syn*- and *anti*-2PT were furthermore calculated with all method/basis set combinations used in Section 3.2.2. for the structure optimization. The calculated values are listed in Table B.3 in the Appendix and will be discussed in Section 4.4.4. in comparison with the experimental values.

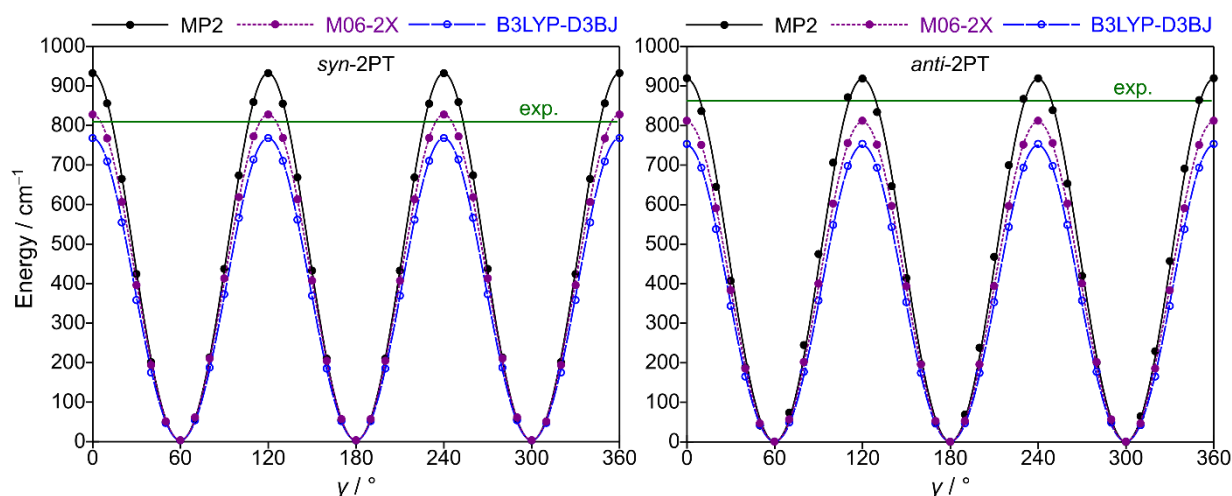


Figure 4.3: Left hand side: The potential energy curve of *syn*-2PT obtained by rotating the methyl group around the C8–C9 bond in 10° steps calculated at the different levels of theory with the 6-311++G(d,p) basis set. The predicted rotational barriers are 929.3 cm^{-1} (MP2), 823.8 cm^{-1} (M06-2X) and 764.5 cm^{-1} (B3LYP-D3BJ). The experimental value of 806.9 cm^{-1} is shown by a horizontal line. Relative energies are given in respect to the lowest energy conformations with $E_{\text{MP2}} = -743.531202$ Hartree, $E_{\text{M06-2X}} = -744.905143$ Hartree, and $E_{\text{B3LYP-D3BJ}} = -745.122921$ Hartree. **Right hand side:** The potential energy curve of *anti*-2PT obtained by rotating the methyl group around the C8–C9 bond in 10° steps calculated at the different levels

of theory with the 6-311++G(d,p) basis set. The predicted rotational barriers are 919.9 cm^{-1} (MP2), 811.7 cm^{-1} (M06-2X) and 753.0 cm^{-1} (B3LYP-D3BJ). The experimental value of 864.5 cm^{-1} is shown by a horizontal line. Relative energies are given in respect to the lowest energy conformations with $E_{\text{MP2}} = -743.529686$ Hartree, $E_{\text{M06-2X}} = -744.904023$ Hartree, and $E_{\text{B3LYP-D3BJ}} = -745.121888$ Hartree. The Fourier coefficients of the parameterized potentials for both conformers are given in Table B.4 in the Appendix. (Figure modified from Ref. [1].)

4.3. Microwave Spectroscopy

4.3.1. Experimental Setup

A broadband scan from 9.0 to 14.8 GHz as a series of overlapping spectra with a step width of 0.25 MHz was recorded using a molecular jet FTMW spectrometer operating in the frequency range from 2.0 to 26.5 GHz [33]. 2PT was purchased from TCI Europe, Zwijndrecht, Belgium, with a stated purity of 97 % and used without further purification. The substance was placed on a pipe cleaner upstream the nozzle with a backing pressure of 2 bar helium as the carrier gas. All signals appearing in the survey spectrum were later remeasured at higher resolution with an experimental accuracy of 2 kHz [69]. Figure 4.4 shows a part of the broadband scan from 9200 to 9500 MHz, where the arbitrary intensity is given in a logarithmic scale.

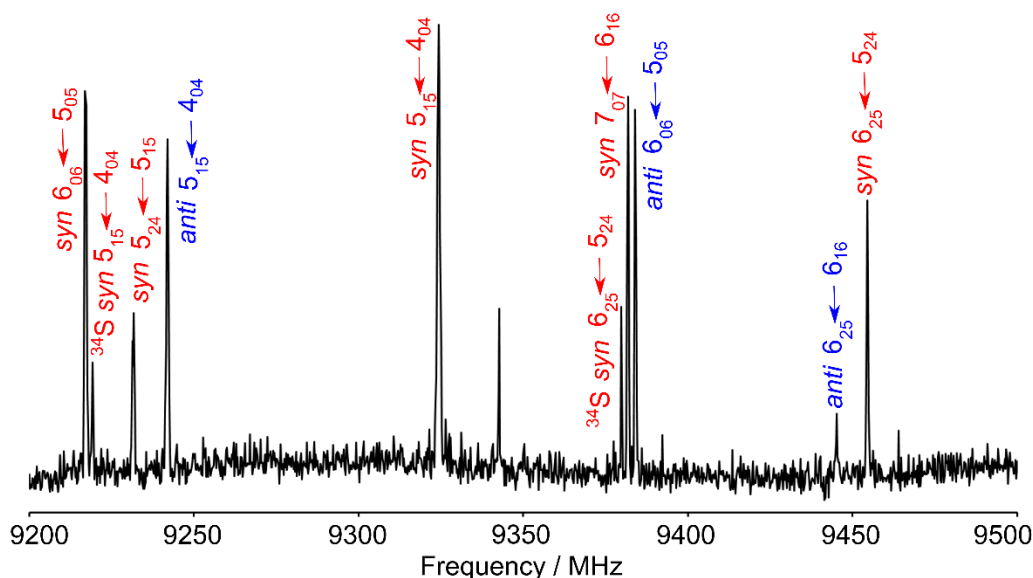


Figure 4.4: Broadband scan of 2PT in the frequency range from 9200 to 9500 MHz recorded by overlapping spectra with 50 co-added decays per each spectrum. The arbitrary intensity is given in a logarithmic scale. The rotational temperature is estimated to be about 1-2 K. Each

line is labelled by the rotational quantum numbers of the transition $J''_{K''_a K''_c} \leftarrow J'_{K'_a K'_c}$ and the corresponding conformer. (Figure modified from Ref. [1].)

4.3.2. Spectral Assignment

The spectral assignment was started with the most stable *syn*-conformer. The rotational constants $A_e = 3394.9$ MHz, $B_e = 877.0$ MHz and $C_e = 703.1$ MHz calculated at the MP2/6-311++G(d,p) level of theory were used to predict the rigid-rotor spectrum of *syn*-2PT. From the calculated dipole moment components of $\mu_a = 1.48$ D, $\mu_b = 3.86$ D and $\mu_c = 0.06$ D, strong *b*-type, weaker *a*-type and no *c*-type transitions were expected in the spectrum. The assignment was straightforward, as the predicted rotational constants were sufficiently accurate.

After the spectrum of the *syn*-conformer was assigned, many lines with slightly lower intensity remained unassigned. The rigid rotor spectra of the *syn*-C₁-, *anti*- and *anti*-C₁-conformers were predicted and compared with the spectrum in which all lines belonging to *syn*-2PT had been excluded. Figure 4.5 clearly visualizes that almost all remaining lines belong to the *anti*-conformer. After the assignment of *anti*-2PT, only very few weak lines in the spectrum were unassigned, indicating that the *syn*-C₁ conformer is not present, although the calculated energies reported in Table 4.1 might suggest this.

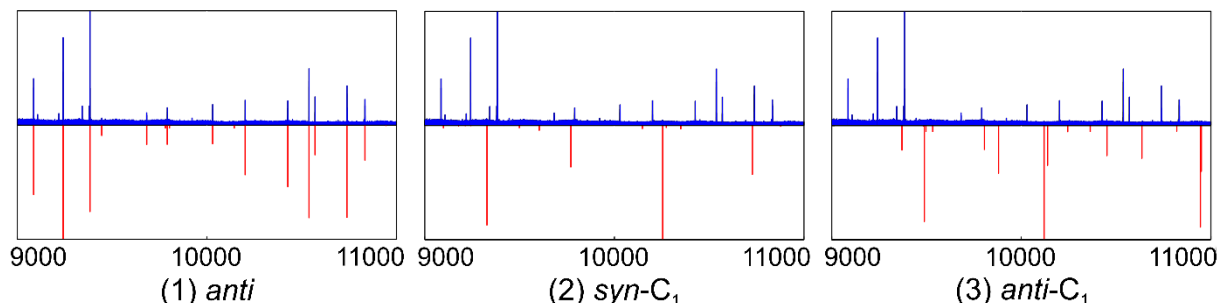


Figure 4.5: The upper trace of all sub-figures illustrates the experimental broadband scan from 9000 to 11000 MHz where all lines belonging to *syn*-2PT have been excluded. The lower trace of figure (1) shows the fitted spectrum of *anti*-2PT and those of figures (2) and (3) the theoretical spectrum of *syn*-C₁-2PT and *anti*-C₁-2PT, respectively. The present figure indicates that beside *syn*-2PT only the *anti*-conformer is present in the experimental spectrum. (Figure modified from Ref. [1].)

In the high resolution spectra small splittings from 2 to 50 kHz were observed for both conformers. They arise from the internal rotation of the methyl group and were primarily analysed for rotational transitions with high *J* and *K* quantum numbers. Figure 4.6 shows a high resolution measurement of the *b*-type $11_{1,10} \leftarrow 10_{2,9}$ transition which illustrates a typical

splitting into an A and an E symmetry species. For several transitions further smaller splittings were found, which might be caused by spin-spin or spin-rotation coupling of the hydrogen atoms, but most of the transitions only appeared broader. The average line width at half height (FWHM) is 20 kHz, although the variation between different transitions is significant. The estimated measurement accuracy, corresponding to $1/10^{\text{th}}$ of the average line width, is 2 kHz.

In total, 150 A and 51 E symmetry species lines were assigned for the *syn*-conformer of 2PT, as well as 103 A and 32 E species lines for the *anti*-conformer. The much smaller number of E species lines is due to the high rotational barrier, causing unresolved splittings in most of the transitions. As expected, only *a*- and *b*-type transitions were observed. The molecular parameters obtained from a fit using the program *XIAM* [40] are collected in Table 4.2. The assigned frequencies are listed in Table B.5 and B.6 in the Appendix. The angles between the methyl rotor and the principal axes could not be fitted and were fixed to values calculated at the MP2/6-311++G(d,p) level of theory, which predicts a non-planar geometry for both *syn*- and *anti*-2PT, in agreement with the results from isotopic substitution (see Section 4.3.4 and discussions which follow). The influence of the fixed values on the fit quality is, however, not significant. For comparison, the fits with the angles between the methyl rotor and the principal axes fixed to values calculated at the B3LYP-D3BJ/6-311++G(d,p) level, which predicts a planar geometry for both conformers, are given in Table B.7 in the Appendix. Because only transitions in the torsional ground state are available, the rotational constant F_0 of the methyl group could not be fitted and was fixed to 160 GHz, a value often found for methyl rotors.

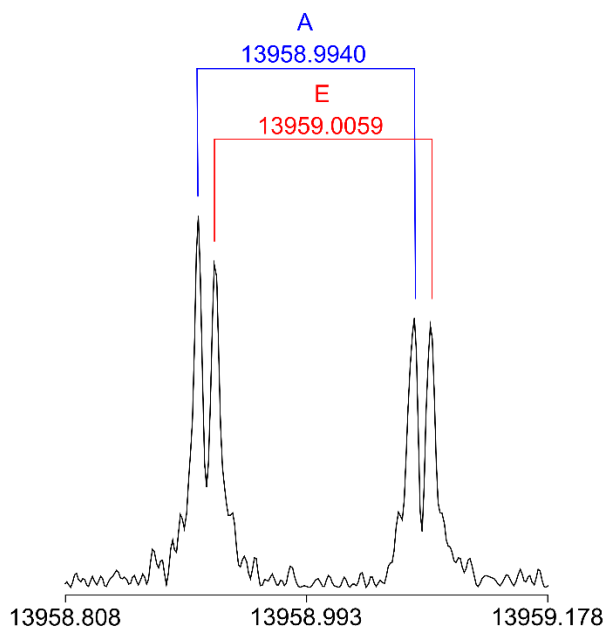


Figure 4.6: A high resolution spectrum of the *b*-type transition $11_{1,10} \leftarrow 10_{2,9}$ of *syn*-2PT. The splittings indicated by brackets are due to the Doppler effect; the frequencies are given in MHz.

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The polarization frequency is 13958.98 MHz. The A and E symmetry species are found at 13958.9940 MHz and 13959.0059 MHz, respectively, corresponding to a torsional splitting of 11.9 kHz. For this spectrum, 1168 free induction decays were co-added. (Figure modified from Ref. [1].)

Table 4.2: Molecular parameters of the *syn*- and *anti*-conformers of 2PT obtained with the program XIAM.

Par. ^a	Unit	<i>syn</i>	Calc. ^b	<i>anti</i>	Calc. ^b
A_0	MHz	3427.43880(19)	3393.970	3274.03476(39)	3234.681
B_0	MHz	877.177065(48)	865.960	905.747009(78)	897.435
C_0	MHz	704.893298(31)	695.289	716.231432(37)	709.719
D_J	kHz	0.01812(15)	0.0178	0.02330(31)	0.0237
D_{JK}	kHz	0.0749(27)	0.0718	0.0621(69)	0.0313
D_K	kHz	0.4473(93)	0.4816	1.842(58)	0.5442
d_1	kHz	-0.00370(10)	-0.0039	-0.00639(30)	-0.0059
d_2	kHz	-0.000275(69)	-0.0004	-0.00138(25)	-0.0092
V_3	cm ⁻¹	806.94(54)	929.3	864.5(88)	919.9
$\angle(i,a)$	deg	19.9 ^c	19.9	11.2 ^c	11.2
$\angle(i,b)$	deg	70.4 ^c	70.4	80.9 ^c	80.9
$\angle(i,c)$	deg	86.9 ^c	86.9	83.4 ^c	83.4
N_A/N_E^d	-	150/51		103/32	
σ^e	kHz	2.6		2.5	

^a All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. ^b Ground state rotational constants and centrifugal distortion constants from anharmonic frequency calculations, all other parameters from optimisations at the MP2/6-311++G(d,p) level of theory. ^c Fixed to the calculated values predicting a non-planar geometry, in agreement with the results from isotopic substitutions. ^d Number of A and E species transitions. ^e Standard deviation of the fit.

4.3.3. Isotopologues

As mentioned in Section 4.2.1., quantum chemical calculations predicted the propionyl group of the *syn*- and *anti*-conformers to be either perfectly in-plane or slightly tilted out of the thiophene frame, depending on the level of theory in use. To investigate this issue experimentally, it was searched for the spectra of the ^{34}S and three ^{13}C -isotopologues C(6), C(8) and C(9) in natural abundances of 4.25% and 1.07%, respectively [70], by using the method described in Section 3.3.3. and Ref. [1].

Only the ^{13}C isotopologues at the positions relevant to determine the orientation of the propionyl moiety were investigated. The search was time-consuming since ^{13}C signals of 2PT were quite weak and often underlay the much more intense ^{12}C signals. The C(2) atom lies very close to the centre of mass of the molecule. Therefore, the spectrum of its ^{13}C -isotopologue could not be captured because all signals are at nearly the same frequencies as those of the main isotopologue. Assuming that the thiophene ring is planar as expected for an aromatic system, the ^{34}S -isotopologue was chosen to substitute $^{13}\text{C}(2)$. The molecular parameters of four isotopologues of *syn*-2PT are collected in Table 4.3. The lists of fitted transitions and their residuals are available in Tables B.8 in the Appendix. Only the ^{34}S -isotopologue of *anti*-2PT could be assigned, but the number of lines is small (see also Table B.8). For the three *anti*-2PT ^{13}C -isotopologues, there were not enough observable transitions to support a convincing assignment, as the transitions were too weak or covered by much stronger ^{12}C signals. In addition, the transitions often fell in the resonance region of the spectrometer and were thus further masked by cavity resonance.

No internal rotation splittings were found for all measured isotopologue transitions.

Table 4.3: Rotational constants (in MHz) and centrifugal distortion constant D_J (in kHz) of four isotopologues of *syn*-2PT obtained with the program *XIAM*.

Par. ^a	³⁴ S	¹³ C(6)	¹³ C(8)	¹³ C(9)
A_0	3376.65668(41)	3426.27459(41)	3409.99595(54)	3424.61165(29)
B_0	870.92399(28)	875.10430(27)	869.790462(27)	857.46947(20)
C_0	698.70339(37)	703.50933(12)	699.391506(15)	691.999904(95)
D_J	0.0217(52)	0.01812 ^b	0.01812 ^b	0.01812 ^b
N^c	23	15	14	12
σ^d	3.9	2.5	3.0	1.6

^a All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. ^b Values of all centrifugal distortion constants except D_J of the ³⁴S species could not be fitted and are fixed to those of the main isotopologue given in Table 4.2. ^c Number of lines. ^d Standard deviation of the fit in kHz.

4.3.4. Structure Determination

The partial r_s structure of *syn*-2PT was derived from multiple isotopic data by using the rotational constants of the parent species given in Table 4.2 and those obtained for the four isotopologues collected in Table 4.3. The position of each substituted atom was first calculated using Kraitchman's equations [39] implemented in the program KRA available from the PROSPE website [49], which provides the absolute atomic coordinates in the principal axis system. The uncertainties were calculated according to Costain's rule [88]. The signs of the atom coordinates were taken to be consistent with the optimized geometry. The resulting atomic coordinates are given in Table 4.4. The bond lengths, bond angles, and the desired dihedral angle $\theta = \angle(\text{S1}, \text{C6}, \text{C8}, \text{C9})$ were determined with the program EVAL, also available at the PROSPE website [49], and are given in Table 4.5. These geometry parameters are compared with those of the equilibrium structure r_e obtained from geometry optimizations with the MP2, B3LYP-D3BJ and M06-2X methods. It has to be noted that the predicted values refer to the equilibrium configuration of the molecule, while vibrational effects affect the substitution geometry. This limits the accuracy of the obtained r_s structural parameters. A better alternative would be the semi-experimental equilibrium structure [89][90] which is unfortunately not possible due to the limited number of assigned isotopologues for *syn*-2PT.

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Table 4.4: Experimental atom positions of the partial substitution r_s structure of *syn*-2PT obtained by isotopic substitutions with Kraitchman's equations [39] as implemented in the program KRA [49]. For comparison, atom positions of the equilibrium r_e structures optimized at the MP2/6-311++G(d,p), B3LYP-D3BJ/6-311++G(d,p) and M06-2X/6-311++G(d,p) levels of theory are also given. Standard errors in parentheses are in the unit of the least significant digits.

	r_s			r_e^{MP2}		
	$ a / \text{\AA}$	$ b / \text{\AA}$	$ c / \text{\AA}$	$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$
S1	1.4459(10)	1.0663(14)	0.025(58)	1.456117	−1.068910	−0.001120
C6	1.1694(13)	0.2197(68)	0.046(32)	−1.185448	−0.244282	0.007579
C8	2.21342(68)	0.8730(17)	0.060(25)	−2.210229	0.878001	0.051818
C9	3.64496(41)	0.3512(43)	0.050(29)	−3.643985	0.365936	−0.032649
	r_e^{B3LYP}			r_e^{M06-2X}		
	$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$	$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$
S1	1.465167	−1.075649	0.000070	1.458905	−1.069740	−0.000049
C6	−1.184143	−0.241682	−0.000106	−1.186286	−0.241721	0.000022
C8	−2.222044	0.872099	−0.000075	−2.212429	0.876447	0.000077
C9	−3.656592	0.354577	0.000247	−3.640857	0.351739	0.000033

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Table 4.5: Bond lengths (in Å), bond angles and the $\angle(\text{S1}, \text{C6}, \text{C8}, \text{C9})$ dihedral angle (in degrees) of *syn*-2PT deduced from the atom coordinates given in Table 4.4. The signs of the r_s atom coordinates used to determine these parameters were taken to be consistent with the optimized geometry as indicated in the superscript.

	r_s^{MP2}	r_e^{MP2}	$r_s^{B3LYP-D3BJ}$	$r_e^{B3LYP-D3BJ}$	r_s^{M06-2X}	r_e^{M06-2X}
C6–C8	1.5113(52)	1.5204	1.5113(52)	1.5224	1.5113(52)	1.5177
C8–C9	1.5277(33)	1.5248	1.5277(33)	1.5250	1.5237(18)	1.5218
S1–C6–C8	151.62(33)	149.71	151.62(33)	150.45	151.62(33)	149.92
C6–C8–C9	113.56(31)	112.60	113.56(30)	113.14	113.66(26)	112.37
S1–C6–C8–C9	173.0(42)	178.36	–173.0(42)	–179.98	177.1(42)	180.00

4.4. Discussion

4.4.1. Conformational Stability

Four stable conformers of 2PT were predicted by quantum chemistry. Regarding the orientation of the carbonyl group, a *syn*- and an *anti*-form are stable. Their stability arises from interactions between the aromatic ring and the carbonyl group, as well as conjugation effects which favour planar forms due to a maximum overlap between the π -orbitals. The higher stability of the *syn*-form of 2PT is mainly due to electrostatic interaction between the oxygen atom of the carbonyl group and the sulphur atom in the ring [73]. The opposite charges on the oxygen and sulphur atoms stabilise the *syn*-conformers, as visualised in Figure 4.7 with the charge data obtained from NBO calculations [74] performed using the *Gaussian 16* program package [41]. For each of the *anti*- and *syn*-forms, two further conformers are stable. They differ by the orientation of the ethyl group (nearly in-plane or out-of-plane C_1), resulting in four conformers for 2PT. The stability between the forms varies in different molecules. The energetically most favourable conformer predicted by all levels of theory in use, *syn*-2PT, has a *syn*-orientation between the oxygen and sulphur atoms and an in-plane or “nearly in-plane” propionyl group. This is in agreement with the intensity observed in the spectrum under the used measurement conditions, where the most intense signals belong to *syn*-2PT. The *anti*- C_1 conformer is predicted to be highest in energy, which is confirmed by the experiment as it was not observed in the microwave spectrum. The stability of *syn*- C_1 - and *anti*-2PT is controversial because some levels predict that *syn*- C_1 is more stable, while *anti*-2PT is more stable in calculations at other levels. The latter matches the result from experiments, as beside *syn*-2PT, only *anti*-2PT was assigned. The spectrum of *anti*-2PT is slightly weaker than that of *syn*-2PT, but also quite intense, as illustrated in Figure 4.4. From the values of the dipole moment components given in Table 4.1, *a*-type transitions of *anti*-2PT are expected to be higher in intensity than those of *syn*-2PT. However, experimentally both *a*- and *b*-type transitions of the *syn*-conformer are always stronger, further confirming the energetical favourability of this conformer. The *a*- and *b*-dipole moment components of the two non-assigned C_1 conformers are very similar to the corresponding assigned ones. Therefore, low dipole moments are not the reason for their non-visibility in the spectrum. Obviously, a planar orientation of the ethyl group has a more significant impact on the conformational stability over electrostatic effects which would favour *syn*- C_1 -2PT over *anti*-2PT.

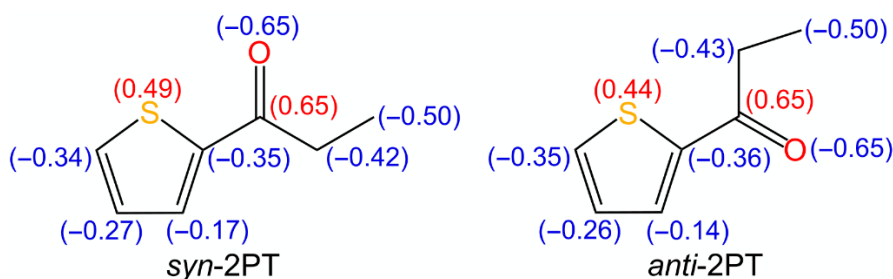


Figure 4.7: Charge distribution in *syn*- and *anti*-2PT obtained from NBO calculations at the MP2/6-311++G(d,p) level of theory. (Figure modified from Ref. [1].)

4.4.2. Quality of the Fits

In total 201 and 135 lines of the *syn*- and *anti*-conformers, respectively, were assigned and fitted with the program *XIAM*. The fit of *syn*-2PT has a standard deviation of 2.6 kHz, the fit of *anti*-2PT one of 2.5 kHz, which is in good agreement with the measurement accuracy of 2 kHz. The quality of both fits is therefore satisfactory. All rotational and centrifugal distortion constants are determined with high accuracy. The angles between the internal rotor axis and the principal axes cannot be fitted and have therefore been fixed to the values determined from geometry optimizations at the MP2/6-311++G(d,p) level of theory, as this level predicted a tilt angle of the ethyl group, which is consistent with results from the structure determination given in Section 4.3.4.

4.4.3. Molecular Parameters

The experimentally deduced rotational constants are in good agreement with the B_e constants predicted at the MP2/6-311++G(d,p) level of theory, which has eased the assignment process significantly. The basis set variation (see Table B.3 in the Appendix) shows, that the predicted rotational constants differ by 1% or less from the experimental values for most method-basis set combinations. The error compensations at the B3LYP-D3BJ/cc-pVTZ level of theory yield B_e constants which are in exact agreement with the experimental values of both conformers, followed by those of the Truhlar's M06-2X/cc-pVDZ level. Though it is not physically meaningful to compare predicted B_e constants with experimental B_0 constants, the B3LYP-D3BJ/cc-pVTZ and M06-2X/cc-pVDZ levels offer cost-efficient calculations with accidentally good accuracy to be useful in guiding the assignment of vibrational ground state microwave spectra. Therefore, they are recommended for molecules related to 2PT.

The distance of the C(6)–C(8) and the C(8)–C(9) bonds of 1.5113(52) and 1.5277(33) Å are typical values for a C–C single bond in an ethyl moiety, as found in previous investigations

where experimental bond lengths are reported for the ethyl group [87]. The dihedral angle $\theta = \angle(\text{S1}, \text{C6}, \text{C8}, \text{C9}) = 173.0(42)^\circ$ deduced from the partial r_s structure confirms a non-planar heavy atom skeleton of the most stable *syn*-conformer, which is predicted at some MP2 levels of theory. Because the signs of the coordinates cannot be determined from Kraitichman's equations, the quantum chemistry level chosen for the signs of the coordinates slightly affects the obtained structural properties. This especially influences the *c*-coordinates since their signs are level-dependent. It is not surprising, because the values of the *c*-coordinates are close to zero, which is also the reason why they are determined with much less accuracy than those of the *a*- and *b*-coordinates (see Table 4.4). The dihedral angle θ is affected most significantly by the sign choice for the *c*-coordinates and varies between $173.0(42)^\circ$ and $177.1(42)^\circ$ (see Table 4.4). Though there is only a thin border between “planar” and “not planar” because the tilt angle, if it exists, is quite small, a comparison with the predicted θ values of either 180° in the case of a planar structure or about 178° for a non-planar structure shows that the experimental structure of 2PT is *not* planar. The experimentally determined *c*-coordinates given in Table 4.4 also confirm this conclusion.

The inertial defects $\Delta_c = I_c - I_a - I_b$ of the *syn*- and *anti*- conformers are $-6.635 \text{ u}\text{\AA}^2$ and $-6.720 \text{ u}\text{\AA}^2$, respectively. The inertial defects $\Delta_c = I_c - I_a - I_b$ of “perfect C_s ” molecules containing an ethyl group, for example the *cis-trans* conformer of ethylnitrite ($\Delta_c = -6.422 \text{ u}\text{\AA}^2$) [91] and the C_s conformer of 2-ethylfuran ($-6.483 \text{ u}\text{\AA}^2$) [87] indicate the contribution of four out-of-plane hydrogen atoms on this parameter. The inertial defect of $-6.635 \text{ u}\text{\AA}^2$ for *syn*-2PT and $-6.720 \text{ u}\text{\AA}^2$ for the *anti*-conformer is higher than those of *cis-trans*-ethylnitrite and 2-ethylfuran, further supporting a non-planar structure of *syn*-2PT and *anti*-2PT. A truly non-planar conformer with a completely out-of-plane ethyl group however would have a significantly higher inertial defect, as the C_1 conformer of 2-ethylfuran ($-29.851 \text{ u}\text{\AA}^2$) [87] shows.

4.4.4. Methyl Internal Rotation

Barriers to internal rotation of ethyl methyl groups are usually higher than 1000 cm^{-1} , which often means the torsional splittings cannot be resolved. Therefore, in many investigations, no information on the methyl torsion was reported, though the molecules contain one or more methyl groups, e.g. in Ref. [92][93][94][95][96]. In some cases where the barrier heights could be determined, values of over 1000 cm^{-1} have often been found [97][98]. For 2PT, the barrier to internal rotation of $806.94(54) \text{ cm}^{-1}$ for the *syn*-conformer and $864.5(88) \text{ cm}^{-1}$ for the *anti*-conformer is significantly lower. This can be explained by the presence of the carbonyl group to which the ethyl group is attached, similar to the cases of ethyl methyl ketone

(763.87(65) cm^{-1}) [80], diethyl ketone (771.93(27) cm^{-1}) [62], methyl propionate (820.46(99) cm^{-1}) [85], propionic acid (818(11) cm^{-1}) [99] and propionyl fluoride (839(21) cm^{-1}) [100]. Though the number of investigated molecules containing a propionyl group (an ethyl group attached to a carbonyl bond) is rather small, there are enough data points to support the conclusion that the torsional barrier of the methyl group in the propionyl moiety is always around 800 cm^{-1} .

Comparing the experimentally deduced rotational barriers with the calculated ones (see Table B.3 in the Appendix) shows that, like the prediction of the acetyl methyl barrier in 2AT (Chapter 3, [4]), the prediction of the propionyl barrier is just as difficult and largely inaccurate. While for *syn*-2PT the B3LYP-D3 method calculates overall the values closest to the experimentally determined ones, the accuracy still remains highly dependent on the chosen basis set. Overall, only 10 out of the 96 employed method/basis set combinations are accurate to within 10 cm^{-1} of the experimental value. For the *anti*-conformer the accuracy is even lower, with only 3 out of 96 calculations achieving a deviation of less than 10 cm^{-1} . Furthermore, in the case of *anti*-2PT the performance of the B3LYP-D3 method is significantly worse, meaning that no clear trend can be deduced to judge which method/basis set combination is suitable to predict torsional barriers for propionyl groups.

4.5. Conclusion

Quantum chemical calculations predict four stable conformers for 2PT with different orientations of the propionyl group. The microwave spectra of two conformers, *syn*- and *anti*-2PT, were assigned under molecular jet conditions. The very small splittings due to internal rotation could be resolved for both conformers. Analysing the splittings with the program *XIAM* yielded torsional barriers of 806.94(54) cm^{-1} for the *syn*- and 864.5(88) cm^{-1} for the *anti*-conformer. Though the *syn*-configuration is favoured by electrostatic interactions of the opposite charges of the oxygen and sulphur atoms, the conformational stability of 2PT is decided by the orientation of the ethyl group. The planarity of 2PT is a controversial issue for calculations at different levels of theory, regarding whether the propionyl group is in-plane with the thiophene ring or not. Partial r_s structure determination from isotopic substitution of the most stable *syn*-conformer convincingly confirmed that 2PT is not planar. There is a tiny, but non-zero tilt angle between the ethyl group and the thiophene ring.

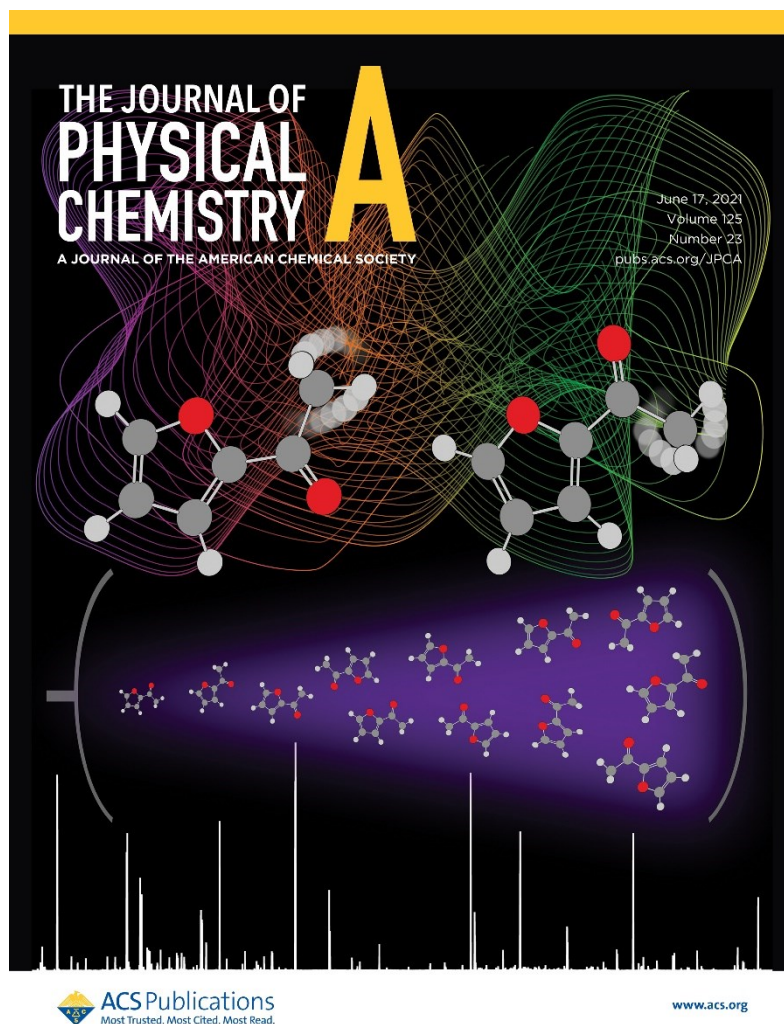
5. 2-Acetylfuran

The main text passages of this chapter have already been published in Ref. [2]:

Christina Dindić, Arne
Lüchow, Natalja Vogt, Jean
Demaion and Ha Vinh Lam
Nguyen

**Equilibrium Structure in
the Presence of Methyl
Internal Rotation:
Microwave Spectroscopy
and Quantum Chemistry
Study of Two Conformers
of 2-Acetylfuran**

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Parts of the publication are reproduced (and adapted) with permission from *J. Phys. Chem. A* 2021, 125, 4986-4997. Copyright 2021 American Chemical Society. Christina Dindić performed measurements, quantum chemical calculations, spectral assignments and wrote the main part of the manuscript. Ha Vinh Lam Nguyen, Arne Lüchow, Natalja Vogt and Jean Demaison co-wrote the manuscript. The quantum chemical calculations and structure determination performed by Natalja Vogt and Jean Demaison featured in the publication have not been reproduced in this dissertation. Figures taken from Ref. [2] have been modified for consistent formatting in this dissertation.

5.1. Introduction

2-acetylfuran (2AF) is the oxygen analogue to 2AT (Chapter 3, [4]). It was investigated to gain insights into the effect the heteroatom in the ring has on both the molecular structure and internal rotation. It is known from the literature that the barriers to methyl internal rotation in oxygen containing molecules are higher than those in their sulphur analogues. Some examples of the barriers in general cases are dimethyl sulphide (735.8 cm^{-1}) [26] vs dimethyl ether (944.3 cm^{-1}) [27] or methyl thioformate (127.5 cm^{-1}) [28] vs methyl formate (370.9 cm^{-1}) [29]. For molecules containing a furan or thiophene moiety, available examples are 194.1 cm^{-1} for 2-methylthiophene [30] vs. 412.9 cm^{-1} for 2-methylfuran [31], 258.8 cm^{-1} for 3-methylthiophene [101] vs. 380.5 cm^{-1} for 3-methylfuran [102], or 248.0 cm^{-1} for 2,5-dimethylthiophene [21] vs. 439.1 cm^{-1} for 2,5-dimethylfuran [22]. It was of interest to see if the pair 2AF and 2AT would follow this trend.

5.2. Quantum Chemical Calculations

5.2.1. Conformational Analysis

To sample the conformations of 2AF, the dihedral angle $\alpha = \angle(\text{O1}-\text{C2}-\text{C6}=\text{O7})$ was varied in steps of 10° (for atom numbering see Figure 5.1). All other geometry parameters were optimized at the MP2/6-311++G(d,p) [42][59] level using the *Gaussian 16* program package [41]. This level was applied because it has yielded reliable rotational constants to guide the assignment in many previous investigations found in the literature [103][104][105]. As expected from the proton magnetic resonance study on 2AF [106] and studies on similar molecules [107][24][108] two conformers were found at $\alpha = 0^\circ$ (called *syn*) and 180° (called *anti*) on the potential energy curve illustrated in Figure 5.2.

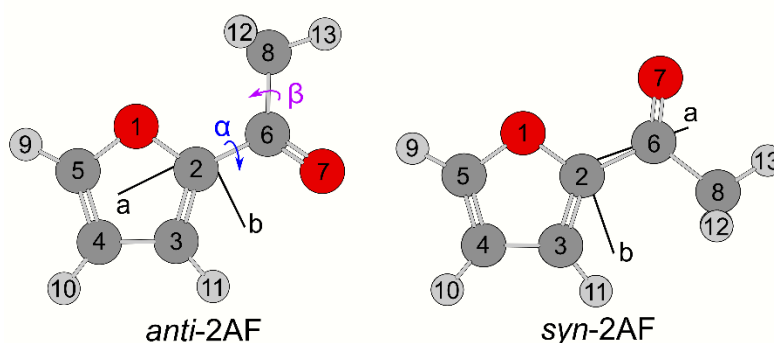


Figure 5.1: Molecular structures of the two conformers of 2AF optimized at the MP2/6-311++G(d,p) level of theory in their principal axes of inertia. Atom numbering is given for both conformers; the dihedral angles $\alpha = \angle(\text{O1}-\text{C2}-\text{C6}=\text{O7})$ and $\beta = \angle(\text{C2}-\text{C6}-\text{C8}-\text{H})$ are defined

for *anti*-2AF. Oxygen atoms are marked in red, carbon atoms in dark grey, and hydrogen atoms in light grey. H14 lies behind H12. (Figure modified from Ref. [2].)

The structures of two conformers (corresponding to minima on the potential energy function in Figure 5.2) were first optimized under full geometry relaxation, revealing C_s symmetry. The atomic coordinates are given in Table C.1 in the Appendix. Frequency calculations confirmed both to be stable conformers. The more favourable structure, *anti*-2AF, is 5 kJ/mol lower in energy than *syn*-2AF (including zero-point corrections). This is essentially the same as the energy difference found for the two conformers of 2-acetyl-5-methylfuran [24]. The quantum chemical results are summarized in Table 5.1.

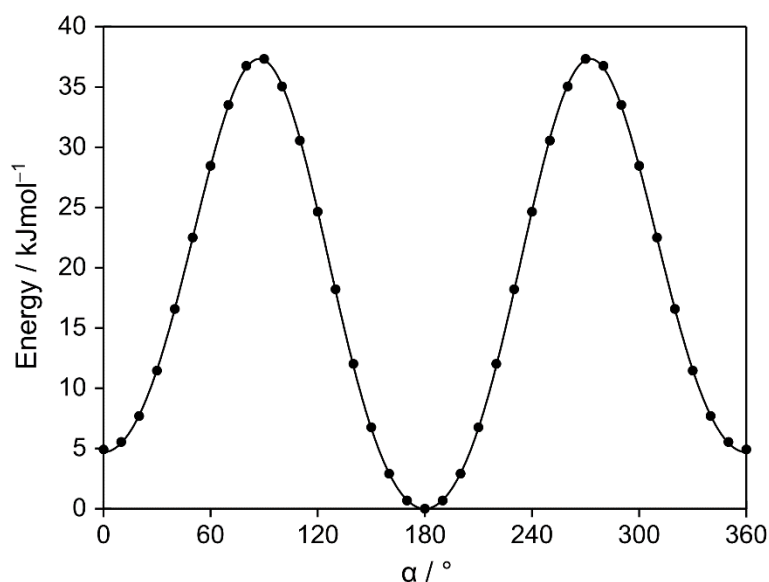


Figure 5.2: The relaxed potential energy scan of 2AF obtained by rotating the acetyl group about the C2–C6 bond, i.e. varying the angle α in 10° steps, calculated at the MP2/6-311++G(d,p) level of theory. The energies are given relative to the lowest energy conformation at 180° with $E = -381.7257264$ Hartree, which corresponds to the *anti*-conformer. (Figure modified from Ref. [2].)

5.2.2. Basis Set Variations

As described in Section 3.2.2. the structures of both conformers were re-optimized using different combinations of methods and basis sets also with *Gaussian 16* [41]. The resulting rotational constants are given in Tables C.2 and C.3 in the Appendix and will be discussed later in comparison to the experimentally determined values.

Table 5.1: Equilibrium rotational constants, dipole moments, and the relative energy including zero-point corrections (E_{rel}) between the two conformers of 2AF calculated at the MP2/6-311++G(d,p) level of theory.

	Unit	<i>anti</i>	<i>syn</i>
A_e	MHz	4820.6	4859.5
B_e	MHz	1630.5	1616.4
C_e	MHz	1227.7	1222.2
μ_a	D	2.89	-2.34
μ_b	D	-2.25	4.06
μ_c	D	0.00	0.00
E_{rel}	kJ·mol ⁻¹	0.00 ^a	5.02

^a Absolute value at -381.61688694 Hartree.

5.2.3. Methyl Internal Rotation

To predict the barrier to internal rotation of the methyl group, geometry optimizations at the MP2/6-311++G(d,p) level of theory were carried out by varying the dihedral angle $\beta = \angle(\text{C2-C6-C8-H})$ in steps of 10° , while allowing all other parameters to relax. The threefold potentials obtained for both conformers are shown in Figure 5.3, yielding predicted V_3 terms of 284.0 cm^{-1} and 234.8 cm^{-1} for *anti*- and *syn*-2AF, respectively; the coefficients of the Fourier expansion used to plot the potential curves can be found in Table C.4. A-E splittings from a methyl torsion with such hindering barriers were expected to be resolved in the microwave spectrum with the experimental setup in use.

The barriers to internal rotation of *anti*- and *syn*-2AF were furthermore calculated with all method/basis set combinations used in Section 5.2.2. for the structure optimization. The calculated values are listed in Table C.2 and C.3 in the Appendix and will be discussed in Section 5.4.4. in comparison with the experimental values.

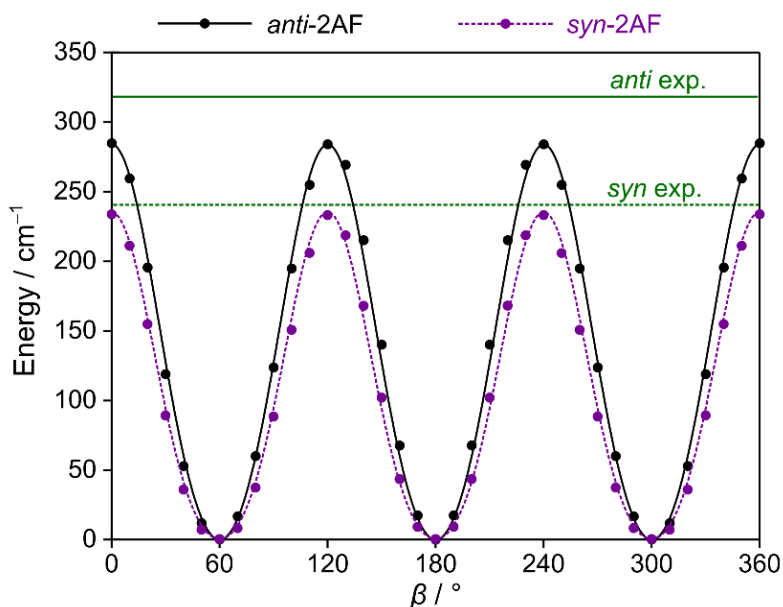


Figure 5.3: Potential energy curves of *anti*- and *syn*-2AF depending on the rotation of the methyl group about the C6-C8 bond upon variation of β . Calculations were carried out at the MP2/6-311++G(d,p) level of theory. The predicted V_3 potentials are 284.0 cm^{-1} and 234.8 cm^{-1} for *anti*- and *syn*-2AF, respectively; the respective experimental values of 319.8 cm^{-1} and 239.8 cm^{-1} are marked by horizontal lines. (Figure modified from Ref. [2].)

5.3. Microwave Spectroscopy

5.3.1. Experimental Setup

A scan from 11.0 to 15.3 GHz as a series of overlapping spectra with a step width of 0.25 MHz was recorded using a molecular jet FTMW spectrometer operating in the frequency range from 2.0 to 26.5 GHz [33]. 2AF was purchased from Sigma-Aldrich, Eschborn, Germany, with a stated purity of 99 % and used without further purification. The substance was put on a piece of pipe cleaner and placed upstream the nozzle with a backing pressure of about 2 bar helium as the carrier gas. All signals appearing in the survey spectrum were later remeasured at higher resolution with an experimental accuracy of 2 kHz [69].

5.3.2. Spectral Assignment

Based on the equilibrium rotational constants B_e calculated at the MP2/6-311++G(d,p) level of theory given in Table 5.1, the rigid rotor spectrum of *anti*-2AF was predicted using the program *XIAM* [40], as this conformer was expected to be energetically more favourable. The predicted spectrum matched the experimental one very well and the assignment was straightforward,

starting with the very intense $J = 4 \leftarrow 3$ *a*- and *b*-type transitions with K_a and $K_c = 0$ or 1. Splittings between the A and E torsional components of most transitions are relatively small, ranging from a few kHz to about 50 MHz, which simplified the extension of the rigid rotor fit to include the effect of methyl internal rotation. An example of the $6_{16} \leftarrow 5_{15}$ transition is shown in Figure 5.4.

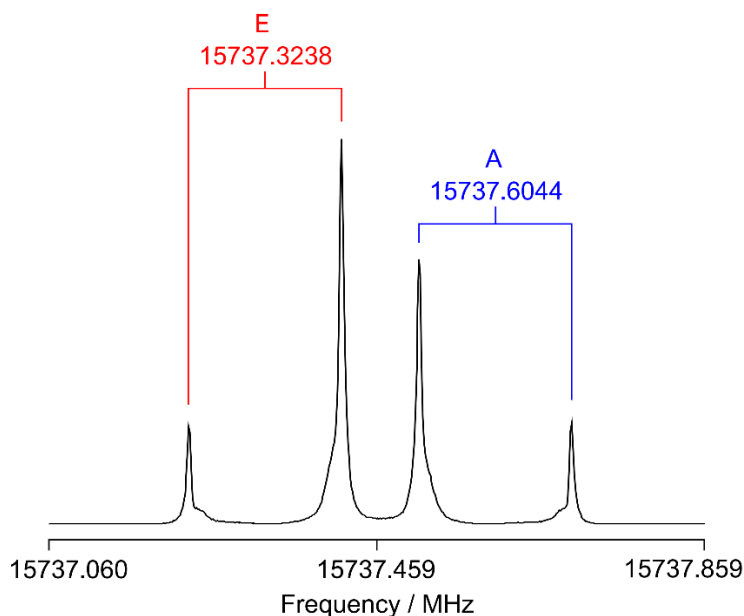


Figure 5.4: A high resolution measurement of the $6_{16} \leftarrow 5_{15}$ transition of *anti*-2AF recorded at 15737.46 MHz. For this spectrum 115 decays were co-added. The splittings indicated by brackets are due to the Doppler effect; the mean frequency is the transition frequency. The A-E torsional splitting is 280.6 kHz. (Figure modified from Ref. [2].)

After *anti*-2AF was assigned, many lines with weaker intensity remained in the spectrum, which could be assigned to *syn*-2AF following the same procedure. In total 141 A and 152 E species transitions were measured for *anti*-2AF as well as 106 A and 107 E lines for *syn*-2AF. The average line width at half height (FWHH) is 20 kHz. Therefore, the estimated measurement accuracy, corresponding to $1/10^{\text{th}}$ of the average line width, is 2 kHz. Most assigned transitions for both conformers are *a*- and *b*-type, as expected from the calculated dipole moment components given in Table 5.1. A few E species *c*-type and *x*-type transitions (ΔK_a and ΔK_c are both even) occurred as given in the frequency lists. For those perturbation allowed transitions, the K_a and K_c quantum numbers have no meaning and they only indicate the order of energy. The molecular parameters of both conformers obtained from the fits using the program *XIAM* are collected in Table 5.2. The assigned frequencies are listed in Table C.5 and C.6 in the Appendix. Because of the strong correlation between the rotational constant F_0 of

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the acetyl methyl group and the V_3 potential term, it was decided to set F_0 to the value calculated at the MP2/6-311++G(d,p) level.

Table 5.2: Experimental spectroscopic parameters of *anti*- and *syn*-2AF obtained with the program XIAM.

Par. ^a	Unit	<i>anti</i>	<i>syn</i>
A_0	MHz	4852.12131(18)	4902.42528(31)
B_0	MHz	1631.236495(66)	1615.10359(13)
C_0	MHz	1230.588617(57)	1224.656525(52)
D_J	kHz	0.06702(44)	0.06485(50)
D_{JK}	kHz	0.1091(19)	0.0778(28)
D_K	kHz	0.5826(86)	0.714(12)
d_1	kHz	−0.02009(22)	−0.01771(33)
d_2	kHz	−0.00260(12)	−0.00190(23)
V_3	cm ^{−1}	319.777(12)	239.780(13)
F_0	GHz	158.0 ^b	158.1 ^b
$D_{p_i^2 J}$	kHz	51.02(69)	74.42(54)
$D_{p_i^2 K}$	kHz	−216.1(26)	−539.2(31)
$D_{p_i^2 -}$	kHz		28.25(50)
$\angle(i, a)$	deg	60.3104(50)	53.7374(75)
$\angle(i, b)$	deg	29.6896(50)	36.2626(75)
$\angle(i, c)$	deg	90.0 ^c	90.0 ^c
Δ_c^d	uÅ ²	−3.289	−3.326
N_A/N_E^e	-	141/152	106/107
σ^f	kHz	2.8	2.2

^a All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. ^b Fixed to the calculated value. ^c Fixed due to symmetry. ^d Pseudo inertial defect. ^e Number of A and E species transitions. ^f Standard deviation of the fit.

5.3.3. Isotopologues

After transitions of both conformers had been assigned and removed from the scan, many lines still remained. It was suspected that they belong to the ¹³C-isotopologues of the more stable *anti*-conformer. To predict the ¹³C transition frequencies, the method described in Section 3.3.3. and Ref. [1] was used, and all ¹³C-isotopologues of *anti*-2AF could be assigned in their natural abundances of 1.07% [70]. Many isotopologue signals were visible in the scan as shown in Figure 5.5. In the high resolution measurements splittings caused by methyl internal rotation could be resolved, allowing the determination of the torsional barrier. Due to the position near the centre of mass of the molecule (see Figure 5.1), many transitions of ¹³C(2)

were overshadowed by those of the parent species. Nevertheless, as the difference between the $^{13}\text{C}(2)$ and the main isotopologue frequencies increases with higher K -quantum numbers, it was possible to observe 15 A and 13 E species $^{13}\text{C}(2)$ transitions with $K_a \geq 1$. Lines of the two ^{18}O -isotopologues with natural abundances of 0.21% [70] were not visible in the scan, but the search by performing small scans around the predicted frequencies with a higher number of co-added decays per each scan step was successful. The assigned transitions of all *anti*-2AF isotopologues are listed in Table C.7 in the Appendix; the fitted molecular parameters obtained with the program *XIAM* are given in Table 5.3. The A and E species of the parent species as well as the isotopologues were also fitted individually with the program *SFLAMS* [12] to confirm the assignments; the fits are given in Table C.8 in the Appendix.

A few signals belonging to the ^{13}C -isotopologues of *syn*-2AF could be measured, but there were not enough transitions to achieve any satisfactory fit. A few weak lines remained unassigned in the spectrum, belonging to neither one of the two parent species nor their isotopologues. They might be due to complexes or impurities.

Based on the data of the assigned isotopologues a structure determination for *anti*-2AF was possible, which can be found in Ref. [2].

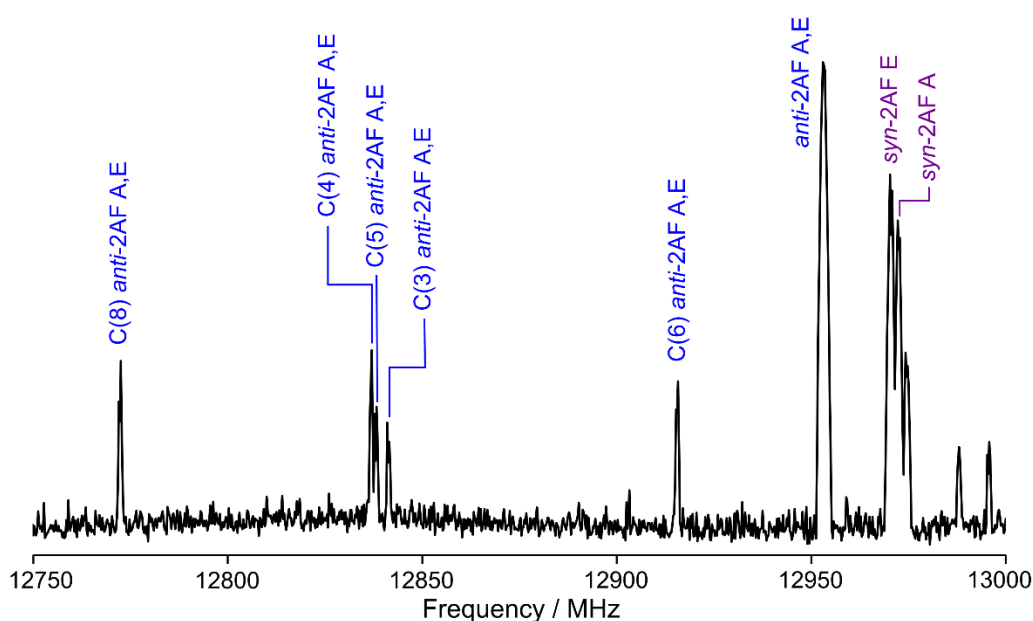


Figure 5.5: A portion of the scan of 2AF in the frequency range from 12750 to 13000 MHz recorded by overlapping spectra with 50 co-added decays per each spectrum. Lines belonging to the $4_{14} \leftarrow 3_{03}$ transition are labelled with the corresponding conformer and torsional species. Lines belonging to the ^{13}C -isotopologues are marked with the atom position in parentheses. The intensities are given in a logarithmic scale in an arbitrary unit. The temperature of the molecular jet was approximately 1-2 K. (Figure modified from Ref. [2].)

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Table 5.3: Molecular parameters of the ^{18}O - and ^{13}C -isotopologues of *anti*-2AF obtained with the program *XIAM*.

Par. ^a	Unit	$^{18}\text{O}(1)$	$^{13}\text{C}(2)$	$^{13}\text{C}(3)$	$^{13}\text{C}(4)$	$^{13}\text{C}(5)$	$^{13}\text{C}(6)$	$^{18}\text{O}(7)$	$^{13}\text{C}(8)$
A_0	MHz	4753.7145(11)	4851.26803(18)	4788.23180(31)	4836.0802(10)	4826.69153(30)	4851.62252(34)	4733.6625(57)	4785.32782(48)
B_0	MHz	1625.85294(28)	1631.32190(18)	1626.61962(13)	1605.28043(13)	1609.52367(12)	1620.83887(11)	1588.78241(10)	1608.39059(17)
C_0	MHz	1221.13177(20)	1230.58544(21)	1223.828070(78)	1214.751159(84)	1216.583064(70)	1224.630867(79)	1198.81329(10)	1213.29183(11)
D_J	kHz	0.0668(14)	0.06702 ^b	0.06709(67)	0.06568(74)	0.06498(63)	0.06632(59)	0.0645(12)	0.06688(95)
D_{JK}	kHz	0.1091 ^b	0.1091 ^b	0.0962(94)	0.1011(51)	0.1091 ^b	0.0988(52)	0.1091 ^b	0.0863(93)
d_1	kHz	-0.0196(17)	-0.02009 ^b	-0.01907(64)	-0.02017(64)	-0.01883(65)	-0.01835(58)	-0.02009 ^b	-0.0193(10)
d_2	kHz	-0.00260 ^b	-0.00260 ^b	-0.00202(61)	-0.00315(50)	-0.00210(59)	-0.00180(43)	-0.00260 ^b	-0.00321(89)
V_3	cm^{-1}	319.771(77)	319.933(31)	319.673(28)	319.677(24)	319.656(28)	319.894(23)	319.607(63)	319.929(37)
$D_{p_{IK}^2}$	kHz	-216.1 ^b	-216.1 ^b	-207(16)	-167(19)	-176.2(84)	-202.5(95)	-216.1 ^b	-205(13)
$\angle(i,a)$	deg	60.892(29)	60.301(13)	60.023(11)	59.981(10)	60.758(10)	60.3897(92)	61.795(25)	59.582(16)
$\angle(i,b)$	deg	29.1075(29)	29.698(13)	29.976(11)	30.018(10)	29.241(10)	29.6103(92)	28.204(25)	30.418(16)
Δ_c^c	$\text{u}\text{\AA}^2$	-3.291	-3.290	-3.289	-3.289	-3.289	-3.289	-3.289	-3.289
N_A/N_E^d	-	22/21	15/13	42/38	43/38	48/33	43/38	20/20	45/37
σ^e	kHz	2.1	2.5	1.7	1.5	1.6	1.6	1.6	2.3

^a All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. $\angle(i,c)$ is fixed to 90° due to symmetry in all fits. F_0 is fixed to the calculated value (158.0 GHz). ^b Values of all centrifugal distortion constants and the higher order parameters $D_{p_{IJ}^2}$, $D_{p_{IK}^2}$, and $D_{p_{I-}^2}$ were fixed to those of the main isotopologue listed in Table 5.2 if no error in parentheses is given. ^c Pseudo inertial defect. ^d Number of A and E species transitions. ^e Standard deviation of the fit.

5.4. Discussion

5.4.1. Conformational Stability

The preferred stability of five-membered heterocycles with a carbonyl-group-containing substituent at the second position of the ring for either a *syn*- or an *anti*-orientation has been extensively studied [73] and demonstrated in many microwave spectroscopic investigations where information on conformations of a molecule and their stability can be deduced with confidence. In furan derivatives, electrostatic interactions between the oxygen atom of the ring and that of the carbonyl group, both carrying a negative charge, decrease the stability of the *syn* form, making the *anti*-conformer the more stable one, as proven in the cases of furfural [107], 5-methylfurfural [108], 2-acetyl-5-methylfuran [24], and 2AF. The greater stability of the *anti*-orientation in 2AF due to electrostatic interactions is shown in Figure 5.6 by the charge distribution obtained from NBO calculations [74] performed using the *Gaussian 16* program package [41].

Compared to the observations found for similar thiophene derivatives such as 2AT (Chapter 3, [4]), 2PT (Chapter 4, [1]) and 2-thiophenecarboxaldehyde [71][72] it becomes clear that the heteroatom in the ring significantly affects the conformational stability. In the thiophenes the *syn*-conformer is always the energetically more stable one. Obviously, exchanging oxygen with sulphur reverses the conformational stability. A reason for the preference of one form (*syn* or *anti*) may be the different electrostatic interaction between the oxygen atom of the carbonyl group and the sulphur in the thiophene ring of 2AT or the oxygen atom in the furan ring of 2AT. The negative charges on the oxygen atoms of 2AF stabilise the *anti*-conformer [2], while the *syn*-form is favoured by the opposite charges on the oxygen and sulphur atoms in 2AT, as visualised also in Figures 3.7 and 5.6 with the charge data obtained from NBO calculations [41]. [4]

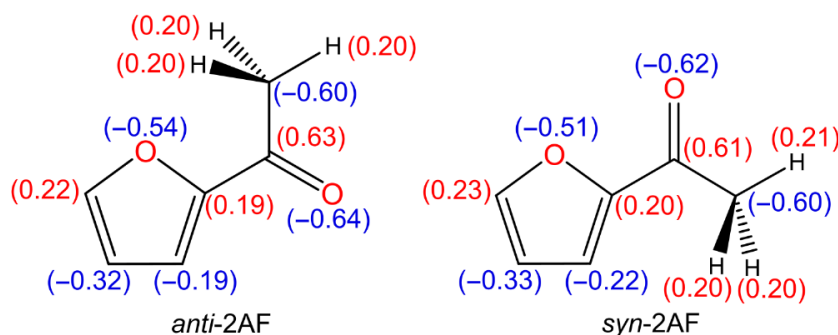


Figure 5.6: Charge distribution in *anti*- and *syn*-2AF obtained from NBO calculations at the MP2/6-311++G(d,p) level of theory. (Figure modified from Ref. [2].)

5.4.2. Quality of the Fits

The standard deviation of all fits is between 1.5 and 2.8 kHz, close to the measurement accuracy of about 2 kHz of the spectrometer. The three rotational constants were determined with high accuracy for both conformers and all assigned isotopologues. The centrifugal distortion constants D_J , D_{JK} , D_K , d_1 , and d_2 were also deduced with high accuracy for both 2AF conformers but not all of them could be determined for each isotopologue. The same is true for the higher order terms $D_{p_l^2 J}$ and $D_{p_l^2 K}$, while $D_{p_l^2 -}$ could be determined only for *syn*-2AF, which has a lower V_3 term. These parameters describe the centrifugal distortion of the methyl group upon internal rotation.

5.4.3. Molecular Parameters

Comparing the rotational constants predicted for the equilibrium structure r_e using different methods and basis sets (see Tables C.2 and C.3 in the Appendix) with the experimentally determined ones, the best agreement was achieved for both conformers with the B3LYP-D3(BJ) method in combination with the 6-311G(d,p) basis set with or without diffuse functions. Error compensation, giving the right answer for the wrong reason, is most likely responsible. Applying the three levels B3LYP-D3BJ/6-311G(d,p), B3LYP-D3BJ/6-311+G(d,p), and B3LYP-D3BJ/6-311++G(d,p), an excellent match was found between the X_e and X_0 rotational constants for 2-acetyl-5-methylfuran [24], but the agreement for furfural [107] and 5-methylfurfural [108] is only moderate, as given in Table C.9 of the Appendix. Therefore, these levels only seem to be cost-efficient methods to access starting values of the rotational constants to guide the assignment for furfural derivatives with an acetyl substituent.

The inertial defects $\Delta_c = I_c - I_a - I_b$ of the *anti*- and *syn*- conformers are -3.289 uÅ^2 and -3.326 uÅ^2 , respectively. For the isotopologues of *anti*-2AF the value changes only marginally. For an in depth discussion on the structure of 2AF, see Ref. [2].

5.4.4. Methyl Internal Rotation

The barrier hindering the internal rotation of the methyl group is well-determined for both conformers and all heavy atom isotopologues of the *anti*-conformer. The barrier height of the parent species of *anti*-2AF is $319.777(12) \text{ cm}^{-1}$. While the value found for its isotopologues is not exactly the same, it varies only within a range of $\pm 0.2 \text{ cm}^{-1}$ (less than 0.1 %). The barrier to internal rotation is thus almost independent from isotopic substitution, as also found for many molecules with methyl internal rotation in the literature [109][110][111] as well as the sulphur analogue 2AT (Chapter 3, [4]). In some special cases like malonaldehyde, isotopic substitution

breaks the molecular symmetry so strongly, that the proton tunnelling is quenched and splittings arising from this LAM vanish [112]. But obviously for 2AF, it does not have sufficient impact to affect the methyl torsion.

A comparison between the experimental and predicted values of the rotational barriers for 2AF (see Table C.2 and C.3 in the Appendix) shows that, similar to *syn*-2AT (see Section 3.4.4.), the MP2 and M06-2X methods perform best, although there is significant variation depending on the basis set in use. For *anti*-2AF the calculations at the MP2/6-311G(3df,3pd) and M06-2X/6-311++(3df,3pd) levels of theory stand out as the only ones accurate to within 10 cm⁻¹. For the *syn*-conformer the same basis set does not perform as well. Here the M06-2X/(aug-)cc-pVTZ and MP2/6-311G(df,pd) levels are better.

Figure 5.7 shows several furan derivatives containing at least one methyl internal rotor. The comparison clearly illustrates the dependence of the methyl torsion on electrostatic interactions which expand over the aromatic system. The presence of a carbonyl substituent with its negative mesomeric and inductive effects decreases the torsional barrier of the ring methyl group (marked in blue in Figure 5.7) of 2-methylfuran (**1**) (412.9 cm⁻¹) [31] notably to about 360 cm⁻¹ in both 5-methylfurfural (**3**) [108] and 2-acetyl-5-methylfuran (**5**) [24]. The positive inductive effect of a methyl group affects the electronic distribution in the furan ring differently, and thus causes an increase of the ring methyl torsional barrier in 2,5-dimethylfuran (**2**) [22] to 439.1461(83) cm⁻¹ in comparison with 2-methylfuran.

The barrier height of the acetyl methyl group (marked in red in Figure 5.7) in *syn*- (**4a**) and *anti*-2AF (**4b**) is higher than that of the corresponding conformer of 2-acetyl-5-methylfuran (**5a** and **5b**) [24]. The only structural difference between the two molecules is the addition of a methyl group on the furan ring, making the moiety connected to the acetyl group longer. Recently, *Andresen et al.* reported on the so-called chain-length effects observed for linear aliphatic ketones containing an acetyl group. The torsional barrier of the acetyl methyl group is lower in ketones with longer alkyl chain [11]. The same effects might explain the torsional barrier of 2-acetyl-5-methylfuran being lower than that of 2AF. The difference is more pronounced for the *syn*-conformers (239.8 cm⁻¹ in 2AF (**4b**) vs. 212.7 cm⁻¹ in 2-acetyl-5-methylfuran (**5b**)) than for the *anti*-conformers (319.8 cm⁻¹ (**4a**) vs. 307.8 cm⁻¹ (**5a**), respectively), because for the former, the methyl group “senses” a longer substituent when a methyl group is added at the fifth position of the ring than it does in the *anti*-conformation.

The barrier height of 239.780(13) cm⁻¹ of *syn*-2AF is significantly lower than that of the *anti*-conformer, which is also the observation found for 2-acetyl-5-methylfuran (see Figure 5.7) as well as for methyl vinyl ketone (*ap* conformer with 434 cm⁻¹ and *sp* conformer with 377 cm⁻¹)

[113] and ionone (*ap* conformers with about 440 cm⁻¹ and *sp* conformers with approximately 350 cm⁻¹, respectively) [114]. Currently, it is known that different electronic configurations within a conjugated double bond system significantly change the torsional barrier of an acetyl methyl group, but more data points are needed to draw a conclusion to explain this observation.

When the sulphur analogue 2AT (**6a** and **6b**) (Chapter 3, [4]) is compared with the *syn*- and *anti*-conformers of 2AF it becomes apparent however that here the higher rotational barrier is found for *syn*-2AT, counter to both similar acetyl furans. The more stable conformer seems to possess a higher barrier to internal rotation of the acetyl methyl group. From the discussion on conformational stability, this supports the suspicion that electrostatic interaction plays an important role for the acetyl methyl torsion.

Furthermore, the direct comparison of the barrier heights of *syn*-2AT and *syn*-2AF (330.2 cm⁻¹ vs. 239.8 cm⁻¹), as well as *anti*-2AT and *anti*-2AF (296.0 cm⁻¹ vs. 319.8 cm⁻¹), surprisingly shows that for the *syn*-conformers, the higher torsional barrier is observed for the sulphur analogue. This is in contrast to the frequent observation that the torsional barriers of methyl internal rotors in oxygen analogues are higher (see Section 5.1.), which remains true for the *anti*-conformer. There is no explanation for this strange observation at this point, but electrostatic effects could be a reason.

2-Acetylfuran

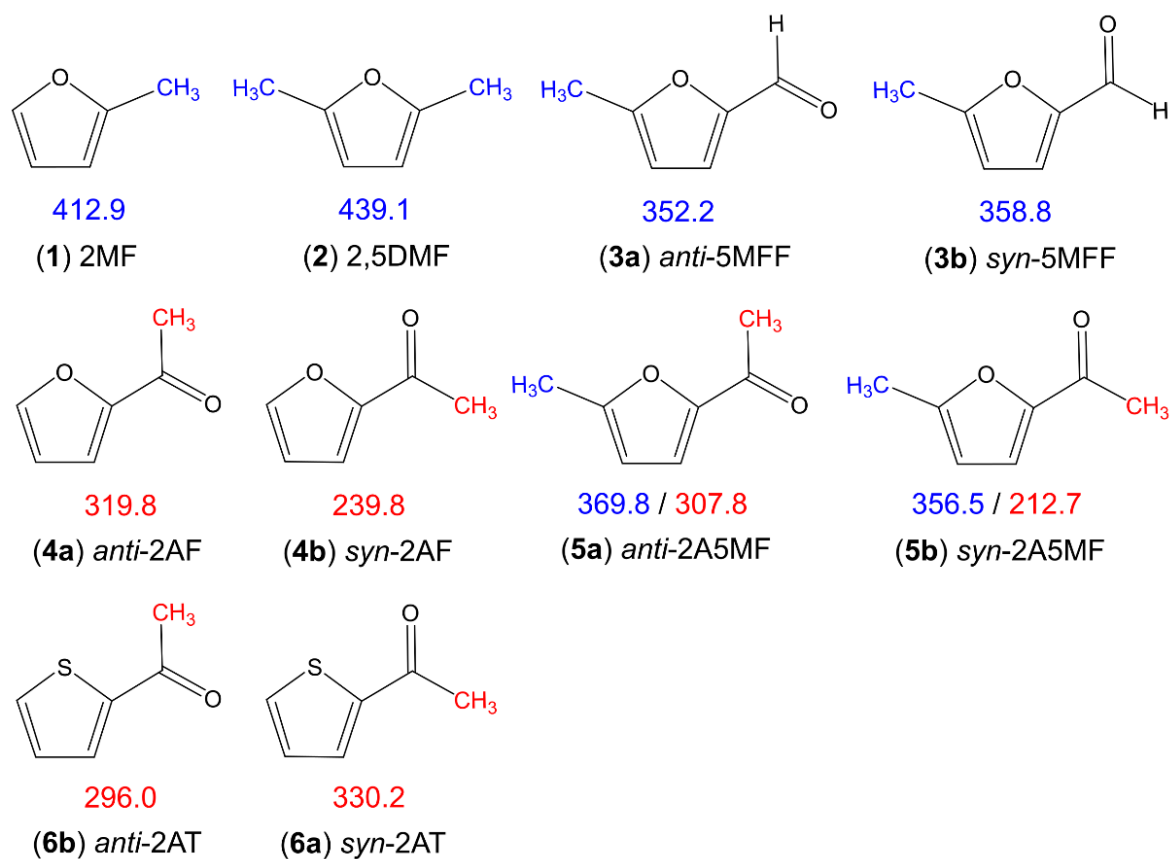


Figure 5.7: Torsional barriers in cm^{-1} of (1) 2-methylfuran [31], (2) 2,5-dimethylfuran [22], (3) *anti*- and *syn*-5-methylfurfural [108], (4) *anti*- and *syn*-2AF (this work, [2]), (5) *anti*- and *syn*-2-acetyl-5-methylfuran [24] and (6) *syn*- and *anti*-2AT (Chapter 3, [4]). For 2-acetyl-5-methylfuran, the barriers of the two methyl groups are color-coded. (Figure modified from Ref. [2].)

5.5. Conclusion

Two conformers, *anti* and *syn*, were identified in the microwave spectrum of 2AF. The spectra of ^{13}C - and ^{18}O -isotopologues of the energetically more stable *anti*-conformer were also studied. The barriers to internal rotation of $319.777(12) \text{ cm}^{-1}$ and $239.780(13) \text{ cm}^{-1}$ were deduced for *anti*- and *syn*-2AF, respectively, from the A-E torsional splittings observed in the spectrum. A comparison with other furan derivatives with at least one methyl rotor indicates that electrostatic effects expand through the conjugated π -electron system of the heteroaromatic ring, allowing substituents to influence the methyl torsion. A-E splittings were also observed for all heavy atom isotopologues of *anti*-2AF, leading to the conclusion that isotopic substitution only has a negligible influence on the barrier height. A comparison with the sulphur analogue 2AT showed, that the heteroatom in the ring significantly influences the conformational stability, as furans favour the *anti*-conformation, while in thiophenes the *syn* form is more stable due to the different electrostatic interactions between the heteroatom and the acetyl oxygen. Regarding the methyl internal rotation of the acetyl group it was surprisingly found that *syn*-2AT possesses a higher rotational barrier than *syn*-2AF, despite the fact that barriers to methyl internal rotation are usually higher in oxygen analogues. This observation has not been conclusively explained yet.

IV Two-Top Molecules

Molecules featuring one methyl internal rotation, such as the three previously investigated in this dissertation but also a myriad of others [102][113][115][116][117][118], have already been studied extensively. The number of investigations decreases significantly however if the number of internal rotors increases. While dozens of two-top molecules studied by high resolution spectroscopy can still be found in the literature [119][120][121], only a single one of them, 2,5-dimethylthiophene [21], features a thiophene ring.

Molecules featuring internal rotation with conjugated π -double bonds are of special interest as electronic effects can be transferred across a longer range, often enabling interactions between two internal rotors. Examples are investigations on a number of benzene derivatives featuring two methyl internal rotations such as three isomers of dimethylanisole [13][14][15], three isomers of dimethylbenzaldehyde [16], *o*- and *m*-xylene [17][18], two isomers of dimethylfluorobenzene [19][20], 4-methylacetophenone [12], or some five-membered aromatic rings like the 2,5-isomers of dimethylthiophene [21], dimethylfuran [22], and dimethylpyrrole [23] or 2-acetyl-5-methylfuran [24] and 4,5-dimethylthiazole [25]. In these studies, it was clearly proven that steric hindrance arising from a neighbouring substituent increases the torsional barrier of a methyl group attached to the aromatic ring, but also that electrostatic effects can be transferred across the π -conjugated system and influence the methyl torsion. While it is easy to expect whether steric effects may occur, the exact nature of electrostatic interactions has not been fully explored yet, mainly due to the very limited number of studies on aromatic heterocycles containing more than one methyl internal rotation.

Therefore, this part of the dissertation aims at a better understanding of these long-range effects with a systematic investigation on such molecules with several methyl rotors. The three molecules investigated here are 2-acetyl-3-methylthiophene (2A3MT, Chapter 6), 2-acetyl-4-methylthiophene (2A4MT, Chapter 7) and 2-acetyl-5-methylthiophene (2A5MT, Chapter 8), illustrated in Figure 1, which are all derivatives of 2AT (Chapter 3, [4]).

In all three of them the π -conjugated system of thiophene is extended by the carbonyl group, therefore connecting the two methyl torsions. Barrier heights determined for the two tops will yield valuable data to evaluate the effects of both steric hindrance and electrostatic interactions in thiophene derivatives [3].

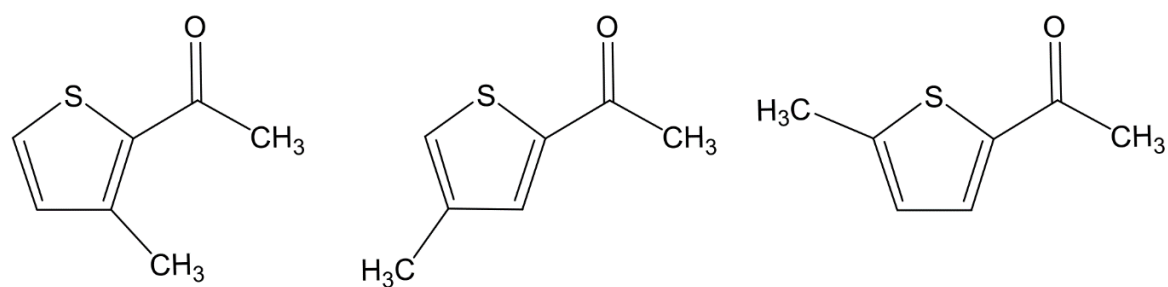


Figure 1: Two-top molecules investigated in this dissertation. From left to right: 2A3MT (Chapter 6), 2A4MT (Chapter 7) and 2A5MT (Chapter 8).

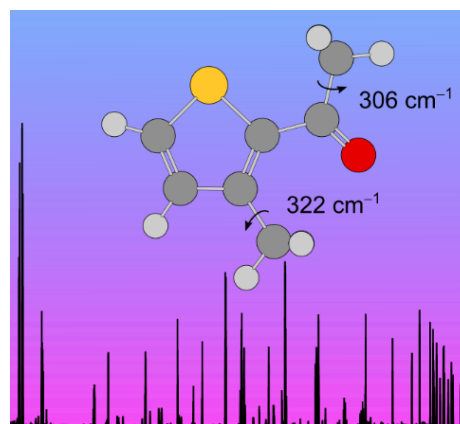
6. 2-Acetyl-3-Methylthiophene

The main text passages of this chapter have already been published in Ref. [3]:

Christina Dindić and Ha Vinh Lam Nguyen

Microwave Spectrum of Two-Top Molecule: 2-Acetyl-3-Methylthiophene

ChemPhysChem **2021**, 22, 2420-2428.



Parts of the publication are reproduced (and adapted) with permission from *ChemPhysChem* 2021, 22, 2420-2428; Copyright © 2021 John Wiley and Sons. Christina Dindić performed measurements, quantum chemical calculations, spectral assignments and wrote the main part of the manuscript. Ha Vinh Lam Nguyen co-wrote the manuscript. Marc Kreutzer is gratefully acknowledged for his contribution to the measurements and assignments during his research project at the RWTH Aachen University. Figures taken from Ref. [3] have been modified for consistent formatting in this dissertation.

6.1. Quantum Chemical Calculations

6.1.1. Conformational Analysis

Similar to the previous three molecules investigated in this dissertation, the conformational landscape of 2A3MT is only influenced by the orientation of the substituents attached to the thiophene ring. Unlike the previous molecules, 2A3MT possesses two substituents, an acetyl and a methyl group. As the rotation of the methyl group about the C3–C9 bond (for atom numbering see Figure 6.1) does not create new conformers, only the acetyl group has to be rotated for a conformational search. Thus, it was reasonable to expect two conformers, *syn* and *anti*, once again. For the conformational analysis the dihedral angle $\alpha = \angle(\text{S1}-\text{C2}-\text{C6}=\text{O7})$ (for atom numbering see Figure 6.1) was varied in steps of 10° while all other geometry parameters were optimized at the MP2/6-311++G(d,p) [42][59] level of theory using the *Gaussian 16* program package [41]. The calculated energies were parameterized using a Fourier expansion with the corresponding coefficients given in Table D.1 of the Appendix. With

these Fourier coefficients the potential energy curve shown in Figure 6.2 could be drawn. Surprisingly, it does not exhibit the expected two minima at 0° and 180° , corresponding to the typical *syn*- and *anti*-conformers, respectively, but similar a very wide valley around 0° and a flat double minimum around 180° . To explore these areas α was varied in steps of 1° between -10° and 10° as well as 160° and 200° as shown in Figure 6.3. A very shallow double minimum was found in the area between -5° and 5° , with the minima lying at $\pm 1.6^\circ$, as can be clearly recognized in calculations with a step width of 0.1° shown in the inset of Figure 6.3. For the area between 160° and 200° , also shown in Figure 6.3, the two equivalent minima lie at 171° and 189° , but the potential curve is not continuous and exhibits a sudden break between 181° and 182° . According to these calculations, both the *anti*- and the *syn*-conformer of 2A3MT exist as two equivalent, non-planar forms, where the acetyl moiety is tilted by 9.0° and 1.6° out of the thiophene plane, respectively, similar to 2AT. However, since (i) the structures of both similar molecules 2AT and 2AF were experimentally determined to be planar by isotopic substitutions [4][2], (ii) the investigation on 2PT showed that the planarity of a thiophene derivative with a carbonyl group containing substituent depends strongly on the level of theory in use (Section 4.2.2., [1]), and (iii) similar observations having been made for nitroxoline [122], another molecule containing conjugated π -double bonds, the calculations were repeated using the B3LYP-D3BJ method. The potential energy curves, also illustrated in Figures 6.2 and 6.3, exhibit the expected course with only two minima, showing that both conformers of 2A3MT are planar. Subsequently, full structure optimizations were performed at both levels of theory, with additional frequency calculations confirming the two obtained conformers to be stable. The calculated rotational constants, dipole moment components, dihedral angles, and energy differences are summarized in Table 6.1; the atomic coordinates are given in Table D.2 of the Appendix. The *anti*-conformer is predicted to be much more stable than the *syn* one.

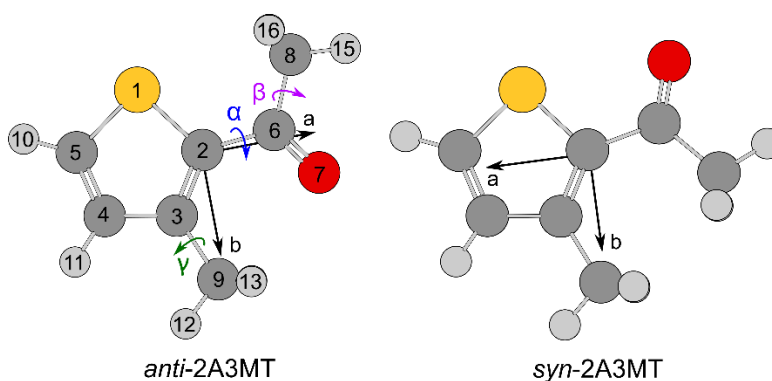


Figure 6.1: Molecular structures of the two conformers of 2A3MT optimized at the B3LYP-D3BJ/6-311++G(d,p) level of theory in their principal axes of inertia. Atom numbering and the dihedral angles $\alpha = \angle(\text{S1-C2-C6=O7})$, $\beta = \angle(\text{C2-C6-C8-H15})$, and $\gamma = \angle(\text{C2-C3-C9-H12})$ are defined for *anti*-2A3MT. The sulphur atom is marked in yellow, oxygen atom in red, carbon

atoms are in dark grey, and hydrogen atoms in light grey. H14 lies behind H13, H17 behind H16. (Figure modified from Ref. [3].)

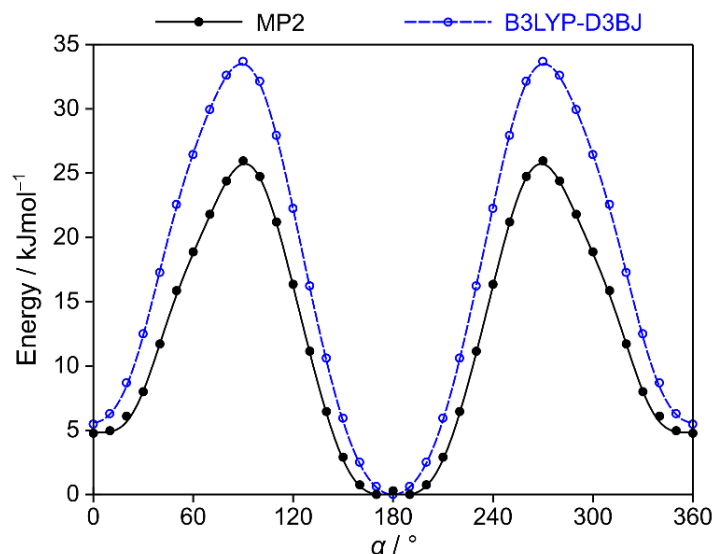


Figure 6.2: The potential energy curves of 2A3MT obtained by rotating the acetyl group about the C2–C6 bond (for atom numbering see Figure 6.1). Calculations were performed at the MP2/6-311++G(d,p) and B3LYP-D3BJ/6-311++G(d,p) levels of theory by varying the dihedral angle α in a grid of 10° . The relative energies are given in respect to the lowest energy conformation with $E_{MP2} = -743.5343631$ Hartree and $E_{B3LYP-D3BJ} = -745.1266413$ Hartree. (Figure modified from Ref. [3].)

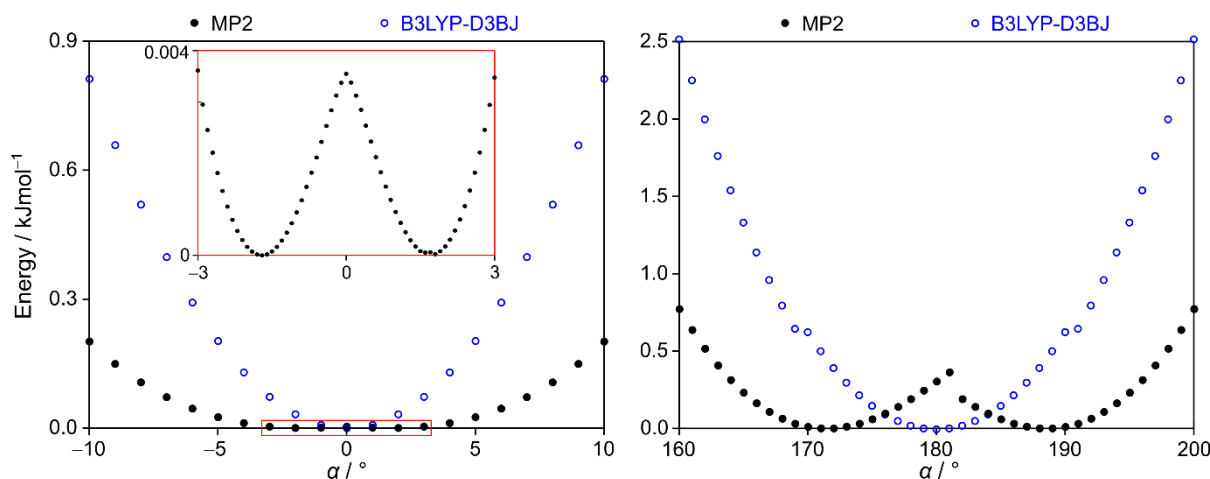


Figure 6.3: Left hand side: The portion between -10° and 10° of the potential energy curves of 2A3MT given in Figure 6.2 where the dihedral angle α was varied in a grid of 1° . The relative energies are given in respect to the lowest energy points with $E_{MP2} = -743.5325478$ Hartree and $E_{B3LYP-D3BJ} = -745.1245546$ Hartree. The inset shows the region between -3° and 3° in a step width of 0.1° calculated at the MP2/6-311++G(d,p) level of theory with the lowest energy

point at $E_{MP2,inset} = -743.5325481$ Hartree. **Right hand side:** The portion between 160° and 200° where the dihedral angle α was varied in a grid of 1° . The relative energies are given in respect to the lowest energy points with $E_{MP2} = -743.5343669$ Hartree and $E_{B3LYP-D3BJ} = -745.1266413$ Hartree. (Figure modified from Ref. [3].)

Table 6.1: Rotational constants (in MHz), dipole moments (in D), dihedral angles (in degrees), and relative energies (in $\text{kJ}\cdot\text{mol}^{-1}$) for the two conformers of 2A3MT calculated with the MP2 and B3LYP-D3BJ methods and the 6-311++G(d,p) basis set.

Par.	<i>MP2</i>		<i>B3LYP-D3BJ</i>	
	<i>anti</i>	<i>syn</i>	<i>anti</i>	<i>syn</i>
A_e	1991.5	1990.2	1990.5	1994.8
B_e	1406.2	1397.8	1407.0	1395.1
C_e	836.9	829.7	832.7	829.4
$ \mu_a $	2.11	1.60	2.54	1.55
$ \mu_b $	1.40	4.49	1.24	3.94
$ \mu_c $	0.43	0.08	0.00	0.00
α	171.47	-1.68	180.00	0.01
β	173.80	179.08	-179.99	179.99
γ	-173.21	177.91	-179.99	179.99
ΔE^a	0.0	4.6	0.0	6.9

^a Energy differences including zero-point corrections relative to the most stable conformer *anti*-2A3MT with $E_{MP2} = -743.402494$ Hartree and $E_{B3LYP-D3BJ} = -744.992915$ Hartree.

6.1.2. Basis Set Variations

Due to the discrepancies between the MP2 and B3LYP methods used for the structure optimizations, as well as a benchmarking effort attempting to find a level of theory which allows for a cost-efficient yet reasonably accurate prediction of rotational constants to ease the assignment of microwave spectra of similar molecules, geometry optimizations were repeated using different methods and basis sets (see Section 3.2.2.). All calculations were exclusively performed for *anti*-2A3MT, as only this conformer was eventually observed in the microwave

spectrum. The results are given in Table D.3 in the Appendix and will be discussed in comparison to the experimental values in Section 6.4.2.

6.1.3. Methyl Internal Rotations

The acetyl methyl and the ring methyl group are both internal rotors. The barriers hindering the internal rotation were calculated by varying the dihedral angles $\beta = \angle(\text{C2-C6-C8-H15})$ and $\gamma = \angle(\text{C2-C3-C9-H12})$ in 10° steps. All other geometry parameters were optimized at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory because (i) it was unclear at this point whether the geometry of 2A3MT is planar as predicted with the B3LYP-D3BJ method or non-planar as given by the MP2 method, and (ii) in some previous studies, MP2 calculations often overestimate and B3LYP ones underestimate values of torsional barriers [1][21][10]. Using both methods thus enables a better estimation. The resulting potential energy curves for *anti*-2A3MT are shown in Figure 6.4, those of *syn*-2A3MT in Figure D.1 in the Appendix. Coefficients of the Fourier expansion used to plot the potential curves can be found in Table D.4. Again, further discussions will only focus on *anti*-2A3MT.

As expected, the values predicted with the MP2 method are larger than those of the B3LYP-D3BJ calculations. For the acetyl methyl group of *anti*-2A3MT, barriers of 316.1 cm^{-1} (MP2) and 182.7 cm^{-1} (B3LYP-D3BJ) were calculated. The respective values for the ring methyl group are 424.8 cm^{-1} and 263.4 cm^{-1} . Further discrepancies between the two methods are the different V_6 contributions, resulting in a double minimum potential for the MP2 curves but a typical three-fold potential for the B3LYP-D3BJ curves, as can be clearly recognized in a portion of the curves between 40° and 80° recalculated in 2° steps (see the inset of Figure 6.4). This observation is likely due to the couplings between the two methyl torsions, which is more significant in MP2 calculations, as shown in the lower trace of Figure 6.4. The rotation of one methyl group induces an oscillation of up to 15° of the other methyl group in calculations with the MP2 method, whereas almost no oscillation is observed in B3LYP-D3BJ calculations. Due to the rearrangement of the acetyl group upon methyl torsions, the MP2 potential curve shows a sudden discontinuation at 66° , the B3LYP-D3BJ exhibits two at 48° and 70° .

2-Acetyl-3-Methylthiophene

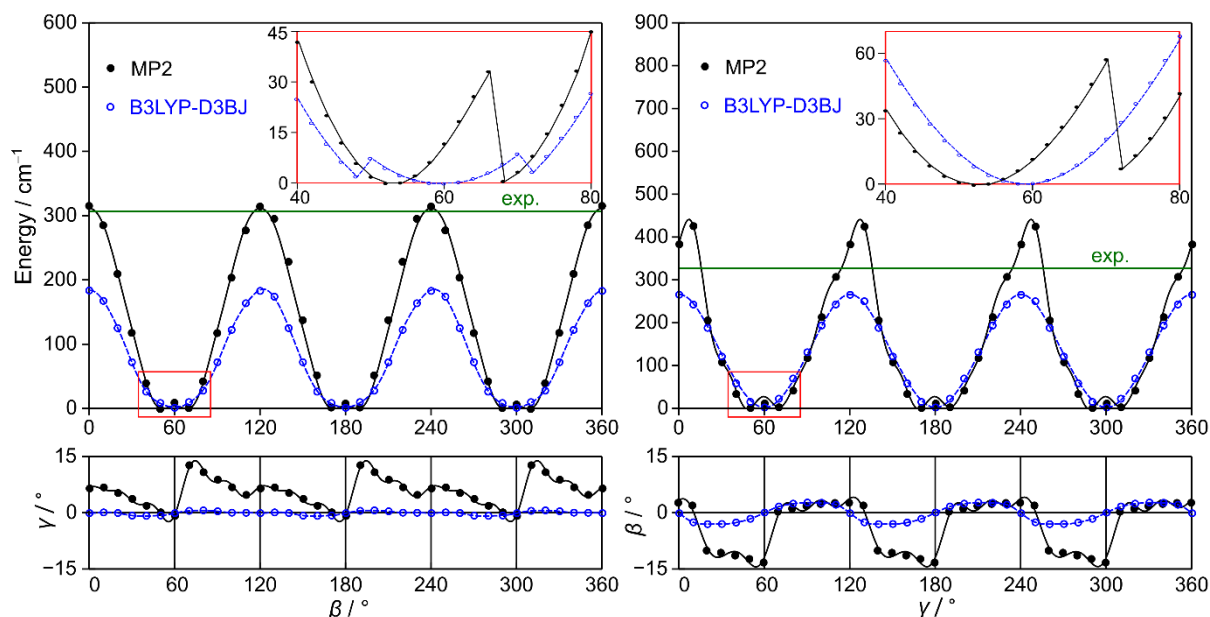


Figure 6.4: Left hand side: The potential energy curves of *anti*-2A3MT obtained by rotating the acetyl methyl group about the C6–C8 bond by varying the dihedral angle β in steps of 10° . The calculations were performed using the 6-311++G(d,p) basis set with either the MP2 or the B3LYP-D3BJ method. The energies are given relative to the lowest energy with $E_{MP2} = -743.5343577$ Hartree and $E_{B3LYP-D3BJ} = -745.1266412$ Hartree. The calculated barrier heights are 316.1 cm^{-1} (MP2) and 182.7 cm^{-1} (B3LYP-D3BJ); the experimental value of 306.2 cm^{-1} is marked by a horizontal line. The MP2 potential exhibits a flat double minimum at $\beta \approx 60^\circ$, 180° , and 300° . The inset shows the portion between 40° and 80° obtained by varying β in steps of 2° . The energy data points are connected by a non-parameterized curve, which is only present for a better tracing. The lower trace depicts the oscillation of the ring methyl group upon the rotation of the acetyl methyl group. The deviations of the dihedral angle γ are given relative to the values of -173.21° (MP2) and -179.99° (B3LYP-D3BJ) of the fully optimized geometries.

Right hand side: The potential energy curves of *anti*-2A3MT obtained by rotating the ring methyl group about the C3–C9 bond by varying the dihedral angle γ in steps of 10° . The energies are given relative to the lowest energy with $E_{MP2} = -743.5343619$ Hartree and $E_{B3LYP-D3BJ} = -745.1266402$ Hartree. The calculated barrier heights are 424.8 cm^{-1} (MP2) and 263.4 cm^{-1} (B3LYP-D3BJ); the experimental value of 321.8 cm^{-1} is marked by a horizontal line. The inset shows the portion between 40° and 80° with γ varied in steps of 2° . The curve connecting the energy points are not parameterized. The MP2 potential curve shows a sudden discontinuation at 69° , while the B3LYP-D3BJ one is continuous. On the lower trace is the oscillation of the acetyl methyl group upon the ring methyl torsion. The deviations of the dihedral angle β are given relative to the values of 173.80° (MP2) and -179.99° (B3LYP-D3BJ) of the fully optimized geometries. (Figure modified from Ref. [3].)

2-Acetyl-3-Methylthiophene

The barriers to internal rotation of the *anti*-conformer were furthermore also predicted at all levels of theory mentioned in Section 6.2.2. The calculated values are listed in Table D.3 in the Appendix; a selection of calculations using the 6-311++G(d,p) basis set are given in Table 6.2. and will later in Section 6.3.4. be compared with the experimental results.

Table 6.2: Torsional barriers (in cm^{-1}) of the acetyl methyl and ring methyl group in *anti*-2A3MT calculated with different methods in combination with the 6-311++G(d,p) basis set. The deviations between the experimental values and the calculated ones are given as absolute values (in cm^{-1}) as well as in percent relative to the experimental values in parentheses.

Method	Acetyl	Dev.	Ring	Dev.
MP2	316.1	−10 (−3)	424.8	−103 (32)
B3LYP-D3	228.9	77 (25)	306.3	16 (5)
B3LYP-D3BJ	182.7	124 (40)	263.4	58 (18)
CAM-B3LYP-D3BJ	205.5	101 (33)	257.6	64 (20)
M06-2X	288.4	18 (6)	369.8	−48 (−15)
ω B97X-D	248.9	57 (19)	243.9	78 (24)
Experimental	306.2		321.8	

In order to study the top-top interactions in more detail, the two-dimensional potential energy surfaces (2D-PES) depending on the dihedral angles β and γ were calculated. Due to symmetry, only data points in the range from 0° to 120° for both β and γ were necessary. The energy points obtained with the MP2 method once again showed discontinuities due to the rearrangement of the entire acetyl group, similar to the observation illustrated in Figure 6.4. Therefore, the data points, available in the Appendix (Table D.5), could not be parameterized. Thus, only the 2D-PES calculated with the B3LYP-D3BJ method is shown in Figure 6.5, where the potential energies were parameterized with a Fourier expansion, the coefficients of which are listed in Table D.6, taking into account the correct symmetry of the methyl groups. The 2D-PES also visualizes that coupling between the two rotors exists, as the minima have oblate rather than circular forms, which would be the case if there were no top-top interaction.

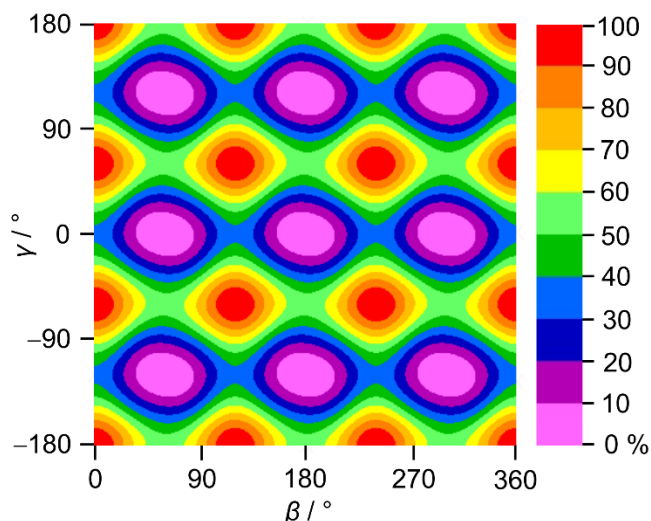


Figure 6.5: Two-dimensional potential energy surface of *anti*-2A3MT calculated at the B3LYP-D3BJ/6-311++G(d,p) level of theory in dependence of the dihedral angles β and γ , which were varied in a grid of 10° while all other geometry parameters were optimized. The colour code gives the relative energy (in percent) on a scale between the minimum $E_{\min} = -745.124411$ Hartree (0%) and the maximum $E_{\max} = -745.126640$ Hartree (100 %). (Figure modified from Ref. [3])

6.2. Microwave Spectroscopy

6.2.1. Experimental Setup

A scan from 9.0 to 15.8 GHz was recorded with a molecular jet FTMW spectrometer operating in the frequency range from 2.0 to 26.5 GHz [33] as a series of overlapping spectra with a step width of 250 kHz. For each measurement 50 free-induction decays were co-added. 2A3MT was purchased from Sigma-Aldrich, Schnelldorf, Germany, with a stated purity of 98 % and used without any further purification. The substance was put on a 5 cm piece of pipe cleaner and placed upstream the nozzle with a backing pressure of about 2 bar helium as the carrier gas. All lines of the scan were subsequently remeasured at a higher resolution with an experimental accuracy of 2 kHz [69] in order to resolve the torsional splittings caused by the two methyl tops.

6.2.2. Spectral Assignment

As the *anti*-conformer of 2A3MT was predicted to be energetically more stable, the assignment was started with this conformer using the rotational constants calculated at the MP2/6-311++G(d,p) level of theory given in Table 6.1. These values were used to predict a rigid-rotor spectrum with the program *XIAM* [40] without taking the effects of internal rotation into account. From the calculated dipole moments *a*- and *b*-type transitions were expected to be very strong while *c*-type transitions should not be visible.

The initial assignment was successful without any problems as the four most intense transitions of the entire survey spectrum ($5_{05} \leftarrow 4_{14}$, $5_{15} \leftarrow 4_{14}$, $5_{05} \leftarrow 4_{04}$, $5_{15} \leftarrow 4_{04}$) were less than 2 MHz off from their predicted frequencies. After a satisfactory rigid rotor fit for *anti*-2A3MT had been achieved, the fit was expanded to include the internal rotation effects. Since the two methyl rotors are inequivalent, each transition of 2A3MT splits into five torsional components ($\sigma_1\sigma_2$) = (00), (01), (10), (11), and (12) as shown in Figures 1.3 and 6.6, where σ_1 and σ_2 [14][38] refer to the acetyl methyl and the ring methyl group, respectively. In a first step, two separate one-top fits were build up, consisting of only the (00) and (01) or (10) torsional species, while neglecting the (11) and (12) species representing top-top interactions. Since quantum chemical calculations predicted a higher barrier to internal rotation for the ring methyl group, splittings between the (00) and (10) species were assumed to be smaller than the (00)-(01) ones. However, in the experimental spectrum this difference was not as significant as expected. Furthermore, the (11)-(12) splittings are often at the resolution limit and not distinguishable. In the high resolution measurement of the *a*-type transition $5_{15} \leftarrow 4_{14}$ shown in Figure 6.6, the separations between the (00) and (01), (01) and (10), (10) and (11), and (11) and (12) species are 114.9 kHz, 31.5 kHz, 112.5 kHz, and 4.5 kHz, respectively. Due to the small splittings, it was difficult at the beginning to assign the torsional species correctly, including the (00) species which should follow a semi-rigid rotor Hamiltonian model. In order to identify the correct torsional species two approaches were employed. Firstly, the focus lay on rotational transitions with higher K_a quantum numbers, because the fine splittings are larger and it is thus easier to distinguish a torsional species from the other ones. Secondly, the program *SFLAMS* [12] was employed to fit the (00), (01), and (10) species separately to check the correctness of the assignment. Eventually, two one-top fits with experimental accuracy could be achieved with the program *XIAM* and finally combined in a two-top fit consisting of the (00), (01), and (10) species. The remaining (11) and (12) species could then be predicted, measured, and assigned straightforwardly. The *XIAM* global fit shown in Table 6.3 incorporates 751 lines in total. The number of lines is nearly evenly distributed between the five species, with a slightly larger number for the (00), (01), and (10) species due to their higher spin statistical weight [14]. The assigned transitions are listed in Table D.7 in the Appendix. The

separate fits with the program *SFLAMS* are given in Table D.8. The rotational constant F_0 , describing the moment of inertia of the methyl internal rotor, could not be fitted and was fixed to 158 GHz, a value often found for methyl groups. The average line width at half height is 21 kHz, corresponding to an estimated measurement accuracy of 2.1 kHz, which is 1/10th of the average line width.

After the assignment of the *anti*-conformer, some very weak lines remained in the spectrum. They most likely belong to either the *syn*-conformer or isotopologues of *anti*-2A3MT, but further assignment was not possible due to the small number of lines and their low intensity.

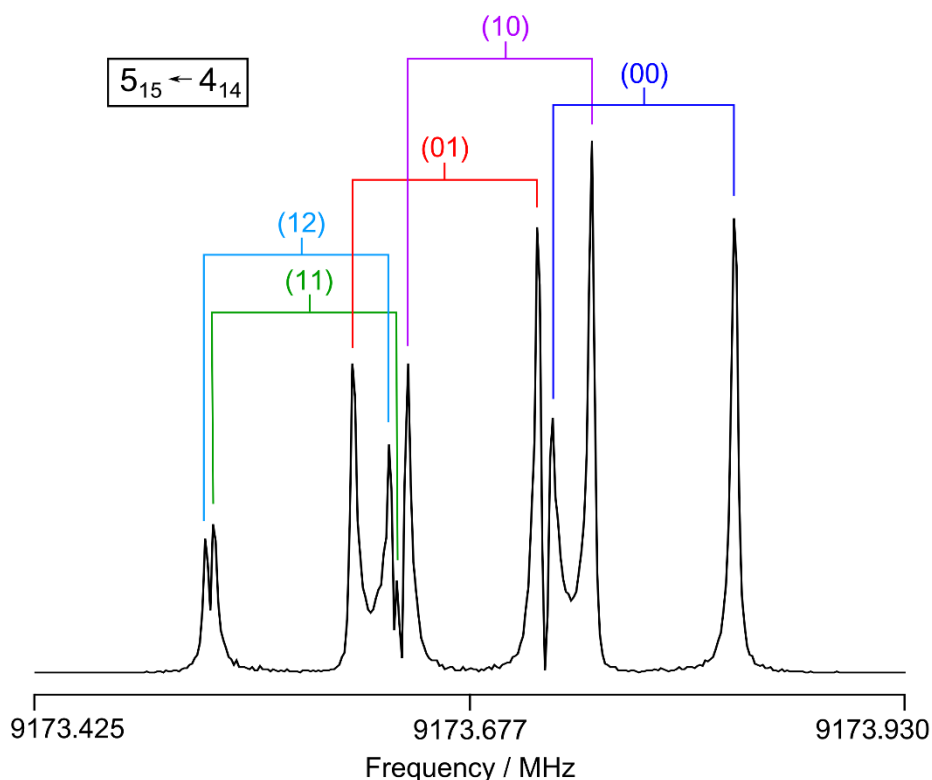


Figure 6.6: A typical high resolution measurement of the *a*-type rotational transition $5_{15} \leftarrow 4_{14}$ of *anti*-2A3MT with its five torsional species (00), (10), (01), (11), and (12). The frequency is given in MHz. The brackets indicate Doppler pairs. The spectrum was recorded at 9173.79 MHz, and 200 free induction decays were co-added. (Figure modified from Ref. [3])

2-Acetyl-3-Methylthiophene

Table 6.3: Experimental spectroscopic parameters of *anti*-2A3MT obtained with the program *XIAM* compared to the predicted values. Rotors 1 and 2 refer to the acetyl methyl and the ring methyl group, respectively.

Par.	Unit	<i>XIAM</i> ^a	MP2 ^b	B3LYP-D3BJ ^b
A_0	MHz	1997.975481(81)	1977.436	1977.164
B_0	MHz	1411.966335(69)	1398.860	1395.869
C_0	MHz	836.288600(23)	826.460	827.099
Δ_J	kHz	0.04798(24)	0.0546	0.0465
Δ_{JK}	kHz	0.0444(12)	0.0255	0.0414
Δ_K	kHz	0.0412(39)	0.0480	0.0383
δ_J	kHz	0.01801(12)	0.0197	0.0176
δ_K	kHz	0.07556(59)	0.1451	0.0941
$V_{3,1}$	cm ⁻¹	306.184(46)	316.1	182.7
$D_{p_i^2 J,1}$	kHz	55.3(11)		
$D_{p_i^2 K,1}$	kHz	-120.6(21)		
$D_{p_i^2 -,1}$	kHz	32.7(35)		
$\angle(i_1, a)$	deg	61.304(20)	65.5	65.1
$\angle(i_1, b)$	deg	28.695(20)	26.3	24.9
$\angle(i_1, c)$	deg	90.0 ^c	81.0	90.0
$V_{3,2}$	cm ⁻¹	321.813(64)	425.8	263.4
$D_{p_i^2 J,2}$	kHz	75.0(12)		
$D_{p_i^2 K,2}$	kHz	55.2(22)		
$D_{p_i^2 -,2}$	kHz	37.6(13)		
$\angle(i_2, a)$	deg	72.128(16)	68.5	69.3
$\angle(i_2, b)$	deg	17.872(16)	21.9	20.7
$\angle(i_2, c)$	deg	90.0 ^c	88.1	90.0
N^d		751		
σ^e	kHz	2.2		

^a All parameters refer to the principal axis system. Watson's A reduction and I^r representation were used. ^b Calculated with the 6-311++G(d,p) basis set. Ground state rotational constants and centrifugal distortion constants obtained from anharmonic frequency calculations are given. The centrifugal distortion constants were transformed from III^r to I^r representation using Eq. (6) of Ref. [123]. ^c Fixed due to symmetry. ^d Number of transitions. ^e Standard deviation of the fit.

6.3. Discussion

6.3.1. Conformational Stability

For 2A3MT only the *anti*-conformer was visible in the spectrum, confirming the predicted higher energetic stability of the *anti*-orientation over the *syn* one. In other thiophene derivatives like 2-thiophenecarboxaldehyde [71][72], and 2PT (Chapter 4, [1]), the *syn*-conformer is more stable than the *anti*-form. The conformational stability was explained by dipole-dipole interactions between the positively charged sulphur atom and the negatively charged oxygen atom of the acetyl group, which still holds true in the case of 2A3MT. NBO calculations [74] performed using the *Gaussian 16* program package [41] yield the charge distribution of 2A3MT depicted in Figure 6.7, showing that the negative partial charge on the carbon atom of the acetyl methyl group is larger than that of the oxygen atom, which stabilizes the *anti*-form over the *syn*-form. Furthermore, the methyl group at the third position of the ring induces steric interactions between the two methyl groups in the *syn*-form where the positive partial charged hydrogen atoms are closest to each other. In contrast, in the *anti*-conformer the negative partial charged oxygen atom of the acetyl group and the positive partial charged hydrogen atoms of the ring methyl group can form a hydrogen bond, thus making the *anti*-orientation significantly more stable, in agreement with the experimental observation. Quantum chemical calculations at all levels of theory also consistently predicted *anti*-2A3MT to be energetically more favourable than the *syn* conformer. Note that the positive partial charge of the sulphur atom causes a negative partial charge on both C(2) and C(5) atoms, while in furfural derivatives, e.g. 2AF (Chapter 5, [2]), they carry a positive partial charge because of the negative partial charge of the oxygen atom in the furan ring.

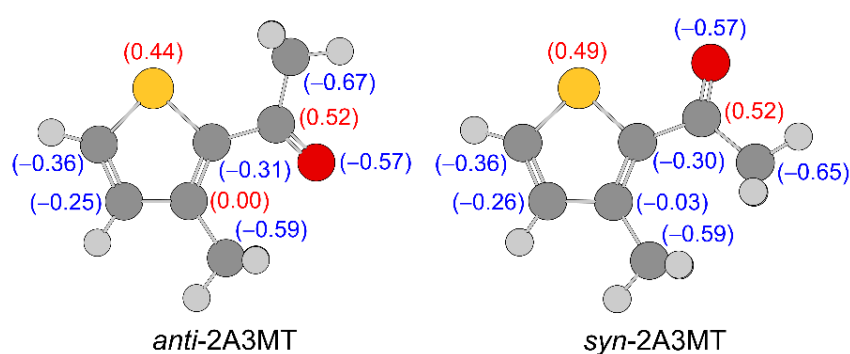


Figure 6.7: Charge distribution in *anti*- and *syn*-2A3MT obtained from NBO calculations at the B3LYP-D3BJ/6-311++G(d,p) level of theory. (Figure modified from Ref. [3])

6.3.2. Quality of the Fit

The *XIAM* fit shown in Table 6.3 with a total of 751 lines has a standard deviation of 2.2 kHz, which is very close to the experimental accuracy of 2.1 kHz and is therefore quite satisfactory. All rotational and centrifugal distortion constants as well as the internal rotation parameters are determined with high accuracy. A comparison between the experimentally determined rotational constants B_0 deduced from the *XIAM* fit and those calculated at different levels of theory B_e (see Table D.3) is not physically meaningful, as the experimental values correspond to the vibrational ground state, while the predicted values belong to the equilibrium structure. Nevertheless, it can be helpful to know which method and basis set combination predicts B_e constants that are closest to B_0 ones, even if the reason is only error compensation. Such benchmark calculations allow for faster and/or more straightforward assignments of the microwave spectra of similar molecules. In the case of *anti*-2A3MT, the MP2/6-31G(d,p) level of theory predicted the *A* rotational constant almost perfectly while *B* and *C* were also less than 1 MHz off. This level of theory has also stood out in many previous works where similar benchmark calculations were performed, especially for molecules containing aromatic rings such as 2-ethylfuran [87], coumarin [124], and *o*-methylanisole [125]. It is of note that the MP2/6-31G(d,p) level predicts a planar structure for *anti*-2A3MT, in contrast to some other MP2 calculations.

A similarly accurate prediction of all three rotational constants is only achieved at the two B3LYP-D3BJ/6-311+(+)G(2d,2p) levels of theory. Overall, most employed levels predict the rotational constants sufficiently close to the experimental values for assignment purposes. Only a small number of them deviate by more than 10 MHz. Notably, large deviations only occur for individual method/basis set combinations without any apparent trends, showing that none of the tested levels are categorically unsuitable for 2A3MT. Resort to more accurate quantum chemical calculations is not attempted, since the present study mainly focuses on the effects of internal rotation arising from two inequivalent methyl rotors, using quantum chemical calculations as a supporting tool, rather than structure determination. In this sense, this benchmark only includes cost-efficient calculations allowing rapid access to rotational constants for an assignment guidance of the microwave spectrum.

6.3.3. Molecular Parameters

Concerning the molecular geometry, calculations at some levels of theory using the MP2 method predicted a non-planar structure with the acetyl group slightly tilted out of the thiophene plane, while all other calculations predicted a planar structure (see Table D.3 in the Appendix). It is noticeable that almost all of them include diffuse functions (+ or ++). The only level without

diffuse function, MP2/6-311G(df,pd), calculates a much smaller tilt angle of only about 2° of the acetyl group (called angle Θ in Table D.3). A structure determination was not possible because the isotopologue lines of *anti*-2A3MT are not sufficiently intense to be measured. From a comparison of the experimental value of $-6.559 \text{ u}\text{\AA}^2$ found for the inertial defect of *anti*-2A3MT with the value of $-9.288 \text{ u}\text{\AA}^2$ calculated using the rotational constants obtained at the MP2/6-311++G(d,p) level, predicting a non-planar structure, and the value of $-6.200 \text{ u}\text{\AA}^2$ obtained at the B3LYP-D3BJ/6-311++G(d,p) level, predicting a planar structure, it is fair to at least suspect that the effective structure is planar. The experimentally determined value is also very close to the inertial defects of other planar molecules with four out-of-plane hydrogen atoms such as the C_s conformer of 2-ethylfuran ($\Delta_c = -6.483 \text{ u}\text{\AA}^2$) [87] and the *cis-trans* conformer of ethylnitrite ($\Delta_c = -6.422 \text{ u}\text{\AA}^2$) [91]. However, since the isotopologue spectra were not observable, the inertial defect is rather an indication, and does not give any conclusive statement on the planarity of 2A3MT.

6.3.4. Methyl Internal Rotation

The barriers to internal rotation of the acetyl methyl and the ring methyl group deduced from the *XIAM* fit are $306.184(46) \text{ cm}^{-1}$ and $321.813(64) \text{ cm}^{-1}$, respectively. Compared to the predicted values, previous studies reported that though the order of magnitude is often correct [1][21][10], MP2 calculations tend to overestimate, while the B3LYP-D3(BJ) ones almost always underestimate the barrier height, which is also true for *anti*-2A3MT (see Table 6.2 and Table D.3 for example). No method/basis set combination manages to calculate both the acetyl methyl and ring methyl torsional barriers well at the same time, given that even small differences of the V_3 value can lead to significant changes in the torsional fine structure.

Microwave spectroscopic studies on methyl torsions in thiophene derivatives are still scarce. Except for the molecules presented in this work, the only investigations reporting on the internal rotation of a methyl group attached to the thiophene ring that can be found in the literature are on 2-methylthiophene (molecule **(7)** in Figure 6.8) [30], 3-methylthiophene (**(8)**) [101] and 2,5-dimethylthiophene (**(9)**) [21]. In all three molecules, no further substituent is in close proximity of the methyl rotor, and the barrier hindering the methyl torsion ranges from 194.1 cm^{-1} in 2-methylthiophene (**(7)**) [30] to 258.8 cm^{-1} in 3-methylthiophene (**(8)**) [101]. Compared to the value of 321.8 cm^{-1} found for the ring methyl group of *anti*-2A3MT (**(10)**), a significant increase due to sterical hindrance caused by the neighbouring acetyl substituent is obvious here.

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For the acetyl methyl group, *Andresen et al.* introduced a classification system linking the torsional barrier with the molecular structure at the other side of the carbonyl bond [10][8][9][11]. This categorization clearly illustrates that electronic effects influence torsional behaviour, although to understand the exact nature of this interaction more data points are necessary. To shed some light on these interactions and with the aim of establishing a distinct “thiophene class”, further thiophene derivatives containing an acetyl substituent will be the subject of the next two chapters in this thesis. As such a discussion including all thiophene derivatives containing an acetyl substituent studied in this thesis can be found in Section 8.3.3.

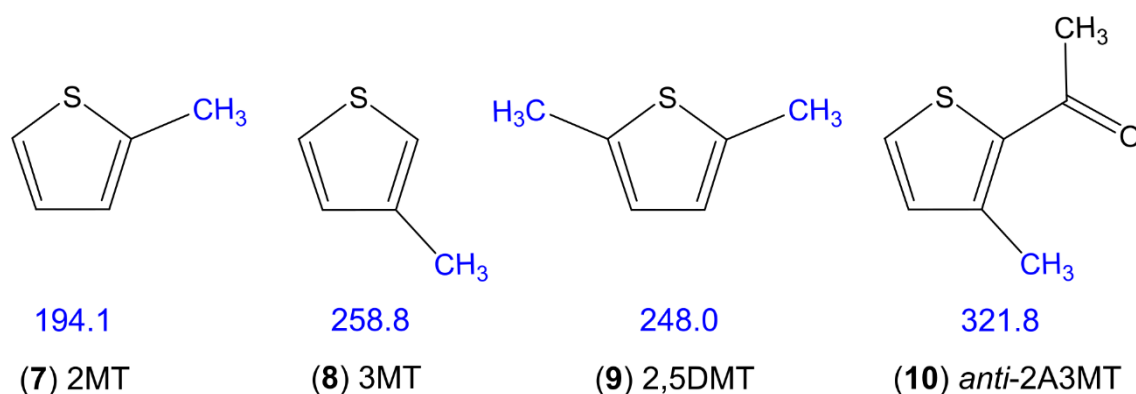


Figure 6.8: Torsional barriers of the ring methyl group given in cm⁻¹ of (7) 2-methylthiophene [30], (8) 3-methylthiophene [101], (9) 2,5-dimethylthiophene [21] and (10) *anti*-2-acetyl-3-methylthiophene (this work, [3]). (Figure modified from Ref. [3])

6.4. Conclusion

The *anti*-conformer of 2A3MT was assigned under molecular jet conditions using Fourier transform microwave spectroscopy with support from quantum chemical calculations. The two non-equivalent internal rotations of the acetyl methyl and the ring methyl groups caused splittings of all rotational transitions into five torsional species. The barriers hindering the methyl torsions were determined to be 306.184(46) cm⁻¹ and 321.813(64) cm⁻¹, respectively. A comparison to the values observed for the ring methyl rotor in 2-methylthiophene [30], 3-methylthiophene [101], and 2,5-dimethylthiophene [21] clearly implies the influence of steric effects. The experimentally determined internal defect suggests that the heavy-atom structure of the molecule is entirely planar, though several MP2 optimizations predict the acetyl group to be tilted out of the thiophene plane.

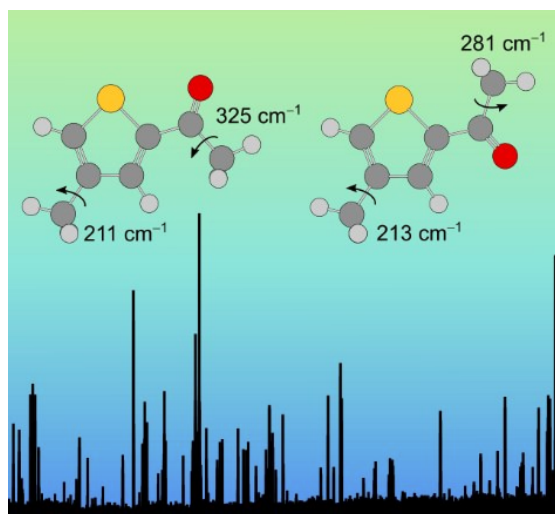
7. 2-Acetyl-4-Methylthiophene

The main text passages of this chapter have already been published in Ref. [5]:

Christina Dindić, Mike Barth and Ha Vinh Lam Nguyen

Two methyl internal rotations of 2-acetyl-4-methylthiophene explored by microwave spectroscopy and quantum chemistry

Spectrochim. Acta A **2022**, 280, 121505.



Parts of the publication are reproduced (and adapted) with permission from *Spectrochim. Acta A* 2022, 280, 121505; Copyright © 2022 Elsevier. Mike Barth performed measurements, quantum chemical calculations and spectral assignments during his Bachelor thesis at the RWTH Aachen University and is gratefully acknowledged for his contribution. Christina Dindić performed additional measurements, quantum chemical calculations, spectral assignments and wrote the main part of the manuscript. Ha Vinh Lam Nguyen and Mike Barth co-wrote the manuscript. Figures taken from Ref. [5] have been modified for consistent formatting in this dissertation.

7.1. Quantum Chemical Calculations

7.1.1. Conformational Analysis

Based on the previous four molecules investigated in this thesis, it was obvious to assume that there are only two stable conformations for 2A4MT, a *syn* or an *anti* form, resulting from the rotation of the acetyl group about the C2–C6 bond (see Figure 7.1 for atom numbering). To confirm this assumption, a conformational analysis was performed by varying the dihedral angle $\alpha = \angle(\text{S1}–\text{C2}–\text{C6}=\text{O7})$ in steps of 10° , while all other geometry parameters were optimized. These calculations were carried out at the MP2/6-311++G(d,p) [42][59] and B3LYP-D3BJ/6-311++G(d,p) [43][44][60][61] levels of theory using the *Gaussian 16* program package [41]. These two levels were applied as the standard starting points of the quantum chemical

analysis. In recent years, the MP2/6-31G(d,p) level of theory was also used more frequently, as this level provided rotational constants in excellent agreement with the experimentally determined ones for many molecules containing an aromatic ring, such as quinoline and isoquinoline [126], coumarin [124], 2-ethylfuran [87], *o*-methylanisole [125], and especially the isomer 2A3MT (Chapter 6, [3]) of 2A4MT. The calculated energies were parameterized using a Fourier expansion with the corresponding coefficients listed in Table E.1 in the Appendix. The energy curves are illustrated in Figure 7.2. As expected, two minima corresponding with the planar *syn*- and *anti*-conformers were found at $\alpha = 0^\circ$ and 180° , respectively, in all three curves. It should be noted that in calculations at the MP2/6-311++G(d,p) level, a very flat double minimum exists at around 180° . A closer look between 165° and 195° with a step width of 1° indicates that the minima lie at $\alpha = 180^\circ \pm 6^\circ$ (see Figure E.1 in the Appendix). This level of theory thus predicts a non-planar enantiomeric pair for the *anti*-conformer of 2A4MT where the acetyl group is tilted out of the thiophene plane by 6° , which is similar to the other thiophene derivatives investigated previously in this work.

Full structure optimizations were performed subsequently, and frequency calculations confirmed the two predicted conformers illustrated in Figure 7.1 as stable. The *syn*-conformer was calculated to be energetically more favourable. The rotational constants, dipole moment components, and relative energies of both conformers obtained at all three levels of theory are given in Table 7.1; the atom coordinates are listed in Table E.2 in the Appendix.

7.1.2. Basis Set Variations

In addition to the initial three levels of theory structure optimizations were also performed using different methods and basis sets (see Section 3.2.2.), both to further the benchmarking efforts as well as to examine the discrepancies regarding the planarity. The results of these calculations for both conformers of 2A4MT are listed in Tables E.3 and E.4 in the Appendix.

2-Acetyl-4-Methylthiophene

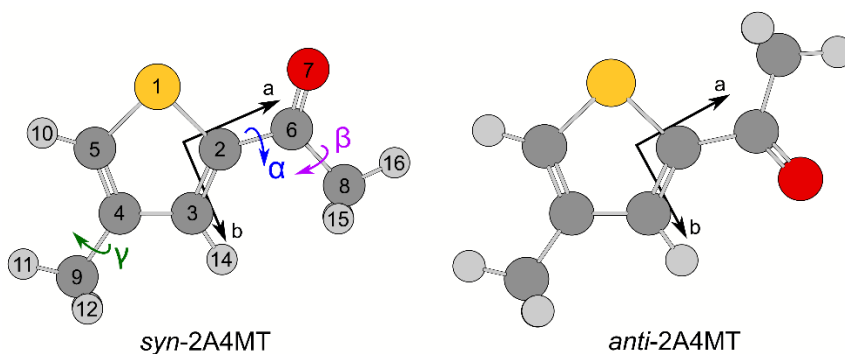


Figure 7.1: The two conformers of 2A4MT in their principal axes of inertia optimized at the B3LYP-D3BJ/6-311++G(d,p) level of theory. The atom numbering is given at *syn*-2A4MT, and the dihedral angles $\alpha = \angle(\text{S1-C2-C6=O7})$, $\beta = \angle(\text{C2-C6-C8-H16})$, and $\gamma = \angle(\text{C5-C4-C9-H11})$ are also shown. The sulphur atom is in yellow, the oxygen atom in red, hydrogen atoms are in grey, and carbon atoms in dark grey. H13 lies behind H12, H17 behind H15.

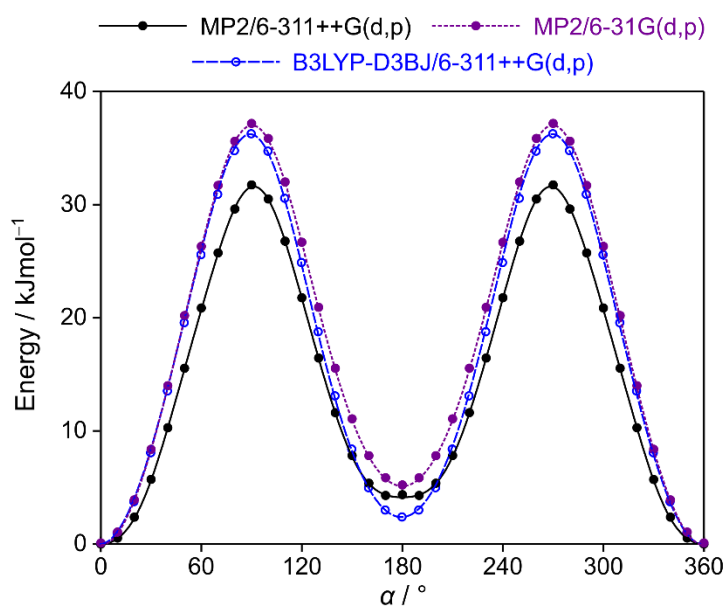


Figure 7.2: The potential energy curves of 2A4MT obtained by rotating the acetyl group about the C2–C6 bond. Calculations were performed at the MP2/6-311++G(d,p), MP2/6-31G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels of theory by varying the dihedral angle α in a grid of 10° . The relative energies are given in respect to the lowest energy conformation with $E_{\text{MP2/6-311++G(d,p)}} = -743.5356644$ Hartree, $E_{\text{MP2/6-31G(d,p)}} = -743.3676980$ Hartree, and $E_{\text{B3LYP-D3BJ}} = -745.1270403$ Hartree.

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Table 7.1: Rotational constants, dipole moments, dihedral angles, and relative energies for the two conformers of 2A4MT calculated at the MP2/6-311++G(d,p), MP2/6-31G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels of theory.

Par.	Unit	MP2/ 6-311++G(d,p)		MP2/ 6-31G(d,p)		B3LYP-D3BJ/ 6-311++G(d,p)	
		<i>syn</i>	<i>anti</i>	<i>syn</i>	<i>anti</i>	<i>syn</i>	<i>anti</i>
A_e	MHz	2625.9	2712.0	2638.1	2703.2	2610.6	2697.8
B_e	MHz	1004.5	988.2	1006.3	993.2	1006.2	990.6
C_e	MHz	733.2	732.7	735.1	732.9	732.9	731.1
$ \mu_a $	D	3.41	2.43	3.38	2.35	3.33	2.36
$ \mu_b $	D	3.41	2.32	3.25	2.19	2.81	2.15
$ \mu_c $	D	0.00	0.39	0.00	0.00	0.00	0.00
α	°	0.00	174.08	0.00	179.99	0.00	180.00
β	°	179.95	171.94	180.00	179.98	179.99	179.99
γ	°	0.39	0.79	0.00	0.04	0.03	0.01
ΔE^a	kJ·mol ⁻¹	0	5.96	0	4.82	0	1.88

^a Energy differences including zero-point corrections relative to the most stable conformer *syn*-2A4MT with $E_{\text{MP2/6-311++G(d,p)}} = -743.4048610$ Hartree, $E_{\text{MP2/6-31G(d,p)}} = -743.2331960$ Hartree and $E_{\text{B3LYP-D3BJ/6-311++G(d,p)}} = -744.9959270$ Hartree.

7.1.3. Methyl Internal Rotations

The barriers hindering the acetyl methyl and the ring methyl torsions were calculated by varying the dihedral angles $\beta = \angle(\text{C2-C6-C8-H16})$ and $\gamma = \angle(\text{C5-C4-C9-H11})$ in 10° steps while all other geometry parameters were optimized. Again, first the MP2/6-311++G(d,p), MP2/6-31G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels were employed. The resulting potential energy curves are shown in Figure 7.3 and Figure 7.4 for *syn*- and *anti*-2A4MT, respectively. The coefficients of the Fourier expansion used to plot the potential curves are given in Table E.5 and E.6 in the Appendix.

The benchmarking effort for the barrier heights of two rotor molecules that was started with 2A3MT (see Section 6.2.3.) is furthered with 2A4MT. The torsional barriers of both conformers were calculated with the same method/basis set combinations used for the structure optimizations. A selection of the results is shown in Table 7.2, where the predicted barrier heights and their deviations from the experimentally found values are given; the complete results can be found in Table E.3 and E.4 in the Appendix.

All curves of *syn*-2A4MT in Figure 7.3 exhibit typical threefold potentials expected for methyl rotors. The values of the barriers predicted at the three levels vary by nearly 150 cm^{-1} for the acetyl methyl group, whereas for the ring methyl group they only differ by about 40 cm^{-1} , indicating that predicting the acetyl methyl torsion is more difficult. When applying a larger set of levels to calculate the barrier heights, this is found to be a general trend, as exemplified in Table 7.2. The lowest trace of Figure 7.3 visualizes the corresponding movement of the second rotor, where only the MP2/6-311++G(d,p) level of theory predicts significant interactions between the acetyl methyl and the ring methyl rotors.

The potential energy curves of *anti*-2A4MT in Figure 7.4 behave very similarly to those of the *syn*-conformer, with the only exception being the double minimum found for the acetyl methyl group in the MP2/6-311++G(d,p) calculations. This behaviour can be explained by the existence of two non-planar forms predicted at this level of theory, which is visualized in the middle trace illustrating the oscillation of the entire acetyl group during the methyl internal rotation.

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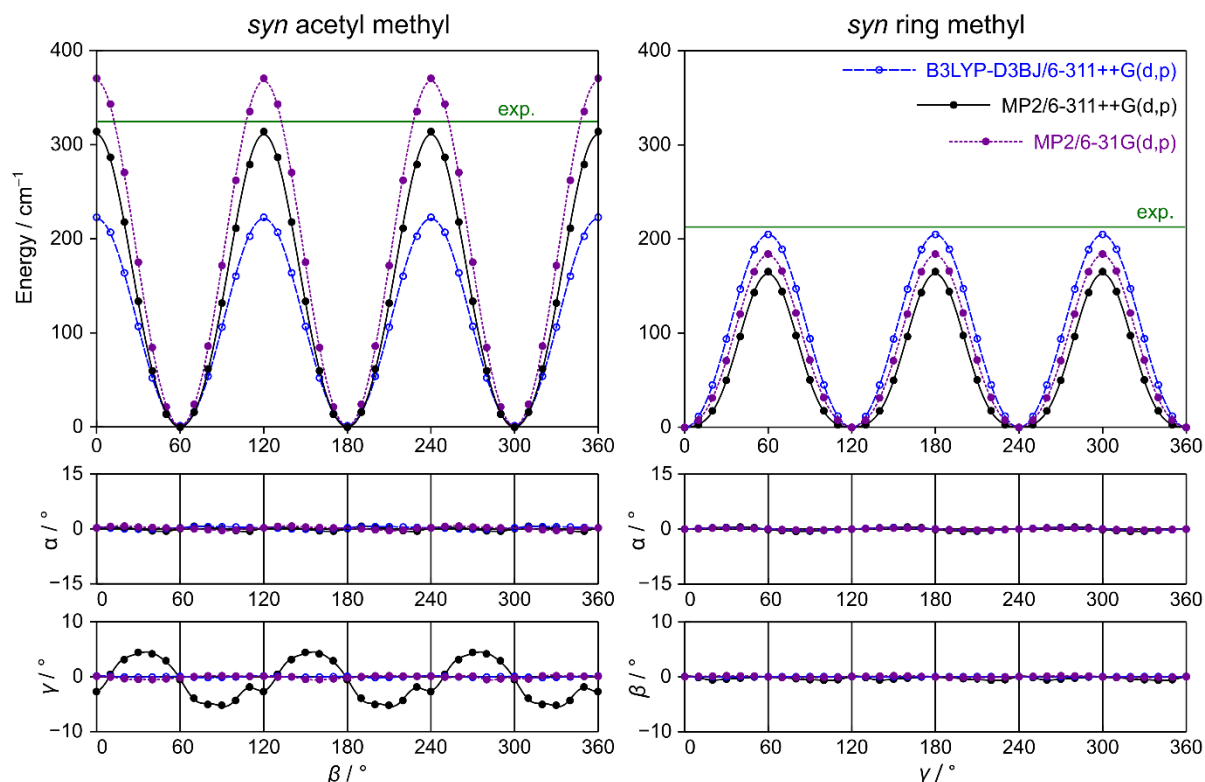


Figure 7.3: Left hand side: The upper trace shows the potential energy curves of the acetyl methyl torsion of *syn*-2A4MT about the C6–C8 bond. Calculations were performed at the MP2/6-311++G(d,p), MP2/6-31G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels of theory by varying the dihedral angle β in a grid of 10° . The calculated torsional barriers are 314.3 cm^{-1} , 370.2 cm^{-1} , and 221.4 cm^{-1} , respectively; the experimental value of 324.9 cm^{-1} is shown by a horizontal line. Relative energies are given in respect to the lowest energy conformations with $E_{\text{MP2/6-311++G(d,p)}} = -745.5356643$ Hartree, $E_{\text{MP2/6-31G(d,p)}} = -743.3676980$ Hartree, and $E_{\text{B3LYP-D3BJ}} = -745.1270402$ Hartree. The middle trace visualizes the oscillation of the acetyl group upon the acetyl methyl rotation and the lowest trace that of the ring methyl group. The deviations of the dihedral angles α and γ are given relative to the values of the fully optimized geometries, which are zero in all cases for α as well as 0.39° (MP2/6-311++G(d,p)), 0.32° (MP2/6-31G(d,p)), and 0.03° (B3LYP-D3BJ) for γ . **Right hand side:** The upper trace shows the potential energy curves of the ring methyl torsion about the C4–C9 bond of *syn*-2A4MT by varying the dihedral angle γ . The calculated torsional barriers are 165.7 cm^{-1} , 184.2 cm^{-1} , and 205.0 cm^{-1} , respectively; the experimental value is 210.7 cm^{-1} . Energy values of the lowest energy conformations are $E_{\text{MP2/6-311++G(d,p)}} = -745.5356644$ Hartree, $E_{\text{MP2/6-31G(d,p)}} = -743.3676980$ Hartree, and $E_{\text{B3LYP-D3BJ}} = -745.1270400$ Hartree. For the middle trace, reference values of α are also zero in all cases. The lower trace visualizes the oscillation of the acetyl methyl group upon the ring methyl rotation. The deviations of the dihedral angle β are

given relative to the values of 179.95° (MP2/6-311++G(d,p)), 179.97° (MP2/6-31G(d,p)), and 179.97° (B3LYP-D3BJ) of the fully optimized geometries.

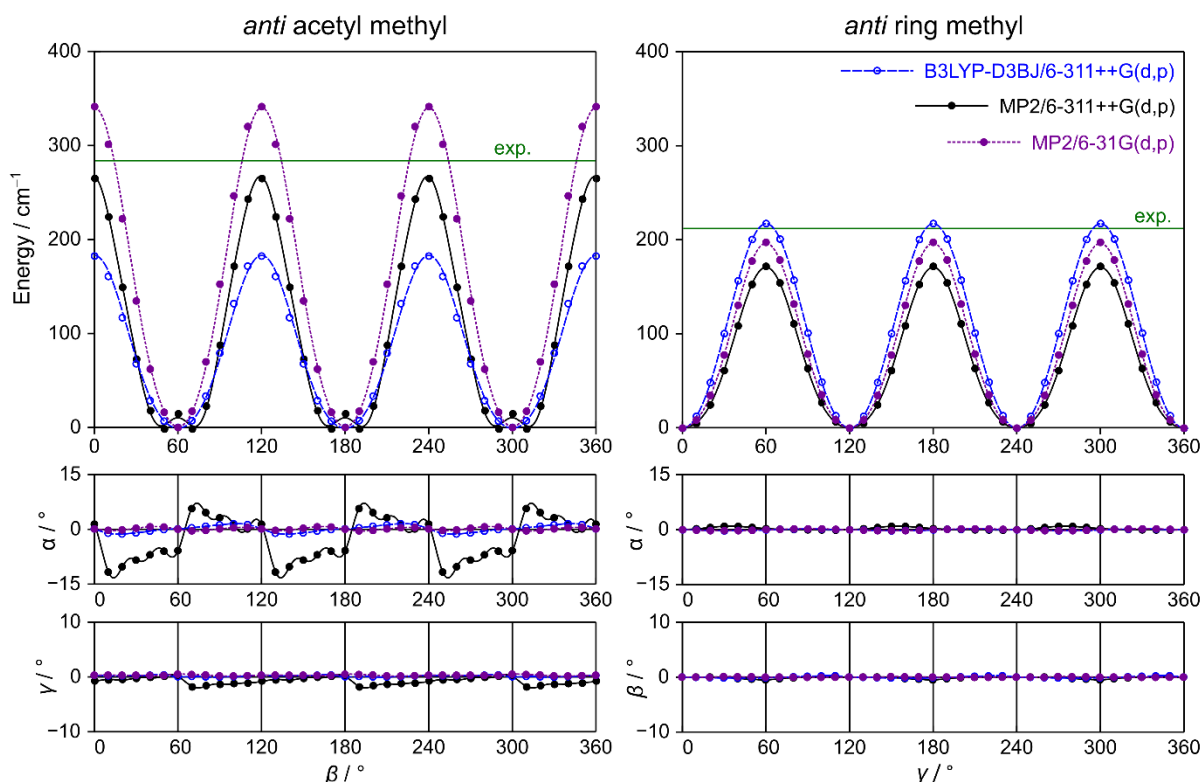


Figure 7.4: Left hand side: The upper trace shows the potential energy curves of the acetyl methyl torsion of *anti*-2A4MT about the C6–C8 bond. Calculations were performed at the MP2/6-311++G(d,p), MP2/6-31G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels of theory by varying the dihedral angle β in a grid of 10°. The calculated torsional barriers are 266.4 cm⁻¹, 341.4 cm⁻¹ and 182.3 cm⁻¹, respectively; the experimental value of 281.2 cm⁻¹ is shown by a horizontal line. Relative energies are given in respect to the lowest energy conformations with $E_{\text{MP2/6-311++G(d,p)}} = -745.5340614$ Hartree, $E_{\text{MP2/6-31G(d,p)}} = -743.3657427$ Hartree, and $E_{\text{B3LYP-D3BJ}} = -745.1261434$ Hartree. The MP2/6-311++G(d,p) calculation predicts double minima around $\beta = 60^\circ$, 180° , and 300° , corresponding with the two enantiomeric forms found in the geometry optimizations. The other two potential energy curves show a typical threefold symmetry. The middle trace visualizes the oscillation of the acetyl group upon the acetyl methyl rotation and the lowest trace that of the ring methyl group. The deviations of the dihedral angles α and γ are given relative to the values of the fully optimized geometries, which are 174.08° (MP2/6-311++G(d,p)), 179.99° (MP2/6-31G(d,p)), and 179.99° (B3LYP-D3BJ) for α , as well as 0.79°, 0.25°, and -0.18°, respectively, for γ . **Right hand side:** The upper trace shows the potential energy curves of the ring methyl torsion about the C4–C9 bond of *anti*-2A4MT by varying the

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dihedral angle γ . The calculated torsional barriers are 172.3 cm^{-1} , 197.7 cm^{-1} and 217.7 cm^{-1} , respectively; the experimental value is 213.0 cm^{-1} . Energy values of the lowest energy conformations are $E_{\text{MP2/6-311++G(d,p)}} = -745.5340612$ Hartree, $E_{\text{MP2/6-31G(d,p)}} = -743.3657427$ Hartree, and $E_{\text{B3LYP-D3BJ}} = -745.1261434$ Hartree. All three curves show the threefold symmetry typical for methyl groups. For the middle trace, reference values of α are the same as for the left hand side figure. The lower trace visualizes the oscillation of the acetyl methyl group upon the ring methyl rotation. The deviations of the dihedral angle β are given relative to the values of 171.94° (MP2/6-311++G(d,p)), 179.99° (MP2/6-31G(d,p)), and 179.97° (B3LYP-D3BJ) of the fully optimized geometries.

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Table 7.2: Torsional barriers (in cm^{-1}) of the acetyl methyl and the ring methyl groups in *syn*- and *anti*-2A4MT calculated with Pople's 6-311++G(d,p) basis set in combination with different methods. The deviations between the experimental and the calculated values are given as absolute values (in cm^{-1}) as well as in percent relative to the experimental values in parentheses.

Method	<i>syn</i> -2A4MT				<i>anti</i> -2A4MT			
	Acetyl	Dev.	Ring	Dev.	Acetyl	Dev.	Ring	Dev.
MP2	314.3	10.6 (3)	165.7	45.0 (21)	266.4	14.8 (5)	172.3	40.7 (19)
MP2 ^a	370.2	−45.3 (−14)	184.2	26.5 (13)	341.4	−60.2 (−21)	197.7	15.3 (7)
B3LYP-D3	257.1	67.8 (21)	203.1	7.6 (4)	223.6	57.6 (20)	216.2	−3.2 (−2)
B3LYP-D3BJ	221.4	103.5 (32)	205.0	5.7 (3)	182.3	98.9 (35)	217.7	−4.7 (−2)
CAM-B3LYP-D3BJ	248.3	76.6 (24)	220.0	−9.3 (−4)	204.3	76.9 (27)	235.3	−22.3 (−10)
M06-2X	335.3	−10.4 (−3)	217.8	−7.1 (−3)	279.0	2.2 (1)	231.0	−18.0 (−8)
ωB97X-D	320.4	4.5 (1)	206.1	4.6 (2)	244.8	36.4 (13)	225.5	−12.5 (−6)
Experimental	324.9		210.7		281.2		213.0	

^a Calculated in combination with the 6-31G(d,p) basis set.

To further study the interactions of the two rotors, two-dimensional potential energy surfaces (2D-PES) depending on the dihedral angles β and γ were calculated at the MP2/6-31G(d,p) and B3LYP-D3BJ/6-311++G(d,p) levels of theory. Only data points in the range from 0° to 120° were necessary for β and γ due to symmetry. The potential energies were parameterized with a Fourier expansion accounting for the correct symmetry of the methyl groups, with the coefficients listed in Table E.7 in the Appendix. The MP2/6-311++G(d,p) level was not used, because the previous investigation on 2A3MT (Chapter 6, [3]) showed that parameterizing the energy points is not possible due to the rearrangement of the acetyl group from one non-planar enantiomer to the other (see Figure E.1). The 2D-PES of *syn*- and *anti*-2A4MT are shown in Figure 7.5.

The 2D-PES for *syn*-2A4MT predicted at the MP2/6-31G(d,p) level displays minima with very oblate rather than circular forms, indicating that there are couplings between the two rotors. This is not the case in calculations at the B3LYP-D3BJ/6-311++G(d,p) level, i.e., the two levels disagree on the presence of top-top interactions. For *anti*-2A4MT, the 2D-PES obtained with both methods show that the interactions exist.

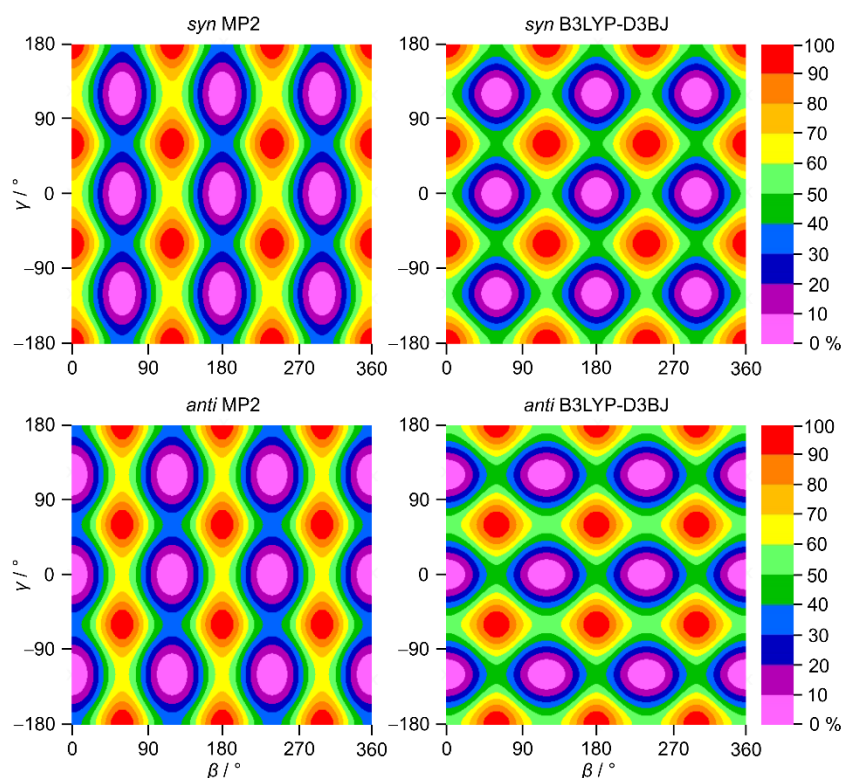


Figure 7.5: The 2D-PES of *syn*- and *anti*-2A4MT calculated at the MP2/6-31G(d,p) and B3LYP-D3BJ/6-311++G(d,p) levels of theory. All geometry parameters were optimized except the two dihedral angles β and γ , which were varied in a grid of 10° . The colour codes indicate the relative energies (in percent) between the minima and the maxima, which are $E_{\min, \text{MP2}} =$

-743.367698 Hartree (0%) and $E_{\text{max,MP2}} = -743.365198$ Hartree (100 %) as well as $E_{\text{min,B3LYP}} = -745.127040$ Hartree (0%) and $E_{\text{max,B3LYP}} = -745.125118$ Hartree (100 %) for the *syn*-conformer. The values for the *anti*-conformer are $E_{\text{min,MP2}} = -743.365743$ Hartree, $E_{\text{max,MP2}} = -743.363317$ Hartree, $E_{\text{min,B3LYP}} = -745.126144$ Hartree, and $E_{\text{max,B3LYP}} = -745.124366$ Hartree (100 %).

7.2. Microwave Spectroscopy

7.2.1. Measurements

A scan from 9.0 to 14.9 GHz was recorded as a series of overlapping spectra with a step width of 250 kHz using a molecular jet Fourier-transform microwave spectrometer operating in the frequency range from 2.0 to 26.5 GHz [33]. For each measurement, 50 free-induction decays were co-added. A portion of the scan is illustrated in Figure 7.6. 2A4MT was purchased from Sigma-Aldrich, Schnelldorf, Germany, with a stated purity of 97 % and used without further purification. Helium as the carrier gas with a backing pressure of 2 bar was flown over the substance, which was put on a pipe cleaner and inserted upstream of the nozzle. All signals appearing in the survey spectrum as well as transitions outside of the initial scan range were later remeasured at higher resolution with an experimental accuracy of 2 kHz [69]. The average line width at half height is 23 kHz, 1/10th of which (2.3 kHz) corresponds to the estimated measurement accuracy.

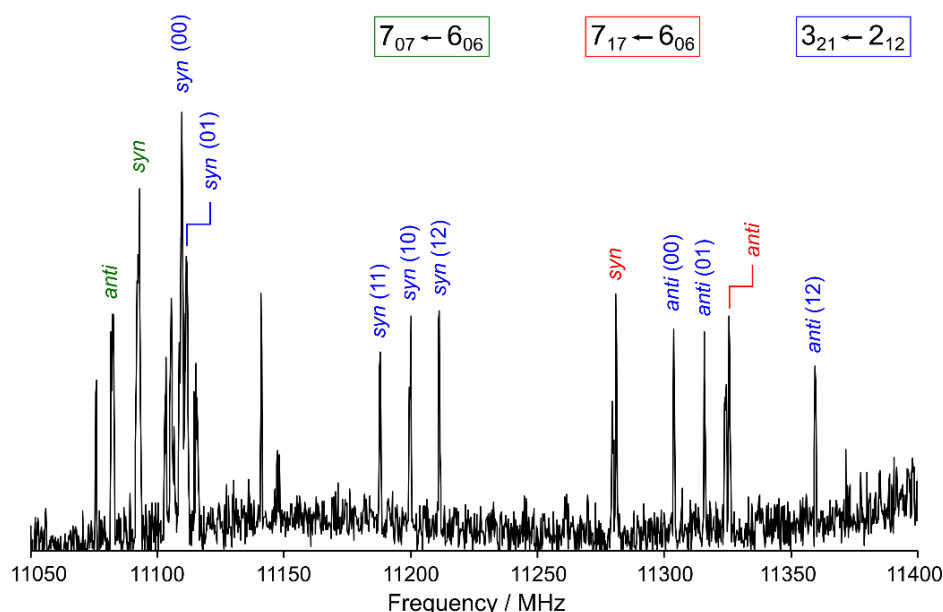


Figure 7.6: A portion of the scan of 2A4MT in the frequency range from 11050 to 11400 MHz recorded by overlapping spectra with 50 co-added decays per each spectrum. Lines belonging

to the $7_{07} \leftarrow 6_{06}$, $7_{17} \leftarrow 6_{06}$, and $3_{21} \leftarrow 2_{12}$ transitions are labelled with the corresponding conformer. For the *b*-type $3_{21} \leftarrow 2_{12}$ transition the torsional species are labelled in parentheses. For the other two transitions, the torsional splittings are too small to be resolved in the scan. The intensities are given in a logarithmic scale in an arbitrary unit. The temperature of the molecular jet was approximately 1-2 K.

7.2.2. Spectral Assignment

As quantum chemical calculations predicted *syn*-2A4MT to be energetically more stable, the assignment was started using the rotational constants of this conformer calculated at the MP2/6-311++G(d,p) level (see Table 7.1). With the program *XIAM* [40] a rigid rotor spectrum was predicted first without taking the effects of internal rotation into account. Due to the calculated dipole moments, strong *a*- and *b*-type transitions and no *c*-type transitions were expected.

An initial assignment was achieved without any issue due to the rather accurately predicted rotational constants. Based on this rigid rotor fit, the effects of internal rotation could then be taken into account. Just as with 2A3MT (Chapter 6, [3]), each rotational transition of 2A4MT splits into five torsional components ($\sigma_1\sigma_2$) = (00), (01), (10), (11), and (12) [14][38] due to the two inequivalent rotors, as shown in Figure 7.7; σ_1 and σ_2 refer to the acetyl methyl and the ring methyl group, respectively. Two separate one top fits were built up first, only accounting for the (00) and (01) or (10) torsional species while neglecting the (11) and (12) species arising from top-top interactions. The identification of the (01) and (10) species was uncomplicated, because the barriers hindering the two methyl torsions differ by about 110 cm⁻¹, resulting in significantly different splitting patterns (see Figure 7.7), which could be straightforwardly assigned.

The assignment of the (11) and (12) species was very problematic when it was attempted to carry out a global fit accounting for both internal rotations. For a large number of transitions of *syn*-2A4MT the lines of the two torsional species are very close. The (11)-(12) splittings are often under the resolution limit. A correct assignment using only predictions of the program *XIAM* was not possible, and different methods had to be employed in addition. The use of combination difference loops (Ritz cycles) as described in Ref. [81] and the program *SFLAMS* for Separately Fitting of Large Amplitude Motion Species [12] made it possible to verify whether the frequencies were of the same species. The separate fits for all five torsional species obtained with *SFLAMS* achieved measurement accuracy, as given in Table 7.3. Once the assignments of individual species was certain, all frequencies were included in a global *XIAM*

fit with a first arbitrary trial for the (11)/(12) assignment. The determination of the correct species could then be achieved easily in the global fit, as the wrong (11)/(12) assignment led to a significant increase of the standard deviation. Ultimately, 890 lines are included in the *XIAM* global fit (see Table 7.4) which has a standard deviation of 3.4 kHz. The assigned transitions are listed in Table E.8 in the Appendix.

After *syn*-2A4MT was assigned, a number of lines still remained in the spectrum. Due to the rather large energy gap between the two conformers predicted with the MP2 method (see Table 7.1), it was first attempted to assign these transitions to the ^{34}S - and ^{13}C -isotopologues of *syn*-2A4MT, which failed. It turned out that the remaining transitions in fact belong to the *anti*-conformer. The analysis of the torsional fine structure of *anti*-2A4MT was successful by using only the program *XIAM*. The final global fit shown in Table 7.4 includes 359 lines. The assigned transitions are listed in Table E.9 in the Appendix.

After both *syn*- and *anti*-2A4MT had been assigned, only a very small number of weak lines remained in the spectrum. They most likely belong to the isotopologues of *syn*-2A4MT, but due to their small number and low intensities, no assignments were possible.

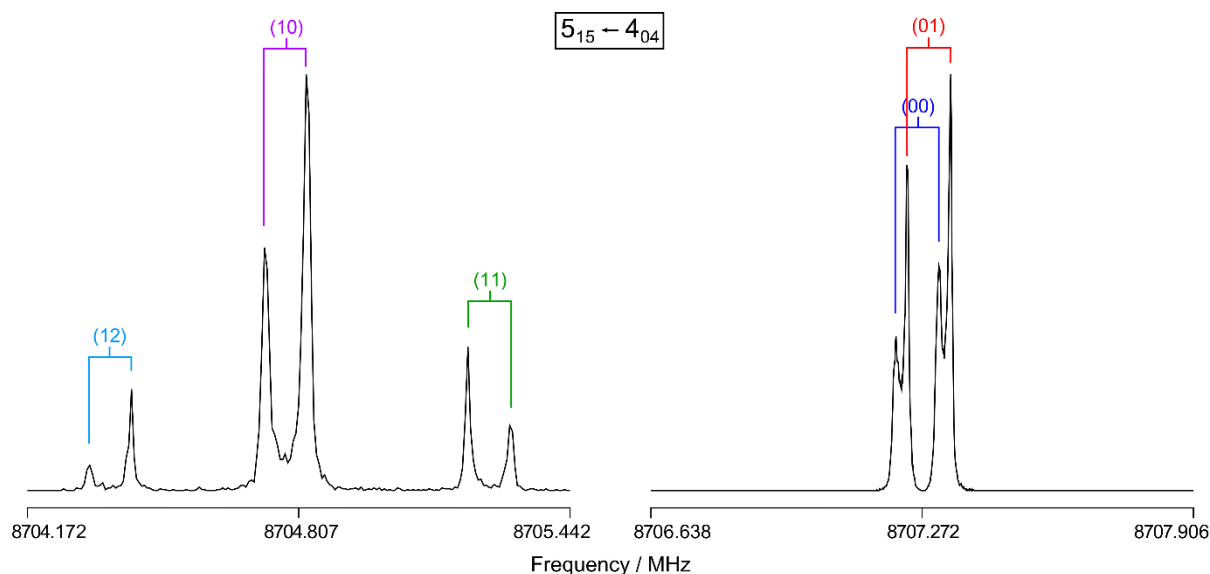


Figure 7.7: Typical high resolution measurements of the *b*-type rotational transition $5_{15} \leftarrow 4_{04}$ of *syn*-2A4MT with its five torsional species (00), (10), (01), (11), and (12). The frequency is given in MHz. The brackets indicate Doppler pairs. The spectra were recorded at 8704.78 MHz and 8707.25 MHz; 145 and 1942 free induction decays were co-added, respectively.

2-Acetyl-4-Methylthiophene

Table 7.3: Molecular parameters obtained from the *SFLAMS* fits of all five torsional species of *syn*-2A4MT.

Par. ^a	Unit	(00)	(01)	(10)	(11)	(12)
<i>A</i>	MHz	2646.24510(16)	2646.16204(12)	2644.34848(23)	2644.26521(22)	2644.26580(21)
<i>B</i>	MHz	1006.336980(47)	1006.281189(41)	1006.237534(76)	1006.181833(75)	1006.181768(82)
<i>C</i>	MHz	735.795173(34)	735.796273(25)	735.795885(46)	735.797123(45)	735.797048(52)
Δ_J	kHz	0.02292(16)	0.02233(17)	0.02336(30)	0.02302(34)	0.02276(37)
Δ_{JK}	kHz	0.0104(18)	0.0089(16)	−0.0179(33)	−0.0166(32)	−0.0155(33)
Δ_K	kHz	0.6307(61)	0.6134(38)	0.517(12)	0.488(11)	0.517(11)
δ_J	kHz	−0.007945(92)	−0.00746(10)	−0.00799(19)	−0.00742(22)	−0.00731(24)
δ_K	kHz	−0.001039(48)	−0.001039(44)	−0.000841(83)	−0.00100(11)	−0.00070(14)
<i>q</i>	MHz		6.08400(26)	74.33572(50)	68.24826(46)	80.42373(44)
<i>q_J</i>	kHz		−0.2076(61)	−0.908(10)	−0.6951(96)	−1.198(10)
<i>q_K</i>	kHz			−10.306(39)	−10.225(35)	−10.382(35)
<i>r</i>	MHz		5.509(16)	17.2710(90)	22.8068(73)	11.709(16)
<i>N</i> ^b		240	221	209	107	113
σ ^c	kHz	3.1	2.3	3.8	2.5	2.8

^a All parameters refer to the principal axis system. Watson's A reduction in the I' representation was used. ^b Number of lines. ^c Standard deviation of the fit.

2-Acetyl-4-Methylthiophene

Table 7.4: Experimental spectroscopic parameters of *syn*- and *anti*-2A4MT obtained with the program *XIAM* compared to the predicted values. Rotors 1 and 2 refer to the acetyl methyl and the ring methyl group, respectively.

Par. ^a	Unit	<i>syn</i> -2A4MT				<i>anti</i> -2A4MT			
		<i>XIAM</i>	MP2/ 6-311++G(d,p) ^b	MP2/ 6-31G(d,p) ^b	B3LYP-D3BJ/ 6-311++G(d,p) ^b	<i>XIAM</i>	MP2/ 6-311++G(d,p) ^b	MP2/ 6-31G(d,p) ^b	B3LYP-D3BJ/ 6-311++G(d,p) ^b
A_0	MHz	2644.92816(15)	2611.638	2627.945	2600.213	2730.5802(27)	2712.743	2689.625	2683.864
B_0	MHz	1006.233649(76)	999.408	999.044	998.622	991.4522(52)	981.774	986.763	983.965
C_0	MHz	735.790760(24)	730.519	730.662	728.277	734.2751(22)	725.227	728.800	726.936
Δ_J	kHz	0.02461(15)	0.0234	0.0230	0.0234	0.02257(24)	0.0231	0.0215	0.0218
Δ_{JK}	kHz	-0.0184(11)	-0.0065	-0.0170	-0.0119	-0.0172(34)	-0.0147	-0.0146	-0.0080
Δ_K	kHz	0.5458(34)	0.4971	0.5096	0.5097	0.524(14)	0.5180	0.4724	0.4853
δ_J	kHz	0.007649(70)	0.0072	0.0071	0.0072	0.00664(10)	0.0064	0.0064	0.0065
δ_K	kHz	0.0462(17)	0.0217	0.0420	0.0440	0.0329(47)	0.0536	0.0375	0.0333
$V_{3,1}$	cm ⁻¹	324.919(94)	314.3	370.2	221.4	281.201(17)	266.4	341.4	182.3
$D_{p_1^2 J}$	kHz	40.63(97)				18.87(27)			
$D_{p_1^2 K}$	kHz	-258.2(28)							
$D_{p_1^2 -}$	kHz	20.71(97)				-1.12(30)			
$\angle(i_1, a)$	deg	67.304(30)	71.6	70.9	71.0	44.487(13)	48.2	47.1	47.5
$\angle(i_1, b)$	deg	22.696(30)	18.4	19.1	19.0	134.488(13)	137.4	137.1	137.5
$\angle(i_1, c)$	deg	90.0 ^c	90.0	90.0	90.0	90.0 ^c	83.1	90.0	90.0
$V_{3,2}$	cm ⁻¹	210.7181(61)	165.7	184.2	205.0	212.9797(41)	172.3	197.7	217.7
$D_{p_2^2 J}$	kHz	8.60(15)				10.65(11)			
$D_{p_2^2 K}$	kHz	22.17(96)							
$D_{p_2^2 -}$	kHz	6.73(14)				8.70(12)			
$\angle(i_2, a)$	deg	148.5832(86)	149.1	149.2	148.1	150.5204(61)	151.2	150.8	150.4
$\angle(i_2, b)$	deg	58.5832(86)	59.1	59.2	58.1	60.5204(61)	61.3	60.8	60.4

2-Acetyl-4-Methylthiophene

$\angle(i_2, c)$	deg	90.0 ^c	90.0	90.0	90.0	90.0 ^c	88.4	90.0	90.0
N^d		890				359			
σ^e	kHz	3.4				2.5			

^a All parameters refer to the principal axis system. Watson's A reduction and I' representation were used. The rotational constants F_0 , describing the moment of inertia of the methyl internal rotors, could not be fitted for either of the conformers and were fixed to 158 GHz, a typical value for methyl groups. ^b Ground state rotational constants and centrifugal distortion constants obtained from anharmonic frequency calculations. ^c Fixed due to symmetry. ^d Number of transitions.

^e Standard deviation of the fit.

7.3. Discussion

7.3.1. Conformational Stability

Five-membered heterocycles containing a carbonyl-substituent at the second position prefer either a *syn*- or an *anti*-conformation due to the maximum overlap between the π -orbitals of the aromatic ring and the carbonyl group, as has been long established [73] and shown in previous microwave spectroscopic investigations, including the ones in this thesis [1][2][3][4][71][24]. Both of these conformers were observed in the microwave spectrum of 2A4MT. Quantum chemical calculations at all employed levels of theory predicted the *syn*-conformer to be energetically more stable. Though it is difficult to give a quantitative statement on the conformational stability due to the lack of dipole moment measurements and the rather unreliable intensity of the experimental setup, the experiments qualitatively confirm this prediction as visualized in Figure 7.6. This is also shown in Table 7.4 by the fact that the number of lines assigned for the *syn* conformer is more than two times that of the *anti* form. The greater stability of *syn*-2A4MT also aligns well with the results found for three other thiophene derivatives, 2-thiophenecarboxaldehyde [71][72], 2AT (Chapter 3, [4]), and 2PT (Chapter 4, [1]), where it was explained by dipole-dipole interactions between the positively charged sulphur atom of the ring and the negatively charged oxygen atom of the carbonyl group. This is also the case for 2A4MT, as shown by NBO calculations [74] performed using the *Gaussian* 16 program package [41] with the results depicted in Figure 7.8.

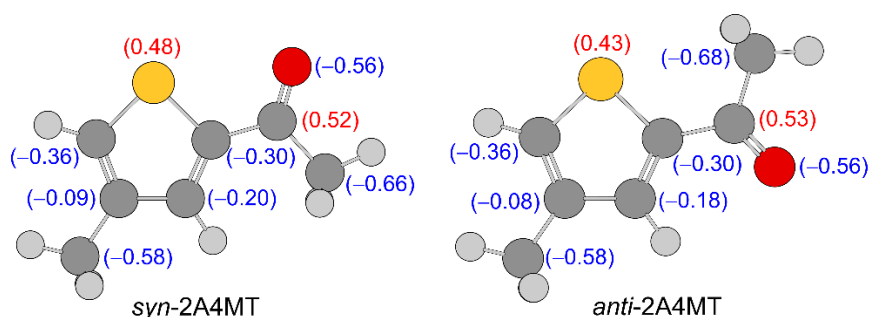


Figure 7.8: Charge distributions in *syn*- and *anti*-2A4MT obtained from NBO calculations at the B3LYP-D3BJ/6-311++G(d,p) level of theory.

7.3.2. Quality of the Fits

For *syn*- and *anti*-2A4MT, 890 and 359 lines could be assigned with the program *XIAM* [40] to standard deviations of 3.4 kHz and 2.5 kHz, respectively. For the *anti*-conformer this value is in good agreement with the experimental accuracy. The slightly higher deviation for the *syn*-conformer is mainly caused by several *b*-type transitions with $K_a = 3 \leftarrow 2$ (see Table E.8). Since the separate fit for the (00) species transitions, which should follow a semi-rigid rotor approximation, has a very similar standard deviation of 3.1 kHz (see Table 7.3) and the predictive power of the fit is quite good, it was not attempted to reduce this further.

7.3.3. Molecular Parameters

In the case of *anti*-2A4MT, some MP2 calculations predict a non-planar structure with a small tilt angle of the acetyl group out of the thiophene plane, the same way as they also perform for 2-acetylthiophene (Chapter 3, [4]) and 2A3MT (Chapter 6, [3]). Given that the inertial defects Δ_c derived from the experimentally determined rotational constants of *syn*- and *anti*-2A4MT are $-6.471 \text{ u}\text{\AA}^2$ and $-6.548 \text{ u}\text{\AA}^2$, respectively, it can be assumed that both conformers are planar, or at least possess effective planar structures. The values are very similar and close to those of other planar molecules with four out-of-plane hydrogen atoms such as the *cis-trans* conformer of ethylnitrite ($\Delta_c = -6.422 \text{ u}\text{\AA}^2$) [91] or the C_s conformer of 2-ethylfuran ($\Delta_c = -6.483 \text{ u}\text{\AA}^2$) [87]. The inertial defect of $-6.559 \text{ u}\text{\AA}^2$ of *anti*-2A3MT (Chapter 6, [3]) is extremely close to that of *anti*-2A4MT. Nevertheless, as no isotopologue data was available for either of the isomers and thus no structure determination was possible, the inertial defect cannot be considered absolute proof of a planar structure.

The results of the benchmark calculations on rotational constants show that for *syn*-2A4MT three levels of theory achieved comparably good predictions: MP2/6-31G(d,p) and MP2/6-311+(+)G(df,pd). The MP2/6-31G(d,p) level already stood out in previously carried out benchmarks for other molecules containing aromatic rings such as *o*-methylanisole [125], 2A3MT (Chapter 6, [3]), coumarin [124], and 2-ethylfuran [87]. It was also recommended by *Kisiel et al.* for quinoline and isoquinoline [126]. For the *anti*-conformer, the result of MP2/6-31G(d,p) is satisfactory, but the MP2/6-311+(+)G(df,pd) and B3LYP-D3BJ/6-311+(+)G(3df,3dp) levels perform better. As mentioned above, some MP2 methods predict non-planar equilibrium structures for *anti*-2A4MT, where the acetyl group is tilted out of the thiophene plane by an angle θ of about 4.7° to 6.7° (see Table E.4), and the MP2/6-311+(+)G(df,pd) levels belong to this group.

7.3.4. Methyl Internal Rotation

The barriers to internal rotation of the acetyl methyl and the ring methyl group deduced from the *XIAM* fit are 324.919(94) cm^{-1} and 210.7181(61) cm^{-1} for *syn*-2A4MT, as well as 281.201(17) cm^{-1} and 212.9797(41) cm^{-1} for *anti*-2A4MT, respectively. Compared to the predicted values visualized in Figures 7.3 and 7.4 in Section 7.1.3., it can be found that the torsional barrier of the ring methyl rotor of both conformers was predicted more accurately. Furthermore, the three employed method/basis set combinations deliver far more similar values for the ring methyl rotor. The values differ by up to 45.4 cm^{-1} for the ring methyl group depending on the employed method, whereas for the acetyl methyl group the variance is more than three times bigger with up to 159.1 cm^{-1} . Similar results can be found with all employed calculation methods listed in Table E.3 and E.4 in the Appendix. The same difficulty in accurately predicting torsional barriers for acetyl methyl groups was also shown in the investigation of 2A3MT (Chapter 6, [3]) as well as other molecules found in the literature such as *N*-acetyl alanine methyl ester [120] or octan-2-one [11]. As such it is not surprising that most method/basis set combinations employed for benchmarking purposes do not calculate both the acetyl methyl and ring methyl torsional barriers well at the same time (see Table E3 and E4 in the Appendix), as was also the case for the previous isomer 2A3MT.

2A4MT was investigated as the next logical step in establishing a possible “thiophene class” of acetyl methyl rotors. The discussion including all thiophene derivatives containing an acetyl substituent studied in this thesis can be found in Section 8.3.3.

To explore the effects of the acetyl group on the internal rotation of the ring methyl group, the torsional barrier of the latter found in 2A3MT and 2A4MT are compared with that of 3-methylthiophene (**8**) [101] (shown in blue in Figure 7.9). The barrier height of 258.8 cm^{-1} found in 3-methylthiophene increases significantly in *anti*-2A3MT (**10**) to 321.8 cm^{-1} due to steric hindrance arising from the neighbouring acetyl group but decreases to about 210 cm^{-1} in 2A4MT (**11**). Since the ring methyl groups of 3-methylthiophene and 2A4MT are both almost steric-free, this demonstrates that electrostatic effects are most probably the reason for this difference. The values found for *syn*- and *anti*-2A4MT are essentially the same, indicating that the influence of the acetyl conformation on the ring methyl torsion is negligible.

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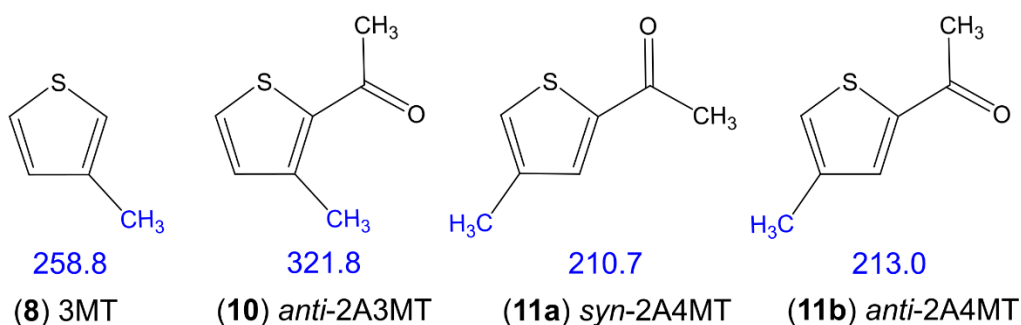
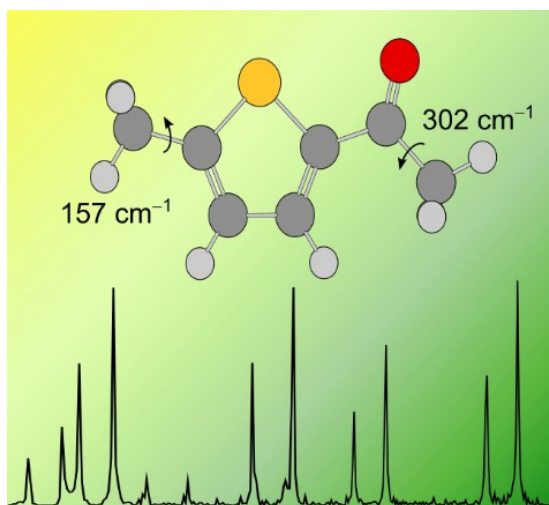


Figure 7.9: The methyl ring torsional barriers of (8) 3-methylthiophene (3MT) [101], (10) *anti*-2-acetyl-3-methylthiophene (Chapter 6, [3]) and (11) 2-acetyl-4-methylthiophene marked in blue, given in cm⁻¹.

7.4. Conclusion

With support from quantum chemical calculations, the microwave spectra of the *syn*- and *anti*-conformers of 2A4MT were successfully assigned. Splittings into quintets due to internal rotations of the two non-equivalent methyl tops allowed the experimental determination of the torsional barriers. Values of 324.919(94) cm⁻¹ and 210.7181(61) cm⁻¹ were found for the acetyl and the ring methyl groups of *syn*-2A4MT, respectively, as well as 281.201(17) cm⁻¹ and 212.9797(41) cm⁻¹ for *anti*-2A4MT. These values are important data points to establish the “thiophene class” with acetylthiophene derivatives as representatives.

8. 2-Acetyl-5-Methylthiophene



Christina Dindić performed measurements, quantum chemical calculations and spectral assignments.

8.1. Quantum Chemical Calculations

8.1.1. Conformational Analysis

The acetyl group is the only moiety in 2-acetyl-5-methylthiophene (2A5MT) whose change in orientation can create conformers and based on the previous molecules investigated in this thesis obviously only two conformers, *syn* and *anti*, are to be expected. For a conformational analysis the dihedral angle $\alpha = \angle(\text{S1-C2-C6=O7})$ (for atom numbering see Figure 8.1) was varied in 10° steps, while all other geometry parameters were optimized at the MP2/6-31G(d,p) [42][59] level of theory using the *Gaussian 16* program package [41]. This level of theory was chosen as it predicted rotational constants which were very close to the experimentally determined ones for the two isomers of 2A5MT, 2A3MT and 2A4MT (Chapter 6 [3], Chapter 7 [5]). The energy points obtained from these calculations were parameterized with a Fourier expansion using the coefficients given in Table F.1 in the Appendix. The resulting potential energy curve given in Figure 8.2 shows that 2A5MT indeed possesses the two expected conformers, which correspond to the minima at $\alpha = 0^\circ$ (*syn*-2A5MT) and $\alpha = 180^\circ$ (*anti*-2A5MT). Subsequent full structure optimizations and frequency calculations confirmed both conformers (shown in Figure 8.1) to be stable. The calculated rotational constants, dipole moments, dihedral angles, and energy difference between the two conformers are given in Table 8.1; the atomic coordinates of both conformers are listed in Table F.2 in the Appendix.

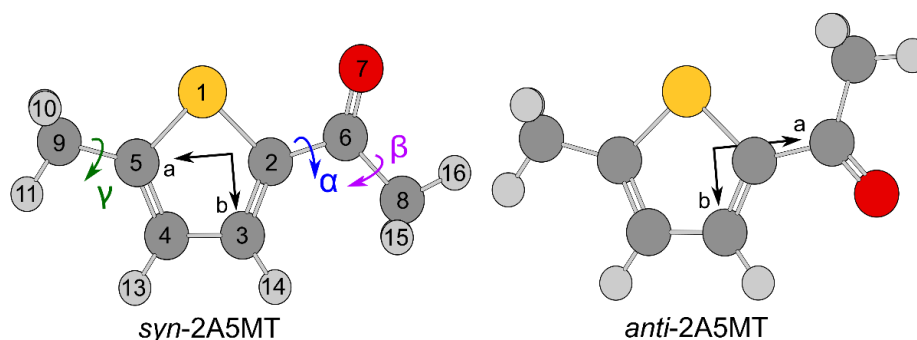


Figure 8.1: Geometries of the two conformers of 2A5MT (*syn* and *anti*) optimized at the MP2/6-31G(d,p) level of theory in the principal axes of inertia. Atom numbering as well as the dihedral angles $\alpha = \angle(\text{S1-C2-C6=O7})$, $\beta = \angle(\text{C2-C6-C8-H15})$, and $\gamma = \angle(\text{S1-C5-C9-H10})$ are defined for *syn*-2A3MT. The sulphur atom is marked in yellow, the oxygen atom in red, carbon atoms are in dark grey, and hydrogen atoms in light grey. H12 lies behind H10, H17 behind H15.

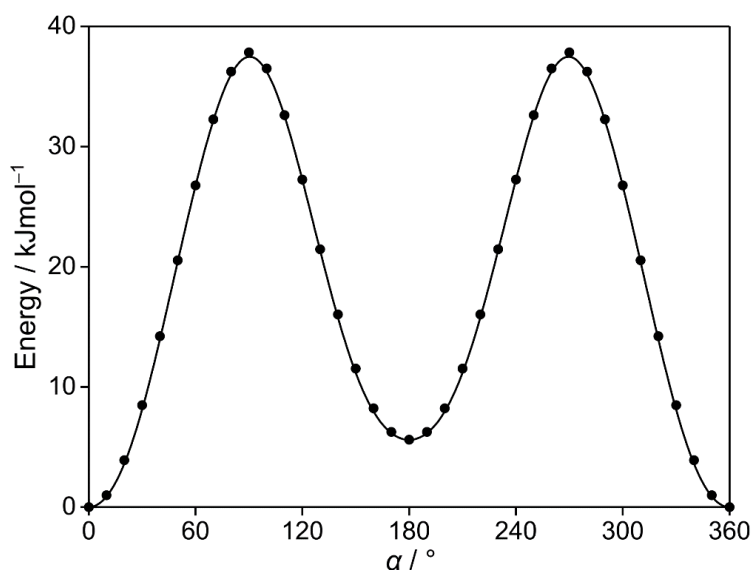


Figure 8.2: The potential energy curve of 2A5MT obtained by rotating the acetyl group about the C2–C6 bond (for atom numbering see Figure 8.1). Calculations were performed at the MP2/6-31G(d,p) level of theory by varying the dihedral angle α in a grid of 10° . The relative energies are given in respect to the lowest energy conformation with $E_{MP2} = -743.3683072$ Hartree.

Table 8.1: Rotational constants, dipole moments, dihedral angles, and relative energies for the two conformers of 2A5MT calculated at the MP2/6-31G(d,p) level of theory.

Par.	Unit	<i>syn</i>	<i>anti</i>
A_e	MHz	3425.2	3356.6
B_e	MHz	927.6	928.8
C_e	MHz	736.6	734.1
$ \mu_a $	D	2.33	3.55
$ \mu_b $	D	3.87	1.58
$ \mu_c $	D	0.00	0.00
α	°	0.00	180.00
β	°	0.00	−0.00
γ	°	179.86	179.98
ΔE^a	kJ·mol ^{−1}	0.0	5.3

^a Energy differences including zero-point corrections relative to the more stable conformer *syn*-2A5MT with $E = -743.2336782$ Hartree.

8.1.2. Basis Set Variations

In addition to the MP2/6-31G(d,p) level of theory, the structure of the more stable and only experimentally assigned conformer *syn*-2A5MT was also optimized using various other method/basis set combinations as explained in Section 3.2.2. The results are summarized in Table F.3 in the Appendix and will be discussed in comparison to the experimental values in Section 8.3.3.

8.1.3. Methyl Internal Rotations

2A5MT possesses two inequivalent internal rotors, the acetyl methyl and the ring methyl group. Thus transitions were expected to split into five torsional components ($\sigma_1\sigma_2$) = (00), (01), (10), (11), and (12) [14][38] like they did for the two previously investigated isomers. In order to predict the barriers to internal rotation, the respective dihedral angles $\beta = \angle(\text{C2-C6-C8-H15})$ and $\gamma = \angle(\text{S1-C5-C9-H10})$ were varied in 10° steps while all other geometry parameters were optimized at the MP2/6-31G(d,p) level of theory. The resulting potential energy curves for *syn*-2A5MT are shown in Figure 8.3, those of *anti*-2A5MT in Figure F.1 in the Appendix. The Fourier coefficients utilized to plot the curves are given in Table F.4 in the Appendix. The potentials

exhibit the typical threefold symmetry expected for methyl groups in all cases. The predicted torsional barriers for *syn*-2A5MT are 359.0 cm^{-1} and 165.5 cm^{-1} for the acetyl methyl and the ring methyl group, respectively. The torsional barriers of both rotors were also calculated for *syn*-2A5MT at other levels used for the geometry optimization. The predicted values are included in Table F.3 in the Appendix. Figure 8.3 also depicts that the other rotor oscillates with an angle of less than 1° , indicating that no coupling between the two rotors is to be expected. The acetyl oscillation frequently observed in similar molecules is also absent.

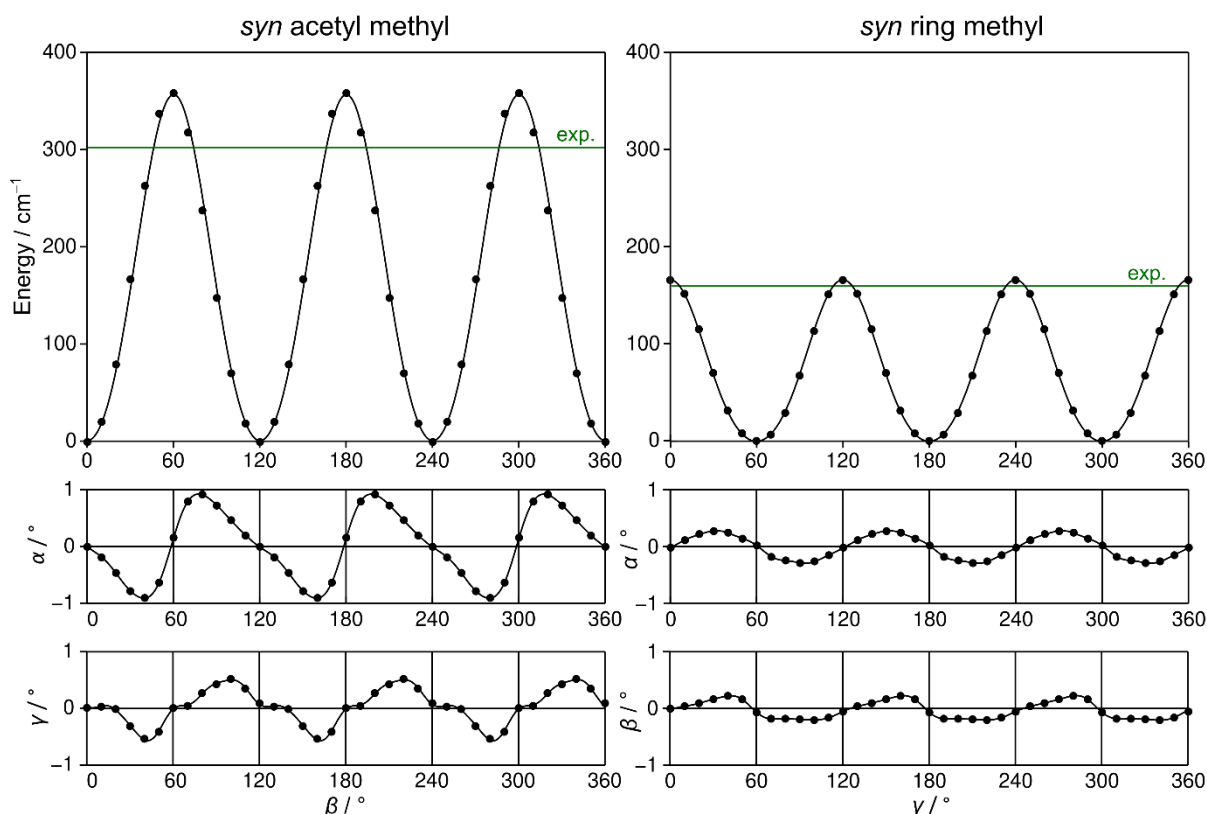


Figure 8.3: **Left hand side:** The potential energy curve of *syn*-2A5MT obtained at the MP2/6-31G(d,p) level of theory by rotating the acetyl methyl group about the C6–C8 bond by varying the dihedral angle β in steps of 10° . The energies are given relative to the lowest energy with $E = -743.3683071$ Hartree. The calculated barrier height is 359.0 cm^{-1} . The middle trace visualizes the oscillation of the acetyl group upon the acetyl methyl rotation and the lowest trace that of the ring methyl group. The deviations of the dihedral angles α and γ are given relative to the values of the fully optimized geometries, which are 0.00° for α and 179.86° for γ . **Right hand side:** The potential energy curve of *syn*-2A5MT obtained by rotating the ring methyl group about the C3–C9 bond by varying the dihedral angle γ in steps of 10° . The energies are given relative to the lowest energy with $E = -743.3683069$ Hartree. The calculated barrier height is 165.5 cm^{-1} . The middle trace visualizes the oscillation of the acetyl group upon the ring methyl rotation and the lowest trace that of the acetyl methyl group. The deviations of

the dihedral angles α and β are given relative to the values of the fully optimized geometries, which are 0.00° for both α and β .

To check whether the coupling between the two rotors can be neglected, a two-dimensional potential energy surface (2D-PES) depending on the dihedral angles β and γ was calculated for *syn*-2A5MT, again at the MP2/6-31G(d,p) level of theory, in order to study the top-top interaction. Due to symmetry, only data points in the range from 0° to 120° were necessary for both β and γ . The potential energies were parameterized with a Fourier expansion with the coefficients listed in Table F.5 in the Appendix. The resulting 2D-PES is given in Figure 8.4. It was only possible to achieve a deviation of 8.0% by fitting the data set but adding cross-coupling coefficients did not enhance the fit, since the values for these terms were negligibly small. Therefore, although the minima are slightly distorted and not circular as in the case of no top-top coupling, no interaction between the acetyl methyl and the ring methyl groups is expected.

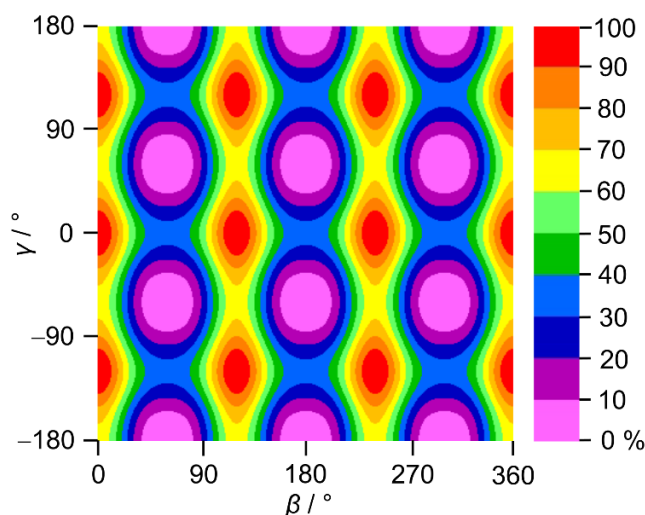


Figure 8.4: Two-dimensional potential energy surface of *syn*-2A5MT calculated at the MP2/6-31G(d,p) level of theory in dependence of the dihedral angles β and γ , which were varied in a grid of 10° while all other geometry parameters were optimized. The colour code gives the relative energy (in percent) on a scale between the minimum $E_{\min} = -743.368307$ Hartree (0%) and the maximum $E_{\max} = -743.365928$ Hartree (100 %).

8.2. Microwave Spectroscopy

A molecular jet Fourier-transform microwave spectrometer operating in the frequency range from 2.0 to 26.5 GHz [33] was used to record the spectrum of 2A5MT. The substance was purchased from TCI Europe, Zwijndrecht, Belgium with a stated purity of >96.0% and used without further purification. As 2A5MT is a solid at room temperature with a melting point between 27 and 28 °C [127], the sample was first heated up until the substance became liquid before a few drops were put on a 5 cm piece of pipe cleaner. The pipe cleaner was placed in a metal tube upstream the nozzle heated to about 40 °C during the measurements. Helium was flown as a carrier gas over the sample with a backing pressure of about 2 bar to transport the substance into the cavity.

Unlike in the previous investigations in this thesis, no broadband scan was recorded for 2A5MT. Instead, an approach similar to the investigation of 2-ethylfuran [87] was employed. Only very small scan portions of about 40 to 300 MHz were recorded around the predicted frequencies of some transitions with the highest expected intensities. This was only possible with results from previous benchmark calculations for the isomers 2A3MT (Chapter 6, [3]) and 2A4MT (Chapter 7, [5]), showing that the rotational constants calculated at the MP2/6-31G(d,p) level of theory are very close to the experimentally determined values. Therefore, the spectrum of the more stable *syn*-2A5MT was first predicted with the program XIAM [40] using the values obtained at this level (see Table 8.1). The first transition that was searched for, $5_{15} \leftarrow 4_{04}$, was predicted at 9568.69 MHz, and the scan was started at 9532 MHz as a series of overlapping spectra with a step width of 0.25 MHz. Three strong lines were observed very close to the expected frequency at 9569.25 MHz, 9573.25 MHz, and 9576.5 MHz, which were subsequently remeasured at a higher resolution with an experimental accuracy of 2 kHz [69]. All three lines appear as a Doppler pair in the high resolution measurements due to the co-axial arrangement between the molecular beam and the resonator, i.e. they are three of the five torsional species expected for a two-top molecule. For rotational barriers in the intermediate range, which both rotors of *syn*-2A5MT were predicted to fall into (see Figure 8.3), the (00) and (01) species often appear as a doublet and the (10), (11) and (12) species as a triplet. Therefore, it was suspected that the three observed lines were the (10), (11) and (12) species of the $5_{15} \leftarrow 4_{04}$ transition, although an assignment was not yet possible at this point.

Next, it was searched for the $6_{16} \leftarrow 5_{05}$ and $7_{17} \leftarrow 6_{06}$ transitions in the same manner and the triplets were found red shifted from the predicted frequencies by less than 30 MHz. Further intense triplets could be found easily afterwards. The identification of all five torsional species was finally possible with the observation of quintets for the *a*-type R-branch $6_{16} \leftarrow 5_{15}$, $7_{17} \leftarrow 6_{16}$, $8_{18} \leftarrow 7_{17}$ due to the relatively small splittings between the species as shown in Figure 8.5.

It was then possible to establish a first fit with the program *XIAM* [40] which only incorporates the (00) species. This (00) fit was rapidly expanded with the (01) and (10) species into two separate one rotor fits and finally into a two-top fit taking all five torsional species into account. At this stage, transitions could be predicted with an accuracy of about 3 kHz, measured, and added to the fit. Ultimately, 427 transitions were included in a two-top fit shown in Table 8.2 with a standard deviation of 2.9 kHz. The standard deviation is very close to the estimated measurement accuracy of 2.7 kHz, corresponding to $1/10^{\text{th}}$ of the average line width at half height (FWHH) of 27 kHz. The assigned transition frequencies are listed in Table F.6 in the Appendix. All scan portions measured between 8000 and 14000 MHz and the fitted spectrum of *syn*-2A5MT are shown in Figure 8.6.

The rotational barriers of the acetyl methyl and the ring methyl group were experimentally determined to be $301.806(35) \text{ cm}^{-1}$ and $157.2651(11) \text{ cm}^{-1}$, respectively. The rotational constants F_0 , describing the moment of inertia of the methyl internal rotors, could not be fitted and were fixed to 158 GHz, a value often found for methyl groups.

It was attempted to assign the *anti*-conformer of 2A5MT in the same manner as *syn*-2A5MT. However, only two very weak lines that potentially belong to *anti*-2A5MT were found, even while using a higher number of 200 co-added decays per measurement to take into account that *anti*-2A5MT is higher in energy than *syn*-2A5MT and may possess lines with lower intensity.

2-Acetyl-5-Methylthiophene

Table 8.2: Experimental spectroscopic parameters of *syn*-2A5MT obtained with the program *XIAM* compared to the predicted values. Top 1 refers to the acetyl methyl group, top 2 to the ring methyl group.

Par. ^a	Unit	<i>XIAM</i>	MP2 ^b
A_0	MHz	3447.62273(27)	3406.116
B_0	MHz	927.022235(89)	922.127
C_0	MHz	737.533474(35)	732.579
Δ_J	kHz	0.02132(36)	0.0200
Δ_{JK}	kHz	/	−0.0015
Δ_K	kHz	0.3161(94)	0.3279
δ_J	kHz	0.00472(17)	0.0046
δ_K	kHz	0.0385(93)	0.0330
$V_{3,1}$	cm ^{−1}	301.811(41)	359.0
$D_{p_i^2 J,1}$	kHz	18.33(59)	
$D_{p_i^2 K,1}$	kHz	−214.6(51)	
$D_{p_i^2 -,1}$	kHz	8.36(61)	
$\angle(i_1, a)$	deg	44.338(31)	47.9
$\angle(i_1, b)$	deg	45.661(31)	42.1
$\angle(i_1, c)$	deg	90.0 ^c	90.0
$V_{3,2}$	cm ^{−1}	157.2612(13)	165.5
$D_{p_i^2 J,2}$	kHz	−3.641(63)	
$D_{p_i^2 K,2}$	kHz	165.64(55)	
$D_{p_i^2 -,2}$	kHz	0.775(67)	
$\angle(i_2, a)$	deg	16.2798(39)	16.6
$\angle(i_2, b)$	deg	73.7202(39)	73.4
$\angle(i_2, c)$	deg	90.0 ^c	90.0
N^d		427	
σ^e	kHz	2.9	

^a All parameters refer to the principal axis system. Watson's A reduction and I^r representation were used. ^b Calculated with the 6-31G(d,p) basis set. Ground state rotational constants and centrifugal distortion constants obtained from anharmonic frequency calculations are given. ^c Fixed due to symmetry. ^d Number of transitions. ^e Standard deviation of the fit.

2-Acetyl-5-Methylthiophene

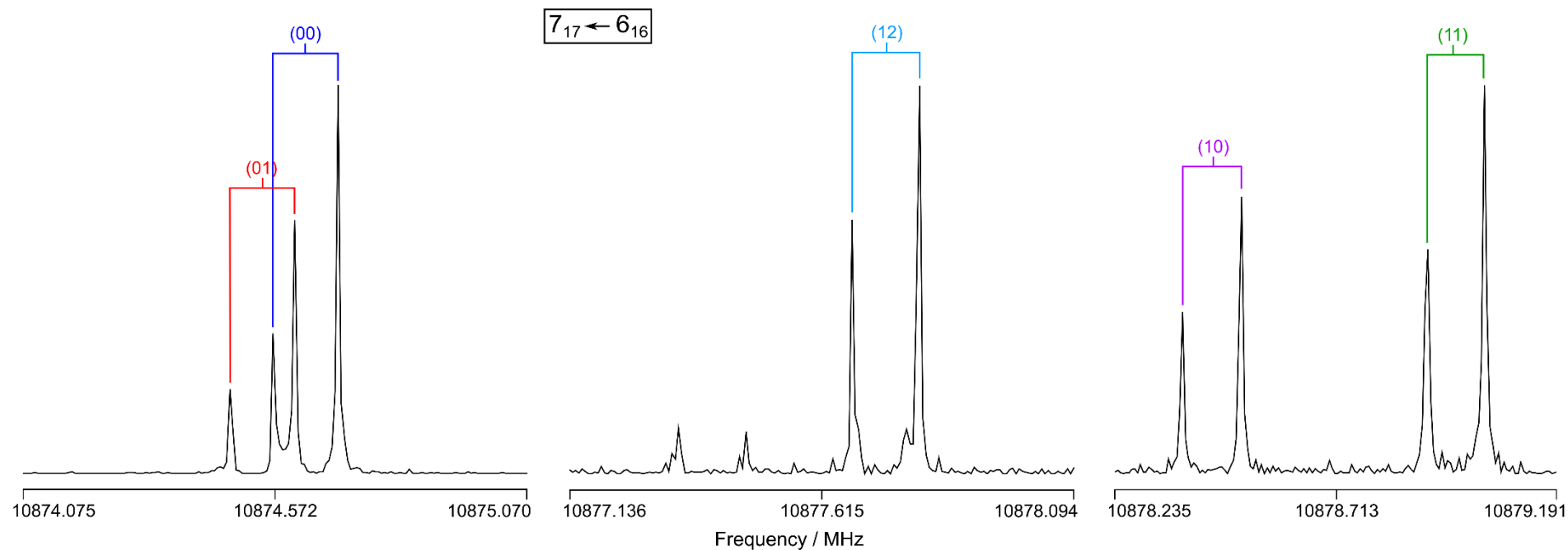


Figure 8.5: High resolution measurements of the a -type transition $7_{17} \leftarrow 6_{16}$ with its five torsional species (00), (10), (01), (11), and (12). The frequency is given in MHz. The brackets indicate Doppler pairs. The spectra were recorded at 10874.75 MHz and 10877.75 MHz, where 50 free induction decays were co-added, and at 10878.97 MHz, with 116 co-added free induction decays.

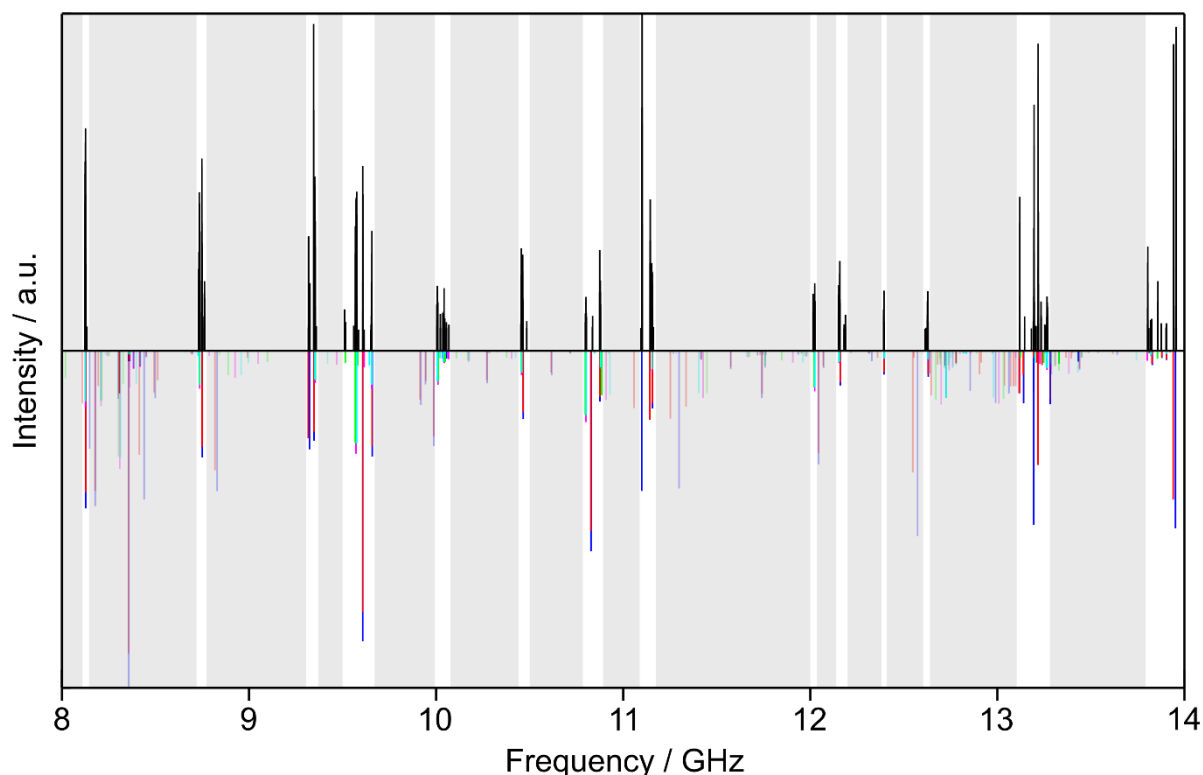


Figure 8.6: Partial scans between 8 and 14 GHz of 2A5MT. The experimental spectrum is shown in the upper trace. In the lower trace the theoretical spectrum of *syn*-2A5MT is displayed as predicted using the molecular parameters obtained from the fit given in Table 8.2. The grey sections were not scanned. The five torsional species are colour coded according to Figure 8.5.

8.3. Discussion

8.3.1. Conformational Stability

Only the most stable of the two expected conformers was observed in the microwave spectrum of 2A5MT, confirming the higher energetic stability predicted for the *syn* form compared to the *anti* form. The preference for the *syn*-conformer has already been established in other thiophene derivatives studied in this thesis. This was explained due to dipole-dipole interactions between the positively charged sulphur atom in the thiophene ring and the negatively charged oxygen of the carbonyl group [1][4][71], which also holds true for 2A5MT, as shown in the results of the NBO calculations [74] given in Figure 8.7.

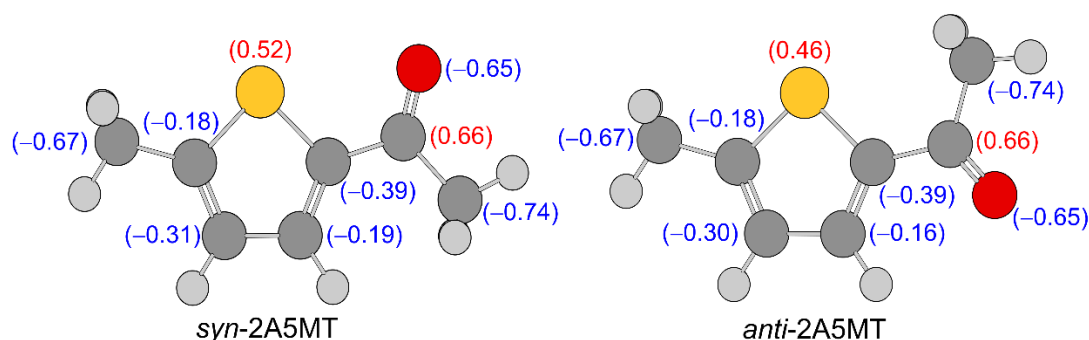


Figure 8.7: Charge distribution in *syn*- and *anti*-2A5MT obtained from NBO calculations at the MP2/6-31G(d,p) level of theory.

In the previous investigations on thiophene derivatives in this dissertation, there were often discrepancies in the calculations of the molecular structures at different levels of theory concerning the planarity. A number of MP2 calculations predicted the molecules to be non-planar due to an out-of-plane tilt of the acetyl group. In the case of *syn*-2A5MT, only the MP2/6-311++G(df,pd) level predicts a non-planar structure with a small tilt angle of about 3°; all other employed levels agree on a planar structure (see Table F.3). Together with the inertial defect of 6.523 uÅ², which is close to those of other planar molecules with four out-of-plane hydrogen atoms such as the *cis-trans* conformer of ethylnitrite ($\Delta_c = -6.422$ uÅ²) [91] and the *C_s* conformer of 2-ethylfuran ($\Delta_c = -6.483$ uÅ²) [87], the planarity question does not arise for *syn*-2A5MT.

8.3.2. Quality of the Fit

The *XIAM* fit given in Table 8.2 includes 451 lines and reaches a standard deviation of 2.9 kHz, satisfactorily close to the measurement accuracy of 2.7 kHz. All rotational and centrifugal distortion constants, except Δ_{JK} which was finally not fitted, as well as the internal rotation parameters were determined with high accuracy.

It is known that a comparison between the calculated rotational constants B_e and the experimentally determined ones B_0 is physically not meaningful, as the first refer to the equilibrium structure and the second to the vibrational ground state. Nevertheless, the benchmarking efforts given in this thesis are still helpful to determine the level of theory which deliver B_e values close to the experimental ones. Even though this agreement is due to error compensations, this allows a more rapid spectral assignment of related molecules in future studies, as shown in the present study on 2A5MT. From the benchmarks carried out for 2A3MT (Chapter 6, [3]) and 2A4MT (Chapter 7, [5]), the measurement time for 2A5MT could be reduced significantly by using B_e rotational constants predicted at the MP2/6-31G(d,p) level of

theory to guide the assignments. However, the benchmarking was still also performed for *syn*-2A5MT (see Section 8.1.2.). The *B* and *C* constants were predicted very accurately with deviations less than 1 MHz, but larger deviation was found for the *A* constant (see Table F.3). The values closest to the experimental ones were provided by the M06-2X/6-31G(d,p) level of theory. It is of note that here also Pople's basis set 6-31G(d,p) is involved. Good results were also achieved when diffusion functions ++ are added, as well as at the B3LYP-D3BJ/6-311(++)G(2d,2p) levels of theory.

8.3.3. Methyl Internal Rotation

The torsional barriers of the ring methyl group and the acetyl methyl group of *syn*-2A5MT were determined to be 301.811(41) cm⁻¹ and 157.2612(13) cm⁻¹, respectively. Compared to the calculated values (see Table 8.2 and Table F.3), the predictions are not very accurate, though generally the ring methyl barrier was better predicted than the acetyl methyl one, similar to the two isomers studied in the previous chapters. Unlike molecular geometries, benchmarking barriers to methyl internal rotation is only at an early stage due to the cost of the calculations. There are no obvious trends regarding methods or basis sets that can be recommended. Only two levels of theory, MP2/6-311+G(d,p) and B3LYP-D3/6-311G(2df,2dp), stand out, which predict values with less than 10 cm⁻¹ deviation from the experimental value for both rotors.

Aromatic rings are of special interest while coupled with multiple methyl internal rotors as the conjugated double bond system is able to transfer electrostatic effects over a longer distance through the π -electrons, making the barrier to methyl torsion sometimes unpredictable. Heterocycles such as thiophene and furan additionally have the influence of the heteroatom on the torsional barrier. It was shown in the literature that changing from sulphur to oxygen increases the barrier, i.e., dimethyl sulfide (736 cm⁻¹) [26] vs. dimethyl ether (944 cm⁻¹) [27], *trans*-ethyl methyl sulfide (693 cm⁻¹) [77] vs. *trans*-ethyl methyl ether (893 cm⁻¹) [128], conformer III of *n*-propyl sulfide (699 cm⁻¹) [104] vs. *trans-trans*-methyl-*n*-propyl ether (1154 cm⁻¹) [129], and S-phenyl thioacetate (48 cm⁻¹) [130] vs. phenyl acetate (137 cm⁻¹) [130]. The same holds true for all methyl rotors attached to the thiophene and the furan rings illustrated in Figure 8.8, but interestingly not for the acetyl methyl rotors. Only two sulphur/oxygen analogue pairs possessing an acetyl methyl rotor have been studied so far, 2-acetylthiophene (molecule **(6)** in Figure 8.8) (Chapter 3, [4]) and 2-acetylfuran (**(4)**) (Chapter 5, [2]) as well as *syn*-2A5MT (**(13)**) and 2-acetyl-5-methylfuran (**(5)**) [24], where the lower torsional barrier of the acetyl methyl group was observed for the *syn*-conformers of the furans. The question why only the acetyl methyl group of the *syn*-conformers and not of the *anti* ones shows this different behaviour is still lacking an answer. To better understand this

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phenomenon, investigations on further acetyl furans such as 2-acetyl-3-methylfuran and 2-acetyl-4-methylfuran, as well as the 3-acetyl isomers of both furans and thiophenes would be helpful and interesting.

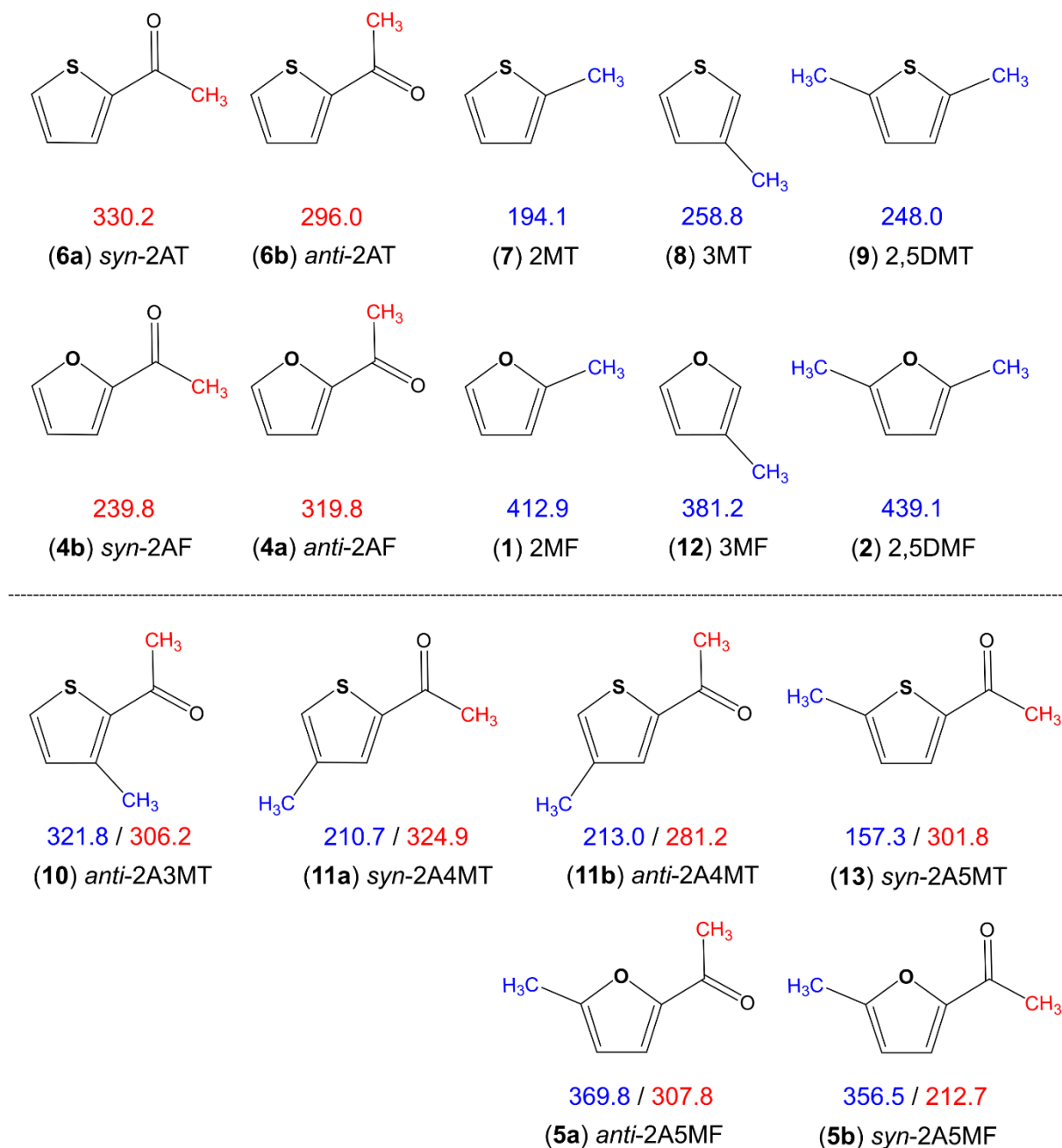


Figure 8.8: Comparison of barriers to internal rotation (in cm^{-1}) of acetyl (green) and ring (blue) methyl groups in thiophene and furan derivatives: (6) 2-acetylthiophene (Chapter 3, [4]), (7) 2-methylthiophene [30], (8) 3-methylthiophene [101], (9) 2,5-dimethylthiophene [21], (4) 2-acetylfuran (Chapter 5, [2]), (1) 2-methylfuran [31], (12) 3-methylfuran [102], (2) 2,5-dimethylfuran [22], (10) *anti*-2-acetyl-3-methylthiophene (Chapter 6, [3]), (11) 2-acetyl-

4-methylthiophene (Chapter 7, [5]), (**13**) *syn*-2-acetyl-5-methylthiophene (Chapter 8) and (**5**) 2-acetyl-5-methylfuran [24].

The various thiophenes and furans shown in Figure 8.8 all possess either a ring methyl group, an acetyl methyl group, or both. The influence of electrostatic effects can be shown by comparing the barriers in (**7**) 2-methylthiophene (194.1 cm^{-1}) [30] and (**9**) 2,5-dimethylthiophene (248.0 cm^{-1}) [21] as well as in their oxygen analogues (**1**) 2-methylfuran (412.9 cm^{-1}) [31] and (**2**) 2,5-dimethylfuran (439.1 cm^{-1}) [22]. The presence of a second methyl group causes an increase of the torsional barrier in both cases. As the methyl groups in the 2- and the 5-positions cannot interact by steric effects, electrostatic effects have to be the reason. Comparison of the ring methyl barriers in (**13**) *syn*-2A5MT (157.3 cm^{-1}) and (**5**) 2-acetyl-5-methylfuran (*syn* 356.5 cm^{-1} , *anti* 369.8 cm^{-1}) [24] demonstrates that different substituents possess different electronic effects. The carbonyl moiety in the acetyl groups with its negative mesomeric and inductive effects causes a decrease of the torsional barrier, and a methyl group causes an increase due to its positive inductive effect when substituted at the same position. The only case where the addition of the acetyl group leads to an increase of the barrier to methyl internal rotation is (**10**) *anti*-2A3MT (321.8 cm^{-1}) (Chapter 6, [3]), compared to (**8**) 3-methylthiophene (258.8 cm^{-1}) [101], due to steric hindrance between the methyl group attached to the ring and the acetyl group. The orientation of the acetyl group has only negligible influences on the barrier of the ring methyl rotor as can be seen in the case of (**11a**) *syn*-2A4MT (210.7 cm^{-1}) and (**11b**) *anti*-2A4MT (213.0 cm^{-1}) (Chapter 7, [5]).

The torsional barrier of the acetyl methyl group is also affected by the ring methyl group. Starting with the values of 330.2 cm^{-1} for *syn*- and 296.0 cm^{-1} for *anti*-2AT, adding a methyl group at the 4- (2A4MT, molecule (**11**) in Figure 8.8) or the 5-position (2A5MT, (**13**)) of the thiophene ring decreases the barrier (Chapter 7, [5]), but adding the methyl group at the 3-position (2A3MT, (**10**)) increases it (Chapter 6, [3]). The same can be observed while comparing 2AF (**4**) (Chapter 5, [2]) with 2-acetyl-5-methylfuran (**5**) [24]. This can be explained by the so-called chain-length effect reported for linear aliphatic ketones containing an acetyl group [11]. Ketones with longer chains feature more prolate character and the acetyl methyl groups possess lower torsional barriers. The effect is reported to be stronger for linear aliphatic ketones with a C_s structure and thus a “straight” chain than those with a C_1 structure and a “bent” chain [11]. The same situation can be found while comparing the molecules in Figure 8.8. In *anti*-2A4MT (**11b**) (Chapter 7, [5]) (-14.8 cm^{-1} compared to *anti*-2AT (Chapter 3, [4])), *syn*-2A5MT (**13**) (-28.4 cm^{-1} compared to *syn*-2AT (Chapter 3, [4])) and *syn*-2-acetyl-5-methylfuran (**5b**) [24] (-27.1 cm^{-1} compared to *syn*-2AF (Chapter 5, [2])), the acetyl methyl and ring methyl group lie on a straight chain, and the torsional barrier of the acetyl methyl group

decreases more than it does for *syn*-2A4MT (**11a**) (Chapter 7, [5]) (-5.3 cm^{-1} compared to *anti*-2AT (**6b**) (Chapter 3, [4])) and *anti*-2-acetyl-5-methylfuran (**5a**) [24] (-12.0 cm^{-1} compared to *syn*-2AF (**4b**) (Chapter 5, [2])), which feature a “bent” chain between the two rotors. In *syn*-2A3MT, the additional methyl group at the 3-position of the ring makes the molecule more globular than *syn*-2AT. Therefore, the barrier hindering the acetyl methyl torsion increases.

Overall, it is noticeable that the barriers of the acetyl methyl group fall into a much wider range for furan derivatives (212.7 cm^{-1} to 319.8 cm^{-1}) than for thiophene derivatives (281.2 cm^{-1} to 330.2 cm^{-1}). At the beginning of this thesis the study of 2AT was begun in the hopes of establishing a “thiophene class” as an extension to the classification system proposed by *Andresen et al.* and *Herbers et al.* for acetyl methyl torsional barriers [11][12]. With the data of four acetylthiophenes now available, it is indeed possible to establish this new category. The barrier heights of acetylthiophene derivatives, and thus the “thiophene class”, are always close to 300 cm^{-1} .

8.4. Conclusion

Previous benchmarking efforts on similar molecules allowed the very rapid assignment of the *syn*-conformer of 2A5MT where only small scan portions of the microwave spectrum were required. The barrier heights were determined for the two inequivalent rotors, the acetyl methyl and the ring methyl groups, to be $301.811(41)\text{ cm}^{-1}$ and $157.2612(13)\text{ cm}^{-1}$, respectively. A comparison with other thiophene derivatives possessing either an acetyl group, a ring methyl group, or both, indicates that electrostatic effects influencing the torsional barriers are transferred through the π -electron system of the heteroaromatic ring. It was also shown that the chain length effects reported for α,β -saturated ketones hold true for 2-acetylthiophene derivatives, i.e. the more prolate the molecular frame, the lower the torsional barrier of the acetyl methyl rotor. The effect of the heteroatom in the ring on the methyl torsion was also investigated by comparing barrier heights in thiophene and furan derivatives. The usual observation that the torsional barrier is higher in oxygen analogues compared to the equivalent sulphur analogues is no longer the case for the *syn*-conformers of 2AF vs. 2AT and 2-acetyl-5-methylfuran vs. 2A5MT. The torsional barriers of acetyl methyl groups in molecules with a thiophene ring attached at the other side of the carbonyl bond are always around 300 cm^{-1} and can thus be grouped together in the so-called “thiophene class”.

V Conclusion

In this thesis six molecules shown in Figure 2 were investigated, all of which contain a heteroaromatic five-membered ring with one carbonyl substituent attached at the 2-position. Due to the planarity of the ring, stable conformers only differ by the orientation of the acetyl substituent. For all molecules a *syn*-conformer and an *anti*-conformer were predicted to be stable, with *syn* and *anti* referring to the orientation of the carbonyl oxygen atom relative to the heteroatom in the ring. The only exception is 2-propionylthiophene (**14**), which has four possible conformers according to quantum chemical calculations. Here the longer propionyl chain can either lie (nearly) in the ring plane or bend out of the ring plane for the *syn* and *anti* orientation of the carbonyl group. The out-of-plane conformers could however not be found experimentally.

For the conformers of 2-propionylthiophene that were found, their planarity is a controversial issue for calculations at different levels of theory, regarding whether the propionyl group lies completely in-plane with the thiophene ring or not. Isotopic substitution allowed for a partial r_s structure determination of the most stable *syn*-conformer, which convincingly confirmed that 2-propionylthiophene is not planar. There is a tiny, but non-zero tilt angle between the ethyl group and the thiophene ring.

In the microwave spectra both the *syn*- and *anti*-conformers were found for 2-acetylthiophene (**6**), 2-propionylthiophene (**14**), 2-acetylfuran (**4**) and 2-acetyl-4-methylthiophene (**11**). For the remaining two molecules, 2-acetyl-3-methylthiophene (**10**) and 2-acetyl-5-methylthiophene (**13**) only the more stable conformer was experimentally detected, which is the *anti* form for the former and the *syn* one for the latter.

For the thiophene derivatives the *syn*-conformer is always predicted to be the energetically more stable one, which is supported experimentally by the intensities in the spectrum and the number of assigned transitions. The only exception is 2-acetyl-3-methylthiophene, where the *syn*-conformer is less stable due to steric interactions between the acetyl group and the ring methyl group. The reason for the higher energetic stability of the *syn*-form in thiophenes stems from a stabilisation due to electrostatic interactions between the opposite charges on the oxygen and sulphur atoms.

Therefore, a change of the heteroatom also affects the relative stability of the conformers. If sulphur as the heteroatom is exchanged by oxygen like in the case of 2-acetylfuran (**4**), the *anti*-conformer becomes energetically more stable. Here, the negative charges on the oxygen atoms destabilise the *syn*-conformer. The conformational stability is thus reversed between acetyl thiophene and acetyl furan derivatives.

Conclusion

Concerning the molecular geometry of the acetylthiophenes, calculations at some levels of theory using the MP2 method predicted a non-planar structure with the acetyl group slightly tilted out of the thiophene plane, but the structure determination for 2-acetylthiophene as well as the inertial defects of the acetylmethylthiophenes lead to the conclusion, that the structures are indeed planar, or at least effectively planar.

The rotational constants of all investigated molecules were calculated at different levels of theory and then compared to the experimentally determined values in a benchmarking effort intended to find method/basis set combinations that predict reliably good values for certain molecule classes and thus ease future assignments of related molecules, even if the comparison between the predicted B_e constants and the experimental B_0 constants is not physically meaningful.

Among all six molecules analysed here, there is no level that delivers the best results for all cases. For 2-propionylthiophene the B3LYP-D3BJ/cc-pVTZ and M06-2X/cc-pVDZ levels of theory performed the best, although it is of note that for this molecule nearly all employed method/basis set combinations yielded values agreeing within 1% with the experimental values.

For 2-acetylthiophene, the level delivering the best agreement with the experimental results is conformer dependent. For *anti*-2AT only the three levels M06-2X/6-311(++)G(d,p) seem to work well, whereas for the *syn*-conformer many levels predict values close to the experimentally determined ones, e.g. the MP2 or B3LYP methods using the (ndf, npd) polarization functions ($n = 1-3$) and the M06-2X and ω B97XD methods using the 6-311G(d,p) basis set with or without diffuse functions.

This is not the same finding as for the furan analogue 2-acetylfuran, where the three B3LYP-D3BJ/6-311(++)G(d,p) levels are recommended. Obviously, furan and thiophene derivatives require different error compensations to access reliable starting values of the rotational constants to guide the spectral assignment

For the three two-top molecules the benchmarking effort was more successful. It was found that for both 2-acetyl-3-methylthiophene and 2-acetyl-4-methylthiophene the MP2/6-31G(d,p) level of theory predicted rotational constants close to the experimental values. Therefore, this level was used to predict the constants for the last isomer in the series, 2-acetyl-5-methylthiophene, which allowed for a much more rapid assignment of the spectrum that only required small scans around the predicted frequencies.

Conclusion

While the rotational constants could be predicted quite accurately for all investigated molecules, the rotational barrier of the acetyl methyl group remains much more difficult to calculate. No apparent trends regarding a suitable method and/or basis set could be found. Further studies going beyond the scope of this thesis are necessary to solve this problem.

The experimentally determined torsional barriers of the acetyl methyl group also lead to another yet unsolved question. From the literature it is known that changing from sulphur to oxygen increases the barrier [77][26][27][104][128][129][130], and while this holds true for all methyl rotors attached to the thiophene and the furan rings investigated up to this date (see Section 8.3.3.), it is interestingly not true for all acetyl methyl rotors.

Only two sulphur/oxygen analogue pairs possessing an acetyl methyl rotor have been studied so far, 2-acetylthiophene (**6**) and 2-acetylfuran (**4**) as well as *syn*-2-acetyl-5-methylthiophene (**13**) and *syn*-2-acetyl-5-methylfuran [24]. In both cases the *syn*-conformer of the furan derivatives unexpectedly possesses the lower torsional barrier. It is still unknown why the acetyl methyl group shows this different behaviour, and why only for the *syn*-conformer and not the *anti* one, but it is nevertheless a clear indication, that the acetyl methyl group has a unique sensitivity to the structure of the moiety attached at the other side of the carbonyl bond.

This sensitivity was previously shown by *Andresen et al.* and *Herbers et al.* who proposed a classification system for acetyl methyl torsional barriers [11][12]. With the molecules investigated in this thesis, it was possible to extend this classification system by the so-called “thiophene class”, as it was shown that the torsional barriers of acetyl methyl groups in molecules with a thiophene ring attached at the other side of the carbonyl bond are always around 300 cm⁻¹ (see Figure 2).

Furthermore, comparisons of the molecules investigated here with other thiophene and furan derivatives possessing either an acetyl group, a ring methyl group, or both indicate that electrostatic effects transferred through the π -electron system of the heteroaromatic ring influence the torsional barriers.

In two-top heteroaromatic molecules the negative mesomeric and inductive effects of the carbonyl moiety in the acetyl group causes a decrease of the torsional barrier of the ring methyl rotor, while a methyl group causes an increase due to its positive inductive effect when substituted at the same position. Steric interactions can influence this effect. The conformation of the acetyl group has barely any influence on the electrostatic effects.

Conclusion

Additionally, it was also shown that the chain length effects reported for α,β -saturated ketones can also be found in 2-acetylthiophene derivatives, i.e., the more prolate the molecular frame, the lower the torsional barrier of the acetyl methyl rotor.

2-propionylthiophene (**14**) does not belong to the “thiophene class” as here the internal rotor is not an acetyl methyl group but an ethyl methyl group. Barriers to internal rotation of ethyl methyl groups are usually higher than 1000 cm^{-1} . For 2-propionylthiophene the barriers are significantly lower with $806.94(54)\text{ cm}^{-1}$ for the *syn*-conformer and $864.5(88)\text{ cm}^{-1}$ for the *anti*-conformer (see Figure 2), which can be explained by the presence of the carbonyl group to which the ethyl group is attached. As similar torsional barriers have been reported for other molecules containing a propionyl group [62][80][85][99][100] the conclusion can be drawn that the torsional barrier of the methyl group in the propionyl moiety is always around 800 cm^{-1} .

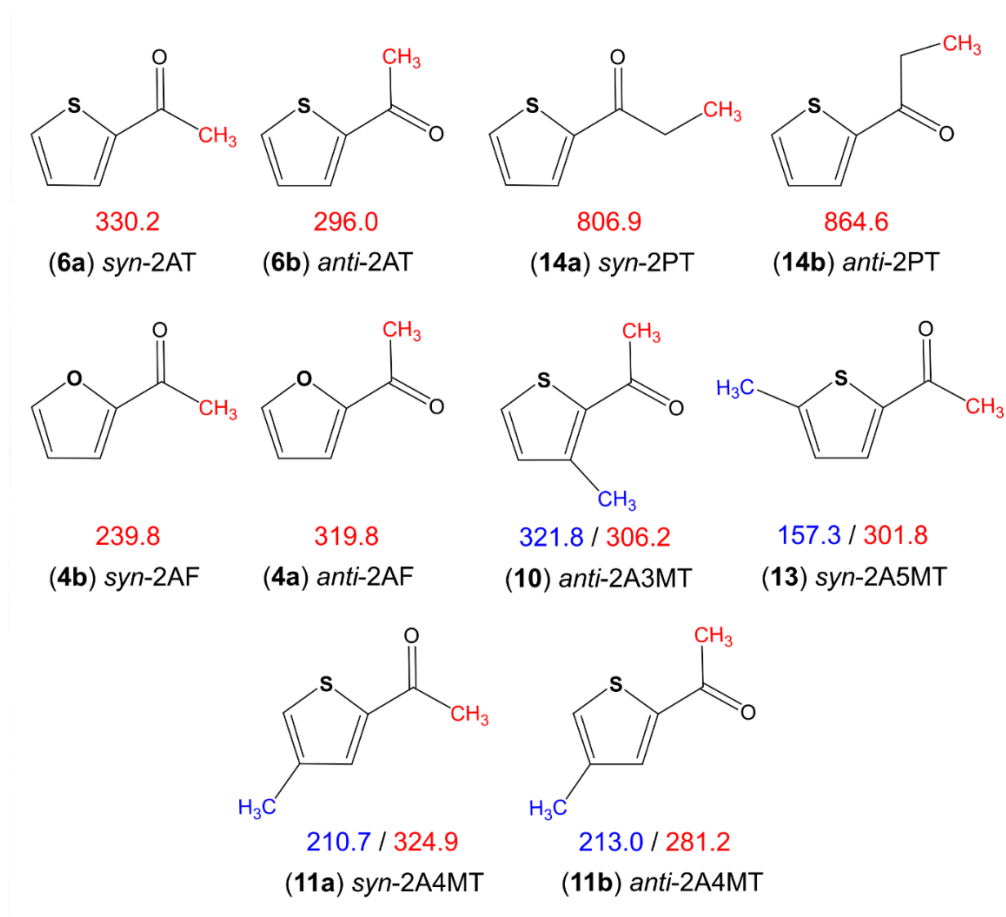


Figure 2: Experimentally observed conformers of (**6**) 2-acetylthiophene (Chapter 3, [4]), (**14**) 2-propionylthiophene (Chapter 4, [1]), (**4**) 2-acetylfuran (Chapter 5, [2]), (**10**) *anti*-2-acetyl-3-methylthiophene (Chapter 6, [3]), (**13**) *syn*-2-acetyl-5-methylthiophene (Chapter 8) and (**11**) 2-acetyl-4-methylthiophene (Chapter 7, [5]) with their torsional barriers given in cm^{-1} . The acetyl methyl group/barrier is marked in red, the ring methyl group/barrier in blue. The energetically more stable conformer is named a, the less stable one b.

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VII Appendix

A. 2-Acetylthiophene

Table A.1: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of 2AT given in Figure 3.2 calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^{12} a_i f_i$ for MP2 and $V(\varphi) = \sum_{i=0}^9 a_i f_i$ for B3LYP-D3BJ.

<i>i</i>	<i>f_i</i>	MP2		B3LYP-D3BJ	
		<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹
0	1	-704.3291215		-705.7867039	
1	cos 1α	-0.0006664	-146.3	-0.0002781	-61.0
2	cos 2α	-0.0054717	-1200.9	-0.0066204	-1453.0
3	cos 3α	-0.0001464	-32.1	-0.0002363	-51.9
4	cos 4α	0.0006446	141.5	0.0004726	103.7
5	cos 5α	-0.0001127	-24.7	-0.0000770	-16.9
6	cos 6α	-0.0000269	-5.9	-0.0000661	-14.5
7	cos 8α	0.0000738	16.2	/	/

Table A.2a: Nuclear Coordinates in the principal axis system of *anti*-2AT and *syn*-2AT optimized at the B3LYP-D3BJ/6-311++G(d,p) level of theory (for atom numbering see Figure 3.1).

	<i>syn</i> -2AT			<i>anti</i> -2AT		
	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å
S1	-0.953154	-1.129718	-0.000215	-0.883991	-1.162249	-0.000024
C3	0.167446	0.208248	-0.000055	0.156924	0.243875	0.000000
C2	-0.500266	1.413605	-0.000303	-0.589429	1.399795	0.000003
C4	-1.910718	1.267983	0.000078	-1.986519	1.164361	0.000022
C5	-2.295419	-0.048616	0.000469	-2.295633	-0.171521	0.000016
C6	1.613275	-0.061779	-0.000076	1.632782	0.166132	-0.000011
O7	2.040571	-1.203321	0.000210	2.299415	1.185138	-0.000023
C8	2.542995	1.135780	0.000104	2.274785	-1.205666	0.000041
H9	-3.300923	-0.441775	0.000841	-3.272775	-0.629977	0.000029
H10	-2.607974	2.094603	0.000147	-2.734473	1.945419	0.000043
H11	0.005232	2.369704	-0.000514	-0.121776	2.374482	0.000003
H12	2.370369	1.757297	-0.882759	1.966055	-1.774429	0.882130
H13	3.572239	0.781490	0.000323	3.357407	-1.093684	-0.000211
H14	2.370000	1.757344	0.882861	1.965661	-1.774741	-0.881706

Appendix A. 2-Acetylthiophene

Table A.2b: Nuclear coordinates in the principal axis system of *anti*-2AT and *syn*-2AT optimized at the MP2/6-311++G(d,p) level of theory (for atom numbering see Figure 3.1).

	<i>syn</i> -2AT			<i>anti</i> -2AT		
	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å
S1	−0.942077	−1.123837	0.000802	0.873736	−1.151212	0.064566
C3	0.160303	0.199028	0.001549	−0.149529	0.236593	0.027211
C2	−0.512946	1.418873	−0.000335	0.600702	1.405593	−0.054691
C4	−1.917553	1.262818	−0.000953	1.990838	1.159925	−0.071778
C5	−2.288941	−0.072805	−0.000715	2.286967	−0.193672	−0.014957
C6	1.614564	−0.058733	−0.000037	−1.631514	0.163058	0.015487
O7	2.051400	−1.204246	−0.001820	−2.298952	1.185481	0.099831
C8	2.526106	1.151338	0.000785	−2.267258	−1.202681	−0.140547
H9	−3.292389	−0.479872	−0.000466	3.261640	−0.664715	−0.001659
H10	−2.630328	2.079818	−0.002002	2.753283	1.928904	−0.126708
H11	−0.004221	2.376749	−0.000395	0.129588	2.381304	−0.095835
H12	2.337220	1.767558	−0.883436	−2.064223	−1.590888	−1.144173
H13	3.562394	0.812270	−0.000693	−3.344780	−1.115302	0.002607
H14	2.339015	1.765316	0.886921	−1.852833	−1.912527	0.582119

Appendix A. 2-Acetylthiophene

Table A.3a: Equilibrium rotational constants, X_e ($X = A, B, C$) and predicted torsional barriers of *syn*-2AT calculated at various levels of theory. The deviations ΔX between the calculated and the ground state experimental values X_0 are given in MHz, the deviation between the calculated and experimental V_3 barrier of the acetyl methyl group is given as ΔV_3 . The relative energy difference (in kJ/mol) is $E_{anti-2AT} - E_{syn-2AT}$.

	<i>A</i> /	ΔA /	<i>B</i> /	ΔB /	<i>C</i> /	ΔC /	ΔE /	V_3 /	ΔV_3 /
Method/Basis Set	MHz	MHz	MHz	MHz	MHz	MHz	kJ/mol	cm ⁻¹	cm ⁻¹
MP2/6-31G(d,p)	3561.3	-26.8	1418.8	2.9	1021.0	-1.1	5.5	374.1	-43.9
MP2/6-31+G(d,p)	3552.2	-35.9	1414.5	-1.4	1018.1	-4.0	5.1	304.9	25.3
MP2/6-31++G(d,p)	3552.2	-35.9	1414.5	-1.4	1018.0	-4.1	4.8	292.5	37.7
MP2/6-311G(d,p)	3560.2	-27.9	1416.8	0.9	1019.9	-2.2	6.2	362.5	-32.3
MP2/6-311+G(d,p)	3555.0	-33.1	1414.5	-1.4	1018.3	-3.8	5.1	326.5	3.7
MP2/6-311++G(d,p)	3554.6	-33.5	1414.5	-1.4	1018.3	-3.8	5.7	320.5	9.7
MP2/6-311G(df,pd)	3585.9	-2.2	1425.0	9.1	1026.3	4.2	5.4	342.7	-12.5
MP2/6-311+G(df,pd)	3580.6	-7.5	1422.2	6.3	1024.4	2.3	4.1	306.7	23.5
MP2/6-311++G(df,pd)	3580.3	-7.8	1422.3	6.4	1024.4	2.3	3.8	304.1	26.1
MP2/6-311G(2d,2p)	3565.5	-22.6	1421.7	5.8	1022.8	0.7	4.8	358.8	-28.6
MP2/6-311+G(2d,2p)	3561.5	-26.6	1420.4	4.5	1021.8	-0.3	3.8	310.9	19.3
MP2/6-311++G(2d,2p)	3561.4	-26.7	1420.4	4.5	1021.8	-0.3	3.7	313.0	17.2
MP2/6-311G(2df,2pd)	3589.8	1.8	1430.2	14.3	1029.2	7.1	4.9	355.6	-25.4
MP2/6-311+G(2df,2pd)	3584.9	-3.2	1428.2	12.3	1027.8	5.7	3.5	303.6	26.6
MP2/6-311++G(2df,2pd)	3584.7	-3.4	1428.1	12.2	1027.7	5.6	3.5	307.8	22.4
MP2/6-311G(3df,3pd)	3596.6	8.5	1429.4	13.5	1029.4	7.3	3.7	358.0	-27.8
MP2/6-311+G(3df,3pd)	3591.2	3.1	1428.6	12.7	1028.6	6.5	3.0	323.0	7.2
MP2/6-311++G(3df,3pd)	3591.1	3.0	1428.6	12.7	1028.5	6.4	3.0	321.2	9.0
MP2/cc-pVDZ	3521.0	-67.1	1405.3	-10.6	1010.8	-11.3	3.7	423.9	-93.7
MP2/cc-pVTZ	3578.8	-9.3	1426.0	10.1	1026.1	4.0	3.6	315.5	14.7
MP2/aug-cc-pVDZ	3507.7	-80.4	1401.3	-14.6	1007.7	-14.4	3.7	296.0	34.2
MP2/aug-cc-pVTZ	3576.6	-11.5	1425.8	9.9	1025.9	3.8	3.5	^a	
B3LYP-D3/6-31G(d,p)	3545.2	-42.9	1404.8	-11.1	1012.5	-9.6	2.6	305.7	24.5

Appendix A. 2-Acetylthiophene

B3LYP-D3/6-31+G(d,p)	3539.9	-48.2	1400.5	-15.4	1009.8	-12.3	2.0	246.4	83.8
B3LYP-D3/6-31++G(d,p)	3539.9	-48.2	1400.4	-15.5	1009.8	-12.3	2.0	242.1	88.1
B3LYP-D3/6-311G(d,p)	3557.6	-30.5	1407.2	-8.7	1014.7	-7.4	3.2	297.2	33.0
B3LYP-D3/6-311+G(d,p)	3554.9	-33.2	1405.0	-10.9	1013.4	-8.7	2.1	256.9	73.3
B3LYP-D3/6-311++G(d,p)	3554.8	-33.3	1405.0	-10.9	1013.3	-8.8	2.1	256.2	74.0
B3LYP-D3/6-311G(df,pd)	3568.8	-19.3	1410.7	-5.2	1017.4	-4.7	3.1	286.9	43.3
B3LYP-D3/6-311+G(df,pd)	3566.7	-21.4	1408.6	-7.3	1016.1	-6.0	2.0	247.4	82.8
B3LYP-D3/6-311++G(df,pd)	3566.6	-21.5	1408.5	-7.4	1016.1	-6.0	1.9	249.3	80.9
B3LYP-D3/6-311G(3df,3pd)	3591.7	3.6	1415.0	-0.9	1021.5	-0.6	2.4	304.2	26.0
B3LYP-D3/6-311+G(3df,3pd)	3587.7	-0.4	1414.4	-1.5	1020.9	-1.2	1.9	281.8	48.4
B3LYP-D3/6-311++G(3df,3pd)	3587.6	-0.5	1414.4	-1.5	1020.8	-1.3	1.9	281.5	48.7
B3LYP-D3/cc-pVDZ	3533.6	-54.5	1402.3	-13.6	1010.3	-11.8	1.3	359.4	-29.2
B3LYP-D3/cc-pVTZ	3578.4	-9.7	1412.2	-3.7	1019.0	-3.1	2.0	281.1	49.1
B3LYP-D3/aug-cc-pVDZ	3531.8	-56.3	1398.9	-17.0	1008.3	-13.8	2.3	267.4	62.8
B3LYP-D3/aug-cc-pVTZ	3577.8	-10.3	1411.7	-4.2	1018.7	-3.4	1.9	267.3	62.9
B3LYP-D3/6-311G(2d,2p)	3575.1	-13.0	1411.5	-4.4	1018.4	-3.7	3.2	316.1	14.1
B3LYP-D3/6-311+G(2d,2p)	3572.1	-16.0	1410.3	-5.6	1017.5	-4.6	2.2	267.1	63.1
B3LYP-D3/6-311++G(2d,2p)	3572.0	-16.1	1410.3	-5.6	1017.5	-4.6	2.2	269.1	61.1
B3LYP-D3/6-311G(2df,2pd)	3584.6	-3.5	1414.1	-1.8	1020.5	-1.6	3.2	320.4	9.8
B3LYP-D3/6-311+G(2df,2pd)	3581.7	-6.4	1412.5	-3.4	1019.4	-2.7	2.1	270.6	59.6
B3LYP-D3/6-311++G(2df,2pd)	3581.7	-6.4	1412.5	-3.4	1019.4	-2.7	2.1	272.8	57.4
B3LYP-D3BJ/6-31G(d,p)	3549.6	-38.5	1409.7	-6.2	1015.4	-6.7	3.7	272.5	57.7
B3LYP-D3BJ/6-31+G(d,p)	3544.0	-44.1	1405.5	-10.4	1012.7	-9.4	3.0	211.7	118.5
B3LYP-D3BJ/6-31++G(d,p)	3544.0	-44.1	1405.5	-10.4	1012.7	-9.4	3.0	207.4	122.8
B3LYP-D3BJ/6-311G(d,p)	3561.9	-26.2	1411.9	-4.0	1017.5	-4.6	4.3	263.9	66.3
B3LYP-D3BJ/6-311+G(d,p)	3559.1	-29.0	1409.9	-6.0	1016.3	-5.8	3.1	221.7	108.5
B3LYP-D3BJ/6-311++G(d,p)	3559.0	-29.1	1409.9	-6.0	1016.2	-5.9	3.1	220.8	109.4
B3LYP-D3BJ/6-311G(df,pd)	3572.6	-15.5	1415.5	-0.4	1020.2	-1.9	4.2	252.8	77.4
B3LYP-D3BJ/6-311+G(df,pd)	3570.2	-17.9	1413.5	-2.4	1019.0	-3.1	3.0	211.6	118.6
B3LYP-D3BJ/6-311++G(df,pd)	3570.1	-18.0	1413.5	-2.4	1019.0	-3.1	2.9	213.4	116.8

Appendix A. 2-Acetylthiophene

B3LYP-D3BJ/6-311G(3df,3pd)	3595.1	7.0	1419.6	3.7	1024.2	2.1	3.5	270.9	59.3
B3LYP-D3BJ/6-311+G(3df,3pd)	3591.1	3.0	1419.1	3.2	1023.6	1.5	2.8	246.3	83.9
B3LYP-D3BJ/6-311++G(3df,3pd)	3591.0	2.9	1419.1	3.2	1023.6	1.5	2.8	246.0	84.2
B3LYP-D3BJ/cc-pVDZ	3538.2	-49.9	1407.2	-8.7	1013.2	-8.9	2.4	326.0	4.2
B3LYP-D3BJ/cc-pVTZ	3582.2	-5.9	1417.0	1.1	1021.7	-0.4	3.0	246.3	83.9
B3LYP-D3BJ/aug-cc-pVDZ	3536.2	-51.9	1403.9	-12.0	1011.3	-10.8	3.2	230.3	99.9
B3LYP-D3BJ/aug-cc-pVTZ	3581.5	-6.6	1416.6	0.7	1021.5	-0.6	2.9	231.7	98.5
B3LYP-D3BJ/6-311G(2d,2p)	3579.2	-8.9	1416.5	0.6	1021.3	-0.8	4.3	283.4	46.8
B3LYP-D3BJ/6-311+G(2d,2p)	3575.8	-12.3	1415.4	-0.5	1020.4	-1.7	3.2	232.2	98.0
B3LYP-D3BJ/6-311++G(2d,2p)	3575.7	-12.4	1415.4	-0.5	1020.4	-1.7	3.2	234.1	96.1
B3LYP-D3BJ/6-311G(2df,2pd)	3588.6	0.5	1419.0	3.1	1023.3	1.2	4.3	286.9	43.3
B3LYP-D3BJ/6-311+G(2df,2pd)	3585.4	-2.7	1417.5	1.6	1022.3	0.2	3.1	235.3	94.9
B3LYP-D3BJ/6-311++G(2df,2pd)	3585.4	-2.7	1417.4	1.5	1022.2	0.1	3.1	237.5	92.7
CAM-B3LYP-D3BJ/6-311G(d,p)	3602.8	14.8	1421.0	5.1	1025.6	3.5	4.3	287.3	42.9
CAM-B3LYP-D3BJ/6-311+G(d,p)	3600.1	12.0	1418.7	2.8	1024.2	2.1	3.2	246.0	84.2
CAM-B3LYP-D3BJ/6-311++G(d,p)	3600.0	11.9	1418.7	2.8	1024.1	2.0	3.1	246.0	84.2
CAM-B3LYP-D3BJ/cc-pVDZ	3576.7	-11.4	1412.5	-3.4	1019.1	-3.0	3.4	340.9	-10.7
CAM-B3LYP-D3BJ/cc-pVTZ	3621.8	33.8	1425.4	9.5	1029.4	7.3	3.1	270.0	60.2
CAM-B3LYP-D3BJ/aug-cc-pVDZ	3579.2	-8.9	1415.9	0.0	1021.1	-1.0	2.5	251.8	78.4
CAM-B3LYP-D3BJ/aug-cc-pVTZ	3622.6	34.5	1426.0	10.1	1029.7	7.6	3.1	255.9	74.3
M06-2X/6-31G(d,p)	3583.2	-4.9	1418.1	2.2	1022.5	0.4	3.8	356.3	-26.1
M06-2X/6-31+G(d,p)	3579.2	-8.9	1414.5	-1.4	1020.3	-1.8	3.3	305.7	24.5
M06-2X/6-31++G(d,p)	3579.2	-8.9	1414.4	-1.5	1020.3	-1.8	3.3	302.1	28.1
M06-2X/6-311G(d,p)	3591.7	3.6	1420.0	4.1	1024.1	2.0	4.3	362.9	-32.7
M06-2X/6-311+G(d,p)	3590.1	2.0	1417.9	2.0	1022.9	0.8	3.3	334.6	-4.4
M06-2X/6-311++G(d,p)	3589.9	1.8	1417.9	2.0	1022.9	0.8	3.2	334.0	-3.8
M06-2X/6-311G(df,pd)	3600.6	12.5	1422.5	6.6	1026.2	4.1	4.1	348.9	-18.7
M06-2X/6-311+G(df,pd)	3599.3	11.3	1420.5	4.6	1025.0	2.9	3.1	321.8	8.4
M06-2X/6-311++G(df,pd)	3599.3	11.3	1420.5	4.6	1025.0	2.9	3.0	324.5	5.7
M06-2X/6-311G(3df,3pd)	3620.9	32.8	1425.9	10.0	1029.5	7.4	3.5	386.1	-55.9

Appendix A. 2-Acetylthiophene

M06-2X/6-311+G(3df,3pd)	3617.6	29.5	1425.7	9.8	1029.2	7.1	3.1	370.8	−40.6
M06-2X/6-311++G(3df,3pd)	3617.5	29.4	1425.7	9.8	1029.2	7.1	3.1	370.9	−40.7
M06-2X/cc-pVDZ	3574.5	−13.6	1416.3	0.4	1020.9	−1.2	2.7	384.9	−54.7
M06-2X/cc-pVTZ	3609.6	21.5	1424.8	8.9	1028.1	6.0	3.2	350.3	−20.1
M06-2X/aug-cc-pVDZ	3572.4	−15.7	1413.0	−2.9	1019.0	−3.1	3.4	328.0	2.2
M06-2X/aug-cc-pVTZ	3609.6	21.5	1424.5	8.6	1027.9	5.8	3.2	344.1	−13.9
ωB97X-D/6-311G(d,p)	3592.6	4.5	1415.7	−0.2	1022.0	−0.1	3.8	289.7	40.5
ωB97X-D/6-311+G(d,p)	3592.5	4.4	1415.6	−0.3	1021.9	−0.2	3.7	290.1	40.1
ωB97X-D/6-311++G(d,p)	3594.3	6.3	1417.7	1.8	1023.2	1.1	4.7	318.1	12.1
ωB97X-D/cc-pVDZ	3570.3	−17.8	1409.3	−6.6	1016.9	−5.2	3.7	355.8	−25.6
ωB97X-D/cc-pVTZ	3614.7	26.6	1422.0	6.1	1027.0	4.9	3.5	312.1	18.1
ωB97X-D/aug-cc-pVDZ	3572.8	−15.3	1412.1	−3.8	1018.6	−3.5	2.9	309.9	20.3
ωB97X-D/aug-cc-pVTZ	3615.1	27.0	1422.2	6.3	1027.2	5.1	3.5	308.4	21.8
CCSD/cc-pVDZ	3521.2	−66.9	1394.6	−21.3	1005.4	−16.7	3.7	423.2	−93.0
Experiment	3588.05		1415.91		1022.07			330.2	

^a Not done due to high quantum chemical cost.

Appendix A. 2-Acetylthiophene

Table A.3b: Equilibrium rotational constants, X_e ($X = A, B, C$) and predicted torsional barriers of *anti*-2AT calculated at various levels of theory. The deviations ΔX between the calculated and the ground state experimental values X_0 are given in MHz, the deviation between the calculated and experimental V_3 barrier of the acetyl methyl group is given as ΔV_3 . Θ is the tilt angle of the acetyl group out of the thiophene plane, *i.e.* deviation of the angle α from 180° .

Method/Basis Set	<i>A</i> / MHz	ΔA / MHz	<i>B</i> / MHz	ΔB / MHz	<i>C</i> / MHz	ΔC / MHz	V_3 / cm ⁻¹	ΔV_3 / cm ⁻¹	Θ / °	Planar
MP2/6-31G(d,p)	3529.8	-25.6	1417.3	-1.5	1017.6	-3.1	352.0	-56.0	0.01	Yes
MP2/6-31+G(d,p)	3525.7	-29.7	1413.7	-5.1	1016.7	-4.0	275.4	20.6	4.91	No
MP2/6-31++G(d,p)	3524.7	-30.7	1412.9	-5.8	1017.6	-3.1	268.0	28.0	5.70	No
MP2/6-311G(d,p)	3530.7	-24.7	1416.9	-1.8	1017.6	-3.2	309.5	-13.5	0.04	Yes
MP2/6-311+G(d,p)	3529.4	-26.0	1415.4	-3.3	1018.5	-2.3	290.9	5.1	4.88	No
MP2/6-311++G(d,p)	3528.4	-27.0	1414.7	-4.0	1019.3	-1.5	284.6	11.4	6.03	No
MP2/6-311G(df,pd)	3557.8	2.4	1426.3	7.5	1024.6	3.8	278.5	17.5	0.02	Yes
MP2/6-311+G(df,pd)	3555.6	0.2	1423.0	4.2	1025.8	5.1	271.5	24.5	6.32	No
MP2/6-311++G(df,pd)	3553.9	-1.5	1422.8	4.0	1026.6	5.9	271.8	24.2	6.85	No
MP2/6-311G(2d,2p)	3539.3	-50.4	1422.1	6.4	1020.9	-1.0	303.1	-7.1	0.03	Yes
MP2/6-311+G(2d,2p)	3538.7	-51.0	1422.7	7.0	1021.1	-0.7	276.5	19.5	0.01	Yes
MP2/6-311++G(2d,2p)	3538.8	-50.9	1422.7	7.0	1021.1	-0.7	274.5	21.5	0.02	Yes
MP2/6-311G(2df,2pd)	3563.5	-26.2	1431.2	15.5	1027.6	5.7	295.4	0.6	0.01	Yes
MP2/6-311+G(2df,2pd)	3563.0	-26.7	1431.1	15.4	1027.5	5.6	267.5	28.5	0.00	Yes
MP2/6-311++G(2df,2pd)	3562.8	-26.9	1431.1	15.4	1027.5	5.6	267.8	28.2	0.00	Yes
MP2/6-311G(3df,3pd)	3571.1	15.7	1431.7	13.0	1028.5	7.7	289.5	6.5	0.01	Yes
MP2/6-311+G(3df,3pd)	3568.6	13.2	1431.8	13.0	1028.3	7.5	265.5	30.5	0.04	Yes
MP2/6-311++G(3df,3pd)	3568.6	13.1	1431.8	13.0	1028.3	7.5	262.1	33.9	0.03	Yes
MP2/cc-pVDZ	3491.0	-64.5	1404.1	-14.7	1007.7	-13.0	378.4	-82.4	0.04	Yes
MP2/cc-pVTZ	3554.8	-0.6	1427.8	9.0	1025.1	4.3	274.8	21.2	0.02	Yes
MP2/aug-cc-pVDZ	3484.7	-70.8	1404.0	-14.7	1007.2	-13.6	269.4	26.6	0.05	Yes

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MP2/aug-cc-pVTZ	3553.9	-1.5	1428.4	9.6	1025.3	4.6	^a		0.03	Yes
B3LYP-D3/6-31G(d,p)	3510.9	-78.7	1404.8	-10.9	1009.6	-12.2	300.4	-4.4	0.00	Yes
B3LYP-D3/6-31+G(d,p)	3509.3	-80.4	1402.9	-12.8	1008.5	-13.3	232.5	63.5	0.00	Yes
B3LYP-D3/6-31++G(d,p)	3509.3	-80.3	1402.9	-12.8	1008.5	-13.3	224.1	71.9	0.00	Yes
B3LYP-D3/6-311G(d,p)	3523.7	-66.0	1407.3	-8.4	1012.0	-9.9	261.1	34.9	0.01	Yes
B3LYP-D3/6-311+G(d,p)	3524.2	-65.4	1407.3	-8.4	1012.0	-9.9	232.6	63.4	0.01	Yes
B3LYP-D3/6-311++G(d,p)	3524.1	-65.5	1407.3	-8.4	1012.0	-9.9	234.1	61.9	0.01	Yes
B3LYP-D3/6-311G(df,pd)	3535.6	-54.1	1411.3	-4.4	1015.0	-6.9	249.1	46.9	0.03	Yes
B3LYP-D3/6-311+G(df,pd)	3536.0	-53.6	1411.4	-4.4	1015.1	-6.8	220.0	76.0	0.03	Yes
B3LYP-D3/6-311++G(df,pd)	3536.0	-53.7	1411.4	-4.3	1015.1	-6.8	223.3	72.7	0.03	Yes
B3LYP-D3/6-311G(3df,3pd)	3560.3	-29.3	1416.6	0.9	1019.8	-2.1	264.8	31.2	0.04	Yes
B3LYP-D3/6-311+G(3df,3pd)	3558.6	-31.1	1417.2	1.4	1019.9	-2.0	253.0	43.0	0.04	Yes
B3LYP-D3/6-311++G(3df,3pd)	3558.5	-31.2	1417.1	1.4	1019.9	-2.0	252.1	43.9	0.04	Yes
B3LYP-D3/cc-pVDZ	3499.7	-89.9	1401.8	-13.9	1007.2	-14.6	330.3	-34.3	0.01	Yes
B3LYP-D3/cc-pVTZ	3547.7	-42.0	1414.2	-1.5	1017.5	-4.4	262.7	33.3	0.03	Yes
B3LYP-D3/aug-cc-pVDZ	3502.9	-86.7	1401.6	-14.1	1007.4	-14.5	254.2	41.8	0.01	Yes
B3LYP-D3/aug-cc-pVTZ	3548.0	-41.6	1414.5	-1.2	1017.7	-4.2	249.1	46.9	0.03	Yes
B3LYP-D3/6-311G(2d,2p)	3542.0	-47.7	1411.8	-3.9	1015.8	-6.1	286.7	9.3	0.01	Yes
B3LYP-D3/6-311+G(2d,2p)	3542.2	-47.5	1412.5	-3.2	1016.1	-5.7	247.1	48.9	0.02	Yes
B3LYP-D3/6-311++G(2d,2p)	3542.1	-47.6	1412.5	-3.2	1016.2	-5.7	250.8	45.2	0.02	Yes
B3LYP-D3/6-311G(2df,2pd)	3552.5	-37.2	1414.8	-0.9	1018.2	-3.7	282.0	14.0	0.01	Yes
B3LYP-D3/6-311+G(2df,2pd)	3552.8	-36.8	1415.2	-0.5	1018.4	-3.4	247.4	48.6	0.05	Yes
B3LYP-D3/6-311++G(2df,2pd)	3552.7	-36.9	1415.3	-0.4	1018.5	-3.4	250.1	45.9	0.04	Yes
B3LYP-D3BJ/6-31G(d,p)	3513.6	-41.8	1410.0	-8.8	1012.5	-8.2	264.9	31.1	0.01	Yes
B3LYP-D3BJ/6-31+G(d,p)	3512.2	-43.2	1408.1	-10.6	1011.5	-9.3	195.3	100.7	0.04	Yes
B3LYP-D3BJ/6-31++G(d,p)	3512.2	-43.2	1408.1	-10.7	1011.4	-9.3	186.5	109.5	0.02	Yes
B3LYP-D3BJ/6-311G(d,p)	3526.5	-28.9	1412.5	-6.3	1014.9	-5.9	221.8	74.2	0.01	Yes
B3LYP-D3BJ/6-311+G(d,p)	3526.9	-28.5	1412.6	-6.2	1015.0	-5.8	192.1	103.9	0.00	Yes
B3LYP-D3BJ/6-311++G(d,p)	3526.8	-28.6	1412.6	-6.2	1015.0	-5.8	193.6	102.4	0.00	Yes
B3LYP-D3BJ/6-311G(df,pd)	3538.0	-17.5	1416.6	-2.1	1018.0	-2.8	208.3	87.7	0.03	Yes

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B3LYP-D3BJ/6-311+G(df,pd)	3538.6	-16.8	1416.7	-2.1	1018.0	-2.7	178.1	117.9	0.03	Yes
B3LYP-D3BJ/6-311++G(df,pd)	3538.6	-16.9	1416.7	-2.0	1018.1	-2.7	181.5	114.5	0.02	Yes
B3LYP-D3BJ/6-311G(3df,3pd)	3562.3	6.8	1422.0	3.3	1022.7	2.0	223.9	72.1	0.03	Yes
B3LYP-D3BJ/6-311+G(3df,3pd)	3561.0	5.6	1422.5	3.8	1022.9	2.1	210.3	85.7	0.01	Yes
B3LYP-D3BJ/6-311++G(3df,3pd)	3560.9	5.5	1422.6	3.9	1022.9	2.2	209.5	86.5	0.06	Yes
B3LYP-D3BJ/cc-pVDZ	3502.5	-52.9	1407.1	-11.6	1010.2	-10.6	292.8	3.2	0.01	Yes
B3LYP-D3BJ/cc-pVTZ	3550.4	-5.0	1419.6	0.8	1020.5	-0.3	221.5	74.5	0.03	Yes
B3LYP-D3BJ/aug-cc-pVDZ	3505.9	-49.5	1407.1	-11.7	1010.4	-10.3	214.5	81.5	0.04	Yes
B3LYP-D3BJ/aug-cc-pVTZ	3550.9	-4.6	1419.9	1.1	1020.7	-0.1	207.6	88.4	0.02	Yes
B3LYP-D3BJ/6-311G(2d,2p)	3544.4	-45.3	1417.1	1.4	1018.7	-3.1	246.5	49.5	0.02	Yes
B3LYP-D3BJ/6-311+G(2d,2p)	3544.7	-45.0	1417.8	2.1	1019.1	-2.8	205.5	90.5	0.02	Yes
B3LYP-D3BJ/6-311++G(2d,2p)	3544.6	-45.1	1417.9	2.1	1019.1	-2.8	209.3	86.7	0.01	Yes
B3LYP-D3BJ/6-311G(2df,2pd)	3554.5	-35.1	1420.1	4.4	1021.1	-0.8	241.1	54.9	0.02	Yes
B3LYP-D3BJ/6-311+G(2df,2pd)	3555.0	-34.6	1420.5	4.8	1021.4	-0.5	205.4	90.6	0.01	Yes
B3LYP-D3BJ/6-311++G(2df,2pd)	3554.9	-34.7	1420.6	4.8	1021.4	-0.5	208.2	87.8	0.01	Yes
CAM-B3LYP-D3BJ/6-311G(d,p)	3564.2	-25.4	1421.5	5.8	1022.7	0.8	239.3	56.7	0.02	Yes
CAM-B3LYP-D3BJ/6-311+G(d,p)	3564.8	-24.9	1421.6	5.9	1022.7	0.9	210.7	85.3	0.01	Yes
CAM-B3LYP-D3BJ/6-311++G(d,p)	3564.8	-24.9	1421.6	5.9	1022.7	0.9	213.2	82.8	0.02	Yes
CAM-B3LYP-D3BJ/cc-pVDZ	3543.7	-45.9	1415.7	0.0	1018.0	-3.8	304.6	-8.6	0.01	Yes
CAM-B3LYP-D3BJ/cc-pVTZ	3588.6	-1.1	1428.8	13.1	1028.4	6.5	240.3	55.7	0.00	Yes
CAM-B3LYP-D3BJ/aug-cc-pVDZ	3540.0	-49.7	1415.9	0.2	1017.8	-4.0	230.3	65.7	0.02	Yes
CAM-B3LYP-D3BJ/aug-cc-pVTZ	3588.1	-1.5	1428.6	12.9	1028.2	6.4	225.9	70.1	0.00	Yes
M06-2X/6-31G(d,p)	3547.2	-8.2	1420.5	1.7	1020.7	0.0	327.8	-31.8	0.01	Yes
M06-2X/6-31+G(d,p)	3546.0	-9.5	1418.6	-0.1	1019.7	-1.1	268.1	27.9	0.02	Yes
M06-2X/6-31++G(d,p)	3546.0	-9.4	1418.7	-0.1	1019.7	-1.1	260.2	35.8	0.02	Yes
M06-2X/6-311G(d,p)	3557.4	2.0	1422.6	3.8	1022.7	1.9	303.1	-7.1	0.01	Yes
M06-2X/6-311+G(d,p)	3558.2	2.8	1422.5	3.7	1022.7	1.9	287.5	8.5	0.00	Yes
M06-2X/6-311++G(d,p)	3558.2	2.7	1422.5	3.8	1022.7	1.9	289.5	6.5	0.01	Yes
M06-2X/6-311G(df,pd)	3567.4	11.9	1425.8	7.0	1025.1	4.4	287.1	8.9	0.03	Yes
M06-2X/6-311+G(df,pd)	3568.3	12.9	1425.6	6.8	1025.1	4.3	271.6	24.4	0.00	Yes

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M06-2X/6-311++G(df,pd)	3568.3	12.9	1425.7	6.9	1025.1	4.4	275.8	20.2	0.01	Yes
M06-2X/6-311G(3df,3pd)	3590.0	34.6	1430.5	11.7	1029.4	8.6	331.3	-35.3	0.03	Yes
M06-2X/6-311+G(3df,3pd)	3588.8	33.4	1431.0	12.3	1029.6	8.8	325.9	-29.9	0.05	Yes
M06-2X/6-311++G(3df,3pd)	3588.8	33.3	1431.0	12.2	1029.6	8.8	324.8	-28.8	0.05	Yes
M06-2X/cc-pVDZ	3538.9	-16.5	1418.1	-0.7	1018.9	-1.9	347.4	-51.4	0.02	Yes
M06-2X/cc-pVTZ	3580.1	24.7	1429.4	10.6	1028.0	7.2	316.0	-20.0	0.04	Yes
M06-2X/aug-cc-pVDZ	3542.6	-12.8	1417.6	-1.2	1018.9	-1.9	304.2	-8.2	0.03	Yes
M06-2X/aug-cc-pVTZ	3581.0	25.6	1429.6	10.8	1028.2	7.4	309.4	-13.4	0.01	Yes
ω B97X-D/6-311G(d,p)	3560.2	-29.5	1417.8	2.1	1020.4	-1.4	232.5	63.5	0.02	Yes
ω B97X-D/6-311+G(d,p)	3560.1	-29.6	1417.8	2.1	1020.4	-1.4	235.0	61.0	0.02	Yes
ω B97X-D/6-311++G(d,p)	3559.4	-30.3	1417.9	2.1	1020.4	-1.5	253.1	42.9	0.00	Yes
ω B97X-D/cc-pVDZ	3539.8	-49.8	1412.1	-3.7	1015.8	-6.0	306.0	-10.0	0.01	Yes
ω B97X-D/cc-pVTZ	3584.6	-5.1	1424.8	9.1	1026.0	4.2	262.1	33.9	0.01	Yes
ω B97X-D/aug-cc-pVDZ	3536.0	-53.6	1411.6	-4.1	1015.3	-6.5	267.0	29.0	0.04	Yes
ω B97X-D/aug-cc-pVTZ	3584.0	-5.7	1424.4	8.7	1025.7	3.9	259.1	36.9	0.01	Yes
CCSD/cc-pVDZ	3484.8	-70.7	1395.1	-23.6	1002.6	-18.2	377.5	-81.5	0.06	Yes
Experiment	3555.44		1418.76		1020.77		296.0			

^a Not done due to high quantum chemical cost.

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Table A.4a: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of *syn*-2AT given in Figure 3.3 calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^2 a_i f_i$.

<i>i</i>	<i>f_i</i>	MP2		B3LYP-D3BJ	
		<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹
0	1	-704.3341292		-705.7929932	
1	cos 3α	0.0007304	160.3	0.0004994	109.6
2	cos 6α	0.0000291	6.4	0.0000117	2.6

Table A.4b: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of *anti*-2AT given in Figure 3.3 calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^5 a_i f_i$.

<i>i</i>	<i>f_i</i>	MP2		B3LYP-D3BJ	
		<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹
0	1	-704.3324313		-705.7919055	
1	cos 3α	0.0006596	144.8	0.0004413	96.9
2	cos 6α	0.0000929	20.4	0.0000353	7.7
3	cos 9α	-0.0000267	-5.9		
4	cos 12α	0.0000202	4.4		
5	cos 15α	-0.0000137	-3.0		

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Table A.5: Observed frequencies ν_{obs} of 312 rotational transitions of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	1	0	1	0	0	0	E	2437.9540	0.3
2	2	0	2	1	0	1	A	4827.2215	-1.0
3	2	0	2	1	0	1	E	4827.0671	-0.3
4	3	0	3	2	0	2	A	7123.4746	-2.5
5	3	0	3	2	0	2	E	7123.2863	1.1
6	4	0	4	3	0	3	A	9302.9890	-3.9
7	4	0	4	3	0	3	E	9302.7953	3.0
8	5	0	5	4	0	4	A	11380.1607	-4.1
9	5	0	5	4	0	4	E	11379.9751	4.1
10	6	0	6	5	0	5	A	13399.7133	-13.6
11	6	0	6	5	0	5	E	13399.5483	5.4
12	7	0	7	6	0	6	A	15404.1691	-7.0
13	7	0	7	6	0	6	E	15404.0070	7.3
14	8	0	8	7	0	7	A	17414.7711	-7.3
15	8	0	8	7	0	7	E	17414.6140	7.4
16	9	0	9	8	0	8	A	19436.1880	-9.3
17	9	0	9	8	0	8	E	19436.0369	9.1
18	10	0	10	9	0	9	A	21466.4740	-9.8
19	10	0	10	9	0	9	E	21466.3247	9.3
20	11	0	11	10	0	10	A	23502.6037	-10.1
21	11	0	11	10	0	10	E	23502.4568	10.7
22	3	0	3	2	1	2	A	5296.1503	-3.8
23	3	0	3	2	1	2	E	5296.3490	-0.7
24	4	0	4	3	1	3	A	7904.6992	-2.7
25	4	0	4	3	1	3	E	7904.7240	-0.6
26	5	0	5	4	1	4	A	10407.7568	-3.5
27	5	0	5	4	1	4	E	10407.6918	2.2
28	6	0	6	5	1	5	A	12779.7295	-4.7
29	6	0	6	5	1	5	E	12779.6164	3.5
30	7	0	7	6	1	6	A	15035.6542	-5.9
31	7	0	7	6	1	6	E	15035.5186	5.7
32	8	0	8	7	1	7	A	17206.9112	-6.5
33	8	0	8	7	1	7	E	17206.7643	6.2
34	9	0	9	8	1	8	A	19323.3404	-8.5
35	9	0	9	8	1	8	E	19323.1915	7.6
36	10	0	10	9	1	9	A	21406.9184	-9.4
37	10	0	10	9	1	9	E	21406.7700	9.2
38	11	0	11	10	1	10	A	23471.8440	-11.9
39	11	0	11	10	1	10	E	23471.6982	9.9
40	1	1	0	0	0	0	E	5004.3114	0.9
41	1	1	1	0	0	0	E	4609.5096	0.4

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42	2	1	2	1	0	1	E	6654.0054	2.5
43	3	1	3	2	0	2	A	8521.7650	−3.1
44	3	1	3	2	0	2	E	8521.3570	4.0
45	4	1	4	3	0	3	A	10275.3962	−1.3
46	4	1	4	3	0	3	E	10275.0790	5.3
47	5	1	5	4	0	4	A	12000.1534	−4.1
48	5	1	5	4	0	4	E	11999.9072	6.2
49	6	1	6	5	0	5	A	13768.2355	−7.4
50	6	1	6	5	0	5	E	13768.0371	7.3
51	7	1	7	6	0	6	A	15612.0298	−7.1
52	7	1	7	6	0	6	E	15611.8559	7.7
53	8	1	8	7	0	7	A	17527.6193	−7.6
54	8	1	8	7	0	7	E	17527.4585	8.1
55	9	1	9	8	0	8	A	19495.7441	−9.1
56	9	1	9	8	0	8	E	19495.5914	9.0
57	10	1	10	9	0	9	A	21497.2314	−10.3
58	10	1	10	9	0	9	E	21497.0822	9.0
59	11	1	11	10	0	10	A	23518.2188	−11.2
60	11	1	11	10	0	10	E	23518.0728	10.3
61	1	1	0	1	0	1	E	2566.3579	1.1
62	3	1	2	3	0	3	A	3757.7619	5.4
63	3	1	2	3	0	3	E	3757.2974	2.9
64	5	1	4	5	0	5	E	6422.8475	−5.2
65	6	1	5	6	0	6	A	8336.8132	1.1
66	7	1	6	7	0	7	A	10516.5378	2.3
67	7	1	6	7	0	7	E	10514.6282	−10.2
68	8	1	7	8	0	8	A	12827.2192	6.7
69	8	1	7	8	0	8	E	12824.8940	−12.4
70	9	1	8	9	0	9	A	15152.1496	11.2
71	9	1	8	9	0	9	E	15149.4339	−12.3
72	4	1	3	3	1	2	A	10429.9204	−1.7
73	4	1	3	3	1	2	E	10429.4559	0.4
74	5	1	4	4	1	3	A	12919.4037	−2.3
75	5	1	4	4	1	3	E	12918.8666	0.6
76	6	1	5	5	1	4	A	15312.6086	−3.4
77	6	1	5	5	1	4	E	15312.0272	1.5
78	7	1	6	6	1	5	A	17583.8957	−3.8
79	7	1	6	6	1	5	E	17583.3068	4.1
80	8	1	7	7	1	6	A	19725.4501	−5.4
81	8	1	7	7	1	6	E	19724.8811	6.5
82	10	1	9	9	1	8	A	23738.9975	−8.5
83	10	1	9	9	1	8	E	23738.4825	10.2
84	2	1	2	1	1	1	A	4482.1968	−2.5
85	2	1	2	1	1	1	E	4482.4490	1.5
86	3	1	3	2	1	2	A	6694.4419	−3.2
87	3	1	3	2	1	2	E	6694.4195	2.1

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88	4	1	4	3	1	3	A	8877.1025	-4.0
89	4	1	4	3	1	3	E	8877.0099	4.0
90	5	1	5	4	1	4	A	11027.7511	-1.8
91	5	1	5	4	1	4	E	11027.6239	4.3
92	6	1	6	5	1	5	A	13148.2441	-6.1
93	6	1	6	5	1	5	E	13148.1048	5.0
94	7	1	7	6	1	6	A	15243.5140	-6.9
95	7	1	7	6	1	6	E	15243.3677	6.4
96	8	1	8	7	1	7	A	17319.7588	-7.3
97	8	1	8	7	1	7	E	17319.6090	7.0
98	9	1	9	8	1	8	A	19382.8962	-8.6
99	9	1	9	8	1	8	E	19382.7469	8.4
100	10	1	10	9	1	9	A	21437.6760	-9.8
101	10	1	10	9	1	9	E	21437.5281	9.5
102	11	1	11	10	1	10	A	23487.4617	-10.4
103	11	1	11	10	1	10	E	23487.3157	11.0
104	5	1	4	4	2	3	A	7676.4351	-2.2
105	5	1	4	4	2	3	E	7677.7043	-1.4
106	6	1	5	5	2	4	A	10907.2980	-1.8
107	6	1	5	5	2	4	E	10907.7288	-2.2
108	7	1	6	6	2	5	A	14080.5150	-1.9
109	7	1	6	6	2	5	E	14080.5225	-0.9
110	8	1	7	7	2	6	A	17110.0454	-1.5
111	8	1	7	7	2	6	E	17109.8106	0.8
112	9	1	8	8	2	7	A	19935.9232	-2.3
113	9	1	8	8	2	7	E	19935.5532	3.3
114	3	2	1	2	0	2	A	17079.6166	-2.8
115	3	2	1	2	0	2	E	17081.0777	3.4
116	4	2	2	3	0	3	A	20119.0534	-4.0
117	4	2	2	3	0	3	E	20118.2935	5.2
118	2	2	1	2	0	2	A	9525.9979	-4.4
119	2	2	1	2	0	2	E	9512.1209	-3.4
120	3	2	2	3	0	3	A	9716.6417	-0.9
121	3	2	2	3	0	3	E	9712.1397	2.5
122	4	2	3	4	0	4	A	10127.6535	-1.0
123	4	2	3	4	0	4	E	10125.1195	1.5
124	5	2	4	5	0	5	A	10829.2383	-0.8
125	5	2	4	5	0	5	E	10827.1467	-0.7
126	2	2	1	2	1	2	A	7698.6793	0.0
127	2	2	1	2	1	2	E	7685.1898	1.0
128	3	2	2	3	1	3	A	8318.3561	4.6
129	3	2	2	3	1	3	E	8314.0688	-0.7
130	4	2	3	4	1	4	A	9155.2571	7.2
131	4	2	3	4	1	4	E	9152.8351	-1.5
132	5	2	4	5	1	5	A	10209.2552	8.7
133	5	2	4	5	1	5	E	10207.2155	-1.9

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134	6	2	5	6	1	6	A	11471.6896	10.9
135	6	2	5	6	1	6	E	11469.6234	−4.5
136	7	2	6	7	1	7	A	12924.0871	3.8
137	7	2	6	7	1	7	E	12921.8492	−5.5
138	8	2	7	8	1	8	A	14539.5758	14.0
139	8	2	7	8	1	8	E	14537.0733	−6.9
140	2	2	0	1	1	0	E	11846.6738	−2.6
141	2	2	0	1	1	1	A	12229.7378	0.6
142	2	2	0	1	1	1	E	12241.4792	1.5
143	3	2	1	2	1	2	A	15252.2990	2.6
144	3	2	1	2	1	2	E	15254.1404	1.7
145	4	2	2	3	1	3	E	18720.2219	1.4
146	5	2	3	4	1	4	E	22731.9240	1.8
147	2	2	1	2	1	1	E	6503.4017	−3.8
148	2	2	0	2	1	1	A	6565.8886	−3.7
149	2	2	0	2	1	1	E	6577.2440	−3.0
150	3	2	1	3	1	2	A	6198.3856	−0.2
151	3	2	1	3	1	2	E	6200.4947	0.2
152	4	2	2	4	1	3	A	5931.3798	1.1
153	4	2	2	4	1	3	E	5931.5397	1.4
154	5	2	3	5	1	4	A	5901.7658	−0.3
155	5	2	3	5	1	4	E	5901.3856	5.7
156	6	2	4	6	1	5	A	6219.5530	2.1
157	6	2	4	6	1	5	E	6218.9050	5.1
158	2	2	0	2	1	2	E	7759.0332	3.0
159	4	2	2	4	1	4	E	9843.2133	−1.3
160	2	2	1	1	1	0	A	11786.9922	−4.2
161	2	2	1	1	1	0	E	11772.8346	−0.3
162	3	2	2	2	1	1	A	13831.1485	−2.6
163	3	2	2	2	1	1	E	13826.7036	0.0
164	4	2	3	3	1	2	A	15672.8880	−2.9
165	4	2	3	3	1	2	E	15670.6177	2.0
166	5	2	4	4	1	3	A	17324.7149	−3.3
167	5	2	4	4	1	3	E	17323.1648	4.1
168	6	2	5	5	1	4	A	18815.9889	−5.7
169	6	2	5	5	1	4	E	18814.8122	7.2
170	7	2	6	6	1	5	A	20199.3007	−7.4
171	7	2	6	6	1	5	E	20198.3777	10.2
172	8	2	7	7	1	6	A	21550.6421	−11.1
173	8	2	7	7	1	6	E	21549.9045	12.2
174	9	2	8	8	1	7	A	22954.8177	−9.8
175	9	2	8	8	1	7	E	22954.2012	13.6
176	3	2	2	2	1	2	E	15008.4882	1.3
177	4	2	3	3	1	3	E	18029.8435	1.0
178	2	2	1	1	1	1	E	12167.6338	−2.5
179	3	2	1	2	1	1	E	14072.3570	1.5

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180	4	2	2	3	1	2	E	16360.9950	1.3
181	3	2	1	3	1	3	E	8559.7185	-2.8
182	4	2	3	3	2	2	A	9714.0026	-2.2
183	4	2	3	3	2	2	E	9715.7755	2.4
184	5	2	4	4	2	3	A	12081.7459	-3.5
185	5	2	4	4	2	3	E	12082.0039	3.5
186	6	2	5	5	2	4	A	14410.6809	-1.6
187	6	2	5	5	2	4	E	14410.5136	3.3
188	7	2	6	6	2	5	A	16695.9207	-4.8
189	7	2	6	6	2	5	E	16695.5927	4.5
190	8	2	7	7	2	6	A	18935.2393	-5.3
191	8	2	7	7	2	6	E	18934.8334	5.9
192	9	2	8	8	2	7	A	21129.6238	-6.0
193	9	2	8	8	2	7	E	21129.1760	6.1
194	3	2	1	2	2	0	A	7504.7592	0.7
195	3	2	1	2	2	0	E	7495.1102	1.7
196	4	2	2	3	2	1	A	10162.9130	-2.0
197	4	2	2	3	2	1	E	10160.5030	3.8
198	5	2	3	4	2	2	A	12889.7915	-1.9
199	5	2	3	4	2	2	E	12888.7107	3.1
200	6	2	4	5	2	3	A	15630.3943	-2.5
201	6	2	4	5	2	3	E	15629.5487	3.0
202	7	2	5	6	2	4	A	18329.3408	-1.7
203	7	2	5	6	2	4	E	18328.4813	2.8
204	8	2	6	7	2	5	A	20948.4078	-2.1
205	8	2	6	7	2	5	E	20947.4784	2.1
206	9	2	7	8	2	6	A	23461.1517	-4.1
207	9	2	7	8	2	6	E	23460.1649	2.3
208	3	2	2	2	2	0	E	7249.4583	1.7
209	4	2	3	3	2	1	E	9470.1223	1.1
210	3	2	1	2	2	1	E	7568.9561	6.1
211	4	2	2	3	2	2	E	10406.1548	3.7
212	8	2	6	7	3	5	A	12086.5886	2.1
213	8	2	6	7	3	5	E	12089.1567	2.6
214	5	3	2	5	0	5	E	23184.9532	-1.9
215	3	3	0	3	2	1	A	11639.5842	-0.8
216	3	3	0	3	2	1	E	11674.4427	-2.4
217	4	3	1	4	2	2	A	11338.8077	0.4
218	4	3	1	4	2	2	E	11366.2811	-3.3
219	5	3	2	5	2	3	A	10848.5264	-1.1
220	5	3	2	5	2	3	E	10860.7213	-1.2
221	6	3	3	6	2	4	A	10220.4406	0.8
222	6	3	3	6	2	4	E	10224.0592	-0.3
223	7	3	4	7	2	5	A	9580.7974	0.7
224	8	3	5	8	2	6	E	9094.5739	1.2
225	3	3	1	2	2	0	A	19140.5194	-0.9

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226	4	3	2	3	2	1	A	21475.1931	-1.5
227	4	3	2	3	2	1	E	21439.8647	1.2
228	5	3	3	4	2	2	A	23634.0644	-2.5
229	5	3	3	4	2	2	E	23616.7249	1.2
230	3	3	0	2	2	0	E	19169.5546	1.0
231	4	3	1	3	2	1	E	21526.7890	5.4
232	5	3	2	4	2	2	E	23749.4308	0.7
233	3	3	1	3	2	1	E	11591.2548	1.8
234	4	3	2	4	2	2	E	11279.3625	-1.8
235	5	3	3	5	2	3	E	10728.0132	-2.9
236	4	3	1	4	2	3	E	12056.6612	-1.2
237	5	3	2	5	2	4	E	12357.8067	-0.9
238	3	3	0	2	2	1	A	19193.2021	-0.1
239	3	3	0	2	2	1	E	19243.3861	-9.0
240	4	3	1	3	2	2	A	21741.2212	-0.9
241	4	3	1	3	2	2	E	21772.4369	1.4
242	5	3	2	4	2	3	A	24426.7294	-1.5
243	5	3	2	4	2	3	E	24439.8108	2.7
244	3	3	0	3	2	2	E	11920.0952	-1.8
245	3	3	1	2	2	1	E	19160.2051	2.1
246	4	3	2	3	2	2	E	21685.5170	1.7
247	5	3	3	4	2	3	E	24307.1022	0.5
248	3	3	1	3	2	2	A	11875.2603	-1.3
249	3	3	1	3	2	2	E	11836.9052	0.3
250	4	3	2	4	2	3	A	12000.6911	1.6
251	4	3	2	4	2	3	E	11969.7403	-2.0
252	5	3	3	5	2	4	A	12240.7305	3.1
253	5	3	3	5	2	4	E	12225.0992	-2.1
254	6	3	4	6	2	5	A	12633.5980	1.4
255	6	3	4	6	2	5	E	12626.5831	-2.5
256	4	3	1	3	3	0	A	9862.1350	-2.3
257	4	3	1	3	3	0	E	9852.3415	3.0
258	5	3	2	4	3	1	A	12399.5108	-2.8
259	5	3	2	4	3	1	E	12383.1479	2.2
260	6	3	3	5	3	2	A	15002.3053	-3.8
261	6	3	3	5	3	2	E	14992.8863	3.6
262	8	3	5	7	3	4	A	20462.4957	-2.1
263	8	3	5	7	3	4	E	20460.5553	4.3
264	9	3	6	8	3	5	A	23288.7693	-1.3
265	9	3	6	8	3	5	E	23287.3590	5.3
266	4	3	2	3	3	1	A	9839.4319	-0.9
267	4	3	2	3	3	1	E	9848.6122	1.7
268	5	3	3	4	3	2	A	12321.7829	-4.5
269	5	3	3	4	3	2	E	12337.3628	3.4
270	6	3	4	5	3	3	A	14803.5470	-4.6
271	6	3	4	5	3	3	E	14811.9973	2.7

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272	7	3	5	6	3	4	A	17273.7335	−4.0
273	8	3	6	7	3	5	A	19720.3064	−4.5
274	8	3	6	7	3	5	E	19720.8662	4.7
275	9	3	7	8	3	6	A	22132.0674	−5.2
276	9	3	7	8	3	6	E	22131.8834	5.8
277	5	3	2	4	3	2	E	12470.0674	1.6
278	5	3	3	4	3	1	E	12250.4415	2.2
279	4	4	1	4	3	2	A	16506.9480	−0.2
280	4	4	1	4	3	2	E	16479.4681	0.2
281	5	4	2	5	3	3	A	16483.7622	1.0
282	5	4	2	5	3	3	E	16441.4346	0.9
283	6	4	3	6	3	4	A	16471.8023	0.9
284	6	4	3	6	3	4	E	16424.8979	−2.2
285	7	4	4	7	3	5	A	16496.7850	0.1
286	7	4	4	7	3	5	E	16458.1726	−4.7
287	4	4	0	4	3	1	A	16480.6679	−0.3
288	4	4	0	4	3	1	E	16503.2533	−2.2
289	5	4	1	5	3	3	E	16551.8925	2.2
290	5	4	1	5	3	2	A	16381.7247	0.6
291	5	4	1	5	3	2	E	16419.1814	−2.5
292	6	4	2	6	3	3	A	16179.7629	−0.1
293	6	4	2	6	3	3	E	16221.8377	−1.9
294	7	4	3	7	3	4	A	15817.3904	−1.1
295	7	4	3	7	3	4	E	15851.2393	−0.2
296	5	4	2	5	3	2	E	16308.7244	−2.9
297	5	4	1	4	4	0	A	12300.5652	−4.3
298	5	4	1	4	4	0	E	12299.0768	2.8
299	6	4	2	5	4	1	A	14800.3429	−5.1
300	6	4	2	5	4	1	E	14795.5410	2.5
301	8	4	4	7	4	3	A	19893.4549	−5.5
302	8	4	4	7	4	3	E	19875.8324	3.8
303	5	4	2	4	4	1	A	12298.5969	−3.4
304	5	4	2	4	4	1	E	12299.3260	0.8
305	6	4	3	5	4	2	A	14791.5874	−4.5
306	6	4	3	5	4	2	E	14795.4621	1.1
307	8	4	5	7	4	4	A	19817.2491	−5.4
308	8	4	5	7	4	4	E	19833.5806	2.9
309	5	5	0	5	4	1	A	21220.7752	3.5
310	5	5	0	5	4	1	E	21232.5895	−2.5
311	5	5	1	5	4	2	A	21222.9759	1.7
312	5	5	1	5	4	2	E	21204.8729	5.0

Appendix A. 2-Acetylthiophene

Table A.6: Observed frequencies ν_{obs} of 245 rotational transitions of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	2	0	2	1	0	1	A	4830.2630	0.0
2	2	0	2	1	0	1	E	4829.9144	-2.1
3	3	0	3	2	0	2	A	7124.0106	-0.4
4	3	0	3	2	0	2	E	7123.6305	-1.6
5	4	0	4	3	0	3	A	9298.1055	0.5
6	4	0	4	3	0	3	E	9297.7760	-0.7
7	5	0	5	4	0	4	A	11369.2812	-0.5
8	5	0	5	4	0	4	E	11369.0267	0.5
9	6	0	6	5	0	5	A	13384.6171	0.1
10	6	0	6	5	0	5	E	13384.4106	0.3
11	7	0	7	6	0	6	A	15386.8784	0.3
12	7	0	7	6	0	6	E	15386.6903	-0.1
13	9	0	9	8	0	8	A	19416.8373	-0.9
14	9	0	9	8	0	8	E	19416.6521	0.0
15	10	0	10	9	0	9	A	21446.0507	-1.6
16	10	0	10	9	0	9	E	21445.8649	-0.5
17	2	1	2	1	1	1	A	4482.8079	-0.1
18	2	1	2	1	1	1	E	4483.0426	1.9
19	3	1	3	2	1	2	A	6694.3484	0.9
20	3	1	3	2	1	2	E	6694.2221	0.0
21	4	1	4	3	1	3	A	8875.3980	0.1
22	4	1	4	3	1	3	E	8875.1785	-0.2
23	5	1	5	4	1	4	A	11023.6480	0.0
24	5	1	5	4	1	4	E	11023.3967	-0.1
25	6	1	6	5	1	5	A	13141.2561	-0.3
26	6	1	6	5	1	5	E	13141.0005	0.3
27	7	1	7	6	1	6	A	15233.4817	0.1
28	7	1	7	6	1	6	E	15233.2327	-0.5
29	8	1	8	7	1	7	A	17306.7845	-0.6
30	8	1	8	7	1	7	E	17306.5497	0.1
31	9	1	9	8	1	8	A	19367.2215	2.2
32	9	1	9	8	1	8	E	19366.9922	-4.8
33	10	1	10	9	1	9	A	21419.5552	-1.4
34	10	1	10	9	1	9	E	21419.3452	-1.1
35	3	0	3	2	1	2	A	5335.9211	1.9
36	3	0	3	2	1	2	E	5335.6510	-3.6
37	4	0	4	3	1	3	A	7939.6766	-0.1
38	4	0	4	3	1	3	E	7939.2060	-3.1
39	5	0	5	4	1	4	A	10433.5601	-0.4
40	5	0	5	4	1	4	E	10433.0542	-2.4
41	6	0	6	5	1	5	A	12794.5289	-0.7

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42	6	0	6	5	1	5	E	12794.0684	-1.8
43	7	0	7	6	1	6	A	15040.1516	0.2
44	7	0	7	6	1	6	E	15039.7597	-0.7
45	8	0	8	7	1	7	A	17203.0132	-0.5
46	8	0	8	7	1	7	E	17202.6861	-0.3
47	9	0	9	8	1	8	A	19313.0659	-0.9
48	9	0	9	8	1	8	E	19312.7888	0.0
49	10	0	10	9	1	9	A	21391.8988	-1.1
50	10	0	10	9	1	9	E	21391.6563	-0.9
51	1	1	1	0	0	0	E	4575.0944	-0.8
52	2	1	2	1	0	1	A	6618.3507	-4.1
53	2	1	2	1	0	1	E	6617.8939	-0.1
54	3	1	3	2	0	2	A	8482.4445	5.2
55	3	1	3	2	0	2	E	8482.2014	1.8
56	4	1	4	3	0	3	A	10233.8307	4.5
57	4	1	4	3	0	3	E	10233.7492	2.9
58	5	1	5	4	0	4	A	11959.3689	-0.3
59	6	1	6	5	0	5	A	13731.3431	-0.7
60	7	1	7	6	0	6	A	15580.2075	-0.8
61	7	1	7	6	0	6	E	15580.1649	1.6
62	8	1	8	7	0	7	A	17500.1145	-0.8
63	8	1	8	7	0	7	E	17500.0232	0.8
64	9	1	9	8	0	8	A	19470.9895	-1.2
65	9	1	9	8	0	8	E	19470.8606	0.4
66	10	1	10	9	0	9	A	21473.7071	-1.9
67	10	1	10	9	0	9	E	21473.5538	-0.7
68	2	1	1	1	1	0	A	5278.9916	0.4
69	3	1	2	2	1	1	A	7884.5543	-0.7
70	3	1	2	2	1	1	E	7883.7584	-0.1
71	4	1	3	3	1	2	A	10443.6288	-0.8
72	4	1	3	3	1	2	E	10442.6438	-2.0
73	5	1	4	4	1	3	A	12931.5750	-0.6
74	5	1	4	4	1	3	E	12930.4432	-3.3
75	6	1	5	5	1	4	A	15319.1476	0.2
76	6	1	5	5	1	4	E	15317.9923	-2.7
77	7	1	6	6	1	5	A	17580.4946	0.4
78	7	1	6	6	1	5	E	17579.4454	-0.6
79	8	1	7	7	1	6	A	19709.8626	1.3
80	8	1	7	7	1	6	E	19708.9856	1.7
81	9	1	8	8	1	7	A	21735.0646	2.0
82	10	1	9	9	1	8	A	23707.0041	3.3
83	10	1	9	9	1	8	E	23706.3611	3.9
84	2	2	1	2	1	2	A	7600.9096	-0.8
85	2	2	1	2	1	2	E	7585.6292	4.0
86	3	2	2	3	1	3	A	8227.9095	1.7
87	3	2	2	3	1	3	E	8223.1713	-1.4

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88	4	2	3	4	1	4	A	9074.7495	−5.8
89	4	2	3	4	1	4	E	9072.0881	−0.6
90	5	2	4	5	1	5	A	10140.9574	−6.8
91	5	2	4	5	1	5	E	10138.5439	−1.2
92	6	2	5	6	1	6	A	11417.0445	−7.3
93	6	2	5	6	1	6	E	11414.3544	−1.0
94	7	2	6	7	1	7	A	12883.3730	−5.4
95	7	2	6	7	1	7	E	12880.1965	−0.5
96	8	2	7	8	1	8	A	14511.7789	−3.2
97	8	2	7	8	1	8	E	14508.0242	0.2
98	9	2	8	9	1	9	A	16269.3996	0.1
99	9	2	8	9	1	9	E	16265.0335	3.1
100	3	3	1	3	2	2	A	11702.8016	1.6
101	3	3	1	3	2	2	E	11661.0107	−2.2
102	4	3	2	4	2	3	A	11832.5516	2.4
103	4	3	2	4	2	3	E	11798.4272	0.4
104	5	3	3	5	2	4	A	12080.4586	2.0
105	5	3	3	5	2	4	E	12063.1522	1.7
106	6	3	4	6	2	5	A	12485.4247	2.7
107	6	3	4	6	2	5	E	12477.8655	−1.1
108	7	3	5	7	2	6	A	13079.7061	0.0
109	7	3	5	7	2	6	E	13075.3548	−0.4
110	8	3	6	8	2	7	A	13885.1520	−0.9
111	8	3	6	8	2	7	E	13881.6506	−0.7
112	3	2	2	2	2	1	A	7321.3452	0.3
113	3	2	2	2	2	1	E	7331.7730	3.4
114	4	2	3	3	2	2	A	9722.2452	−0.2
115	4	2	3	3	2	2	E	9724.0955	0.8
116	5	2	4	4	2	3	A	12089.8546	−2.3
117	6	2	5	5	2	4	A	14417.3434	−0.5
118	6	2	5	5	2	4	E	14416.8106	0.1
119	7	2	6	6	2	5	A	16699.8087	0.5
120	7	2	6	6	2	5	E	16699.0752	0.4
121	8	2	7	7	2	6	A	18935.1902	1.3
122	8	2	7	7	2	6	E	18934.3782	1.6
123	9	2	8	8	2	7	A	21124.8382	1.6
124	9	2	8	8	2	7	E	21124.0051	1.7
125	4	3	2	3	3	1	A	9851.9928	−1.9
126	4	3	2	3	3	1	E	9861.5092	0.6
127	5	3	3	4	3	2	A	12337.7636	−0.7
128	5	3	3	4	3	2	E	12354.5779	1.0
129	6	3	4	5	3	3	A	14822.3089	−0.3
130	6	3	4	5	3	3	E	14831.5264	−0.2
131	7	3	5	6	3	4	A	17294.0915	−0.7
132	7	3	5	6	3	4	E	17296.5640	0.6
133	8	3	6	7	3	5	A	19740.6365	0.8

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134	8	3	6	7	3	5	E	19740.6735	0.8
135	9	3	7	8	3	6	A	22150.4908	0.8
136	9	3	7	8	3	6	E	22149.6328	2.7
137	2	2	1	2	0	2	A	9389.0045	2.3
138	2	2	1	2	0	2	E	9373.6019	−0.8
139	3	2	2	3	0	3	A	9586.3357	−0.4
140	3	2	2	3	0	3	E	9581.7410	0.8
141	4	2	3	4	0	4	A	10010.4761	−0.4
142	4	2	3	4	0	4	E	10008.0610	2.7
143	5	2	4	5	0	5	A	10731.0493	−2.4
144	5	2	4	5	0	5	E	10728.8862	1.0
145	6	2	5	6	0	6	A	11763.7734	−5.2
146	6	2	5	6	0	6	E	11761.2862	0.8
147	7	2	6	7	0	7	A	13076.7083	−0.3
148	7	2	6	7	0	7	E	13073.6700	0.1
149	3	2	1	2	2	0	A	7518.6799	−0.2
150	3	2	1	2	2	0	E	7507.2125	0.9
151	4	2	2	3	2	1	A	10185.6577	−1.0
152	4	2	2	3	2	1	E	10182.3581	2.1
153	5	2	3	4	2	2	A	12920.6521	−1.2
154	5	2	3	4	2	2	E	12918.7918	2.3
155	6	2	4	5	2	3	A	15665.8383	−1.4
156	6	2	4	5	2	3	E	15664.1181	1.2
157	7	2	5	6	2	4	A	18364.8570	−0.4
158	7	2	5	6	2	4	E	18363.0027	−0.7
159	8	2	6	7	2	5	A	20979.4631	0.6
160	8	2	6	7	2	5	E	20977.4620	−2.6
161	9	2	7	8	2	6	A	23482.8412	1.9
162	3	3	0	3	2	1	A	11458.8953	2.4
163	3	3	0	3	2	1	E	11498.5059	0.1
164	4	3	1	4	2	2	A	11149.3572	0.6
165	4	3	1	4	2	2	E	11181.3690	−6.6
166	5	3	2	5	2	3	A	10648.9668	0.1
167	5	3	2	5	2	3	E	10664.2365	−5.4
168	6	3	3	6	2	4	A	10015.9054	−0.4
169	6	3	3	6	2	4	E	10021.4307	−6.5
170	2	2	1	1	1	0	A	11685.6228	−3.7
171	2	2	1	1	1	0	E	11669.4869	2.4
172	3	2	2	2	1	1	A	13727.9771	−3.1
173	3	2	2	2	1	1	E	13723.0930	−4.6
174	4	2	3	3	1	2	A	15565.6670	−3.6
175	4	2	3	3	1	2	E	15563.4302	−3.7
176	5	2	4	4	1	3	A	17211.8939	−4.0
177	5	2	4	4	1	3	E	17210.6398	−1.4
178	6	2	5	5	1	4	A	18697.6624	−3.9
179	6	2	5	5	1	4	E	18697.0075	2.3

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180	8	2	7	7	1	6	A	21433.0215	-0.1
181	2	2	0	1	1	1	A	12134.3571	1.7
182	2	2	0	1	1	1	E	12148.4728	5.4
183	3	2	1	2	1	2	A	15170.2303	2.9
184	3	2	1	2	1	2	E	15172.6379	-0.4
185	4	2	2	3	1	3	A	18661.5429	4.2
186	4	2	2	3	1	3	E	18660.7733	1.1
187	5	2	3	4	1	4	A	22706.8006	6.5
188	5	2	3	4	1	4	E	22704.3858	2.9
189	4	3	1	3	3	0	A	9876.1213	-1.2
190	4	3	1	3	3	0	E	9865.2238	-2.0
191	5	3	2	4	3	1	A	12420.2622	-1.2
192	5	3	2	4	3	1	E	12401.6576	1.8
193	6	3	3	5	3	2	A	15032.7775	-1.3
194	6	3	3	5	3	2	E	15021.3132	1.1
195	7	3	4	6	3	3	A	17732.7939	-1.3
196	7	3	4	6	3	3	E	17727.5857	2.6
197	8	3	5	7	3	4	A	20518.7472	-1.2
198	8	3	5	7	3	4	E	20515.4742	3.3
199	4	1	3	3	2	2	E	4603.3084	1.7
200	5	1	4	4	2	3	E	7809.6565	-2.0
201	6	1	5	5	2	4	A	11038.8234	-1.6
202	6	1	5	5	2	4	E	11037.7961	-4.2
203	7	1	6	6	2	5	A	14201.9737	-1.7
204	7	1	6	6	2	5	E	14200.4305	-5.2
205	9	1	8	8	2	7	A	20011.9038	1.6
206	9	1	8	8	2	7	E	20010.3028	-2.0
207	2	2	0	2	1	1	A	6457.2687	-3.5
208	2	2	0	2	1	1	E	6471.1314	1.9
209	3	2	1	3	1	2	A	6091.3941	-3.3
210	3	2	1	3	1	2	E	6094.5796	-3.0
211	4	2	2	4	1	3	A	5833.4261	-0.5
212	4	2	2	4	1	3	E	5834.2930	0.2
213	7	2	5	7	1	6	A	6953.5611	1.4
214	7	2	5	7	1	6	E	6952.3249	9.8
215	8	2	6	8	1	7	E	8220.8010	5.2
216	9	2	7	9	1	8	E	9967.2635	-1.3
217	10	2	8	10	1	9	E	12110.9938	-4.4
218	3	2	1	2	0	2	A	16958.3182	-1.1
219	3	2	1	2	0	2	E	16960.6174	1.6
220	4	2	2	3	0	3	A	20019.9689	1.9
221	4	2	2	3	0	3	E	20019.3440	4.3
222	3	3	0	2	2	1	A	19028.2122	2.3
223	4	3	1	3	2	2	A	21582.9893	1.8
224	4	3	1	3	2	2	E	21618.9801	5.0
225	5	3	2	4	2	3	A	24281.0066	1.1

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226	5	3	2	4	2	3	E	24296.5345	−1.6
227	3	3	1	2	2	0	A	18973.5105	2.6
228	4	3	2	3	2	1	A	21306.8246	2.1
229	4	3	2	3	2	1	E	21267.2806	2.5
230	5	3	3	4	2	2	A	23458.9305	2.5
231	5	3	3	4	2	2	E	23439.4953	−3.7
232	2	2	0	2	1	2	E	7665.4300	3.3
233	3	2	1	3	1	3	E	8478.4169	0.7
234	2	2	1	2	1	1	E	6391.3275	−0.5
235	2	2	1	1	1	1	E	12068.6685	2.6
236	2	2	0	1	1	0	E	11749.2887	2.7
237	3	2	1	2	2	1	E	7587.0125	−0.6
238	3	2	2	2	1	2	E	14917.3920	−2.9
239	3	2	1	2	1	1	E	13978.3384	−2.7
240	3	3	1	2	2	1	E	18992.7838	1.2
241	3	3	0	2	2	0	E	19005.7156	−1.8
242	3	3	0	3	2	2	E	11753.7491	−0.2
243	4	3	1	3	2	1	E	21363.7337	2.1
244	4	3	1	4	2	3	E	11894.8786	−1.7
245	4	3	2	4	2	2	E	11084.9184	−3.7

Table A.7a: Observed frequencies ν_{obs} of 101 rotational transitions of the $^{34}\text{S}(1)$ isotopologue (for atom numbering see Figure 3.1) of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	4	0	4	3	0	3	E	9228.8710	1.3
2	4	0	4	3	0	3	A	9229.0614	-3.9
3	5	0	5	4	0	4	E	11284.2547	4.2
4	5	0	5	4	0	4	A	11284.4362	-3.8
5	6	0	6	5	0	5	E	13284.3109	4.1
6	6	0	6	5	0	5	A	13284.4834	-3.7
7	7	0	7	6	0	6	A	15271.6819	-5.4
8	7	0	7	6	0	6	E	15271.5219	7.7
9	4	0	4	3	1	3	A	7882.7979	-2.6
10	4	0	4	3	1	3	E	7882.8267	-0.7
11	5	0	5	4	1	4	A	10357.6989	-1.0
12	6	0	6	5	1	5	E	12700.3885	3.9
13	6	0	6	5	1	5	A	12700.4964	-3.1
14	7	0	7	6	1	6	A	14928.8076	-4.9
15	7	0	7	6	1	6	E	14928.6752	4.0
16	8	0	8	7	1	7	A	17075.0724	-3.5
17	8	0	8	7	1	7	E	17074.9291	7.4
18	2	1	2	1	0	1	A	6567.7968	-3.4

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19	2	1	2	1	0	1	E	6567.2672	1.5
20	3	1	3	2	0	2	A	8417.7244	-1.2
21	3	1	3	2	0	2	E	8417.3197	3.7
22	4	1	4	3	0	3	A	10155.8035	-2.0
23	4	1	4	3	0	3	E	10155.4897	4.7
24	5	1	5	4	0	4	A	11868.4243	-3.3
25	5	1	5	4	0	4	E	11868.1803	7.6
26	6	1	6	5	0	5	A	13627.3545	-7.3
27	6	1	6	5	0	5	E	13627.1557	6.0
28	7	1	7	6	0	6	A	15462.7158	-4.7
29	7	1	7	6	0	6	E	15462.5399	7.0
30	8	1	8	7	0	7	A	17368.5627	-6.0
31	8	1	8	7	0	7	E	17368.4004	6.7
32	9	1	9	8	0	8	A	19324.9139	-7.3
33	9	1	9	8	0	8	E	19324.7601	7.7
34	10	1	10	9	0	9	A	21312.7858	-6.2
35	3	1	3	2	1	2	E	6644.7447	1.0
36	4	1	4	3	1	3	A	8809.5357	-4.9
37	4	1	4	3	1	3	E	8809.4442	1.5
38	5	1	5	4	1	4	A	10941.6855	-2.0
39	5	1	5	4	1	4	E	10941.5609	3.5
40	6	1	6	5	1	5	A	13043.3767	2.4
41	6	1	6	5	1	5	E	13043.2243	-3.2
42	7	1	7	6	1	6	A	15119.8391	-6.6
43	7	1	7	6	1	6	E	15119.6972	7.3
44	8	1	8	7	1	7	A	17177.5300	-5.4
45	8	1	8	7	1	7	E	17177.3828	7.8
46	9	1	9	8	1	8	A	19222.4557	-6.0
47	9	1	9	8	1	8	E	19222.3094	10.3
48	2	1	1	1	1	0	A	5240.8323	-0.9
49	2	1	1	1	1	0	E	5240.3113	1.0
50	3	1	2	2	1	1	A	7827.4660	-3.9
51	3	1	2	2	1	1	E	7827.0747	0.3
52	4	1	3	3	1	2	A	10367.8135	-3.3
53	4	1	3	3	1	2	E	10367.3583	-1.8
54	5	1	4	4	1	3	A	12837.3282	-2.7
55	5	1	4	4	1	3	E	12836.8033	0.2
56	6	1	5	5	1	4	A	15206.8897	-5.0
57	6	1	5	5	1	4	E	15206.3250	2.0
58	7	1	6	6	1	5	A	17450.8251	-3.3
59	7	1	6	6	1	5	E	17450.2526	5.5
60	8	1	7	7	1	6	A	19563.5627	-2.9
61	2	2	0	1	1	1	A	12041.2279	-0.5
62	2	2	0	1	1	1	E	12052.5912	1.6
63	3	2	1	2	1	2	A	15055.8407	-0.5
64	3	2	1	2	1	2	E	15057.5716	-1.0

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65	4	2	2	3	1	3	A	18523.3457	1.0
66	4	2	2	3	1	3	E	18522.7812	-1.3
67	5	2	3	4	1	4	A	22541.5712	10.2
68	5	2	3	4	1	4	E	22540.0486	-0.5
69	3	2	2	3	1	3	A	8164.2594	-0.2
70	3	2	2	3	1	3	E	8160.1229	-2.6
71	4	2	3	4	1	4	A	9005.8395	-3.9
72	4	2	3	4	1	4	E	9003.4940	-2.3
73	2	2	1	1	1	0	A	11595.2391	-0.5
74	2	2	1	1	1	0	E	11581.4930	1.9
75	3	2	2	2	1	1	A	13622.2736	-0.8
76	3	2	2	2	1	1	E	13617.9753	-1.2
77	4	2	3	3	1	2	A	15445.9259	-3.0
78	4	2	3	3	1	2	E	15443.7179	2.2
79	5	2	4	4	1	3	A	17079.3562	-2.6
80	5	2	4	4	1	3	E	17077.8409	5.1
81	6	2	5	5	1	4	A	18553.4589	-5.0
82	6	2	5	5	1	4	E	18552.3028	6.5
83	7	2	6	6	1	5	A	19923.3919	-5.1
84	2	2	1	1	1	1	E	11977.9801	-1.0
85	4	2	2	3	2	1	E	10109.9537	0.1
86	3	2	2	2	2	1	A	7267.8631	-4.8
87	3	2	2	2	2	1	E	7276.7979	2.1
88	4	2	3	3	2	2	A	9651.1209	-3.5
89	4	2	3	3	2	2	E	9652.8142	0.7
90	3	3	0	3	2	1	E	11401.2237	-0.6
91	4	3	1	4	2	2	A	11058.6329	3.5
92	4	3	1	4	2	2	E	11085.3667	-3.0
93	5	3	2	5	2	3	A	10561.0786	3.1
94	5	3	2	5	2	3	E	10572.5054	-0.7
95	3	3	0	2	2	1	A	18881.2647	-1.0
96	4	3	1	3	2	2	A	21417.7141	-0.4
97	4	3	1	3	2	2	E	21448.0279	1.2
98	3	3	1	2	2	0	A	18826.8098	0.7
99	3	3	1	2	2	0	E	18773.4359	-3.9
100	4	3	2	3	2	1	A	21142.7914	-1.6
101	4	3	2	3	2	1	E	21108.4245	3.8

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Table A.7b: Observed frequencies ν_{obs} of 15 rotational transitions of the $^{13}\text{C}(2)$ isotopologue (for atom numbering see Figure 3.1) of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	4	1	4	3	0	3	A	10273.8004	-1.0
2	2	2	1	2	1	2	A	7695.9099	-2.3
3	2	2	1	1	1	0	A	11783.8983	-2.3
4	3	2	2	2	1	1	A	13827.8934	2.5
5	3	2	1	2	1	2	A	15249.4457	-1.9
6	4	2	2	3	1	3	A	18718.2489	1.8
7	3	3	0	3	2	1	A	11634.6232	-4.2
8	4	3	1	4	2	2	A	11333.6653	3.1
9	5	3	2	5	2	3	A	10843.1712	0.1
10	3	3	1	2	2	0	A	19135.4367	-0.4
11	4	3	2	3	2	1	A	21469.9412	-0.5
12	5	3	3	4	2	2	A	23628.5288	0.5
13	4	4	1	4	3	2	A	16500.1732	1.7
14	5	4	2	5	3	3	A	16476.9860	0.5
15	5	4	1	5	3	2	A	16374.8112	-0.2

Table A.7c: Observed frequencies ν_{obs} of 52 rotational transitions of the $^{13}\text{C}(3)$ isotopologue (for atom numbering see Figure 3.1) of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	4	0	4	3	0	3	A	9265.1309	-1.0
2	4	0	4	3	0	3	E	9264.9402	-2.9
3	5	0	5	4	0	4	A	11328.1381	-2.0
4	5	0	5	4	0	4	E	11327.9575	-0.7
5	6	0	6	5	0	5	A	13335.7568	-2.3
6	6	0	6	5	0	5	E	13335.5886	2.0
7	9	0	9	8	0	8	A	19346.1255	-3.6
8	9	0	9	8	0	8	E	19345.9766	7.0
9	4	0	4	3	1	3	A	7916.9141	-2.4
10	5	0	5	4	1	4	A	10400.8150	1.2
11	5	0	5	4	1	4	E	10400.7392	-0.7
12	6	0	6	5	1	5	A	12751.9538	4.2
13	6	0	6	5	1	5	E	12751.8306	-0.2
14	7	0	7	6	1	6	A	14988.2157	-2.0
15	7	0	7	6	1	6	E	14988.0750	-1.4

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16	8	0	8	7	1	7	A	17142.2776	−1.6
17	8	0	8	7	1	7	E	17142.1224	−5.1
18	4	1	3	3	1	2	A	10409.9206	2.0
19	3	1	3	2	0	2	A	8447.6690	1.2
20	3	1	3	2	0	2	E	8447.2789	−8.7
21	4	1	4	3	0	3	A	10192.4576	−0.6
22	4	1	4	3	0	3	E	10192.1611	−0.3
23	5	1	5	4	0	4	A	11911.9489	−0.7
24	5	1	5	4	0	4	E	11911.7167	2.7
25	6	1	6	5	0	5	A	13678.1911	−2.2
26	7	1	7	6	0	6	A	15521.2510	−1.7
27	7	1	7	6	0	6	E	15521.0864	9.1
28	8	1	8	7	0	7	A	17435.0070	−1.3
29	9	1	9	8	0	8	A	19399.3285	−4.0
30	4	1	4	3	1	3	A	8844.2458	3.0
31	4	1	4	3	1	3	E	8844.1466	1.8
32	5	1	5	4	1	4	A	10984.6212	−2.1
33	5	1	5	4	1	4	E	10984.4955	−0.2
34	6	1	6	5	1	5	A	13094.3812	−2.7
35	6	1	6	5	1	5	E	13094.2440	3.2
36	7	1	7	6	1	6	A	15178.8150	−3.4
37	7	1	7	6	1	6	E	15178.6720	4.7
38	8	1	8	7	1	7	A	17244.4095	1.9
39	8	1	8	7	1	7	E	17244.2566	4.2
40	2	2	1	1	1	0	A	11632.3654	−0.8
41	3	2	2	2	1	1	A	13667.2744	−0.9
42	4	2	3	3	1	2	A	15497.8261	7.6
43	5	2	4	4	1	3	A	17137.2631	−0.4
44	6	2	5	5	1	4	A	18616.7765	2.8
45	7	2	6	6	1	5	A	19991.9519	−4.0
46	2	2	0	1	1	1	A	12080.6069	−1.8
47	3	2	1	2	1	2	A	15108.2448	−1.4
48	4	2	2	3	1	3	A	18591.3580	0.5
49	3	3	0	2	2	1	A	18941.7165	−0.6
50	4	3	1	3	2	2	A	21488.7657	0.8
51	3	3	1	2	2	0	A	18886.8738	0.2
52	4	3	2	3	2	1	A	21211.8954	−0.7

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Table A.7d: Observed frequencies ν_{obs} of 52 rotational transitions of the $^{13}\text{C}(4)$ isotopologue (for atom numbering see Figure 3.1) of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	4	0	4	3	0	3	A	9205.8244	-1.9
2	4	0	4	3	0	3	E	9205.6329	0.8
3	5	0	5	4	0	4	A	11260.9987	-2.4
4	5	0	5	4	0	4	E	11260.8177	3.1
5	6	0	6	5	0	5	A	13259.2442	-2.5
6	6	0	6	5	0	5	E	13259.0757	5.3
7	3	0	3	2	1	2	A	5242.8148	-3.6
8	3	0	3	2	1	2	E	5242.9937	3.3
9	5	0	5	4	1	4	A	10300.5210	-2.4
10	5	0	5	4	1	4	E	10300.4490	4.4
11	6	0	6	5	1	5	A	12647.2114	-2.5
12	6	0	6	5	1	5	E	12647.0915	2.3
13	7	0	7	6	1	6	A	14879.0763	-2.4
14	4	1	3	3	1	2	A	10322.1764	0.2
15	4	1	3	3	1	2	E	10321.7131	-7.7
16	5	1	4	4	1	3	A	12785.6748	-1.1
17	6	1	5	5	1	4	A	15153.6716	-0.4
18	7	1	6	6	1	5	A	17400.7724	-0.6
19	7	1	6	6	1	5	E	17400.1954	1.0
20	8	1	7	7	1	6	A	19519.3488	1.4
21	3	1	3	2	0	2	A	8431.1589	0.8
22	3	1	3	2	0	2	E	8430.7677	-1.1
23	5	1	5	4	0	4	A	11873.0271	-6.8
24	5	1	5	4	0	4	E	11872.8035	7.8
25	7	1	7	6	0	6	A	15447.5886	5.0
26	7	1	7	6	0	6	E	15447.4066	-0.3
27	8	1	8	7	0	7	A	17343.3760	-4.2
28	3	1	3	2	1	2	A	6624.6517	-1.8
29	3	1	3	2	1	2	E	6624.6252	2.3
30	4	1	4	3	1	3	A	8784.4645	-4.4
31	4	1	4	3	1	3	E	8784.3731	3.6
32	5	1	5	4	1	4	A	10912.5635	7.3
33	5	1	5	4	1	4	E	10912.4295	3.7
34	6	1	6	5	1	5	A	13010.7723	-4.7
35	2	2	1	1	1	0	A	11659.9921	-0.7
36	3	2	2	2	1	1	A	13682.7119	0.9
37	4	2	3	3	1	2	A	15504.9674	-3.8
38	6	2	5	5	1	4	A	18614.4892	-3.6
39	6	2	5	5	1	4	E	18613.3772	-3.2

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40	7	2	6	6	1	5	A	19983.0908	−0.1
41	7	2	6	6	1	5	E	19982.2205	4.5
42	2	2	0	1	1	1	A	12098.5074	−0.6
43	3	2	1	2	1	2	A	15090.3963	6.3
44	4	2	2	3	2	1	A	10058.3707	−2.5
45	5	2	3	4	2	2	A	12757.3388	−0.2
46	6	2	4	5	2	3	A	15469.7088	1.5
47	3	3	0	2	2	1	A	18986.4988	0.1
48	4	3	1	3	2	2	A	21508.3639	1.4
49	5	3	2	4	2	3	A	24166.6037	0.7
50	3	3	1	2	2	0	A	18934.2535	1.2
51	4	3	2	3	2	1	A	21244.5356	−1.1
52	5	3	3	4	2	2	A	23380.5364	−2.3

Table A.7e: Observed frequencies ν_{obs} of 52 rotational transitions of the $^{13}\text{C}(5)$ isotopologue (for atom numbering see Figure 3.1) of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>J</i>	<i>K_a</i>	<i>K_c</i>	Species	<i>V</i> _{obs}	<i>V</i> _{obs} − <i>V</i> _{calc}
	upper level			lower level				MHz	kHz
1	4	0	4	3	0	3	A	9201.5158	−1.1
2	4	0	4	3	0	3	E	9201.3222	−0.5
3	5	0	5	4	0	4	A	11262.1456	−2.4
4	5	0	5	4	0	4	E	11261.9636	3.7
5	8	0	8	7	0	7	A	17237.0861	−2.0
6	3	0	3	2	1	2	A	5185.9231	0.7
7	3	0	3	2	1	2	E	5186.1304	−0.8
8	5	0	5	4	1	4	A	10255.0555	−1.3
9	5	0	5	4	1	4	E	10254.9986	4.1
10	6	0	6	5	1	5	A	12613.1286	−0.5
11	6	0	6	5	1	5	E	12613.0196	4.6
12	7	0	7	6	1	6	A	14855.8710	−3.3
13	7	0	7	6	1	6	E	14855.7400	6.5
14	2	1	2	1	0	1	A	6622.5767	−0.8
15	2	1	2	1	0	1	E	6622.0324	−2.4
16	3	1	3	2	0	2	A	8472.2200	−2.1
17	3	1	3	2	0	2	E	8471.8080	−2.2
18	5	1	5	4	0	4	A	11912.8653	−2.0
19	5	1	5	4	0	4	E	11912.6158	0.9
20	6	1	6	5	0	5	A	13656.0879	−2.9
21	6	1	6	5	0	5	E	13655.8870	4.5
22	7	1	7	6	0	6	A	15472.4960	0.4
23	7	1	7	6	0	6	E	15472.3199	7.6
24	8	1	8	7	0	7	A	17360.6081	−2.9

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25	9	1	9	8	0	8	A	19302.5038	−4.8
26	4	1	4	3	1	3	A	8776.9964	−2.5
27	4	1	4	3	1	3	E	8776.9058	0.0
28	5	1	5	4	1	4	A	10905.7729	−3.1
29	5	1	5	4	1	4	E	10905.6523	2.8
30	6	1	6	5	1	5	A	13005.3693	−2.2
31	6	1	6	5	1	5	E	13005.2321	4.6
32	7	1	7	6	1	6	A	15080.2498	−3.4
33	7	1	7	6	1	6	E	15080.1061	6.3
34	4	1	3	3	1	2	A	10292.8874	−1.7
35	4	1	3	3	1	2	E	10292.4341	−5.3
36	5	1	4	4	1	3	A	12755.2910	−1.2
37	5	1	4	4	1	3	E	12754.7675	−4.9
38	6	1	5	5	1	4	A	15127.3592	2.1
39	6	1	5	5	1	4	E	15126.7893	−1.8
40	3	2	2	2	1	1	A	13799.1296	−2.3
41	4	2	3	3	1	2	A	15624.6643	−0.2
42	6	2	5	5	1	4	A	18745.5455	1.7
43	4	2	2	3	1	3	A	18579.3377	6.8
44	4	2	2	3	2	1	A	10018.5013	−1.0
45	4	2	2	3	2	1	E	10015.9106	0.5
46	5	2	3	4	2	2	A	12703.9302	1.0
47	3	3	0	2	2	1	A	19175.7193	−2.5
48	4	3	1	3	2	2	A	21686.3554	−3.4
49	3	3	1	2	2	0	A	19126.0273	0.7
50	4	3	2	3	2	1	A	21435.3493	−0.9
51	5	3	3	4	2	2	A	23577.3983	0.6
52	3	3	1	3	2	2	A	11951.1091	4.2

Table A.7f: Observed frequencies ν_{obs} of 57 rotational transitions of the $^{13}\text{C}(6)$ isotopologue (for atom numbering see Figure 3.1) of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	3	0	3	2	0	2	E	7082.3227	2.4
2	4	0	4	3	0	3	A	9252.8636	−2.6
3	4	0	4	3	0	3	E	9252.6725	4.9
4	5	0	5	4	0	4	E	11321.6964	5.4
5	6	0	6	5	0	5	E	13332.4374	12.8
6	5	0	5	4	1	4	A	10332.3192	−2.2
7	5	0	5	4	1	4	E	10332.2543	−0.9
8	6	0	6	5	1	5	A	12697.4709	−4.7
9	6	0	6	5	1	5	E	12697.3615	3.7

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10	7	0	7	6	1	6	A	14946.8973	-8.2
11	7	0	7	6	1	6	E	14946.7620	0.9
12	1	1	1	0	0	0	A	4605.1618	-0.2
13	2	1	2	1	0	1	A	6638.7860	-8.4
14	2	1	2	1	0	1	E	6638.2545	3.2
15	3	1	3	2	0	2	A	8497.3292	-4.6
16	4	1	4	3	0	3	A	10242.4220	-6.2
17	5	1	5	4	0	4	A	11957.0091	-5.9
18	5	1	5	4	0	4	E	11956.7635	5.7
19	6	1	6	5	0	5	A	13712.7561	-8.3
20	6	1	6	5	0	5	E	13712.5595	8.2
21	7	1	7	6	0	6	E	15542.8130	6.1
22	8	1	8	7	0	7	E	17444.8320	0.2
23	4	1	3	3	1	2	A	10362.0824	-0.6
24	5	1	4	4	1	3	A	12838.2129	-1.9
25	5	1	4	4	1	3	E	12837.6830	0.0
26	6	1	5	5	1	4	A	15221.0495	-1.2
27	6	1	5	5	1	4	E	15220.4750	3.0
28	4	1	4	3	1	3	A	8827.6014	-2.5
29	4	1	4	3	1	3	E	8827.5122	6.5
30	5	1	5	4	1	4	E	10967.3260	4.0
31	6	1	6	5	1	5	A	13077.6293	-3.5
32	6	1	6	5	1	5	E	13077.4880	3.5
33	7	1	7	6	1	6	A	15162.8256	-12.1
34	7	1	7	6	1	6	E	15162.6830	2.8
35	2	2	1	1	1	0	A	11781.8452	0.7
36	2	2	1	1	1	0	E	11767.5071	1.0
37	3	2	2	2	1	1	A	13815.4714	-2.2
38	4	2	3	3	1	2	A	15649.2106	-7.5
39	5	2	4	4	1	3	A	17295.0990	-3.1
40	5	2	4	4	1	3	E	17293.5410	7.0
41	6	2	5	5	1	4	A	18781.3527	-6.8
42	6	2	5	5	1	4	E	18780.1692	6.8
43	2	2	0	1	1	1	A	12218.4270	1.4
44	3	2	1	2	1	2	A	15215.7355	2.3
45	3	2	1	2	1	2	E	15217.6521	-1.1
46	4	2	2	3	1	3	A	18650.6426	-2.4
47	4	2	2	3	1	3	E	18650.1396	2.9
48	3	2	2	3	1	3	A	8326.2547	5.8
49	3	2	2	3	1	3	E	8321.9001	-2.8
50	3	2	2	2	2	1	A	7268.0645	-6.0
51	3	3	1	2	2	0	A	19133.5990	2.9
52	3	3	1	2	2	0	E	19079.2916	-3.6
53	4	3	2	3	2	1	A	21455.7555	0.4
54	5	3	3	4	2	2	A	23606.3727	0.9
55	5	3	3	4	2	2	E	23588.5896	1.7

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56	3	3	0	3	2	1	A	11683.6259	1.3
57	3	3	0	3	2	1	E	11718.3825	−3.9

Table A.7g: Observed frequencies ν_{obs} of 54 rotational transitions of the $^{13}\text{C}(8)$ isotopologue (for atom numbering see Figure 3.1) of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>J</i>	<i>K_a</i>	<i>K_c</i>	Species	<i>V</i> _{obs}	<i>V</i> _{obs} − <i>V</i> _{calc}
	upper level			lower level				MHz	kHz
1	2	0	2	1	0	1	A	4747.6477	−1.1
2	2	0	2	1	0	1	E	4747.5023	−2.6
3	3	0	3	2	0	2	A	7008.9898	−0.9
4	3	0	3	2	0	2	E	7008.8088	−2.2
5	4	0	4	3	0	3	A	9157.6858	4.0
6	4	0	4	3	0	3	E	9157.4934	2.0
7	5	0	5	4	0	4	A	11206.1878	−2.6
8	5	0	5	4	0	4	E	11206.0082	4.1
9	6	0	6	5	0	5	A	13196.7304	−12.3
10	3	0	3	2	1	2	A	5180.5269	−1.1
11	3	0	3	2	1	2	E	5180.7530	7.2
12	4	0	4	3	1	3	A	7750.8299	0.3
13	4	0	4	3	1	3	E	7750.8796	3.0
14	6	0	6	5	1	5	A	12563.1125	−2.7
15	6	0	6	5	1	5	E	12563.0071	−6.2
16	3	1	2	2	1	1	A	7736.9698	−1.0
17	3	1	2	2	1	1	E	7736.5850	−6.2
18	4	1	3	3	1	2	A	10252.5662	−1.0
19	5	1	4	4	1	3	A	12703.2558	0.6
20	6	1	5	5	1	4	A	15062.2374	0.2
21	3	1	3	2	0	2	A	8415.8404	−2.6
22	3	1	3	2	0	2	E	8415.4245	−1.3
23	4	1	4	3	0	3	A	10143.1645	0.5
24	4	1	4	3	0	3	E	10142.8375	2.4
25	5	1	5	4	0	4	E	11839.5619	6.2
26	6	1	6	5	0	5	A	13576.6959	−7.6
27	6	1	6	5	0	5	E	13576.4912	4.7
28	5	1	5	4	1	4	A	10854.3388	3.1
29	5	1	5	4	1	4	E	10854.2173	5.4
30	6	1	6	5	1	5	A	12943.0729	−3.1
31	6	1	6	5	1	5	E	12942.9397	4.7
32	7	1	7	6	1	6	A	15007.1191	−7.6
33	7	1	7	6	1	6	E	15006.9826	6.5
34	8	1	8	7	1	7	E	17052.2408	5.1
35	2	2	1	1	1	0	A	11677.0879	1.3

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36	3	2	2	2	1	1	A	13689.8922	−0.9
37	4	2	3	3	1	2	A	15505.2311	6.0
38	5	2	4	4	1	3	A	17134.8765	−1.8
39	6	2	5	5	1	4	A	18606.5469	−1.8
40	2	2	0	1	1	1	A	12108.2367	−3.1
41	3	2	1	2	1	2	A	15072.4498	−0.7
42	4	2	2	3	1	3	A	18468.2707	2.9
43	3	2	1	2	2	0	A	7374.2255	0.2
44	4	2	2	3	2	1	A	9983.1967	−0.9
45	5	2	3	4	2	2	A	12660.2135	0.4
46	6	2	4	5	2	3	A	15353.3020	1.1
47	3	3	0	2	2	1	A	19014.2715	−1.4
48	4	3	1	3	2	2	A	21516.4860	−1.1
49	5	3	2	4	2	3	A	24149.7539	−0.3
50	3	3	1	2	2	0	A	18963.9264	−0.4
51	4	3	2	3	2	1	A	21262.2144	0.6
52	3	3	1	3	2	2	A	11819.0809	2.5
53	4	3	2	4	2	3	A	11939.2866	−1.3
54	5	3	3	5	2	4	A	12169.6230	1.3

Table A.8a: Observed frequencies ν_{obs} of 63 rotational transitions of the $^{34}\text{S}(1)$ isotopologue (for atom numbering see Figure 3.1) of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	2	0	2	1	0	1	A	4799.7839	−0.8
2	2	0	2	1	0	1	E	4799.4338	−2.9
3	3	0	3	2	0	2	A	7074.1520	−1.3
4	3	0	3	2	0	2	E	7073.7786	0.1
5	4	0	4	3	0	3	A	9226.1908	1.3
6	4	0	4	3	0	3	E	9225.8724	1.0
7	5	0	5	4	0	4	A	11275.4921	2.4
8	5	0	5	4	0	4	E	11275.2480	1.3
9	6	0	6	5	0	5	A	13271.5844	0.6
10	6	0	6	5	0	5	E	13271.3877	−0.5
11	7	0	7	6	0	6	A	15257.1026	−1.3
12	7	0	7	6	0	6	E	15256.9240	−1.2
13	8	0	8	7	0	7	A	17250.9398	−1.1
14	8	0	8	7	0	7	E	17250.7635	−0.6
15	9	0	9	8	0	8	A	19255.9165	−0.3
16	9	0	9	8	0	8	E	19255.7384	0.2
17	4	0	4	3	1	3	A	7923.4659	0.1
18	4	0	4	3	1	3	E	7922.9792	−1.1
19	5	0	5	4	1	4	A	10388.5892	−2.7

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20	5	0	5	4	1	4	E	10388.0881	3.6
21	6	0	6	5	1	5	A	12719.7455	-0.1
22	7	0	7	6	1	6	A	14937.3648	1.4
23	7	0	7	6	1	6	E	14936.9818	-0.8
24	3	1	3	2	0	2	A	8376.8705	-6.5
25	3	1	3	2	0	2	E	8376.6705	0.8
26	4	1	4	3	0	3	A	10113.0854	-1.9
27	4	1	4	3	0	3	E	10113.0340	0.3
28	5	1	5	4	0	4	A	11827.3248	-3.1
29	5	1	5	4	0	4	E	11827.3452	2.2
30	6	1	6	5	0	5	A	13591.3284	4.1
31	7	1	7	6	0	6	A	15432.9083	-0.7
32	7	1	7	6	0	6	E	15432.8681	-1.0
33	8	1	8	7	0	7	A	17344.0105	0.5
34	9	1	9	8	0	8	A	19303.8247	-0.1
35	9	1	9	8	0	8	E	19303.6969	-1.6
36	4	1	4	3	1	3	A	8810.3638	0.3
37	5	1	5	4	1	4	A	10940.4309	0.8
38	5	1	5	4	1	4	E	10940.1819	1.1
39	6	1	6	5	1	5	A	13039.4856	-0.5
40	6	1	6	5	1	5	E	13039.2355	1.1
41	7	1	7	6	1	6	A	15113.1714	2.9
42	7	1	7	6	1	6	E	15112.9271	0.5
43	9	1	9	8	1	8	A	19210.7578	2.0
44	9	1	9	8	1	8	E	19210.5410	-0.8
45	5	1	4	4	1	3	A	12854.8587	-0.4
46	6	1	5	5	1	4	A	15218.3979	0.4
47	7	1	6	6	1	5	A	17451.3925	-0.6
48	8	1	7	7	1	6	A	19550.9600	-0.5
49	2	2	1	1	1	0	A	11487.0696	-4.4
50	3	2	2	2	1	1	A	13512.7123	-5.1
51	4	2	3	3	1	2	A	15332.3707	7.9
52	2	2	0	1	1	1	A	11940.0670	3.0
53	3	2	1	2	1	2	A	14970.9564	-0.9
54	4	2	2	3	1	3	A	18465.7994	5.4
55	3	2	2	3	1	3	A	8067.4215	-2.6
56	3	3	0	3	2	1	A	11170.2119	1.3
57	4	3	1	4	2	2	A	10852.1345	5.0
58	3	3	1	2	2	0	A	18648.5461	-1.0
59	4	3	2	3	2	1	A	20963.6163	-1.0
60	5	3	3	4	2	2	A	23092.1148	-1.9
61	3	3	0	2	2	1	A	18705.3866	-3.0
62	4	3	1	3	3	0	A	9823.5251	-2.1
63	4	3	1	3	3	0	E	9812.1617	-0.2

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Table A.8b: Observed frequencies ν_{obs} of 10 rotational transitions of the $^{13}\text{C}(4)$ isotopologue (for atom numbering see Figure 3.1) of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	4	0	4	3	0	3	A	9199.6654	0.5
2	6	0	6	5	0	5	A	13244.2061	1.8
3	5	0	5	4	1	4	A	10317.7121	0.9
4	6	0	6	5	1	5	A	12655.3432	-0.8
5	3	1	3	2	0	2	A	8398.6726	0.9
6	4	1	4	3	0	3	A	10131.6664	-2.0
7	5	1	5	4	0	4	A	11838.5763	1.2
8	7	1	7	6	0	6	A	15419.1082	-0.5
9	3	1	3	2	1	2	A	6622.8479	-1.1
10	4	1	4	3	1	3	A	8780.8686	-1.6

Table A.8c: Observed frequencies ν_{obs} of 11 rotational transitions of the $^{13}\text{C}(5)$ isotopologue (for atom numbering see Figure 3.1) of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	4	0	4	3	0	3	A	9196.6294	0.7
2	5	0	5	4	0	4	A	11251.1826	-1.5
3	6	0	6	5	1	5	A	12628.9231	-0.6
4	5	1	5	4	0	4	A	11870.6874	-1.4
5	4	1	4	3	1	3	A	8775.0477	0.4
6	2	2	1	1	1	0	A	11672.5008	-3.7
7	3	2	2	2	1	1	A	13693.5005	3.0
8	4	2	3	3	1	2	A	15514.9364	-2.6
9	5	2	4	4	1	3	A	17149.0402	4.3
10	2	2	0	1	1	1	A	12108.7493	-2.7
11	3	2	1	2	1	2	A	15093.3946	2.2

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Table A.9a: Observed frequencies ν_{obs} of 5 rotational transitions of the $^{13}\text{C}(6)$ isotopologue (for atom numbering see Figure 3.1) of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	5	0	5	4	0	4	A	11309.3166	4.6
2	6	0	6	5	0	5	A	13315.4302	-8.7
3	7	0	7	6	0	6	A	15307.2960	5.0
4	6	0	6	5	1	5	A	12710.1858	0.0
5	5	1	5	4	1	4	A	10961.4417	-1.0

Table A.9b: Observed frequencies ν_{obs} of 9 rotational transitions of the $^{13}\text{C}(3)$ isotopologue (for atom numbering see Figure 3.1) of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>J</i>	<i>K_a</i>	<i>K_c</i>	Species	<i>ν</i> _{obs}	<i>ν</i> _{obs} − <i>ν</i> _{calc}
	upper level			lower level				MHz	kHz
1	4	0	4	3	0	3	A	9258.7938	−16.5
2	5	0	5	4	0	4	A	11315.9877	−4.2
3	6	0	6	5	0	5	A	13319.4859	−61.5
4	4	1	4	3	1	3	A	8841.1585	−12.5
5	5	1	5	4	1	4	A	10978.9239	−27.9
6	6	1	6	5	1	5	A	13085.7459	67.5
7	7	1	7	6	1	6	A	15166.9951	32.5
8	8	1	8	7	1	7	A	17229.5229	0.6
9	2	2	0	1	1	1	A	11991.8085	4.2

Table A.9c: Observed frequencies ν_{obs} of 7 rotational transitions of the $^{13}\text{C}(2)$ and $^{13}\text{C}(8)$ isotopologues (for atom numbering see Figure 3.1) of *anti*-2AT. A fit was not possible.

No.	^{13}C	J	K _a	K _c	J	K _a	K _c	Species	ν_{obs}
		upper level			lower level				[MHz]
1	C(2)	4	1	3	3	1	2	A	10442.6442
2	C(2)	2	2	1	1	1	0	A	11680.9726
3	C(2)	2	2	0	1	1	1	A	12130.4247
4	C(8)	4	0	4	3	0	3	A	9176.9291
5	C(8)	4	1	3	3	1	2	A	10299.0271
6	C(8)	2	2	1	1	1	0	A	11568.2513
7	C(8)	2	2	0	1	1	1	A	12008.2391

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Table A.10: Molecular parameters of $^{13}\text{C}(3)$ - and $^{13}\text{C}(6)$ -isotopologues of *anti*-2AT obtained with the program *XIAM*.

Par. ^a	Unit	$^{13}\text{C}(3)$	$^{13}\text{C}(6)$
A_0	MHz	3507.206(45)	3554.856(54)
B_0	MHz	1417.755(32)	1408.849(13)
C_0	MHz	1016.4673(47)	1015.7426(29)
Δ_c^c	uÅ^2	−3.370	−3.337
N_A^d	-	9	5
σ^e	kHz	46.1	11.1

^a All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. ^b Values of all centrifugal distortion constants were fixed to those of the main isotopologue listed in Table 2. ^c Pseudo inertial defect. ^d Number of A species transitions. ^e Standard deviation of the fit.

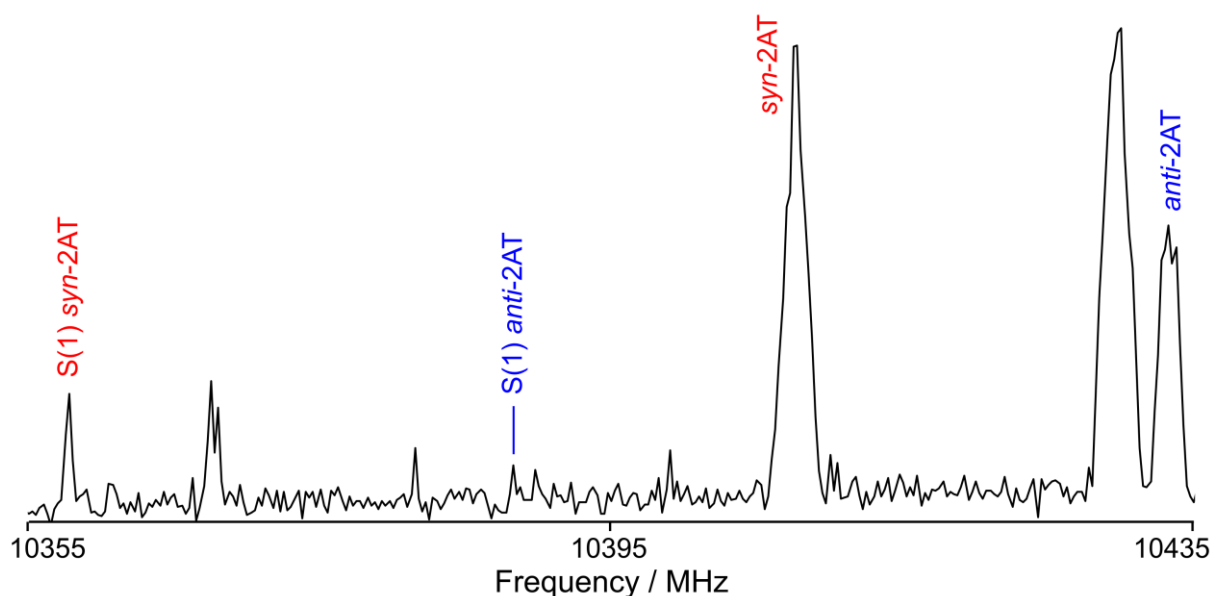


Figure A.1: A portion of the scan of 2AT in the frequency range from 10355 to 10435 MHz recorded by overlapping spectra with 50 co-added decays per each spectrum. Lines belonging to the $5_{05} \leftarrow 4_{14}$ transition of the parent species and of the ^{34}S -isotopologue are labelled with the corresponding conformer. The intensities are given in a logarithmic scale in an arbitrary unit. The temperature of the molecular jet was approximately 1-2 K. (Figure modified from Ref. [4])

B. 2-Propionylthiophene

Table B.1: Coefficients of the one-dimensional Fourier expansion for the potential energy curves calculated using different methods in combination with the basis set 6-311++G(d,p) given in Figure 4.2. The potential is expanded as $V(\varphi) = \sum_{i=0}^6 a_i f_i$.

<i>i</i>	<i>f_i</i>	MP2		B3LYP-D3BJ		M06-2X	
		<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹
0	1	-743.5311916		-745.1229207		-744.9051433	
1	cos α	0.0028798	632.1	0.0029098	638.6	0.0031160	683.9
2	cos 2α	0.0019198	421.3	0.0014663	321.8	0.0013606	298.6
3	cos 3α	0.0013365	293.3	0.0009516	208.8	0.0012842	281.9
4	cos 4α	-0.0000195	-4.3	-0.0002997	-65.8	-0.0003624	-79.5
5	cos 5α	-0.0001154	-25.3	-0.0002322	-51.0	-0.0002568	-56.4
6	cos 6α	-0.0000843	-18.5	-0.0001263	-27.7	-0.0001612	-35.4

Table B.2a: Nuclear coordinates in the principal axis system of *syn*-2PT and *syn*-C₁-2PT calculated at the MP2/6-311++G(d,p) level of theory (for atom numbering see Figure 4.1).

	<i>syn</i>			<i>syn</i> -C ₁		
	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å
S1	1.456117	-1.068910	-0.001120	-1.425833	-0.996238	0.254844
C2	0.238294	0.148986	-0.026017	-0.117773	0.040897	-0.169793
C3	0.799023	1.424550	-0.018429	-0.558553	1.346264	-0.383623
C4	2.212207	1.395798	-0.001248	-1.949355	1.490184	-0.179608
C5	2.702798	0.099129	0.010986	-2.547706	0.289409	0.170759
C6	-1.185448	-0.244282	0.007579	1.240941	-0.522254	-0.308733
O7	-1.511642	-1.426265	0.005583	1.433700	-1.731191	-0.218555
C8	-2.210229	0.878001	0.051818	2.385416	0.456373	-0.480162
C9	-3.643985	0.365936	-0.032649	2.767487	1.065373	0.878463
H10	3.738959	-0.215527	0.018085	-3.592871	0.111123	0.391075
H11	2.847947	2.274112	0.001793	-2.496545	2.419991	-0.287911
H12	0.207180	2.333266	-0.025575	0.102771	2.158244	-0.665391
H13	-2.046611	1.439292	0.980700	3.226298	-0.105303	-0.895256
H14	-1.990902	1.571496	-0.768932	2.110935	1.245735	-1.187078
H15	-3.859336	-0.318246	0.790567	3.040577	0.273916	1.582180
H16	-4.347855	1.201449	0.010884	3.622152	1.738740	0.770310
H17	-3.805358	-0.178476	-0.965846	1.933921	1.630514	1.304393

Appendix B. 2-Propionylthiophene

Table B.2b: Nuclear coordinates in the principal axis system of *anti*-2PT and *anti*-C₁-2PT calculated at the MP2/6-311++G(d,p) level of theory (for atom numbering see Figure 4.1).

	<i>anti</i>			<i>anti</i> -C ₁		
	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å
S1	1.099446	-1.204830	0.078603	0.950111	-1.140002	-0.345710
C2	0.288352	0.316970	0.037589	0.184278	0.387191	-0.108543
C3	1.199980	1.363632	-0.062459	1.103078	1.343126	0.314990
C4	2.539798	0.918524	-0.087529	2.411701	0.826757	0.431822
C5	2.636546	-0.463186	-0.020129	2.477640	-0.519817	0.105100
C6	-1.188412	0.459930	0.014194	-1.269272	0.614848	-0.297548
O7	-1.701405	1.566525	0.118265	-1.722777	1.753125	-0.277448
C8	-2.014906	-0.800719	-0.177295	-2.170530	-0.597062	-0.419678
C9	-3.510253	-0.560055	-0.003688	-2.534641	-1.118626	0.979733
H10	3.532510	-1.070837	-0.007143	3.348220	-1.163379	0.095270
H11	3.405298	1.568197	-0.155130	3.276633	1.400721	0.745249
H12	0.875141	2.396935	-0.112830	0.804975	2.365382	0.519900
H13	-1.793798	-1.186669	-1.181312	-3.071398	-0.281771	-0.952686
H14	-1.654866	-1.562684	0.525883	-1.681298	-1.386698	-1.000875
H15	-3.863945	0.191879	-0.711809	-3.035041	-0.334200	1.554160
H16	-4.065697	-1.487335	-0.167249	-3.208707	-1.976139	0.905548
H17	-3.728552	-0.195626	1.002962	-1.641039	-1.431822	1.527205

Appendix B. 2-Propionylthiophene

Table B.3a: Equilibrium rotational constants, X_e ($X = A, B, C$), predicted torsional barriers and dihedral angles of *syn*-2PT calculated at various levels of theory. The deviations ΔX between the calculated and the ground state experimental values X_0 are given in MHz, the deviation between the calculated and experimental V_3 barrier of the acetyl methyl group is given as ΔV_3 . All optimizations were done under full-symmetry relaxation.

Method/Basis Set	$A /$ MHz	$\Delta A /$ MHz	$B /$ MHz	$\Delta B /$ MHz	$C /$ MHz	$\Delta C /$ MHz	$V_3 /$ cm ⁻¹	$\Delta V_3 /$ cm ⁻¹	$\alpha /$ °	$\beta /$ °
MP2/6-31G(d,p)	3410.4	-17.0	879.3	2.1	705.1	0.2	861.3	-54.4	0.0	180.0
MP2/6-31+G(d,p)	3393.4	-34.0	877.5	0.3	703.6	-1.3	918.1	-111.2	-3.2	174.2
MP2/6-31++G(d,p)	3391.1	-36.3	877.8	0.6	703.8	-1.1	918.3	-111.4	-3.7	172.5
MP2/6-311G(d,p)	3404.6	-22.8	877.6	0.4	703.8	-1.1	861.0	-54.1	0.0	180.0
MP2/6-311+G(d,p)	3396.0	-31.4	876.8	-0.4	703.1	-1.8	935.0	-128.1	-2.4	175.9
MP2/6-311++G(d,p)	3394.9	-32.5	877.0	-0.2	703.1	-1.8	929.3	-122.4	-2.6	175.2
MP2/6-311G(df,pd)	3429.5	2.1	883.0	5.8	708.3	3.4	825.1	-18.2	0.0	180.0
MP2/6-311+G(df,pd)	3418.4	-9.0	882.1	4.9	707.5	2.6	900.6	-93.7	-3.5	174.5
MP2/6-311++G(df,pd)	3418.3	-9.1	882.2	5.0	707.6	2.7	896.0	-31.4	-3.5	174.1
MP2/6-311G(3df,3pd)	3442.3	14.9	885.9	8.7	710.7	5.8	863.7	-56.8	0.0	180.0
MP2/6-311+G(3df,3pd)	3432.6	5.2	885.4	8.2	709.9	5.0	885.4	-78.5	0.0	180.0
MP2/6-311++G(3df,3pd)	3432.7	5.3	885.4	8.2	709.9	5.0	883.2	-76.3	0.0	-180.0
MP2/cc-pVDZ	3370.3	-57.1	870.7	-6.5	698.0	-6.9	890.4	-83.5	0.0	180.0
MP2/cc-pVTZ	3423.4	-4.0	883.9	6.7	708.6	3.7	850.6	-43.7	0.0	180.0
MP2/aug-cc-pVDZ	3351.6	-75.8	869.8	-7.4	696.6	-8.3	855.1	-48.2	0.0	180.0
MP2/aug-cc-pVTZ	3419.5	-7.9	883.9	6.7	708.4	3.5	^a		0.0	180.0
B3LYP-D3/6-31G(d,p)	3395.6	-31.8	870.4	-6.8	698.7	-6.2	786.2	20.7	0.0	-180.0
B3LYP-D3/6-31+G(d,p)	3385.0	-42.4	868.2	-9.0	696.9	-8.0	830.5	-23.6	0.0	-180.0
B3LYP-D3/6-31++G(d,p)	3385.0	-42.4	868.2	-9.0	696.9	-8.0	829.5	-22.6	0.0	-180.0
B3LYP-D3/6-311G(d,p)	3406.5	-20.9	871.5	-5.7	699.9	-5.0	751.4	55.5	0.0	180.0
B3LYP-D3/6-311+G(d,p)	3400.3	-27.1	870.5	-6.7	699.0	-5.9	813.6	-6.7	0.0	180.0
B3LYP-D3/6-311++G(d,p)	3400.1	-27.3	870.5	-6.7	699.0	-5.9	812.6	-5.7	0.0	-180.0
B3LYP-D3/6-311G(df,pd)	3416.5	-10.9	873.8	-3.4	701.8	-3.1	751.4	55.5	0.0	180.0

Appendix B. 2-Propionylthiophene

B3LYP-D3/6-311+G(df,pd)	3410.6	-16.8	872.8	-4.4	700.9	-4.0	813.7	-6.8	0.0	180.0
B3LYP-D3/6-311++G(df,pd)	3410.6	-16.8	872.8	-4.4	700.9	-4.0	811.5	-4.6	0.0	180.0
B3LYP-D3/6-311G(3df,3pd)	3437.9	10.5	876.3	-0.9	704.3	-0.6	795.2	11.7	0.0	-180.0
B3LYP-D3/6-311+G(3df,3pd)	3429.9	2.5	875.8	-1.4	703.6	-1.3	814.8	-7.9	0.0	-180.0
B3LYP-D3/6-311++G(3df,3pd)	3429.7	2.3	875.8	-1.4	703.6	-1.3	814.8	-7.9	0.0	180.0
B3LYP-D3/cc-pVDZ	3385.4	-42.0	868.5	-8.7	697.2	-7.7	819.2	-12.3	0.0	180.0
B3LYP-D3/cc-pVTZ	3423.8	-3.6	874.6	-2.6	702.6	-2.3	782.2	24.7	0.0	180.0
B3LYP-D3/aug-cc-pVDZ	3377.9	-49.5	867.3	-9.9	696.0	-8.9	780.7	26.2	0.0	-180.0
B3LYP-D3/aug-cc-pVTZ	3421.1	-6.3	874.5	-2.7	702.4	-2.5	800.0	6.9	0.0	180.0
B3LYP-D3BJ/6-31G(d,p)	3400.4	-27.0	872.9	-4.3	700.6	-4.3	733.3	73.6	0.0	180.0
B3LYP-D3BJ/6-31+G(d,p)	3389.2	-38.2	870.7	-6.5	698.7	-6.2	783.1	23.8	0.0	-180.0
B3LYP-D3BJ/6-31++G(d,p)	3389.2	-38.2	870.7	-6.5	698.7	-6.2	782.0	24.9	0.0	180.0
B3LYP-D3BJ/6-311G(d,p)	3410.7	-16.7	874.0	-3.2	701.7	-3.2	698.9	108.0	0.0	180.0
B3LYP-D3BJ/6-311+G(d,p)	3404.1	-23.3	873.1	-4.1	700.8	-4.1	765.3	41.6	0.0	-180.0
B3LYP-D3BJ/6-311++G(d,p)	3404.0	-23.4	873.1	-4.1	700.8	-4.1	764.5	42.4	0.0	-180.0
B3LYP-D3BJ/6-311G(df,pd)	3420.5	-6.9	876.3	-0.9	703.6	-1.3	697.6	109.3	0.0	-180.0
B3LYP-D3BJ/6-311+G(df,pd)	3414.1	-13.3	875.4	-1.8	702.7	-2.2	764.1	42.8	0.0	-180.0
B3LYP-D3BJ/6-311++G(df,pd)	3414.0	-13.4	875.4	-1.8	702.7	-2.2	762.0	44.9	0.0	-180.0
B3LYP-D3BJ/6-311G(3df,3pd)	3441.7	14.3	878.8	1.6	706.0	1.1	742.0	64.9	0.0	-180.0
B3LYP-D3BJ/6-311+G(3df,3pd)	3433.2	5.8	878.3	1.1	705.4	0.5	765.1	41.8	0.0	-180.0
B3LYP-D3BJ/6-311++G(3df,3pd)	3433.1	5.7	878.4	1.2	705.4	0.5	765.0	41.9	0.0	-180.0
B3LYP-D3BJ/cc-pVDZ	3390.4	-37.0	871.0	-6.2	699.0	-5.9	768.6	38.3	0.0	180.0
B3LYP-D3BJ/cc-pVTZ	3427.5	0.1	877.2	0.0	704.4	-0.5	730.9	76.0	0.0	-180.0
B3LYP-D3BJ/aug-cc-pVDZ	3382.3	-45.1	869.8	-7.4	697.9	-7.0	733.6	73.3	0.0	-180.0
B3LYP-D3BJ/aug-cc-pVTZ	3424.7	-2.7	877.1	-0.1	704.2	-0.7	750.7	56.2	0.0	-180.0
M06-2X/6-31G(d,p)	3436.0	8.6	878.6	1.4	705.7	0.8	775.9	31.0	0.0	-180.0
M06-2X/6-31+G(d,p)	3427.5	0.1	876.7	-0.5	704.2	-0.7	819.5	-12.6	0.0	180.0
M06-2X/6-31++G(d,p)	3427.5	0.1	876.7	-0.5	704.2	-0.7	820.6	-13.7	0.0	180.0
M06-2X/6-311G(d,p)	3441.7	14.3	879.5	2.3	706.5	1.6	771.4	35.5	0.0	180.0
M06-2X/6-311+G(d,p)	3437.2	9.8	878.6	1.4	705.8	0.9	825.5	-18.6	0.0	180.0

Appendix B. 2-Propionylthiophene

M06-2X/6-311++G(d,p)	3437.1	9.7	878.6	1.4	705.8	0.9	823.8	-16.9	0.0	180.0
M06-2X/6-311G(df,pd)	3449.4	22.0	881.2	4.0	708.0	3.1	762.0	44.9	0.0	180.0
M06-2X/6-311+G(df,pd)	3445.3	17.9	880.3	3.1	707.2	2.3	817.7	-10.8	0.0	180.0
M06-2X/6-311++G(df,pd)	3445.2	17.8	880.3	3.1	707.2	2.3	815.1	-8.2	0.0	180.0
M06-2X/6-311G(3df,3pd)	3469.5	42.1	883.3	6.1	710.1	5.2	821.8	-14.9	0.0	180.0
M06-2X/6-311+G(3df,3pd)	3463.1	35.7	882.9	5.7	709.7	4.8	833.0	-26.1	0.0	180.0
M06-2X/6-311++G(3df,3pd)	3463.0	35.6	882.9	5.7	709.6	4.7	833.1	-26.2	0.0	180.0
M06-2X/cc-pVDZ	3427.0	-0.4	877.4	0.2	704.6	-0.3	796.9	10.0	0.0	180.0
M06-2X/cc-pVTZ	3456.1	28.7	882.6	5.4	709.1	4.2	799.0	7.9	0.0	180.0
M06-2X/aug-cc-pVDZ	3420.5	-6.9	876.1	-1.1	703.6	-1.3	773.5	33.4	0.0	-180.0
M06-2X/aug-cc-pVTZ	3454.9	27.5	882.5	5.3	709.0	4.1	812.5	-5.6	0.0	180.0
CCSD/cc-pVDZ	3372.0	-55.4	863.9	-13.3	693.7	-11.2	890.7	-83.8	0.0	180.0
Experiment	3427.4		877.2		704.9		806.9			

^a Not done due to high quantum chemical cost.

Appendix B. 2-Propionylthiophene

Table B.3b: Equilibrium rotational constants, X_e ($X = A, B, C$), predicted torsional barriers and dihedral angles of *anti*-2PT calculated at various levels of theory. The deviations ΔX between the calculated and the ground state experimental values X_0 are given in MHz, the deviation between the calculated and experimental V_3 barrier of the acetyl methyl group is given as ΔV_3 . All optimizations were done under full-symmetry relaxation.

Method/Basis Set	$A /$ MHz	$\Delta A /$ MHz	$B /$ MHz	$\Delta B /$ MHz	$C /$ MHz	$\Delta C /$ MHz	$V_3 /$ cm^{-1}	$\Delta V_3 /$ cm^{-1}	$\alpha /$ $^\circ$	$\beta /$ $^\circ$
MP2/6-31G(d,p)	3268.9	-5.1	903.6	-2.1	714.1	-2.1	862.1	2.5	-180.0	180.0
MP2/6-31+G(d,p)	3242.8	-31.2	904.3	-1.5	715.3	-1.0	907.1	-42.5	172.8	171.7
MP2/6-31++G(d,p)	3241.1	-32.9	904.5	-1.2	715.5	-0.8	903.3	-38.7	172.8	171.4
MP2/6-311G(d,p)	3267.4	-6.6	902.9	-2.8	713.7	-2.6	868.0	-3.4	-180.0	-180.0
MP2/6-311+G(d,p)	3247.0	-27.0	904.6	-1.1	715.7	-0.5	922.2	-57.6	173.3	172.7
MP2/6-311++G(d,p)	3245.4	-28.6	904.8	-1.0	716.0	-0.2	919.9	-55.3	172.8	172.5
MP2/6-311G(df,pd)	3290.8	16.8	909.1	3.4	718.7	2.4	830.0	34.6	178.8	178.1
MP2/6-311+G(df,pd)	3266.8	-7.2	910.7	5.0	720.9	4.7	884.3	-19.7	172.5	172.1
MP2/6-311++G(df,pd)	3265.7	-8.3	910.8	5.0	721.1	4.9	882.0	-17.4	172.1	172.0
MP2/6-311G(3df,3pd)	3302.2	28.2	913.2	7.5	721.7	5.4	845.4	19.2	-180.0	180.0
MP2/6-311+G(3df,3pd)	3293.8	19.8	913.7	7.9	721.6	5.3	875.1	-10.5	-180.0	180.0
MP2/6-311++G(3df,3pd)	3293.9	19.9	913.7	7.9	721.6	5.3	872.7	-8.1	-180.0	180.0
MP2/cc-pVDZ	3231.7	-42.3	895.7	-10.1	707.5	-8.7	888.5	-23.9	-180.0	180.0
MP2/cc-pVTZ	3284.1	10.1	911.2	5.4	719.5	3.3	841.5	23.1	-180.0	180.0
MP2/aug-cc-pVDZ	3215.3	-58.7	897.6	-8.2	707.9	-8.3	839.9	24.7	-180.0	180.0
B3LYP-D3/6-31G(d,p)	3249.9	-24.1	894.7	-11.1	707.6	-8.6	776.8	87.8	-180.0	-180.0
B3LYP-D3/6-31+G(d,p)	3240.8	-33.2	893.9	-11.9	706.7	-9.5	820.4	44.2	-180.0	180.0
B3LYP-D3/6-31++G(d,p)	3240.7	-33.3	893.9	-11.8	706.7	-9.5	820.5	44.1	-180.0	-180.0
B3LYP-D3/6-311G(d,p)	3260.1	-13.9	895.9	-9.8	708.9	-7.3	738.8	125.8	-180.0	-180.0
B3LYP-D3/6-311+G(d,p)	3253.6	-20.4	896.4	-9.4	708.9	-7.4	802.0	62.6	-180.0	180.0
B3LYP-D3/6-311++G(d,p)	3253.4	-20.6	896.4	-9.3	708.9	-7.3	800.7	63.9	-180.0	180.0
B3LYP-D3/6-311G(df,pd)	3269.7	-4.3	898.7	-7.1	711.1	-5.2	737.9	126.7	-180.0	-180.0
B3LYP-D3/6-311+G(df,pd)	3263.5	-10.5	899.1	-6.6	711.0	-5.2	801.4	63.2	-180.0	180.0

Appendix B. 2-Propionylthiophene

B3LYP-D3/6-311++G(df,pd)	3263.3	-10.7	899.1	-6.6	711.0	-5.2	799.1	65.5	-180.0	180.0
B3LYP-D3/6-311G(3df,3pd)	3291.7	17.7	901.6	-4.1	713.9	-2.3	780.5	84.1	-179.9	180.0
B3LYP-D3/6-311+G(3df,3pd)	3284.1	10.1	902.3	-3.5	714.0	-2.3	803.4	61.2	-180.0	180.0
B3LYP-D3/6-311++G(3df,3pd)	3284.0	10.0	902.3	-3.5	714.0	-2.3	803.2	61.4	-180.0	180.0
B3LYP-D3/cc-pVDZ	3239.1	-34.9	892.9	-12.8	706.1	-10.1	809.6	55.0	180.0	-180.0
B3LYP-D3/cc-pVTZ	3276.8	2.8	900.6	-5.1	712.6	-3.7	771.5	93.1	-180.0	180.0
B3LYP-D3/aug-cc-pVDZ	3233.5	-40.5	893.6	-12.1	706.3	-10.0	761.2	103.4	-180.0	180.0
B3LYP-D3/aug-cc-pVTZ	3274.2	0.2	901.0	-4.7	712.7	-3.5	791.5	73.1	-180.0	180.0
B3LYP-D3BJ/6-31G(d,p)	3247.0	-27.0	899.1	-6.7	710.2	-6.0	723.8	140.8	180.0	-180.0
B3LYP-D3BJ/6-31+G(d,p)	3237.7	-36.3	898.4	-7.4	709.4	-6.9	773.7	90.9	-180.0	-180.0
B3LYP-D3BJ/6-31++G(d,p)	3237.7	-36.3	898.4	-7.4	709.4	-6.9	773.7	90.9	-180.0	180.0
B3LYP-D3BJ/6-311G(d,p)	3256.8	-17.2	900.4	-5.4	711.5	-4.7	686.1	178.5	180.0	180.0
B3LYP-D3BJ/6-311+G(d,p)	3250.0	-24.0	901.0	-4.8	711.6	-4.7	754.3	110.3	-180.0	180.0
B3LYP-D3BJ/6-311++G(d,p)	3249.8	-24.2	901.0	-4.7	711.6	-4.6	753.0	111.6	-180.0	180.0
B3LYP-D3BJ/6-311G(df,pd)	3265.9	-8.1	903.2	-2.5	713.7	-2.5	683.8	180.8	180.0	180.0
B3LYP-D3BJ/6-311+G(df,pd)	3259.4	-14.6	903.8	-1.9	713.8	-2.5	752.3	112.3	-180.0	180.0
B3LYP-D3BJ/6-311++G(df,pd)	3259.2	-14.8	903.9	-1.9	713.8	-2.4	750.1	114.5	-180.0	180.0
B3LYP-D3BJ/6-311G(3df,3pd)	3287.2	13.2	906.4	0.6	716.7	0.4	726.8	137.8	-180.0	-180.0
B3LYP-D3BJ/6-311+G(3df,3pd)	3279.4	5.4	907.1	1.3	716.7	0.5	753.3	111.3	-180.0	180.0
B3LYP-D3BJ/6-311++G(3df,3pd)	3279.3	5.3	907.1	1.3	716.7	0.5	753.2	111.4	-180.0	180.0
B3LYP-D3BJ/cc-pVDZ	3236.5	-37.5	897.3	-8.4	708.7	-7.5	758.9	105.7	-180.0	180.0
B3LYP-D3BJ/cc-pVTZ	3272.7	-1.3	905.3	-0.4	715.3	-0.9	720.1	144.5	-179.9	-180.0
B3LYP-D3BJ/aug-cc-pVDZ	3230.3	-43.7	898.2	-7.5	709.0	-7.3	714.4	150.2	-180.0	-180.0
B3LYP-D3BJ/aug-cc-pVTZ	3269.8	-4.2	905.8	0.1	715.5	-0.7	741.9	122.7	-180.0	180.0
M06-2X/6-31G(d,p)	3286.7	12.7	904.7	-1.0	715.7	-0.6	767.8	96.8	-180.0	-180.0
M06-2X/6-31+G(d,p)	3279.5	5.5	904.0	-1.8	714.9	-1.4	810.2	54.4	-180.0	180.0
M06-2X/6-31++G(d,p)	3279.3	5.3	904.0	-1.7	714.9	-1.4	812.1	52.5	-180.0	180.0
M06-2X/6-311G(d,p)	3293.4	19.4	906.0	0.3	716.8	0.6	761.1	103.5	-180.0	-180.0
M06-2X/6-311+G(d,p)	3288.3	14.3	906.4	0.7	716.8	0.6	813.5	51.1	-180.0	180.0
M06-2X/6-311++G(d,p)	3288.0	14.0	906.5	0.8	716.8	0.6	811.7	52.9	-180.0	-180.0

Appendix B. 2-Propionylthiophene

M06-2X/6-311G(df,pd)	3301.1	27.1	908.2	2.4	718.5	2.2	750.5	114.1	-180.0	-180.0
M06-2X/6-311+G(df,pd)	3296.3	22.3	908.6	2.8	718.5	2.3	804.8	59.8	-179.9	180.0
M06-2X/6-311++G(df,pd)	3296.2	22.2	908.6	2.8	718.5	2.3	802.1	62.5	-179.9	180.0
M06-2X/6-311G(3df,3pd)	3321.5	47.5	911.0	5.2	721.2	4.9	806.0	58.6	-180.0	180.0
M06-2X/6-311+G(3df,3pd)	3315.4	41.4	911.5	5.7	721.2	5.0	820.1	44.5	-180.0	180.0
M06-2X/6-311++G(3df,3pd)	3315.4	41.4	911.5	5.7	721.2	5.0	819.6	45.0	-180.0	180.0
M06-2X/cc-pVDZ	3278.7	4.7	903.5	-2.2	714.6	-1.6	788.1	76.5	-180.0	180.0
M06-2X/cc-pVTZ	3307.7	33.7	910.8	5.0	720.4	4.2	787.8	76.8	-180.0	180.0
M06-2X/aug-cc-pVDZ	3274.7	0.7	903.9	-1.8	714.7	-1.6	754.7	109.9	-180.0	180.0
M06-2X/aug-cc-pVTZ	3306.6	32.6	911.1	5.4	720.6	4.4	802.2	62.4	-180.0	180.0
CCSD/6-311++G(d,p)	3244.2	-29.8	897.9	-7.8	711.0	-5.3	^a		173.6	174.6
CCSD/cc-pVDZ	3223.0	-51.0	889.8	-15.9	703.5	-12.8	889.2	-24.6	-180.0	180.0
Experiment	3274.0		905.7		716.2		864.6			

^a Not done due to high quantum chemical cost.

Appendix B. 2-Propionylthiophene

Table B.4: Coefficients of the one-dimensional Fourier expansion for the potential energy curve of *syn*- and *anti*-2PT given in Figure 4.3 calculated using different methods in combination with the basis set 6-311++G(d,p). The potential is expanded as $V(\varphi) = \sum_{i=0}^2 a_i f_i$.

	<i>i</i>	<i>f_i</i>	MP2		B3LYP-D3BJ		M06-2X	
			<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹
<i>syn</i>	0	1	-743.591750		-745.1212221		-744.9032898	
	1	cos 3α	0.0021111	463.3	0.0017355	380.9	0.0018733	411.1
	2	cos 6α	0.0000805	17.7	0.0000429	9.4	0.0000232	5.1
<i>anti</i>	0	1	-743.527634		-745.1202321		-744.9022638	
	1	cos 3α	0.0020904	458.8	0.0017067	374.6	0.001843	404.6
	2	cos 6α	0.0000442	9.7	0.0000582	12.8	0.000031	6.9

Table B.5: Observed frequencies ν_{obs} of 201 rotational transitions of *syn*-2PT with $\nu_{\text{obs}} - \nu_{\text{calc}}$ values from a fit with the program *XIAM*.

No.	J	K _a	K _c	J	K _a	K _c	Species	ν_{obs} MHz	$\nu_{\text{obs}} - \nu_{\text{calc}}$ kHz
	upper level			lower level					
1	2	0	2	1	0	1	A	3155.7033	-0.3
2	3	0	3	2	0	2	A	4712.5964	-0.2
3	4	0	4	3	0	3	A	6245.1040	-0.2
4	5	0	5	4	0	4	A	7747.4055	-0.1
5	6	0	6	5	0	5	A	9217.1304	-0.3
6	7	0	7	6	0	6	A	10656.5614	-0.7
7	8	0	8	7	0	7	A	12072.2521	-0.5
8	9	0	9	8	0	8	A	13472.8402	-0.3
9	10	0	10	9	0	9	A	14866.3298	0.2
10	11	0	11	10	0	10	A	16258.3959	-0.1
11	12	0	12	11	0	11	A	17652.1589	-0.2
12	13	0	13	12	0	12	A	19048.8281	0.7
13	14	0	14	13	0	13	A	20448.5041	-0.1
14	16	0	16	15	0	15	A	23255.1592	0.6
15	4	0	4	3	1	3	A	4088.6400	2.1
16	5	0	5	4	1	4	A	5868.4507	1.2
17	6	0	6	5	1	5	A	7640.2300	1.5
18	7	0	7	6	1	6	A	9381.8094	3.4
19	8	0	8	7	1	7	A	11078.0117	1.9
20	9	0	9	8	1	8	A	12722.2717	0.8
21	10	0	10	9	1	9	A	14315.5702	1.0
22	11	0	11	10	1	10	A	15863.7818	-0.5
23	12	0	12	11	1	11	A	17374.9293	0.8
24	13	0	13	12	1	12	A	18857.1752	-0.4
25	14	0	14	13	1	13	A	20317.7589	0.3
26	15	0	15	14	1	14	A	21762.5782	1.3

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27	2	1	1	2	0	2	A	2903.2592	−2.4
28	3	1	2	3	0	3	A	3189.8822	−2.4
29	4	1	3	4	0	4	A	3599.9412	−0.8
30	5	1	4	5	0	5	A	4153.8831	4.6
31	7	1	6	7	0	7	A	5764.5981	3.9
32	9	1	8	9	0	9	A	8074.3749	3.8
33	12	1	11	12	0	12	A	12500.6450	3.1
34	13	1	12	13	0	13	A	14093.0648	1.2
35	14	1	13	14	0	14	A	15689.6540	2.6
36	2	1	2	1	0	1	A	5542.1227	−3.7
37	3	1	3	2	0	2	A	6869.0581	−4.8
38	4	1	4	3	0	3	A	8124.0624	2.1
39	4	1	4	3	0	3	E	8124.0531	−3.0
40	5	1	5	4	0	4	A	9324.3027	−5.1
41	6	1	6	5	0	5	A	10491.8819	−4.9
42	7	1	7	6	0	6	A	11650.8002	−4.7
43	8	1	8	7	0	7	A	12822.8173	−4.9
44	9	1	9	8	0	8	A	14023.6003	−0.6
45	10	1	10	9	0	9	A	15260.9402	−3.1
46	11	1	11	10	0	10	A	16535.6252	−1.4
47	12	1	12	11	0	11	A	17843.8116	0.6
48	13	1	13	12	0	12	A	19179.5728	−0.3
49	14	1	14	13	0	13	A	20536.7220	0.2
50	16	1	16	15	0	15	A	23294.2702	−0.6
51	2	1	1	1	1	0	A	3336.4190	−0.4
52	3	1	2	2	1	1	A	4999.2197	0.1
53	4	1	3	3	1	2	A	6655.1615	−0.2
54	5	1	4	4	1	3	A	8301.3421	0.1
55	6	1	5	5	1	4	A	9934.3305	0.7
56	7	1	6	6	1	5	A	11550.0786	−0.1
57	8	1	7	7	1	6	A	13143.9449	−0.2
58	9	1	8	8	1	7	A	14710.9244	−0.5
59	10	1	9	9	1	8	A	16246.2460	−1.4
60	11	1	10	10	1	9	A	17746.4094	−0.6
61	12	1	11	11	1	10	A	19210.4969	−1.2
62	3	1	3	2	1	2	A	4482.6395	−0.5
63	4	1	4	3	1	3	A	5967.5940	0.0
64	5	1	5	4	1	4	A	7445.3513	−0.4
65	6	1	6	5	1	5	A	8914.9840	−0.6
66	7	1	7	6	1	6	A	10376.0476	−1.3
67	8	1	8	7	1	7	A	11828.5789	−0.4
68	9	1	9	8	1	8	A	13273.0309	−0.4
69	10	1	10	9	1	9	A	14710.1827	−0.2
70	11	1	11	10	1	10	A	16141.0128	−0.1
71	12	1	12	11	1	11	A	17566.5806	0.2
72	13	1	13	12	1	12	A	18987.9215	0.3

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73	14	1	14	13	1	13	A	20405.9769	0.8
74	15	1	15	14	1	14	A	21821.5508	1.0
75	8	1	7	7	2	6	A	7510.1492	-3.1
76	8	1	7	7	2	6	E	7510.1669	3.1
77	9	1	8	8	2	7	A	9666.8532	-2.1
78	9	1	8	8	2	7	E	9666.8696	3.4
79	10	1	9	9	2	8	A	11824.3636	-2.7
80	10	1	9	9	2	8	E	11824.3775	1.0
81	11	1	10	10	2	9	A	13958.9940	-1.9
82	11	1	10	10	2	9	E	13959.0059	0.7
83	12	1	11	11	2	10	A	16046.7625	-2.1
84	12	1	11	11	2	10	E	16046.7749	2.0
85	13	1	12	12	2	11	A	18066.7423	-2.3
86	13	1	12	12	2	11	E	18066.7515	-0.2
87	2	2	0	1	1	1	A	11167.9304	2.7
88	2	2	0	2	1	1	A	7659.2230	-5.6
89	3	2	1	3	1	2	A	7439.8230	-6.0
90	3	2	1	3	1	2	E	7439.8154	-2.3
91	4	2	2	4	1	3	E	7189.5319	1.7
92	5	2	3	5	1	4	A	6942.6837	3.2
93	5	2	3	5	1	4	E	6942.6665	-2.0
94	8	2	6	8	1	7	A	6606.4561	1.5
95	8	2	6	8	1	7	E	6606.4430	-1.3
96	2	2	1	2	1	2	A	8167.6285	-2.2
97	2	2	1	2	1	2	E	8167.6122	0.9
98	3	2	2	3	1	3	A	8431.1924	-5.8
99	3	2	2	3	1	3	E	8431.1837	-0.2
100	4	2	3	4	1	4	A	8785.3091	-3.9
101	4	2	3	4	1	4	E	8785.2966	-3.0
102	5	2	4	5	1	5	E	9231.5466	2.8
103	6	2	5	6	1	6	A	9771.0678	-7.4
104	6	2	5	6	1	6	E	9771.0595	-2.4
105	7	2	6	7	1	7	A	10404.1395	-4.6
106	7	2	6	7	1	7	E	10404.1360	5.2
107	9	2	8	9	1	9	A	11945.4863	-5.6
108	9	2	8	9	1	9	E	11945.4711	-7.2
109	10	2	9	10	1	10	A	12847.0857	-3.7
110	10	2	9	10	1	10	E	12847.0801	4.6
111	12	2	11	12	1	12	A	14883.4917	-2.9
112	12	2	11	12	1	12	E	14883.4766	-3.6
113	4	2	2	3	1	3	A	14878.1253	3.1
114	4	2	2	3	1	3	E	14878.1124	2.7
115	5	2	3	4	1	4	E	16964.9971	1.3
116	6	2	4	5	1	5	E	19249.1869	0.7
117	3	2	2	2	1	1	A	12397.0044	5.0
118	4	2	3	3	1	2	A	13719.4901	1.4

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119	4	2	3	3	1	2	E	13719.4726	-2.8
120	5	2	4	4	1	3	A	14955.9286	5.7
121	5	2	4	4	1	3	E	14955.9068	-3.1
122	6	2	5	5	1	4	A	16109.0887	5.2
123	7	2	6	6	1	5	A	17183.8739	2.4
124	7	2	6	6	1	5	E	17183.8549	-3.9
125	8	2	7	7	1	6	A	18188.0177	2.9
126	9	2	8	8	1	7	A	19132.8082	2.1
127	9	2	8	8	1	7	E	19132.7901	-3.6
128	10	2	9	9	1	8	A	20033.6647	3.2
129	10	2	9	9	1	8	E	20033.6479	-1.6
130	11	2	10	10	1	9	A	20910.1484	4.9
131	11	2	10	10	1	9	E	20910.1318	-0.2
132	2	2	0	3	1	3	A	3693.4207	-6.7
133	3	2	1	2	2	0	A	4779.8172	-2.8
134	4	2	2	3	2	1	A	6404.8735	-1.4
135	5	2	3	4	2	2	A	8054.4797	-0.6
136	6	2	4	5	2	3	A	9729.5416	-0.5
137	7	2	5	6	2	4	A	11426.2378	-0.8
138	8	2	6	7	2	5	A	13136.3442	-2.9
139	3	2	2	2	2	1	A	4746.2100	2.6
140	3	2	2	2	2	1	E	4746.2157	3.1
141	4	2	3	3	2	2	A	6321.7094	0.5
142	5	2	4	4	2	3	A	7891.5962	0.4
143	6	2	5	5	2	4	A	9454.5026	0.0
144	7	2	6	6	2	5	A	11009.1174	-0.4
145	8	2	7	7	2	6	A	12554.2219	-0.1
146	9	2	8	8	2	7	A	14088.7367	0.2
147	10	2	9	9	2	8	A	15611.7805	0.1
148	3	3	1	2	2	0	A	17924.9233	4.1
149	4	3	2	3	2	1	A	19489.4971	2.4
150	4	3	2	3	2	1	E	19489.4067	1.0
151	5	3	3	4	2	2	A	21021.3322	1.0
152	5	3	3	4	2	2	E	21021.2940	2.0
153	6	3	4	5	2	3	A	22498.7213	1.0
154	6	3	4	5	2	3	E	22498.6948	2.2
155	3	3	0	2	2	1	A	17933.6158	1.4
156	3	3	0	2	2	1	E	17933.8408	-4.6
157	4	3	1	3	2	2	A	19533.3540	2.5
158	4	3	1	3	2	2	E	19533.4011	3.6
159	5	3	2	4	2	3	A	21153.7564	-1.8
160	3	3	0	3	2	1	E	13145.5850	4.0
161	5	3	2	5	2	3	A	12974.0602	-2.5
162	6	3	3	6	2	4	A	12790.7184	3.6
163	6	3	3	6	2	4	E	12790.6994	0.7
164	8	3	5	8	2	6	A	12179.8988	1.9

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165	8	3	5	8	2	6	E	12179.8775	1.6
166	4	3	2	4	2	3	A	13209.8354	0.4
167	4	3	2	4	2	3	E	13209.7486	0.7
168	5	3	3	5	2	4	A	13254.9473	-3.3
169	5	3	3	5	2	4	E	13254.9167	4.4
170	6	3	4	6	2	5	A	13332.3161	-1.2
171	6	3	4	6	2	5	E	13332.2930	2.5
172	7	3	5	7	2	6	A	13452.4578	2.4
173	7	3	5	7	2	6	E	13452.4332	1.1
174	8	3	6	8	2	7	A	13626.0119	-0.8
175	8	3	6	8	2	7	E	13625.9924	1.6
176	9	3	7	9	2	8	A	13863.2060	-0.6
177	9	3	7	9	2	8	E	13863.1852	-0.2
178	4	3	1	4	2	2	A	13086.4264	-1.1
179	4	3	1	4	2	2	E	13086.4740	2.3
180	6	3	3	5	2	4	A	22808.3610	4.4
181	6	3	3	5	2	4	E	22808.3413	0.2
182	5	3	2	4	3	1	A	7942.1169	1.4
183	5	3	2	4	3	1	E	7942.0647	-1.7
184	6	3	3	5	3	2	A	9546.1950	0.8
185	6	3	3	5	3	2	E	9546.1807	-2.0
186	7	3	4	6	3	3	A	11161.1629	-2.3
187	5	3	3	4	3	2	A	7936.7101	-1.3
188	5	3	3	4	3	2	E	7936.7597	-0.6
189	6	3	4	5	3	3	A	9531.8671	-2.3
190	6	3	4	5	3	3	E	9531.8811	0.5
191	7	3	5	6	3	4	A	11129.2568	0.9
192	8	3	6	7	3	5	A	12727.7789	-0.4
193	4	4	0	4	3	1	A	18438.2480	0.5
194	5	4	1	5	3	2	A	18425.2556	-3.9
195	6	4	2	6	3	3	A	18400.3063	2.4
196	7	4	3	7	3	4	A	18356.0687	-3.0
197	4	4	1	4	3	2	A	18440.0479	-0.7
198	5	4	2	5	3	3	A	18432.4090	-3.3
199	6	4	3	6	3	4	A	18421.5439	-1.6
200	7	4	4	7	3	5	A	18408.4348	-3.5
201	4	4	1	5	3	2	A	10496.1272	1.8

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Table B.6: Observed frequencies ν_{obs} of 135 rotational transitions of *anti*-2PT, with $\nu_{\text{obs}} - \nu_{\text{calc}}$ values from a fit with the program *XIAM*.

No.	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>J</i>	<i>K_a</i>	<i>K_c</i>	Species	<i>V_{obs}</i>	<i>V_{obs}—V_{calc}</i>
	upper level			lower level				MHz	kHz
1	2	0	2	1	0	1	A	3233.0313	−0.9
2	3	0	3	2	0	2	A	4822.4766	−0.3
3	4	0	4	3	0	3	A	6380.7904	−0.7
4	5	0	5	4	0	4	A	7901.5837	0.0
5	6	0	6	5	0	5	A	9384.0023	0.5
6	7	0	7	6	0	6	A	10833.7562	0.5
7	8	0	8	7	0	7	A	12261.1817	0.2
8	9	0	9	8	0	8	A	13677.2371	0.0
9	10	0	10	9	0	9	A	15090.2141	0.6
10	12	0	12	11	0	11	A	17922.7399	0.3
11	13	0	13	12	0	12	A	19344.2815	0.8
12	14	0	14	13	0	13	A	20768.8765	0.1
13	15	0	15	14	0	14	A	22195.8273	0.0
14	16	0	16	15	0	15	A	23624.4912	1.1
15	3	0	3	2	1	2	A	2632.7742	−0.4
16	3	0	3	2	1	2	E	2632.7765	−0.6
17	4	0	4	3	1	3	A	4438.5437	3.1
18	4	0	4	3	1	3	E	4438.5395	−3.5
19	5	0	5	4	1	4	A	6251.9501	−0.3
20	6	0	6	5	1	5	A	8043.6780	0.2
21	7	0	7	6	1	6	A	9791.0736	−1.1
22	8	0	8	7	1	7	A	11482.1107	−0.3
23	9	0	9	8	1	8	A	13115.3559	−0.1
24	9	0	9	8	1	8	E	13115.3605	3.6
25	10	0	10	9	1	9	A	14696.7963	−1.1
26	10	0	10	9	1	9	E	14696.7991	1.1
27	11	0	11	10	1	10	A	16235.8761	0.3
28	12	0	12	11	1	11	A	17742.4807	0.2
29	13	0	13	12	1	12	A	19225.3272	0.6
30	14	0	14	13	1	13	A	20691.3810	0.2
31	15	0	15	14	1	14	A	22145.8753	−2.0
32	5	1	4	5	0	5	A	4172.0012	0.8
33	5	1	4	5	0	5	E	4171.9960	−2.1
34	6	1	5	6	0	6	A	4989.6610	1.7
35	6	1	5	6	0	6	E	4989.6548	−2.3
36	11	1	10	11	0	11	A	11653.7128	−1.0
37	11	1	10	11	0	11	E	11653.7101	−1.0
38	2	1	2	1	0	1	A	5422.7354	0.9
39	2	1	2	1	0	1	E	5422.7290	−3.0
40	3	1	3	2	0	2	A	6764.7284	1.1

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41	3	1	3	2	0	2	E	6764.7230	-1.8
42	4	1	4	3	0	3	A	8030.4244	0.0
43	4	1	4	3	0	3	E	8030.4186	-3.2
44	5	1	5	4	0	4	A	9241.9082	0.5
45	5	1	5	4	0	4	E	9241.9051	-0.2
46	6	1	6	5	0	5	A	10426.6839	1.1
47	6	1	6	5	0	5	E	10426.6790	-1.4
48	7	1	7	6	0	6	A	11612.8290	2.7
49	7	1	7	6	0	6	E	11612.8241	0.0
50	8	1	8	7	0	7	A	12823.0596	-3.0
51	9	1	9	8	0	8	A	14070.6551	1.9
52	9	1	9	8	0	8	E	14070.6431	-8.5
53	10	1	10	9	0	9	A	15359.1143	0.0
54	11	1	11	10	0	10	A	16685.0363	0.7
55	11	1	11	10	0	10	E	16685.0289	-5.6
56	13	1	13	12	0	12	A	19421.7763	-0.1
57	14	1	14	13	0	13	A	20818.8259	-0.5
58	15	1	15	14	0	14	A	22227.7322	-1.5
59	16	1	16	15	0	15	A	23644.7147	0.4
60	2	1	1	1	1	0	A	3433.4649	-2.0
61	2	1	1	1	1	0	E	3433.4680	1.1
62	3	1	2	2	1	1	A	5143.1642	1.1
63	3	1	2	2	1	1	E	5143.1586	-4.5
64	4	1	3	3	1	2	A	6843.8542	-0.6
65	5	1	4	4	1	3	A	8531.5979	-0.7
66	6	1	5	5	1	4	A	10201.6615	0.9
67	7	1	6	6	1	5	A	11848.4320	0.1
68	8	1	7	7	1	6	A	13465.5925	0.9
69	9	1	8	8	1	7	A	15046.7483	0.9
70	11	1	10	10	1	9	A	18083.6850	1.1
71	12	1	11	11	1	10	A	19540.4734	1.1
72	2	1	2	1	1	1	A	3054.4417	-3.1
73	2	1	2	1	1	1	E	3054.4448	-0.1
74	3	1	3	2	1	2	A	4575.0247	-0.4
75	4	1	4	3	1	3	A	6088.1737	-0.2
76	5	1	5	4	1	4	A	7592.2751	0.7
77	6	1	6	5	1	5	A	9086.3594	0.7
78	7	1	7	6	1	6	A	10570.1456	0.3
79	8	1	8	7	1	7	A	12043.9926	0.6
80	9	1	9	8	1	8	A	13508.7730	0.9
81	10	1	10	9	1	9	A	14965.6979	-0.3
82	11	1	11	10	1	10	A	16416.1349	0.0
83	13	1	13	12	1	12	A	19302.8228	0.6
84	14	1	14	13	1	13	A	20741.3308	0.1
85	2	2	0	1	1	1	A	10738.7473	-1.0
86	2	2	0	1	1	1	E	10738.7402	-2.3

Appendix B. 2-Propionylthiophene

87	3	2	1	2	1	2	A	12593.6948	4.2
88	3	2	1	2	1	2	E	12593.6757	-7.7
89	4	2	2	3	1	3	A	14605.1746	2.0
90	4	2	2	3	1	3	E	14605.1721	6.9
91	5	2	3	4	1	4	A	16810.8115	1.3
92	7	2	5	6	1	6	A	21950.3955	-1.1
93	3	2	1	3	1	2	A	6881.9978	3.6
94	3	2	1	3	1	2	E	6881.9837	-3.3
95	4	2	2	4	1	3	A	6624.6432	-3.3
96	5	2	3	5	1	4	A	6386.8651	5.7
97	5	2	3	5	1	4	E	6386.8521	-0.1
98	2	2	1	1	1	0	A	10538.3083	-5.0
99	3	2	2	2	1	1	A	11970.7775	-0.3
100	3	2	2	2	1	1	E	11970.7733	3.5
101	4	2	3	3	1	2	A	13307.0155	-1.9
102	4	2	3	3	1	2	E	13307.0101	0.5
103	5	2	4	4	1	3	A	14548.7730	0.1
104	5	2	4	4	1	3	E	14548.7617	-3.5
105	6	2	5	5	1	4	A	15699.9803	0.1
106	6	2	5	5	1	4	E	15699.9710	-1.6
107	7	2	6	6	1	5	A	16767.6598	2.0
108	7	2	6	6	1	5	E	16767.6477	-2.5
109	8	2	7	7	1	6	A	17762.9468	3.4
110	2	2	1	2	1	2	A	7673.3808	1.2
111	2	2	1	2	1	2	E	7673.3732	3.0
112	3	2	2	3	1	3	A	7964.2862	0.2
113	4	2	3	4	1	4	A	8355.5172	2.3
114	5	2	4	5	1	5	A	8848.8538	3.1
115	6	2	5	6	1	6	A	9445.3031	5.2
116	6	2	5	6	1	6	E	9445.2860	-4.3
117	8	2	7	8	1	8	A	10944.2207	4.4
118	8	2	7	8	1	8	E	10944.2015	-7.2
119	4	2	2	3	2	1	A	6586.5063	-0.7
120	5	2	3	4	2	2	A	8293.8110	-0.5
121	6	2	4	5	2	3	A	10030.2289	-0.1
122	7	2	5	6	2	4	A	11787.9939	3.3
123	8	2	6	7	2	5	A	13554.4712	1.2
124	4	2	3	3	2	2	A	6479.4045	1.8
125	5	2	4	4	2	3	A	8085.6106	0.3
126	6	2	5	5	2	4	A	9682.8069	1.0
127	7	2	6	6	2	5	A	11269.3384	0.3
128	8	2	7	7	2	6	A	12843.7204	2.8
129	4	3	2	4	2	3	A	12350.9653	-1.6
130	5	3	2	4	3	1	A	8151.6731	-1.4
131	6	3	3	5	3	2	A	9803.2117	4.8
132	8	3	5	7	3	4	A	13156.3934	-1.0

Appendix B. 2-Propionylthiophene

133	5	3	3	4	3	2	A	8143.4489	−0.2
134	5	3	3	4	3	2	E	8143.4539	−7.0
135	6	3	4	5	3	3	A	9781.4585	3.0

Table B.7: Molecular parameters of *syn*-2PT and *anti*-2PT obtained with the program *XIAM* where the angles between the internal rotor axis and the principal axes of inertia are fixed to values predicted at the B3LYP-D3BJ/6-311++G(d,p) level of theory.

Par. ^a	Unit	<i>syn</i>	<i>Calc.</i> ^b	<i>anti</i>	<i>Calc.</i> ^b
A_0	MHz	3427.43880(19)	3383.114	3274.03476(39)	3222.920
B_0	MHz	877.177067(48)	866.872	905.747027(78)	895.759
C_0	MHz	704.893296(31)	696.450	716.231414(37)	707.766
D_J	kHz	0.01812(15)	0.0175	0.02330(31)	0.0228
D_{JK}	kHz	0.0749(27)	0.0820	0.0621(69)	0.0419
D_K	kHz	0.4474(93)	0.4541	1.842(58)	0.4957
d_1	kHz	−0.00370(10)	−0.0039	−0.00639(30)	−0.0056
d_2	kHz	−0.000275(69)	−0.0004	−0.00138(25)	−0.0004
V_3	cm ^{−1}	807.00(54)	764.5	865.4(88)	753.0
$\angle(i,a)$	deg	19.9 ^c	19.9	9.9 ^c	9.9
$\angle(i,b)$	deg	70.2 ^c	70.2	80.1 ^c	80.1
$\angle(i,c)$	deg	90.0 ^c	90.0	90.0 ^c	90.0
N_A/N_E^d	-	150/51		103/32	
σ^e	kHz	2.6		2.5	

^a All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. ^b Ground state rotational constants and centrifugal distortion constants from anharmonic frequency calculations, all other parameters from optimisations at the MP2/6-311++G(d,p) level of theory. ^c Fixed to the calculated values predicting a planar geometry. ^d Number of A and E species transitions. ^e Standard deviation of the fit.

Appendix B. 2-Propionylthiophene

Table B.8a: Observed frequencies ν_{obs} of 23 rotational transitions of the ^{34}S isotopologue of *syn*-2PT with $\nu_{\text{obs}} - \nu_{\text{calc}}$ values from a fit with the program *XIAM*.

No.	J	K _a	K _c	J	K _a	K _c	ν_{obs}	$\nu_{\text{obs}} - \nu_{\text{calc}}$
	upper level			lower level			[MHz]	[kHz]
1	2	0	2	1	0	1	3130.6784	−0.1
2	3	0	3	2	0	2	4674.7172	−1.0
3	4	0	4	3	0	3	6194.0013	−0.3
4	5	0	5	4	0	4	7682.6943	0.5
5	6	0	6	5	0	5	9138.5519	1.6
6	2	1	2	1	0	1	5472.7622	−3.2
7	5	1	5	4	0	4	9219.1284	−1.8
8	6	1	6	5	0	5	10376.0502	−0.8
9	7	1	7	6	0	6	11525.3196	−0.2
10	3	1	3	2	1	2	4445.3162	−0.2
11	4	1	4	3	1	3	5917.6849	−1.1
12	5	1	5	4	1	4	7382.7606	−0.2
13	3	1	2	2	1	1	4961.7111	1.0
14	4	1	3	3	1	2	6604.9657	0.2
15	5	1	4	4	1	3	8238.2752	0.1
16	2	2	0	1	1	1	11009.4573	−3.3
17	3	2	1	2	1	2	12785.4664	−0.5
18	4	2	2	3	1	3	14696.4655	−7.9
19	4	2	3	3	1	2	13536.1898	4.1
20	3	2	1	3	1	2	7307.0851	−10.1
21	6	2	5	5	2	4	9379.2202	0.7
22	3	3	0	2	2	1	17673.5653	6.1
23	3	3	1	2	2	0	17664.7218	5.5

Appendix B. 2-Propionylthiophene

Table B.8b: Observed frequencies ν_{obs} of 15 rotational transitions of the $^{13}\text{C}(6)$ isotopologue (for atom numbering see Figure 4.1) of *syn*-2PT with $\nu_{\text{obs}} - \nu_{\text{calc}}$ values from a fit with the program *XIAM*.

No.	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>V_{obs}</i>	<i>V_{obs} - V_{calc}</i>
	upper level			lower level			MHz	kHz
1	2	0	2	1	0	1	3148.8581	-0.6
2	3	0	3	2	0	2	4702.4997	0.9
3	4	0	4	3	0	3	6231.9455	1.1
4	5	0	5	4	0	4	7731.4034	1.0
5	2	1	2	1	0	1	5536.8014	0.1
6	3	1	3	2	0	2	6861.2767	-4.0
7	4	1	4	3	0	3	8114.0453	-1.3
8	5	1	5	4	0	4	9312.1487	-1.9
9	3	1	3	2	1	2	4473.3385	0.3
10	5	1	5	4	1	4	7430.0502	1.9
11	2	2	0	1	1	1	11162.2901	3.0
12	3	2	1	2	1	2	12945.8286	-4.3
13	4	2	2	3	1	3	14862.9280	-1.0
14	3	2	2	2	1	1	12389.3421	2.0
15	4	2	3	3	1	2	13709.4111	2.5

Table B.8c: Observed frequencies ν_{obs} of 14 rotational transitions of the $^{13}\text{C}(8)$ isotopologue (for atom numbering see Figure 4.1) of *syn*-2PT, with $\nu_{\text{obs}} - \nu_{\text{calc}}$ resulting from a fit with the program *XIAM*.

No.	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>V_{obs}</i>	<i>V_{obs} - V_{calc}</i>
	upper level			lower level			MHz	kHz
1	3	0	3	2	0	2	4674.5215	0.2
2	4	0	4	3	0	3	6194.9983	-0.9
3	5	0	5	4	0	4	7685.7609	1.6
4	2	1	2	1	0	1	5508.1655	-3.6
5	3	1	3	2	0	2	6824.9792	-0.4
6	4	1	4	3	0	3	8070.5414	2.3
7	5	1	5	4	0	4	9261.7360	-2.2
8	3	1	3	2	1	2	4446.8861	0.4
9	5	1	5	4	1	4	7386.1996	1.2
10	5	1	4	4	1	3	8232.9167	0.8
11	2	2	0	1	1	1	11108.0603	2.8
12	3	2	1	2	1	2	12880.6632	5.2
13	4	2	2	3	1	3	14785.7556	-5.1
14	4	2	3	3	1	2	13640.5904	-1.7

Appendix B. 2-Propionylthiophene

Table B.8d: Observed frequencies ν_{obs} of 12 rotational transitions of the $^{13}\text{C}(9)$ isotopologue (for atom numbering see Figure 4.1) of *syn*-2PT with $\nu_{\text{obs}} - \nu_{\text{calc}}$ values from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	ν_{obs}	$\nu_{\text{obs}} - \nu_{\text{calc}}$
	upper level			lower level			MHz	kHz
1	2	0	2	1	0	1	3091.1949	0.5
2	3	0	3	2	0	2	4617.5420	-1.3
3	4	0	4	3	0	3	6121.4372	-0.3
4	2	1	2	1	0	1	5500.6074	-2.6
5	4	1	4	3	0	3	8039.4466	-0.7
6	5	1	5	4	0	4	9220.0956	0.3
7	5	1	5	4	1	4	7302.0868	1.3
8	2	2	0	1	1	1	11139.0376	-1.7
9	3	2	1	2	1	2	12884.8388	0.7
10	4	2	2	3	1	3	14757.6418	-0.1
11	3	2	2	2	1	1	12349.8256	2.6
12	4	2	3	3	1	2	13650.0156	-0.4

Table B.8e: Observed frequencies ν_{obs} of 4 rotational transitions of the ^{34}S isotopologue of *anti*-2PT with $\nu_{\text{obs}} - \nu_{\text{calc}}$ values from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	ν_{obs}	$\nu_{\text{obs}} - \nu_{\text{calc}}$
	upper level			lower level			MHz	kHz
1	2	2	0	1	1	1	10558.2584	-0.2
2	5	1	5	4	0	4	9134.7002	2.1
3	6	0	6	5	0	5	9318.5508	0.0
4	6	1	6	5	0	5	10310.7978	-1.7

C. 2-Acetylfuran

Table C.1: Nuclear coordinates in the principal axis system of *anti*-2AF and *syn*-2AF calculated at the MP2/6-311++G(d,p) level of theory (for atom numbering see Figure 5.1).

	<i>anti</i> -2AF			<i>syn</i> -2AF		
	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å
O1	0.716015	−1.044956	0.000098	−0.814718	−1.042969	0.000094
C2	0.051515	0.148521	−0.000265	−0.045904	0.078549	0.000229
C3	0.955812	1.191906	−0.000213	−0.854413	1.202121	0.000024
C4	2.247666	0.597414	−0.000173	−2.196002	0.729068	−0.000086
C5	2.042594	−0.762522	0.000350	−2.107248	−0.643122	−0.000106
C6	−1.422266	0.125708	0.000046	1.417798	−0.097743	0.000047
O7	−2.046524	1.179402	0.000358	1.928160	−1.209304	−0.000098
C8	−2.090677	−1.230332	−0.000249	2.232638	1.180047	−0.000057
H9	2.705866	−1.614405	0.000434	−2.842779	−1.433515	−0.000111
H10	3.207492	1.093765	0.000281	−3.106999	1.309974	−0.000312
H11	0.693346	2.239934	−0.000830	−0.517175	2.229047	0.000235
H12	−3.172232	−1.092066	0.000308	3.292138	0.922721	0.000285
H13	−1.784284	−1.800876	−0.882131	1.998520	1.778774	−0.885606
H14	−1.783498	−1.801857	0.880698	1.998034	1.779334	0.884974

Appendix C. 2-Acetylfuran

Table C.2: Equilibrium rotational constants, X_e ($X = A, B, C$) and predicted torsional barriers of *anti*-2AF calculated at various levels of theory. The deviations ΔX between the calculated and the ground state experimental values X_0 are given in MHz, the deviation between the calculated and experimental V_3 barrier of the acetyl methyl group is given as ΔV_3 . All optimizations were done under full-symmetry relaxation.

Method/Basis Set	$A /$ MHz	$\Delta A /$ MHz	$B /$ MHz	$\Delta B /$ MHz	$C /$ MHz	$\Delta C /$ MHz	$V_3 /$ cm ⁻¹	$\Delta V_3 /$ cm ⁻¹
MP2/6-31G(d,p)	4820.6	-31.5	1632.4	1.2	1228.7	-1.9	308.2	11.6
MP2/6-31+G(d,p)	4814.4	-37.7	1626.8	-4.4	1225.1	-5.5	308.0	11.8
MP2/6-31++G(d,p)	4814.1	-38.0	1626.9	-4.3	1225.1	-5.4	307.9	11.9
MP2/6-311G(d,p)	4824.1	-28.0	1633.0	1.8	1229.3	-1.3	247.5	72.3
MP2/6-311+G(d,p)	4820.6	-31.6	1630.5	-0.7	1227.7	-2.9	275.5	44.3
MP2/6-311++G(d,p)	4820.6	-31.6	1630.5	-0.7	1227.7	-2.9	284.0	35.8
MP2/6-311G(df,pd)	4855.6	3.4	1643.5	12.2	1237.2	6.6	227.8	92.0
MP2/6-311+G(df,pd)	4854.8	2.7	1640.0	8.8	1235.2	4.6	257.1	62.7
MP2/6-311++G(df,pd)	4854.3	2.2	1640.1	8.8	1235.2	4.6	264.7	55.1
MP2/6-311G(2d,2p)	4839.6	-12.5	1638.5	7.3	1233.3	2.7	297.3	22.5
MP2/6-311+G(2d,2p)	4838.8	-13.3	1636.3	5.1	1232.0	1.4	283.4	36.4
MP2/6-311++G(2d,2p)	4838.7	-13.4	1636.3	5.1	1232.0	1.4	288.1	31.7
MP2/6-311G(2df,2pd)	4860.8	8.7	1648.5	17.3	1240.3	9.7	299.0	20.8
MP2/6-311+G(2df,2pd)	4860.1	8.0	1645.5	14.3	1238.6	8.0	279.5	40.3
MP2/6-311++G(2df,2pd)	4859.8	7.7	1645.6	14.4	1238.7	8.1	284.2	35.6
MP2/6-311G(3df,3pd)	4862.8	10.7	1646.3	15.0	1239.2	8.6	323.5	-3.7
MP2/6-311+G(3df,3pd)	4859.7	7.6	1643.9	12.6	1237.7	7.1	294.8	25.0
MP2/6-311++G(3df,3pd)	4859.7	7.6	1643.9	12.6	1237.7	7.1	292.2	27.6
MP2/cc-pVDZ	4777.9	-74.3	1622.9	-8.3	1220.7	-9.9	289.3	30.5
MP2/cc-pVTZ	4850.8	-1.4	1643.3	12.1	1236.8	6.2	275.7	44.1
MP2/aug-cc-pVDZ	4766.4	-85.7	1615.3	-16.0	1215.6	-15.0	293.6	26.2
MP2/aug-cc-pVTZ	4849.1	-3.0	1642.1	10.8	1236.0	5.4	275.1	44.7
B3LYP-D3/6-31G(d,p)	4831.6	-20.5	1629.1	-2.1	1227.5	-3.1	222.7	97.1

Appendix C. 2-Acetylfuran

B3LYP-D3/6-31+G(d,p)	4831.2	-20.9	1624.8	-6.4	1225.1	-5.5	195.9	123.9
B3LYP-D3/6-31++G(d,p)	4831.3	-20.8	1624.7	-6.5	1225.0	-5.6	195.7	124.1
B3LYP-D3/6-311G(d,p)	4851.3	-0.8	1632.3	1.1	1230.6	0.0	193.0	126.8
B3LYP-D3/6-311+G(d,p)	4853.0	0.9	1630.6	-0.6	1229.8	-0.8	200.1	119.7
B3LYP-D3/6-311++G(d,p)	4852.8	0.7	1630.6	-0.6	1229.8	-0.8	203.9	115.9
B3LYP-D3/6-311G(df,pd)	4866.5	14.4	1636.7	5.5	1234.1	3.5	188.4	131.4
B3LYP-D3/6-311+G(df,pd)	4867.9	15.8	1634.6	3.4	1233.0	2.4	195.9	123.9
B3LYP-D3/6-311++G(df,pd)	4867.7	15.6	1634.7	3.5	1233.0	2.4	200.7	119.1
B3LYP-D3/6-311G(3df,3pd)	4878.7	26.6	1638.7	7.5	1236.0	5.4	256.5	63.3
B3LYP-D3/6-311+G(3df,3pd)	4877.4	25.3	1637.0	5.8	1234.9	4.3	241.0	78.8
B3LYP-D3/6-311++G(3df,3pd)	4877.4	25.3	1637.0	5.8	1234.9	4.3	239.5	80.3
B3LYP-D3/cc-pVDZ	4821.0	-31.1	1627.2	-4.0	1225.9	-4.7	232.7	87.1
B3LYP-D3/cc-pVTZ	4872.8	20.7	1636.7	5.5	1234.4	3.8	223.2	96.6
B3LYP-D3/aug-cc-pVDZ	4827.5	-24.6	1623.5	-7.7	1224.2	-6.4	217.9	101.9
B3LYP-D3/aug-cc-pVTZ	4873.2	21.1	1636.1	4.9	1234.1	3.5	227.1	92.7
B3LYP-D3/6-311G(2d,2p)	4867.3	15.2	1636.1	4.9	1233.7	3.1	241.6	78.2
B3LYP-D3/6-311+G(2d,2p)	4867.8	15.7	1634.5	3.3	1232.8	2.2	224.7	95.1
B3LYP-D3/6-311++G(2d,2p)	4867.7	15.6	1634.5	3.3	1232.8	2.2	226.9	92.9
B3LYP-D3/6-311G(2df,2pd)	4874.8	22.7	1638.5	7.3	1235.6	5.0	247.9	71.9
B3LYP-D3/6-311+G(2df,2pd)	4875.6	23.5	1636.5	5.3	1234.5	3.9	230.5	89.3
B3LYP-D3/6-311++G(2df,2pd)	4875.6	23.5	1636.5	5.3	1234.5	3.9	232.5	87.3
B3LYP-D3BJ/6-31G(d,p)	4835.9	-16.3	1628.6	-2.7	1227.5	-3.1	218.7	101.1
B3LYP-D3BJ/6-31+G(d,p)	4835.2	-17.0	1624.2	-7.0	1225.0	-5.6	193.1	126.7
B3LYP-D3BJ/6-31++G(d,p)	4835.2	-16.9	1624.2	-7.1	1225.0	-5.6	192.9	126.9
B3LYP-D3BJ/6-311G(d,p)	4856.1	4.0	1631.7	0.5	1230.6	0.0	188.2	131.6
B3LYP-D3BJ/6-311+G(d,p)	4856.8	4.7	1630.1	-1.2	1229.7	-0.9	196.1	123.7
B3LYP-D3BJ/6-311++G(d,p)	4856.7	4.5	1630.1	-1.1	1229.7	-0.9	199.8	120.0
B3LYP-D3BJ/6-311G(df,pd)	4870.4	18.2	1635.8	4.6	1233.8	3.2	183.5	136.3
B3LYP-D3BJ/6-311+G(df,pd)	4871.5	19.4	1633.9	2.6	1232.8	2.2	192.0	127.8
B3LYP-D3BJ/6-311++G(df,pd)	4871.4	19.2	1633.9	2.7	1232.8	2.2	196.8	123.0

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B3LYP-D3BJ/6-311G(2d,2p)	4871.3	19.2	1635.4	4.2	1233.6	3.0	238.2	81.6
B3LYP-D3BJ/6-311+G(2d,2p)	4871.8	19.7	1633.8	2.6	1232.7	2.1	221.8	98.0
B3LYP-D3BJ/6-311++G(2d,2p)	4871.7	19.6	1633.8	2.6	1232.7	2.1	224.1	95.7
B3LYP-D3BJ/6-311G(2df,2pd)	4878.7	26.6	1637.9	6.7	1235.5	4.9	243.9	75.9
B3LYP-D3BJ/6-311+G(2df,2pd)	4879.3	27.2	1635.7	4.5	1234.3	3.7	227.4	92.4
B3LYP-D3BJ/6-311++G(2df,2pd)	4879.2	27.1	1635.7	4.5	1234.3	3.7	229.4	90.4
B3LYP-D3BJ/6-311G(3df,3pd)	4882.6	30.5	1638.0	6.8	1235.8	5.2	253.6	66.2
B3LYP-D3BJ/6-311+G(3df,3pd)	4881.0	28.8	1636.2	5.0	1234.7	4.1	238.0	81.8
B3LYP-D3BJ/6-311++G(3df,3pd)	4881.0	28.8	1636.2	5.0	1234.7	4.1	236.6	83.2
B3LYP-D3BJ/cc-pVDZ	4825.0	-27.1	1626.7	-4.6	1225.8	-4.8	214.8	105.0
B3LYP-D3BJ/cc-pVTZ	4876.8	24.7	1636.1	4.8	1234.3	3.7	223.9	95.9
B3LYP-D3BJ/aug-cc-pVDZ	4831.7	-20.5	1623.2	-8.1	1224.2	-6.3	228.0	91.8
B3LYP-D3BJ/aug-cc-pVTZ	4877.1	25.0	1635.5	4.2	1234.0	3.4	219.7	100.1
CAM-B3LYP-D3BJ/6-311G(d,p)	4901.7	49.6	1643.6	12.4	1240.3	9.7	203.9	115.9
CAM-B3LYP-D3BJ/6-311+G(d,p)	4902.4	50.3	1642.0	10.8	1239.4	8.8	214.7	105.1
CAM-B3LYP-D3BJ/6-311++G(d,p)	4902.2	50.1	1642.0	10.8	1239.4	8.8	218.4	101.4
CAM-B3LYP-D3BJ/cc-pVDZ	4870.2	18.1	1638.5	7.3	1235.4	4.8	231.2	88.6
CAM-B3LYP-D3BJ/cc-pVTZ	4921.7	69.6	1647.8	16.6	1243.9	13.3	245.1	74.7
CAM-B3LYP-D3BJ/aug-cc-pVDZ	4876.7	24.6	1634.7	3.5	1233.7	3.1	235.1	84.7
CAM-B3LYP-D3BJ/aug-cc-pVTZ	4922.2	70.1	1647.1	15.9	1243.5	12.9	240.0	79.8
M06-2X/6-31G(d,p)	4872.6	20.4	1640.9	9.7	1236.9	6.3	277.8	42.0
M06-2X/6-31+G(d,p)	4871.9	19.8	1637.0	5.7	1234.6	4.0	258.8	61.0
M06-2X/6-31++G(d,p)	4872.0	19.9	1636.9	5.7	1234.6	4.0	259.9	59.9
M06-2X/6-311G(d,p)	4889.0	36.9	1643.8	12.6	1239.6	9.0	262.6	57.2
M06-2X/6-311+G(d,p)	4890.1	38.0	1642.3	11.0	1238.8	8.2	275.1	44.7
M06-2X/6-311++G(d,p)	4889.9	37.8	1642.3	11.1	1238.8	8.2	279.3	40.5
M06-2X/6-311G(df,pd)	4899.6	47.5	1646.9	15.7	1242.0	11.4	255.4	64.4
M06-2X/6-311+G(df,pd)	4901.4	49.2	1645.2	13.9	1241.1	10.5	267.6	52.2
M06-2X/6-311++G(df,pd)	4901.2	49.1	1645.2	14.0	1241.1	10.6	273.4	46.4
M06-2X/6-311G(3df,3pd)	4912.2	60.1	1648.6	17.3	1243.7	13.1	336.8	-17.0

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M06-2X/6-311+G(3df,3pd)	4910.9	58.7	1647.4	16.1	1243.0	12.4	326.2	-6.4
M06-2X/6-311++G(3df,3pd)	4910.9	58.7	1647.3	16.1	1242.9	12.3	325.1	-5.3
M06-2X/cc-pVDZ	4864.0	11.9	1640.0	8.8	1235.9	5.3	278.1	41.7
M06-2X/cc-pVTZ	4906.7	54.5	1647.4	16.1	1242.7	12.1	301.9	17.9
M06-2X/aug-cc-pVDZ	4868.4	16.3	1636.1	4.9	1234.0	3.4	279.3	40.5
M06-2X/aug-cc-pVTZ	4907.8	55.7	1647.0	15.7	1242.5	11.9	306.0	13.8
ω B97X-D/6-311G(d,p)	4893.0	40.9	1640.7	9.5	1238.1	7.5	229.9	89.9
ω B97X-D/6-311+G(d,p)	4892.8	40.7	1640.7	9.5	1238.1	7.5	234.5	85.3
ω B97X-D/6-311++G(d,p)	4891.8	39.7	1642.1	10.9	1238.8	8.2	221.9	97.9
ω B97X-D/cc-pVDZ	4862.1	10.0	1636.3	5.1	1233.7	3.1	248.2	71.6
ω B97X-D/cc-pVTZ	4911.8	59.7	1645.8	14.6	1242.1	11.5	259.4	60.4
ω B97X-D/aug-cc-pVDZ	4867.0	14.9	1633.1	1.9	1232.2	1.6	261.0	58.8
ω B97X-D/aug-cc-pVTZ	4912.5	60.4	1645.5	14.3	1242.0	11.4	266.5	53.3
CCSD/cc-pVDZ	4797.2	-54.9	1616.5	-14.7	1218.4	-12.2	295.3	24.5
Experiment	4852.1		1631.2		1230.6		239.8	

Appendix C. 2-Acetylfuran

Table C.3: Equilibrium rotational constants and torsional barriers of *syn*-2AF calculated at various levels of theory. The deviations ΔX between the calculated and the ground state experimental values X_0 are given in MHz, the deviation between the calculated and experimental V_3 barrier of the acetyl methyl group is given as ΔV_3 . All optimizations were done under full-symmetry relaxation.

Method/Basis Set	A / MHz	ΔA / MHz	B / MHz	ΔB / MHz	C / MHz	ΔC / MHz	V_3 / cm⁻¹	ΔV_3 / cm⁻¹
MP2/6-31G(d,p)	4864.9	-37.6	1616.4	1.3	1222.5	-2.2	290.1	-50.3
MP2/6-31+G(d,p)	4857.1	-45.3	1611.3	-3.8	1219.1	-5.6	212.2	27.6
MP2/6-31++G(d,p)	4857.0	-45.5	1611.3	-3.8	1219.1	-5.6	205.6	34.2
MP2/6-311G(d,p)	4863.6	-38.8	1618.3	3.2	1223.6	-1.1	264.3	-24.5
MP2/6-311+G(d,p)	4859.5	-42.9	1616.4	1.3	1222.2	-2.4	230.6	9.2
MP2/6-311++G(d,p)	4859.5	-42.9	1616.4	1.3	1222.2	-2.4	234.8	5.0
MP2/6-311G(df,pd)	4893.1	-9.4	1628.5	13.3	1231.2	6.5	237.6	2.2
MP2/6-311+G(df,pd)	4892.8	-9.7	1625.7	10.6	1229.6	4.9	206.6	33.2
MP2/6-311++G(df,pd)	4892.3	-10.1	1625.8	10.7	1229.6	4.9	209.1	30.7
MP2/6-311G(2d,2p)	4879.9	-22.5	1622.6	7.5	1226.9	2.2	257.0	-17.2
MP2/6-311+G(2d,2p)	4878.8	-23.6	1621.0	5.9	1226.0	1.3	210.2	29.6
MP2/6-311++G(2d,2p)	4878.6	-23.8	1621.1	6.0	1226.0	1.3	211.9	27.9
MP2/6-311G(2df,2pd)	4901.8	-0.6	1632.4	17.3	1233.9	9.2	249.8	-10.0
MP2/6-311+G(2df,2pd)	4899.2	-3.2	1630.3	15.2	1232.5	7.8	205.9	33.9
MP2/6-311++G(2df,2pd)	4899.0	-3.4	1630.3	15.2	1232.5	7.8	207.3	32.5
MP2/6-311G(3df,3pd)	4905.4	2.9	1629.5	14.3	1232.5	7.8	268.4	-28.6
MP2/6-311+G(3df,3pd)	4899.0	-3.5	1628.4	13.3	1231.5	6.8	226.7	13.1
MP2/6-311++G(3df,3pd)	4898.8	-3.6	1628.5	13.3	1231.5	6.8	224.7	15.1
MP2/cc-pVDZ	4815.7	-86.8	1608.1	-7.0	1214.8	-9.9	331.3	-91.5
MP2/cc-pVTZ	4889.5	-12.9	1628.3	13.2	1230.8	6.1	215.4	24.4
MP2/aug-cc-pVDZ	4804.4	-98.0	1600.4	-14.8	1209.7	-15.0	223.4	16.4
MP2/aug-cc-pVTZ	4888.1	-14.3	1627.0	11.9	1230.0	5.3	203.2	36.6
B3LYP-D3/6-31G(d,p)	4879.4	-23.0	1611.8	-3.3	1220.8	-3.9	216.0	23.8

Appendix C. 2-Acetylfuran

B3LYP-D3/6-31+G(d,p)	4879.2	-23.2	1607.3	-7.8	1218.2	-6.5	145.3	94.5
B3LYP-D3/6-31++G(d,p)	4879.3	-23.1	1607.3	-7.8	1218.2	-6.5	142.3	97.5
B3LYP-D3/6-311G(d,p)	4900.9	-1.5	1614.6	-0.5	1223.7	-1.0	195.2	44.6
B3LYP-D3/6-311+G(d,p)	4902.3	-0.1	1612.8	-2.3	1222.8	-1.9	160.8	79.0
B3LYP-D3/6-311++G(d,p)	4902.1	-0.3	1612.8	-2.3	1222.8	-1.9	160.5	79.3
B3LYP-D3/6-311G(df,pd)	4914.6	12.2	1618.4	3.3	1226.7	2.0	178.6	61.2
B3LYP-D3/6-311+G(df,pd)	4916.5	14.1	1616.5	1.4	1225.8	1.1	147.4	92.4
B3LYP-D3/6-311++G(df,pd)	4916.3	13.9	1616.6	1.5	1225.8	1.1	150.6	89.2
B3LYP-D3/6-311G(2d,2p)	4917.7	15.3	1618.1	3.0	1226.7	2.0	215.5	24.3
B3LYP-D3/6-311+G(2d,2p)	4917.2	14.8	1617.0	1.9	1226.1	1.4	171.4	68.4
B3LYP-D3/6-311++G(2d,2p)	4917.1	14.7	1617.1	2.0	1226.1	1.4	171.1	68.7
B3LYP-D3/6-311G(2df,2pd)	4924.9	22.5	1620.2	5.1	1228.4	3.7	214.1	25.7
B3LYP-D3/6-311+G(2df,2pd)	4924.8	22.4	1618.7	3.6	1227.5	2.8	172.9	66.9
B3LYP-D3/6-311++G(2df,2pd)	4924.7	22.3	1618.8	3.7	1227.5	2.8	172.7	67.1
B3LYP-D3/6-311G(3df,3pd)	4929.5	27.1	1619.8	4.7	1228.4	3.7	214.0	25.8
B3LYP-D3/6-311+G(3df,3pd)	4925.4	23.0	1619.2	4.1	1227.8	3.1	184.7	55.1
B3LYP-D3/6-311++G(3df,3pd)	4925.4	23.0	1619.2	4.1	1227.8	3.1	182.6	57.2
B3LYP-D3/cc-pVDZ	4866.4	-36.0	1610.6	-4.5	1219.4	-5.3	265.1	-25.3
B3LYP-D3/cc-pVTZ	4921.5	19.1	1619.2	4.1	1227.6	2.9	178.7	61.1
B3LYP-D3/aug-cc-pVDZ	4873.9	-28.5	1606.7	-8.4	1217.6	-7.1	178.8	61.0
B3LYP-D3/aug-cc-pVTZ	4922.1	19.7	1618.7	3.6	1227.3	2.6	170.5	69.3
B3LYP-D3BJ/6-31G(d,p)	4884.0	-18.4	1612.4	-2.7	1221.4	-3.3	196.8	43.0
B3LYP-D3BJ/6-31+G(d,p)	4883.9	-18.5	1607.8	-7.3	1218.8	-5.8	126.3	113.5
B3LYP-D3BJ/6-31++G(d,p)	4883.9	-18.5	1607.8	-7.3	1218.8	-5.9	123.3	116.5
B3LYP-D3BJ/6-311G(d,p)	4905.5	3.1	1615.1	0.0	1224.3	-0.4	175.6	64.2
B3LYP-D3BJ/6-311+G(d,p)	4906.7	4.2	1613.3	-1.8	1223.3	-1.3	140.2	99.6
B3LYP-D3BJ/6-311++G(d,p)	4906.5	4.1	1613.3	-1.8	1223.3	-1.3	139.9	99.9
B3LYP-D3BJ/6-311G(df,pd)	4919.2	16.8	1618.8	3.7	1227.3	2.6	158.0	81.8
B3LYP-D3BJ/6-311+G(df,pd)	4920.8	18.4	1617.0	1.9	1226.3	1.7	126.1	113.7
B3LYP-D3BJ/6-311++G(df,pd)	4920.6	18.2	1617.0	1.9	1226.3	1.7	129.3	110.5

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B3LYP-D3BJ/6-311G(2d,2p)	4922.4	20.0	1618.5	3.4	1227.3	2.6	195.7	44.1
B3LYP-D3BJ/6-311+G(2d,2p)	4921.6	19.2	1617.5	2.4	1226.6	1.9	150.3	89.5
B3LYP-D3BJ/6-311++G(2d,2p)	4921.5	19.1	1617.5	2.4	1226.6	1.9	150.0	89.8
B3LYP-D3BJ/6-311G(2df,2pd)	4929.5	27.1	1620.6	5.5	1228.9	4.2	193.6	46.2
B3LYP-D3BJ/6-311+G(2df,2pd)	4929.1	26.7	1619.1	4.0	1228.0	3.3	151.6	88.2
B3LYP-D3BJ/6-311++G(2df,2pd)	4929.1	26.7	1619.2	4.1	1228.0	3.3	151.3	88.5
B3LYP-D3BJ/6-311G(3df,3pd)	4933.7	31.3	1620.0	4.9	1228.8	4.1	194.0	45.8
B3LYP-D3BJ/6-311+G(3df,3pd)	4929.7	27.2	1619.6	4.5	1228.3	3.7	163.0	76.8
B3LYP-D3BJ/6-311++G(3df,3pd)	4929.6	27.2	1619.6	4.5	1228.3	3.7	160.9	78.9
B3LYP-D3BJ/cc-pVDZ	4871.0	-31.4	1611.0	-4.1	1219.9	-4.7	245.0	-5.2
B3LYP-D3BJ/cc-pVTZ	4926.0	23.5	1619.6	4.5	1228.1	3.5	157.5	82.3
B3LYP-D3BJ/aug-cc-pVDZ	4878.5	-23.9	1607.4	-7.8	1218.3	-6.4	156.2	83.6
B3LYP-D3BJ/aug-cc-pVTZ	4926.2	23.8	1618.9	3.8	1227.7	3.1	149.0	90.8
CAM-B3LYP-D3BJ/6-311G(d,p)	4955.6	53.2	1626.0	10.9	1233.7	9.0	194.5	45.3
CAM-B3LYP-D3BJ/6-311+G(d,p)	4956.9	54.5	1624.1	9.0	1232.7	8.0	159.7	80.1
CAM-B3LYP-D3BJ/6-311++G(d,p)	4956.7	54.3	1624.1	9.0	1232.7	8.0	160.2	79.6
CAM-B3LYP-D3BJ/cc-pVDZ	4921.6	19.2	1621.6	6.5	1229.1	4.4	258.2	-18.4
CAM-B3LYP-D3BJ/cc-pVTZ	4975.0	72.6	1630.5	15.4	1237.4	12.7	178.3	61.5
CAM-B3LYP-D3BJ/aug-cc-pVDZ	4928.3	25.9	1617.5	2.4	1227.2	2.5	174.9	64.9
CAM-B3LYP-D3BJ/aug-cc-pVTZ	4975.4	73.0	1629.8	14.7	1237.0	12.3	169.1	70.7
M06-2X/6-31G(d,p)	4922.7	20.3	1623.7	8.6	1230.3	5.7	261.8	-22.0
M06-2X/6-31+G(d,p)	4923.0	20.6	1619.8	4.7	1228.2	3.5	199.8	40.0
M06-2X/6-31++G(d,p)	4922.9	20.5	1619.8	4.7	1228.2	3.5	195.4	44.4
M06-2X/6-311G(d,p)	4938.8	36.4	1626.6	11.5	1233.0	8.3	247.6	-7.8
M06-2X/6-311+G(d,p)	4940.1	37.6	1625.2	10.1	1232.3	7.6	224.9	14.9
M06-2X/6-311++G(d,p)	4939.8	37.4	1625.3	10.2	1232.3	7.6	225.3	14.5
M06-2X/6-311G(df,pd)	4948.5	46.1	1629.5	14.4	1235.2	10.6	227.2	12.6
M06-2X/6-311+G(df,pd)	4950.8	48.3	1627.9	12.8	1234.5	9.8	207.5	32.3
M06-2X/6-311++G(df,pd)	4950.6	48.1	1628.0	12.9	1234.5	9.8	212.0	27.8
M06-2X/6-311G(3df,3pd)	4963.2	60.8	1630.7	15.6	1236.8	12.2	283.0	-43.2

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M06-2X/6-311+G(3df,3pd)	4959.5	57.0	1630.5	15.4	1236.5	11.8	262.4	-22.6
M06-2X/6-311++G(3df,3pd)	4959.4	57.0	1630.6	15.4	1236.5	11.8	260.7	-20.9
M06-2X/cc-pVDZ	4911.9	9.5	1623.6	8.5	1229.7	5.0	287.6	-47.8
M06-2X/cc-pVTZ	4954.7	52.3	1630.8	15.7	1236.3	11.7	239.3	0.5
M06-2X/aug-cc-pVDZ	4916.5	14.0	1619.9	4.8	1227.9	3.2	233.7	6.1
M06-2X/aug-cc-pVTZ	4955.8	53.4	1630.4	15.3	1236.2	11.5	235.8	4.0
ω B97X-D/6-311G(d,p)	4941.4	39.0	1624.8	9.7	1232.1	7.4	191.8	48.0
ω B97X-D/6-311+G(d,p)	4941.2	38.8	1624.8	9.7	1232.1	7.4	193.3	46.5
ω B97X-D/6-311++G(d,p)	4939.5	37.1	1626.3	11.2	1232.8	8.1	215.2	24.6
ω B97X-D/cc-pVDZ	4908.0	5.6	1621.4	6.3	1228.2	3.5	268.5	-28.7
ω B97X-D/cc-pVTZ	4958.5	56.1	1630.5	15.4	1236.4	11.7	211.5	28.3
ω B97X-D/aug-cc-pVDZ	4913.0	10.6	1618.3	3.2	1226.7	2.0	222.5	17.3
ω B97X-D/aug-cc-pVTZ	4959.0	56.6	1630.3	15.2	1236.3	11.6	211.7	28.1
CCSD/cc-pVDZ	4844.3	-58.1	1600.8	-14.3	1212.5	-12.2	331.7	-91.9
Experiment	4902.4		1615.1		1224.7		319.8	

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Table C.4: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of *anti*- and *syn*-2AF given in Figure 5.3 calculated at the MP2/6-311++G(d,p) level of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^2 a_i f_i$.

<i>anti</i> -2AF			<i>syn</i> -2AF		
<i>i</i>	f_i	a_i / Hartree	a_i / cm ⁻¹	a_i / Hartree	a_i / cm ⁻¹
0	1	-381.7251125		-381.7233774	
1	cos 3 α	0.0006468	142.0	0.0005350	117.4
2	cos 6 α	0.0000331	7.3	0.0000535	11.7

Table C.5: Observed frequencies ν_{obs} of 293 rotational transitions of *anti*-2AF with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>J</i>	<i>K_a</i>	<i>K_c</i>	Species	<i>V</i> _{obs}	<i>V</i> _{obs} − <i>V</i> _{calc}
	upper level			lower level				[MHz]	[kHz]
1	2	0	2	1	0	1	A	5688.7409	0.9
2	2	0	2	1	0	1	E	5688.4292	−1.9
3	3	0	3	2	0	2	A	8447.0826	0.1
4	3	0	3	2	0	2	E	8446.6958	−0.7
5	4	0	4	3	0	3	A	11111.6951	−0.5
6	4	0	4	3	0	3	E	11111.2984	−0.8
7	5	0	5	4	0	4	A	13676.3249	0.3
8	5	0	5	4	0	4	E	13675.9669	0.0
9	6	0	6	5	0	5	A	16159.7298	0.0
10	6	0	6	5	0	5	E	16159.4275	0.4
11	7	0	7	6	0	6	A	18596.1692	−0.2
12	7	0	7	6	0	6	E	18595.9112	0.5
13	8	0	8	7	0	7	A	21017.0136	−1.0
14	8	0	8	7	0	7	E	21016.7814	0.5
15	9	0	9	8	0	8	A	23440.4036	7.5
16	9	0	9	8	0	8	E	23440.1724	−0.4
17	3	0	3	2	1	2	E	5591.5659	−2.7
18	4	0	4	3	1	3	A	8739.7131	−0.7
19	4	0	4	3	1	3	E	8739.3590	−2.6
20	5	0	5	4	1	4	A	11834.6106	0.2
21	5	0	5	4	1	4	E	11834.1079	−2.5
22	6	0	6	5	1	5	A	14821.3088	0.3
23	6	0	6	5	1	5	E	14820.7629	−1.5
24	7	0	7	6	1	6	A	17679.8733	−0.2
25	7	0	7	6	1	6	E	17679.3498	−1.4
26	8	0	8	7	1	7	A	20420.0777	−0.8
27	8	0	8	7	1	7	E	20419.6077	−0.8
28	9	0	9	8	1	8	A	23066.3704	−1.8
29	9	0	9	8	1	8	E	23065.9598	−1.3

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30	1	1	1	0	0	0	A	6083.0065	-2.0
31	1	1	1	0	0	0	E	6081.9240	-0.1
32	3	1	3	2	0	2	A	10819.0609	-3.5
33	3	1	3	2	0	2	E	10818.6356	1.4
34	4	1	4	3	0	3	A	12953.4055	-4.3
35	4	1	4	3	0	3	E	12953.1585	2.8
36	5	1	5	4	0	4	A	15014.7425	-3.4
37	5	1	5	4	0	4	E	15014.6323	2.7
38	6	1	6	5	0	5	A	17076.0219	-3.8
39	6	1	6	5	0	5	E	17075.9899	3.2
40	7	1	7	6	0	6	E	19193.0861	3.0
41	8	1	8	7	0	7	A	21391.0365	-2.0
42	8	1	8	7	0	7	E	21390.9943	1.8
43	9	1	9	8	0	8	A	23667.8451	-1.8
44	9	1	9	8	0	8	E	23667.7619	0.5
45	1	1	0	1	0	1	A	3621.8206	1.1
46	1	1	0	1	0	1	E	3622.0541	1.1
47	4	1	3	4	0	4	A	5835.6214	7.1
48	4	1	3	4	0	4	E	5834.4467	4.0
49	5	1	4	5	0	5	A	7296.0487	-8.1
50	5	1	4	5	0	5	E	7294.1788	2.6
51	6	1	5	6	0	6	A	9173.9067	-6.7
52	6	1	5	6	0	6	E	9171.1505	0.7
53	7	1	6	7	0	7	A	11432.5064	-5.4
54	7	1	6	7	0	7	E	11428.7760	-1.8
55	8	1	7	8	0	8	A	13984.8812	-3.0
56	8	1	7	8	0	8	E	13980.1941	-2.0
57	9	1	8	9	0	9	A	16716.5745	0.3
58	9	1	8	9	0	9	E	16711.0269	-1.2
59	10	1	9	10	0	10	A	19515.6696	3.9
60	10	1	9	10	0	10	E	19509.3911	1.8
61	2	1	2	1	0	1	A	8544.1923	-3.6
62	2	1	2	1	0	1	E	8543.5597	0.7
63	2	1	1	1	1	0	A	6124.5905	1.5
64	2	1	1	1	1	0	E	6123.7435	0.4
65	3	1	2	2	1	1	A	9163.8869	0.6
66	3	1	2	2	1	1	E	9163.1381	0.8
67	4	1	3	3	1	2	A	12172.8377	0.1
68	4	1	3	3	1	2	E	12171.9356	-0.6
69	5	1	4	4	1	3	A	15136.7682	1.1
70	5	1	4	4	1	3	E	15135.6994	-1.0
71	6	1	5	5	1	4	A	18037.5873	0.8
72	6	1	5	5	1	4	E	18036.3994	-1.2
73	7	1	6	6	1	5	A	20854.7687	1.0
74	7	1	6	6	1	5	E	20853.5374	-1.4
75	8	1	7	7	1	6	A	23569.3884	1.4

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76	8	1	7	7	1	6	E	23568.1984	-0.7
77	4	1	3	4	1	4	A	3993.9050	4.9
78	4	1	3	4	1	4	E	3992.5858	-0.4
79	5	1	4	5	1	5	A	5957.6426	7.2
80	5	1	4	5	1	5	E	5955.5124	-1.1
81	6	1	5	6	1	6	A	8257.6093	-8.2
82	6	1	5	6	1	6	E	8254.5893	-0.9
83	7	1	6	7	1	7	A	10835.5692	-6.5
84	7	1	6	7	1	7	E	10831.6025	-2.9
85	8	1	7	8	1	8	A	13610.8567	-3.6
86	8	1	7	8	1	8	E	13605.9810	-3.4
87	2	1	2	1	1	1	A	5323.1136	-0.7
88	2	1	2	1	1	1	E	5323.3907	0.6
89	4	1	4	3	1	3	A	10581.4279	-0.1
90	4	1	4	3	1	3	E	10581.2179	-0.2
91	3	1	3	2	1	2	A	7963.6040	-4.4
92	3	1	3	2	1	2	E	7963.5060	-0.2
93	5	1	5	4	1	4	A	13173.0321	0.4
94	5	1	5	4	1	4	E	13172.7729	-0.2
95	6	1	6	5	1	5	A	15737.6044	0.0
96	6	1	6	5	1	5	E	15737.3238	-0.2
97	7	1	7	6	1	6	A	18276.8089	-0.7
98	7	1	7	6	1	6	E	18276.5231	-0.4
99	8	1	8	7	1	7	A	20794.1016	-0.8
100	8	1	8	7	1	7	E	20793.8198	-0.4
101	9	1	9	8	1	8	A	23293.8219	-1.1
102	9	1	9	8	1	8	E	23293.5483	-1.5
103	5	1	4	4	2	3	A	6804.1628	6.6
104	5	1	4	4	2	3	E	6805.5256	-0.7
105	6	1	5	5	2	4	A	10610.1206	1.2
106	6	1	5	5	2	4	E	10609.8903	-2.1
107	7	1	6	6	2	5	A	14450.5468	5.6
108	7	1	6	6	2	5	E	14449.4549	-3.6
109	8	1	7	7	2	6	A	18256.0637	2.7
110	8	1	7	7	2	6	E	18254.4671	-4.4
111	9	1	8	8	2	7	A	21951.4851	2.5
112	9	1	8	8	2	7	E	21949.6352	-4.5
113	3	2	1	2	0	2	A	22480.4817	1.7
114	3	2	1	2	0	2	E	22484.1084	2.9
115	3	2	2	3	0	3	A	13859.5954	1.2
116	3	2	2	3	0	3	E	13852.4653	2.4
117	4	2	3	4	0	4	A	14168.2270	1.9
118	4	2	3	4	0	4	E	14164.6203	3.4
119	5	2	4	5	0	5	A	14723.5255	1.6
120	5	2	4	5	0	5	E	14720.6879	3.4
121	6	2	5	6	0	6	A	15578.1392	-0.8

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122	6	2	5	6	0	6	E	15575.2332	3.1
123	7	2	6	7	0	7	A	16745.8364	-1.4
124	7	2	6	7	0	7	E	16742.5081	2.6
125	8	2	7	8	0	8	A	18205.4880	0.3
126	8	2	7	8	0	8	E	18201.5650	3.9
127	2	2	0	1	1	1	A	16223.6784	2.5
128	2	2	0	1	1	1	E	16241.6788	-6.7
129	3	2	1	2	1	2	A	19625.0287	4.7
130	3	2	1	2	1	2	E	19628.9788	1.2
131	4	2	2	3	1	3	A	23417.6407	-7.7
132	4	2	2	3	1	3	E	23417.2515	1.5
133	2	2	0	1	1	0	E	15839.7948	-6.6
134	2	2	1	1	1	0	A	15787.8239	-2.0
135	2	2	1	1	1	0	E	15766.9489	6.9
136	3	2	2	2	1	1	A	18249.0059	-2.3
137	3	2	2	2	1	1	E	18241.7930	-1.4
138	4	2	3	3	1	2	A	20505.4449	-3.5
139	5	2	4	4	1	3	A	22564.2291	-5.1
140	5	2	4	4	1	3	E	22562.2085	-0.2
141	6	2	5	5	1	4	A	24441.8071	-5.9
142	6	2	5	5	1	4	E	24440.4821	1.2
143	2	2	0	2	1	1	A	9698.3456	-3.3
144	2	2	0	2	1	1	E	9716.0597	1.3
145	2	2	1	2	1	1	E	9643.1979	-1.1
146	3	2	2	3	1	2	E	9078.6561	-1.0
147	2	2	0	2	1	2	E	10918.2971	1.7
148	3	2	1	3	1	3	E	11665.4724	1.1
149	2	2	1	2	1	2	A	10865.4508	1.4
150	2	2	1	2	1	2	E	10845.4337	-2.3
151	3	2	2	3	1	3	A	11487.6124	0.1
152	3	2	2	3	1	3	E	11480.5246	-0.6
153	4	2	3	4	1	4	A	12326.5171	6.2
154	4	2	3	4	1	4	E	12322.7614	1.0
155	5	2	4	5	1	5	A	13385.1096	7.1
156	5	2	4	5	1	5	E	13382.0224	0.6
157	6	2	5	6	1	6	A	14661.8417	-2.4
158	6	2	5	6	1	6	E	14658.6716	1.1
159	7	2	6	7	1	7	A	16148.8996	-2.1
160	7	2	6	7	1	7	E	16145.3347	1.6
161	8	2	7	8	1	8	A	17831.4633	-0.5
162	8	2	7	8	1	8	E	17827.3512	1.7
163	9	2	8	9	1	9	A	19688.3974	1.7
164	9	2	8	9	1	9	E	19683.6550	2.2
165	3	2	1	3	1	2	A	9258.9218	-3.3
166	3	2	1	3	1	2	E	9263.6023	-1.0
167	4	2	2	4	1	3	A	8842.3211	0.7

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168	4	2	2	4	1	3	E	8843.4457	0.0
169	5	2	3	5	1	4	A	8569.7496	0.7
170	5	2	3	5	1	4	E	8569.8151	2.2
171	6	2	4	6	1	5	A	8555.1361	0.6
172	6	2	4	6	1	5	E	8554.6654	4.8
173	7	2	5	7	1	6	A	8891.0817	1.5
174	7	2	5	7	1	6	E	8890.0798	9.3
175	8	2	6	8	1	7	A	9648.4948	-7.7
176	2	2	1	1	1	1	E	16168.8322	6.1
177	3	2	1	2	1	1	E	18426.7399	-0.6
178	3	2	2	2	1	2	E	19444.0313	-0.2
179	3	2	2	2	2	1	A	8585.7719	0.6
180	3	2	2	2	2	1	E	8598.5979	2.5
181	4	2	3	3	2	2	A	11420.3266	0.1
182	4	2	3	3	2	2	E	11423.4539	0.6
183	5	2	4	4	2	3	A	14231.6233	0.0
184	5	2	4	4	2	3	E	14232.0353	0.8
185	6	2	5	5	2	4	A	17014.3467	0.8
186	6	2	5	5	2	4	E	17013.9727	0.0
187	7	2	6	6	2	5	A	19763.8678	0.6
188	7	2	6	6	2	5	E	19763.1865	0.4
189	8	2	7	7	2	6	A	22476.6650	0.5
190	8	2	7	7	2	6	E	22475.8366	0.1
191	9	2	8	8	2	7	A	25150.7552	0.3
192	9	2	8	8	2	7	E	25149.8523	-0.8
193	4	2	2	3	2	1	A	11756.2333	0.5
194	4	2	2	3	2	1	E	11751.7796	1.0
195	5	2	3	4	2	2	A	14864.1967	1.1
196	5	2	3	4	2	2	E	14862.0689	1.2
197	6	2	4	5	2	3	A	18022.9742	1.0
198	6	2	4	5	2	3	E	18021.2496	1.3
199	7	2	5	6	2	4	A	21190.7137	1.3
200	7	2	5	6	2	4	E	21188.9497	1.0
201	8	2	6	7	2	5	A	24326.8113	1.9
202	8	2	6	7	2	5	E	24324.9002	0.0
203	4	2	2	3	2	2	E	11936.7265	1.7
204	4	2	3	3	2	1	E	11238.5072	0.1
205	8	2	6	7	3	5	A	9749.7011	-1.6
206	8	2	6	7	3	5	E	9754.2146	3.2
207	9	2	7	8	3	6	A	14039.4541	0.3
208	3	3	0	3	2	2	E	17180.8486	0.3
209	4	3	1	4	2	3	E	17275.3506	0.7
210	5	3	2	5	2	4	E	17480.0572	-2.3
211	3	3	1	3	2	2	A	17128.2716	0.5
212	3	3	1	3	2	2	E	17085.0716	-3.6
213	4	3	2	4	2	3	A	17220.4189	1.0

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214	4	3	2	4	2	3	E	17178.8854	−3.5
215	5	3	3	5	2	4	A	17400.0900	1.0
216	5	3	3	5	2	4	E	17371.0154	−0.5
217	6	3	4	6	2	5	A	17700.8577	1.1
218	6	3	4	6	2	5	E	17685.9934	1.0
219	7	3	5	7	2	6	A	18154.8612	0.3
220	7	3	5	7	2	6	E	18147.0340	2.3
221	8	3	6	8	2	7	A	18789.9625	1.5
222	8	3	6	8	2	7	E	18784.7018	1.5
223	3	3	1	3	2	1	E	16900.1237	−5.4
224	4	3	2	4	2	2	E	16665.6147	−2.7
225	5	3	3	5	2	3	E	16227.7104	−0.9
226	6	3	4	6	2	4	E	15535.4098	−2.3
227	3	3	0	3	2	1	A	16956.4006	1.1
228	3	3	0	3	2	1	E	16995.9017	−0.5
229	4	3	1	4	2	2	A	16724.1731	1.2
230	4	3	1	4	2	2	E	16762.0776	−0.8
231	5	3	2	5	2	3	A	16311.2019	0.8
232	5	3	2	5	2	3	E	16336.7516	−3.3
233	6	3	3	6	2	4	A	15707.7150	−0.3
234	6	3	3	6	2	4	E	15719.1545	−4.3
235	7	3	4	7	2	5	A	14961.8244	−2.5
236	7	3	4	7	2	5	E	14966.2562	−4.5
237	8	3	5	8	2	6	A	14176.5275	−0.3
238	8	3	5	8	2	6	E	14178.2553	−3.3
239	9	3	6	9	2	7	A	13488.9616	−0.9
240	9	3	6	9	2	7	E	13489.5316	1.0
241	4	3	2	3	3	1	A	11512.4739	0.5
242	4	3	2	3	3	1	E	11517.2698	2.8
243	5	3	3	4	3	2	A	14411.2945	0.1
244	5	3	3	4	3	2	E	14424.1639	2.4
245	6	3	4	5	3	3	A	17315.1142	0.6
246	6	3	4	5	3	3	E	17328.9507	1.5
247	7	3	5	6	3	4	A	20217.8722	0.7
248	7	3	5	6	3	4	E	20224.2261	0.7
249	8	3	6	7	3	5	A	23111.7654	0.7
250	8	3	6	7	3	5	E	23113.5058	0.7
251	4	3	1	3	3	0	A	11524.0075	2.3
252	4	3	1	3	3	0	E	11517.9552	0.3
253	5	3	2	4	3	1	A	14451.2248	0.0
254	5	3	2	4	3	1	E	14436.7425	−1.6
255	6	3	3	5	3	2	A	17419.4877	0.3
256	6	3	3	5	3	2	E	17403.6528	0.5
257	7	3	4	6	3	3	A	20444.8246	0.6
258	7	3	4	6	3	3	E	20436.0518	1.2
259	8	3	5	7	3	4	A	23541.5121	1.8

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260	8	3	5	7	3	4	E	23536.9009	2.7
261	4	4	0	4	3	1	A	23878.1739	0.7
262	4	4	0	4	3	1	E	23897.7996	-2.2
263	6	4	2	6	3	3	A	23688.7381	-0.2
264	4	4	1	5	3	2	A	9426.8607	0.3
265	4	4	0	5	3	3	A	9480.3486	6.2
266	4	4	1	4	3	2	A	23891.5480	-0.7
267	4	4	1	4	3	2	E	23866.7365	-1.6
268	5	4	2	5	3	3	A	23867.8100	0.4
269	6	4	3	6	3	4	A	23842.5734	0.4
270	6	4	3	6	3	4	E	23791.5169	0.7
271	8	4	5	8	3	6	A	23847.7796	4.2
272	5	4	2	4	4	1	A	14387.5557	0.4
273	5	4	2	4	4	1	E	14387.2496	4.1
274	6	4	3	5	4	2	A	17289.8776	0.6
275	6	4	3	5	4	2	E	17290.6471	3.7
276	7	4	4	6	4	3	A	20204.2344	0.3
277	7	4	4	6	4	3	E	20208.1698	3.1
278	8	4	5	7	4	4	A	23130.6044	-0.1
279	8	4	5	7	4	4	E	23140.6139	5.1
280	5	4	1	4	4	0	A	14388.2579	0.2
281	5	4	1	4	4	0	E	14387.0090	-1.9
282	6	4	2	5	4	1	A	17293.0195	0.1
283	6	4	2	5	4	1	E	17290.3497	-2.1
284	7	4	3	6	4	2	A	20214.6075	0.2
285	7	4	3	6	4	2	E	20208.4081	-2.1
286	8	4	4	7	4	3	A	23158.7010	0.1
287	8	4	4	7	4	3	E	23146.0435	-2.8
288	6	5	1	5	5	0	A	17259.5709	-8.5
289	6	5	1	5	5	0	E	17258.4939	-3.1
290	6	5	2	5	5	1	A	17259.5507	7.5
291	6	5	2	5	5	1	E	17258.7777	6.0
292	8	6	2	7	6	1	A	23028.1255	-5.5
293	8	6	2	7	6	1	E	23026.6750	-5.6

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Table C.6: Observed frequencies ν_{obs} of 213 rotational transitions of *syn*-2AF with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs} [MHz]	$\nu_{obs}-\nu_{calc}$ [kHz]
	upper level			lower level					
1	1	0	1	0	0	0	A	2840.0347	0.7
2	1	0	1	0	0	0	E	2839.4376	0.4
3	2	0	2	1	0	1	A	5647.2818	1.2
4	2	0	2	1	0	1	E	5646.2312	0.1
5	3	0	3	2	0	2	A	8390.4604	0.2
6	3	0	3	2	0	2	E	8389.1862	-0.1
7	4	0	4	3	0	3	A	11045.2937	0.5
8	4	0	4	3	0	3	E	11044.0149	0.0
9	5	0	5	4	0	4	A	13604.2470	-0.8
10	5	0	5	4	0	4	E	13603.0981	-0.7
11	6	0	6	5	0	5	A	16082.7797	0.0
12	6	0	6	5	0	5	E	16081.7879	0.2
13	7	0	7	6	0	6	A	18512.1622	-0.7
14	7	0	7	6	0	6	E	18511.2892	-0.6
15	8	0	8	7	0	7	A	20922.9796	-0.4
16	8	0	8	7	0	7	E	20922.1755	0.4
17	9	0	9	8	0	8	A	23334.2474	0.2
18	9	0	9	8	0	8	E	23333.4743	-0.6
19	3	0	3	2	1	2	A	5459.9605	-2.4
20	3	0	3	2	1	2	E	5462.8335	0.1
21	4	0	4	3	1	3	A	8590.9116	-0.7
22	4	0	4	3	1	3	E	8591.5079	1.1
23	5	0	5	4	1	4	A	11677.1447	-0.2
24	5	0	5	4	1	4	E	11676.6972	0.2
25	6	0	6	5	1	5	A	14663.0384	0.8
26	6	0	6	5	1	5	E	14662.1161	-1.3
27	7	0	7	6	1	6	A	17525.2443	0.8
28	7	0	7	6	1	6	E	17524.1563	-0.2
29	8	0	8	7	1	7	A	20269.6905	0.7
30	8	0	8	7	1	7	E	20268.5897	0.7
31	9	0	9	8	1	8	A	22918.2807	1.5
32	9	0	9	8	1	8	E	22917.2305	1.4
33	1	1	0	1	0	1	A	3679.1205	1.3
34	2	1	1	2	0	2	A	4102.6105	2.9
35	3	1	2	3	0	3	E	4796.5656	0.6
36	4	1	3	4	0	4	A	5822.0824	-4.3
37	4	1	3	4	0	4	E	5820.0571	2.3
38	5	1	4	5	0	5	A	7232.4777	-2.7
39	5	1	4	5	0	5	E	7228.2040	0.2
40	6	1	5	6	0	6	A	9050.2240	-4.4

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41	6	1	5	6	0	6	E	9043.1578	0.1
42	8	1	7	8	0	8	A	13746.3717	-1.5
43	8	1	7	8	0	8	E	13733.1745	-1.6
44	1	1	0	0	0	0	E	6526.3853	1.3
45	1	1	1	0	0	0	A	6128.4489	-0.5
46	2	1	2	1	0	1	A	8577.7817	3.8
47	2	1	2	1	0	1	E	8572.5847	0.6
48	3	1	3	2	0	2	A	10844.8410	-0.1
49	3	1	3	2	0	2	E	10841.6965	2.1
50	4	1	4	3	0	3	A	12972.3982	2.0
51	4	1	4	3	0	3	E	12970.4168	0.1
52	5	1	5	4	0	4	A	15023.9913	1.4
53	5	1	5	4	0	4	E	15022.7680	-1.1
54	6	1	6	5	0	5	A	17069.6989	-0.2
55	6	1	6	5	0	5	E	17068.9208	-0.3
56	7	1	7	6	0	6	A	19165.4508	-2.2
57	7	1	7	6	0	6	E	19164.8755	-0.5
58	8	1	8	7	0	7	A	21338.9472	-0.7
59	8	1	8	7	0	7	E	21338.4201	-0.8
60	9	1	9	8	0	8	A	23591.2716	-0.5
61	9	1	9	8	0	8	E	23590.7230	-0.1
62	5	1	4	5	1	5	A	5812.7346	-3.7
63	5	1	4	5	1	5	E	5808.5337	0.2
64	2	1	2	1	1	1	A	5289.3617	-0.8
65	2	1	2	1	1	1	E	5295.2099	0.8
66	3	1	3	2	1	2	A	7914.3435	-0.4
67	3	1	3	2	1	2	E	7915.3411	-0.4
68	4	1	4	3	1	3	A	10518.0154	0.2
69	4	1	4	3	1	3	E	10517.9097	1.1
70	5	1	5	4	1	4	A	13096.8873	0.3
71	5	1	5	4	1	4	E	13096.3678	0.5
72	6	1	6	5	1	5	A	15649.9566	-0.4
73	6	1	6	5	1	5	E	15649.2505	-0.3
74	7	1	7	6	1	6	A	18178.5328	-0.8
75	7	1	7	6	1	6	E	18177.7428	0.2
76	8	1	8	7	1	7	A	20685.6584	0.6
77	8	1	8	7	1	7	E	20684.8352	0.5
78	9	1	9	8	1	8	A	23175.3034	-0.8
79	9	1	9	8	1	8	E	23174.4767	-0.7
80	2	1	1	1	1	1	E	6473.1051	-1.3
81	2	1	1	1	1	0	A	6070.7727	3.6
82	2	1	1	1	1	0	E	6063.5338	-0.7
83	3	1	2	2	1	1	A	9084.7260	1.4
84	3	1	2	2	1	1	E	9081.5013	0.1
85	4	1	3	3	1	2	A	12070.5088	0.8
86	4	1	3	3	1	2	E	12067.5031	-1.6

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87	5	1	4	4	1	3	E	15011.2473	−0.4
88	6	1	5	5	1	4	A	17900.5287	1.0
89	6	1	5	5	1	4	E	17896.7407	−1.0
90	7	1	6	6	1	5	A	20709.1263	1.1
91	7	1	6	6	1	5	E	20705.1687	−0.8
92	8	1	7	7	1	6	A	23422.1627	0.2
93	2	1	2	1	1	0	E	4885.6365	−0.8
94	5	1	4	4	2	3	A	6449.9779	1.6
95	5	1	4	4	2	3	E	6480.8444	1.3
96	6	1	5	5	2	4	E	10236.0851	−1.0
97	7	1	6	6	2	5	A	14038.9782	4.2
98	7	1	6	6	2	5	E	14043.6070	−1.3
99	8	1	7	7	2	6	A	17832.9375	5.3
100	6	1	5	5	2	3	E	9138.4400	1.0
101	3	2	2	3	0	3	A	14097.4756	1.2
102	4	2	3	4	0	4	E	14350.4603	0.9
103	2	2	0	1	1	1	A	16359.4958	2.0
104	2	2	0	1	1	1	E	16470.2781	−4.2
105	2	2	0	1	1	0	E	16060.7080	−2.4
106	2	2	1	1	1	1	E	16221.6314	3.6
107	2	2	1	1	1	0	A	15936.0012	−3.1
108	2	2	1	1	1	0	E	15812.0610	5.1
109	3	2	2	2	1	1	A	18385.3265	−0.5
110	3	2	2	2	1	1	E	18309.5249	−2.3
111	4	2	3	3	1	2	A	20635.1714	−1.8
112	4	2	3	3	1	2	E	20597.9089	−0.4
113	2	2	0	2	1	1	A	9898.0195	−1.5
114	3	2	1	3	1	2	A	9463.0207	−2.5
115	3	2	1	3	1	2	E	9522.1047	1.0
116	4	2	2	4	1	3	A	9041.8371	0.9
117	4	2	2	4	1	3	E	9065.3363	−0.3
118	5	2	3	5	1	4	E	8758.3010	−1.7
119	6	2	4	6	1	5	A	8697.2803	−0.6
120	6	2	4	6	1	5	E	8700.0407	−2.1
121	2	2	0	2	1	2	E	11175.0737	0.6
122	3	2	1	2	1	2	A	19719.8639	5.8
123	3	2	1	2	1	2	E	19781.5022	0.1
124	4	2	2	3	1	3	E	23476.8984	0.2
125	3	2	1	2	1	1	E	18603.6069	2.0
126	4	2	2	3	1	2	E	21132.8404	−0.9
127	3	2	1	3	1	3	E	11866.1645	3.9
128	4	2	2	4	1	4	E	12958.9903	0.7
129	3	2	2	3	1	2	E	9228.0231	−3.0
130	3	2	2	2	1	2	E	19487.4227	−1.8
131	5	2	4	4	1	3	A	22691.9880	2.6
132	5	2	4	4	1	3	E	22671.9030	−0.3

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133	6	2	5	5	1	4	A	24570.6764	−2.5
134	6	2	5	5	1	4	E	24558.3027	−0.3
135	4	2	2	3	1	3	A	23454.8314	−3.8
136	4	2	3	4	1	3	E	8530.4039	−0.7
137	2	2	1	2	1	2	A	11037.3487	3.1
138	2	2	1	2	1	2	E	10926.4149	−3.7
139	3	2	2	3	1	3	A	11643.0946	1.1
140	3	2	2	3	1	3	E	11572.0807	−2.3
141	4	2	3	4	1	4	A	12459.6484	−0.6
142	4	2	3	4	1	4	E	12424.0584	0.8
143	5	2	4	5	1	5	A	13490.0903	8.2
144	5	2	4	5	1	5	E	13469.1898	0.7
145	6	2	5	6	1	6	A	14733.4608	0.6
146	6	2	5	6	1	6	E	14717.5854	−0.2
147	7	2	6	7	1	7	A	16183.1314	0.6
148	8	2	7	8	1	8	A	17825.9484	0.9
149	5	2	4	4	2	2	E	13606.5673	0.5
150	5	2	3	4	2	3	E	15239.1456	−0.2
151	3	2	2	2	2	1	A	8520.0937	2.0
152	4	2	3	3	2	2	A	11334.5709	0.1
153	4	2	3	3	2	2	E	11369.8851	1.9
154	5	2	4	4	2	3	A	14127.3195	−0.6
155	5	2	4	4	2	3	E	14141.4992	0.4
156	6	2	5	5	2	4	A	16893.3337	−1.3
157	6	2	5	5	2	4	E	16897.6463	−1.1
158	8	2	7	7	2	6	A	22328.4735	−0.9
159	3	2	1	2	2	0	A	8649.7284	1.6
160	3	2	1	2	2	0	E	8606.4258	−3.2
161	4	2	2	3	2	1	A	11649.3213	0.3
162	4	2	2	3	2	1	E	11610.7352	−2.4
163	5	2	3	4	2	2	A	14722.6074	0.9
164	5	2	3	4	2	2	E	14704.2125	−1.3
165	6	2	4	5	2	3	A	17848.0073	−0.1
166	6	2	4	5	2	3	E	17838.4807	−1.1
167	7	2	5	6	2	4	A	20987.2895	0.1
168	7	2	5	6	2	4	E	20980.5259	−1.8
169	8	2	6	7	2	5	A	24101.4972	0.8
170	4	2	2	3	2	2	E	11904.8150	−0.2
171	6	2	5	5	2	3	E	15800.0006	0.3
172	3	3	1	3	2	2	A	17438.4762	−1.3
173	3	3	1	3	2	2	E	17310.8703	−3.8
174	4	3	2	4	2	3	A	17524.7161	1.3
175	5	3	3	5	2	4	A	17693.1838	0.1
176	5	3	3	5	2	4	E	17535.0465	1.6
177	6	3	4	6	2	5	A	17975.8525	0.8
178	6	3	4	6	2	5	E	17847.2415	6.1

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179	7	3	5	7	2	6	A	18403.6805	−2.6
180	3	3	0	3	2	1	A	17277.7841	0.5
181	4	3	1	4	2	2	A	17059.5865	2.8
182	5	3	2	5	2	3	A	16668.5118	3.1
183	3	3	0	4	2	3	A	6105.6321	−1.5
184	4	3	2	4	2	2	E	16830.7227	−2.8
185	5	3	3	5	2	3	E	16437.4001	2.2
186	4	3	1	3	3	0	A	11431.1225	1.5
187	5	3	2	4	3	1	E	14312.3298	−6.4
188	5	3	3	4	3	2	A	14295.7874	−1.6
189	5	3	3	4	3	2	E	14310.8898	3.6
190	6	3	4	5	3	3	A	17176.0016	−1.4
191	6	3	4	5	3	3	E	17209.8412	3.4
192	7	3	5	6	3	4	A	20056.0344	−1.3
193	7	3	5	6	3	4	E	20100.9648	0.1
194	8	3	6	7	3	5	A	22928.7757	−1.6
195	6	3	3	5	3	2	A	17269.5911	−1.5
196	7	3	4	6	3	3	A	20260.1544	−1.2
197	7	3	4	6	3	3	E	20209.1816	−4.9
198	6	3	3	6	2	4	A	16090.0959	2.0
199	7	3	4	7	2	5	A	15362.9556	−4.6
200	4	4	0	4	3	1	A	24319.3982	−1.9
201	5	4	1	5	3	2	A	24261.3925	0.3
202	5	4	2	5	3	3	A	24308.4985	0.7
203	5	4	1	4	4	0	A	14273.5220	−1.6
204	6	4	2	5	4	1	A	17153.4315	−3.4
205	5	4	2	4	4	1	A	14272.9220	−0.2
206	5	4	2	4	4	1	E	14271.6242	4.1
207	6	4	3	5	4	2	A	17150.7390	−4.3
208	6	4	3	5	4	2	E	17150.2470	5.2
209	7	4	4	6	4	3	A	20039.9471	−4.7
210	7	4	4	6	4	3	E	20042.2998	5.8
211	6	5	2	5	5	1	E	17120.4041	5.0
212	6	5	1	5	5	0	E	17119.4836	−4.3
213	7	5	3	6	5	2	E	19994.6654	5.2

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Table C.7a: Observed frequencies ν_{obs} of 43 rotational transitions of the $^{18}\text{O}(1)$ isotopologue (for atom numbering see Figure 5.1) of *anti*-2AF with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J upper level	K_a	K_c	J lower level	K_a	K_c	Species	ν_{obs} [MHz]	$\nu_{obs}-\nu_{calc}$ [kHz]
1	2	0	2	1	0	1	A	5657.3723	1.9
2	2	0	2	1	0	1	E	5657.0584	-2.7
3	3	0	3	2	0	2	A	8396.0266	0.0
4	3	0	3	2	0	2	E	8395.6467	2.9
5	5	0	5	4	0	4	A	13576.2866	-0.8
6	5	0	5	4	0	4	E	13575.9423	-0.4
7	6	0	6	5	0	5	A	16034.5987	-1.5
8	6	0	6	5	0	5	E	16034.3126	0.9
9	7	0	7	6	0	6	A	18448.5970	-1.8
10	7	0	7	6	0	6	E	18448.3542	1.5
11	4	0	4	3	1	3	A	8761.3007	4.2
12	4	0	4	3	1	3	E	8760.9132	0.2
13	5	0	5	4	1	4	A	11826.5765	-5.3
14	5	0	5	4	1	4	E	11826.0664	0.0
15	6	0	6	5	1	5	A	14778.3314	-2.0
16	6	0	6	5	1	5	E	14777.7877	0.1
17	2	1	2	1	0	1	A	8417.3928	-2.8
18	2	1	2	1	0	1	E	8416.8085	-2.4
19	3	1	3	2	0	2	A	10672.0189	-1.8
20	3	1	3	2	0	2	E	10671.6338	0.2
21	4	1	4	3	0	3	A	12786.9954	-0.8
22	4	1	4	3	0	3	E	12786.7805	1.4
23	5	1	5	4	0	4	A	14832.5535	-0.7
24	5	1	5	4	0	4	E	14832.4678	1.0
25	6	1	6	5	0	5	A	16883.1857	4.7
26	6	1	6	5	0	5	E	16883.1624	1.5
27	3	1	3	2	1	2	A	7911.9945	-1.0
28	3	1	3	2	1	2	E	7911.8856	1.8
29	4	1	4	3	1	3	A	10511.0010	-1.1
30	4	1	4	3	1	3	E	10510.7895	0.2
31	5	1	5	4	1	4	A	13082.8458	-2.9
32	5	1	5	4	1	4	E	13082.5906	0.1
33	6	1	6	5	1	5	A	15626.9125	-1.7
34	3	1	2	2	1	1	A	9124.3269	0.8
35	3	1	2	2	1	1	E	9123.5838	-0.1
36	4	1	3	3	1	2	A	12117.7003	0.3
37	4	1	3	3	1	2	E	12116.8017	1.9
38	5	1	4	4	1	3	A	15063.5009	1.5
39	5	1	4	4	1	3	E	15062.4353	0.4

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40	6	1	5	5	1	4	A	17942.4882	0.9
41	6	1	5	5	1	4	E	17941.3106	0.2
42	7	1	6	6	1	5	A	20733.0734	1.2
43	7	1	6	6	1	5	E	20731.8626	-1.5

Table C.7b: Observed frequencies ν_{obs} of 28 rotational transitions of the $^{13}\text{C}(2)$ isotopologue (for atom numbering see Figure 5.1) of *anti*-2AF with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				[MHz]	[kHz]
1	2	2	1	1	1	0	A	15785.2588	-2.4
2	2	2	1	1	1	0	E	15764.4411	-4.2
3	3	2	2	2	1	1	A	18246.4378	0.7
4	3	2	2	2	1	1	E	18239.2556	3.0
5	2	2	1	2	1	2	A	10862.8990	1.6
6	2	2	1	2	1	2	E	10842.9475	-0.7
7	3	2	2	3	1	3	A	11485.2101	2.9
8	3	2	2	3	1	3	E	11478.1458	-2.4
9	4	2	3	4	1	4	A	12324.3086	2.4
10	4	2	3	4	1	4	E	12320.5647	-3.4
11	3	2	1	2	1	2	A	19622.8398	1.7
12	3	2	1	2	1	2	E	19626.7677	-1.1
13	4	2	2	3	1	3	E	23415.4907	0.1
14	3	3	0	3	2	1	A	16951.8222	0.4
15	3	3	0	3	2	1	E	16991.2573	1.2
16	4	3	1	4	2	2	A	16719.4443	-4.0
17	4	3	1	4	2	2	E	16757.2631	-1.9
18	5	3	2	5	2	3	A	16306.2563	1.0
19	5	3	2	5	2	3	E	16331.7145	-1.7
20	6	3	3	6	2	4	E	15713.9159	2.0
21	3	3	1	3	2	2	A	17123.8146	3.4
22	3	3	1	3	2	2	E	17080.6915	0.9
23	4	3	2	4	2	3	A	17216.0209	0.8
24	5	3	3	5	2	4	A	17395.8086	0.1
25	6	3	4	6	2	5	A	17696.7624	-2.2
26	6	3	4	6	2	5	E	17681.9669	2.4
27	4	4	0	4	3	1	A	23871.8529	-2.6
28	4	4	1	4	3	2	A	23885.2484	1.7

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Table C.7c: Observed frequencies ν_{obs} of 80 rotational transitions of the $^{13}\text{C}(3)$ isotopologue (for atom numbering see Figure 5.1) of *anti*-2AF with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J	K_a	K_c	J	K_a	K_c	Species	V_{obs}	$V_{obs}-V_{calc}$
	upper level			lower level				[MHz]	[kHz]
1	2	0	2	1	0	1	A	5664.9958	-0.9
2	2	0	2	1	0	1	E	5664.6893	-1.8
3	3	0	3	2	0	2	A	8409.1316	0.0
4	3	0	3	2	0	2	E	8408.7507	-0.7
5	4	0	4	3	0	3	A	11057.4015	-0.5
6	4	0	4	3	0	3	E	11057.0137	0.1
7	6	0	6	5	0	5	A	16070.4759	-0.4
8	6	0	6	5	0	5	E	16070.1820	0.3
9	7	0	7	6	0	6	A	18491.2376	-0.1
10	7	0	7	6	0	6	E	18490.9850	-0.3
11	8	0	8	7	0	7	A	20898.0831	-0.2
12	8	0	8	7	0	7	E	20897.8549	0.9
13	9	0	9	8	0	8	A	23308.4703	-0.3
14	9	0	9	8	0	8	E	23308.2513	0.5
15	4	0	4	3	1	3	A	8745.8217	0.1
16	4	0	4	3	1	3	E	8745.4777	-1.1
17	5	0	5	4	1	4	A	11820.2686	2.6
18	5	0	5	4	1	4	E	11819.7800	-1.4
19	6	0	6	5	1	5	A	14783.3397	0.2
20	6	0	6	5	1	5	E	14782.8153	0.5
21	7	0	7	6	1	6	A	17617.1637	1.1
22	7	0	7	6	1	6	E	17616.6609	0.0
23	8	0	8	7	1	7	A	20333.4358	0.7
24	8	0	8	7	1	7	E	20332.9866	1.9
25	9	0	9	8	1	8	A	22957.6632	1.0
26	9	0	9	8	1	8	E	22957.2677	-0.5
27	3	1	3	2	0	2	A	10720.7189	6.9
28	3	1	3	2	0	2	E	10720.2862	0.0
29	4	1	4	3	0	3	A	12841.5100	2.7
30	4	1	4	3	0	3	E	12841.2555	0.8
31	5	1	5	4	0	4	A	14891.5082	0.1
32	5	1	5	4	0	4	E	14891.3864	-3.0
33	6	1	6	5	0	5	A	16944.5484	-3.0
34	6	1	6	5	0	5	E	16944.5063	0.3
35	7	1	7	6	0	6	A	19055.8835	-2.4
36	7	1	7	6	0	6	E	19055.8555	0.9
37	8	1	8	7	0	7	A	21248.8905	-1.1
38	8	1	8	7	0	7	E	21248.8366	0.0
39	3	1	2	2	1	1	A	9132.2924	-0.3

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40	3	1	2	2	1	1	E	9131.5524	1.1
41	4	1	3	3	1	2	A	12129.3162	0.4
42	4	1	3	3	1	2	E	12128.4243	0.9
43	5	1	4	4	1	3	A	15079.8239	0.1
44	5	1	4	4	1	3	E	15078.7691	0.1
45	6	1	5	5	1	4	A	17965.0541	−0.2
46	6	1	5	5	1	4	E	17963.8856	0.7
47	7	1	6	6	1	5	A	20763.8525	0.7
48	7	1	6	6	1	5	E	20762.6427	−2.5
49	8	1	7	7	1	6	A	23457.1748	−0.2
50	8	1	7	7	1	6	E	23456.0152	0.3
51	4	1	4	3	1	3	A	10529.9266	−0.3
52	4	1	4	3	1	3	E	10529.7191	−0.8
53	5	1	5	4	1	4	A	13107.4013	−1.5
54	5	1	5	4	1	4	E	13107.1479	−0.4
55	6	1	6	5	1	5	A	15657.4140	−0.5
56	6	1	6	5	1	5	E	15657.1385	−0.6
57	7	1	7	6	1	6	A	18181.8110	0.2
58	7	1	7	6	1	6	E	18181.5308	0.5
59	8	1	8	7	1	7	A	20684.2434	−0.1
60	8	1	8	7	1	7	E	20683.9669	−0.3
61	2	2	1	1	1	0	A	15589.3839	−6.3
62	4	2	3	3	1	2	A	20278.8057	5.1
63	2	2	0	1	1	1	A	16028.3708	1.5
64	3	2	1	2	1	2	A	19424.2965	−1.0
65	4	2	2	3	2	1	A	11718.7207	−0.9
66	4	2	2	3	2	1	E	11714.3895	0.7
67	6	2	4	5	2	3	A	17971.0731	−1.5
68	6	2	4	5	2	3	E	17969.3745	−0.7
69	7	2	5	6	2	4	A	21128.1645	0.1
70	7	2	5	6	2	4	E	21126.4230	0.7
71	4	2	3	3	2	2	A	11374.0416	−0.3
72	4	2	3	3	2	2	E	11377.0606	1.3
73	5	2	4	4	2	3	A	14172.5412	−2.0
74	5	2	4	4	2	3	E	14172.9258	0.3
75	5	3	3	4	3	2	A	14356.8508	1.2
76	5	3	3	4	3	2	E	14370.0966	1.9
77	6	3	4	5	3	3	A	17249.8454	−0.9
78	6	3	4	5	3	3	E	17263.4949	0.0
79	7	3	5	6	3	4	A	20141.2861	0.7
80	7	3	5	6	3	4	E	20147.3187	−1.3

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Table C.7d: Observed frequencies ν_{obs} of 81 rotational transitions of the $^{13}\text{C}(4)$ isotopologue (for atom numbering see Figure 5.1) of *anti*-2AF with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J upper level	K_a	K_c	J lower level	K_a	K_c	Species	ν_{obs} [MHz]	$\nu_{obs}-\nu_{calc}$ [kHz]
1	2	0	2	1	0	1	A	5606.9401	0.4
2	2	0	2	1	0	1	E	5606.6410	-0.6
3	3	0	3	2	0	2	A	8328.6894	-3.2
4	3	0	3	2	0	2	E	8328.3164	-1.8
5	4	0	4	3	0	3	A	10960.9760	0.2
6	4	0	4	3	0	3	E	10960.5875	-0.8
7	5	0	5	4	0	4	A	13496.7781	1.5
8	5	0	5	4	0	4	E	13496.4243	0.3
9	6	0	6	5	0	5	A	15952.5992	-0.7
10	6	0	6	5	0	5	E	15952.2998	-0.1
11	8	0	8	7	0	7	A	20751.1837	5.1
12	8	0	8	7	0	7	E	20750.9429	-5.4
13	9	0	9	8	0	8	A	23143.0652	-0.7
14	9	0	9	8	0	8	E	23142.8472	0.0
15	6	0	6	5	1	5	A	14577.4204	-0.7
16	6	0	6	5	1	5	E	14576.8958	-0.2
17	7	0	7	6	1	6	A	17410.0327	0.2
18	7	0	7	6	1	6	E	17409.5228	0.3
19	8	0	8	7	1	7	A	20125.7511	0.8
20	8	0	8	7	1	7	E	20125.2868	-1.1
21	9	0	9	8	1	8	A	22747.2323	-1.3
22	9	0	9	8	1	8	E	22746.8296	2.3
23	4	1	4	3	0	3	A	12837.1329	-2.5
24	4	1	4	3	0	3	E	12836.8691	0.1
25	5	1	5	4	0	4	A	14871.9584	3.0
26	5	1	5	4	0	4	E	14871.8286	0.7
27	6	1	6	5	0	5	A	16903.0961	-2.1
28	6	1	6	5	0	5	E	16903.0530	0.9
29	7	1	7	6	0	6	A	18985.9587	-0.3
30	7	1	7	6	0	6	E	18985.9359	0.8
31	8	1	8	7	0	7	A	21147.0106	-0.3
32	8	1	8	7	0	7	E	21146.9686	0.3
33	9	1	9	8	0	8	A	23386.1890	-0.1
34	9	1	9	8	0	8	E	23386.1099	-0.2
35	2	1	1	1	1	0	A	6030.8732	0.7
36	2	1	1	1	1	0	E	6030.0264	1.3
37	3	1	2	2	1	1	A	9024.5153	0.3
38	3	1	2	2	1	1	E	9023.7860	-0.4
39	4	1	3	3	1	2	A	11989.4657	-0.5

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40	4	1	3	3	1	2	E	11988.5946	−0.8
41	5	1	4	4	1	3	A	14911.9433	−0.7
42	5	1	4	4	1	3	E	14910.9122	−1.1
43	6	1	5	5	1	4	A	17774.9689	−0.2
44	7	1	6	6	1	5	A	20559.1380	0.8
45	3	1	3	2	1	2	A	7854.4556	0.0
46	3	1	3	2	1	2	E	7854.3665	0.7
47	4	1	4	3	1	3	A	10437.6671	1.4
48	4	1	4	3	1	3	E	10437.4660	−0.6
49	5	1	5	4	1	4	A	12995.7955	−0.2
50	5	1	5	4	1	4	E	12995.5470	−0.2
51	6	1	6	5	1	5	A	15527.9196	0.2
52	6	1	6	5	1	5	E	15527.6481	−0.1
53	9	1	9	8	1	8	E	22990.0903	0.2
54	4	2	3	3	2	2	A	11254.5396	0.7
55	4	2	3	3	2	2	E	11257.9266	0.7
56	5	2	4	4	2	3	A	14026.6205	0.3
57	5	2	4	4	2	3	E	14027.1331	−0.1
58	6	2	5	5	2	4	A	16771.5546	1.3
59	6	2	5	5	2	4	E	16771.2363	−0.4
60	7	2	6	6	2	5	A	19484.8911	1.8
61	7	2	6	6	2	5	E	19484.2488	−1.0
62	4	2	2	3	2	1	A	11573.9880	3.1
63	4	2	2	3	2	1	E	11569.3239	−1.6
64	5	2	3	4	2	2	A	14629.8246	−0.5
65	5	2	3	4	2	2	E	14627.6673	1.2
66	6	2	4	5	2	3	A	17736.8437	0.1
67	6	2	4	5	2	3	E	17735.1479	1.8
68	7	3	5	6	3	4	A	19918.1787	−1.6
69	7	3	5	6	3	4	E	19925.1530	0.1
70	5	3	3	4	3	2	A	14197.5575	−0.9
71	5	3	3	4	3	2	E	14209.8716	1.2
72	6	3	4	5	3	3	A	17058.1156	−0.7
73	7	3	5	6	3	4	A	19918.1797	−0.6
74	5	3	2	4	3	1	A	14234.4657	−0.2
75	5	3	2	4	3	1	E	14220.6060	−0.9
76	6	3	3	5	3	2	A	17154.6940	−0.5
77	6	3	3	5	3	2	E	17138.6121	0.7
78	7	3	4	6	3	3	A	20128.5831	−1.6
79	7	3	4	6	3	3	E	20119.2971	0.8
80	5	4	2	4	4	1	A	14174.5898	0.8
81	6	4	3	5	4	2	A	17033.0945	0.2

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Table C.7e: Observed frequencies ν_{obs} of 81 rotational transitions of the $^{13}\text{C}(5)$ isotopologue (for atom numbering see Figure 5.1) of *anti*-2AF with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J upper level	K_a	K_c	J lower level	K_a	K_c	Species	ν_{obs} [MHz]	$\nu_{obs}-\nu_{calc}$ [kHz]
1	2	0	2	1	0	1	A	5618.5595	-0.1
2	3	0	3	2	0	2	A	8344.8439	0.9
3	3	0	3	2	0	2	E	8344.4620	-0.8
4	4	0	4	3	0	3	A	10980.4156	1.3
5	4	0	4	3	0	3	E	10980.0227	-0.4
6	5	0	5	4	0	4	A	13518.5431	0.6
7	5	0	5	4	0	4	E	13518.1893	0.0
8	6	0	6	5	0	5	A	15976.4778	-0.2
9	6	0	6	5	0	5	E	15976.1806	0.9
10	7	0	7	6	0	6	A	18386.9869	-0.6
11	7	0	7	6	0	6	E	18386.7345	0.4
12	8	0	8	7	0	7	A	20780.8710	0.2
13	8	0	8	7	0	7	E	20780.6442	1.0
14	3	0	3	2	1	2	A	5486.6677	2.8
15	3	0	3	2	1	2	E	5486.5942	-1.3
16	5	0	5	4	1	4	A	11660.6608	-2.1
17	6	0	6	5	1	5	A	14618.8895	-0.8
18	6	0	6	5	1	5	E	14618.3392	0.2
19	7	0	7	6	1	6	A	17451.8748	-0.1
20	7	0	7	6	1	6	E	17451.3462	0.2
21	8	0	8	7	1	7	A	20167.7781	-1.2
22	8	0	8	7	1	7	E	20167.3038	-0.4
23	9	0	9	8	1	8	A	22789.8407	-1.6
24	9	0	9	8	1	8	E	22789.4305	2.5
25	4	1	4	3	0	3	A	12838.2917	-2.1
26	4	1	4	3	0	3	E	12838.0586	1.9
27	5	1	5	4	0	4	A	14876.1316	1.4
28	5	1	5	4	0	4	E	14876.0333	3.3
29	6	1	6	5	0	5	A	16911.5946	4.1
30	6	1	6	5	0	5	E	16911.5691	1.3
31	7	1	7	6	0	6	A	19000.0739	-5.1
32	8	1	8	7	0	7	A	21167.4893	-0.4
33	8	1	8	7	0	7	E	21167.4608	1.2
34	9	1	9	8	0	8	A	23413.0722	0.4
35	9	1	9	8	0	8	E	23413.0011	0.2
36	3	1	3	2	1	2	A	7868.7492	-3.9
37	3	1	3	2	1	2	E	7868.6532	0.5
38	4	1	4	3	1	3	A	10456.2053	-0.4
39	4	1	4	3	1	3	E	10455.9991	-0.4

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40	5	1	5	4	1	4	A	13018.2494	-1.2
41	5	1	5	4	1	4	E	13017.9966	0.2
42	6	1	6	5	1	5	A	15553.9988	-4.1
43	6	1	6	5	1	5	E	15553.7267	-0.4
44	7	1	7	6	1	6	A	18064.9668	0.4
45	7	1	7	6	1	6	E	18064.6852	0.2
46	8	1	8	7	1	7	A	20554.3967	-1.4
47	8	1	8	7	1	7	E	20554.1211	0.5
48	3	1	2	2	1	1	A	9046.0074	0.4
49	3	1	2	2	1	1	E	9045.2730	0.9
50	4	1	3	3	1	2	A	12017.3847	0.3
51	4	1	3	3	1	2	E	12016.5001	0.3
52	5	1	4	4	1	3	A	14945.5159	-0.7
53	5	1	4	4	1	3	E	14944.4686	-0.1
54	6	1	5	5	1	4	A	17813.0842	0.3
55	6	1	5	5	1	4	E	17811.9173	0.7
56	7	1	6	6	1	5	A	20600.3407	0.1
57	7	1	6	6	1	5	E	20599.1278	-0.2
58	8	1	7	7	1	6	A	23288.7766	0.3
59	8	1	7	7	1	6	E	23287.6002	-0.9
60	2	2	1	1	1	0	A	15697.4975	-0.3
61	3	2	2	2	1	1	A	18130.6708	2.3
62	3	2	2	2	1	1	E	18123.5283	0.1
63	4	2	3	3	1	2	A	20363.0929	1.7
64	4	2	3	3	1	2	E	20359.8098	-2.7
65	5	2	4	4	1	3	A	22401.5230	-3.3
66	4	2	2	3	2	1	A	11602.7437	0.2
67	5	2	3	4	2	2	A	14667.6229	0.4
68	6	2	4	5	2	3	A	17783.4144	1.2
69	7	2	5	6	2	4	A	20910.0802	-1.2
70	4	2	3	3	2	2	A	11278.4291	-0.6
71	5	2	4	4	2	3	A	14055.8203	0.8
72	6	2	5	5	2	4	A	16805.6389	1.0
73	7	2	6	6	2	5	A	19523.3867	0.7
74	5	3	2	4	3	1	A	14267.1945	0.3
75	6	3	3	5	3	2	A	17195.3992	-1.1
76	5	3	3	4	3	2	A	14229.3354	0.1
77	5	3	3	4	3	2	E	14241.6943	2.2
78	6	3	4	5	3	3	A	17096.3710	0.2
79	6	3	4	5	3	3	E	17110.0254	-1.6
80	8	3	6	7	3	5	A	22820.9182	0.2
81	8	3	6	7	3	5	E	22822.7255	1.1

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Table C.7f: Observed frequencies ν_{obs} of 81 rotational transitions of the $^{13}\text{C}(6)$ isotopologue (for atom numbering see Figure 5.1) of *anti*-2AF with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				[MHz]	[kHz]
1	3	0	3	2	0	2	A	8401.3200	0.2
2	3	0	3	2	0	2	E	8400.9369	-0.9
3	4	0	4	3	0	3	A	11054.0272	0.3
4	4	0	4	3	0	3	E	11053.6333	-0.1
5	5	0	5	4	0	4	A	13608.3399	0.2
6	5	0	5	4	0	4	E	13607.9827	-1.0
7	8	0	8	7	0	7	A	20917.5413	0.0
8	8	0	8	7	0	7	E	20917.3101	0.5
9	3	0	3	2	1	2	A	5532.3762	2.9
10	3	0	3	2	1	2	E	5532.3187	-1.4
11	4	0	4	3	1	3	A	8664.7038	1.8
12	4	0	4	3	1	3	E	8664.3527	-1.8
13	5	0	5	4	1	4	A	11746.6562	-2.9
14	5	0	5	4	1	4	E	11746.1596	-2.6
15	7	0	7	6	1	6	A	17573.3262	0.2
16	7	0	7	6	1	6	E	17572.8023	-0.7
17	8	0	8	7	1	7	A	20305.6284	-0.6
18	8	0	8	7	1	7	E	20305.1578	0.2
19	3	1	3	2	0	2	A	10790.6426	-2.0
20	3	1	3	2	0	2	E	10790.2178	1.1
21	4	1	4	3	0	3	A	12915.7071	-0.4
22	4	1	4	3	0	3	E	12915.4559	1.0
23	5	1	5	4	0	4	A	14967.0642	3.3
24	5	1	5	4	0	4	E	14966.9469	0.5
25	6	1	6	5	0	5	A	17016.5349	-3.5
26	6	1	6	5	0	5	E	17016.5040	1.4
27	7	1	7	6	0	6	A	19119.8707	1.3
28	7	1	7	6	0	6	E	19119.8515	-0.3
29	8	1	8	7	0	7	A	21302.8673	-1.9
30	8	1	8	7	0	7	E	21302.8306	1.5
31	3	1	3	2	1	2	A	7921.7000	1.8
32	3	1	3	2	1	2	E	7921.5979	-1.1
33	4	1	4	3	1	3	A	10526.3824	-0.3
34	4	1	4	3	1	3	E	10526.1760	-0.1
35	5	1	5	4	1	4	A	13105.3797	-0.6
36	5	1	5	4	1	4	E	13105.1237	-1.2
37	6	1	6	5	1	5	A	15657.8174	0.2
38	6	1	6	5	1	5	E	15657.5406	0.8
39	8	1	8	7	1	7	A	20690.9567	-0.2

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40	8	1	8	7	1	7	E	20690.6777	0.6
41	3	1	2	2	1	1	A	9108.7258	0.5
42	3	1	2	2	1	1	E	9107.9859	1.0
43	4	1	3	3	1	2	A	12100.4576	1.0
44	4	1	3	3	1	2	E	12099.5669	0.1
45	5	1	4	4	1	3	A	15048.3816	0.5
46	5	1	4	4	1	3	E	15047.3269	−0.8
47	6	1	5	5	1	4	A	17934.9419	0.2
48	6	1	5	5	1	4	E	17933.7674	−1.1
49	7	1	6	6	1	5	A	20740.1425	0.9
50	7	1	6	6	1	5	E	20738.9218	−0.9
51	8	1	7	7	1	6	A	23445.3026	0.0
52	8	1	7	7	1	6	E	23444.1232	2.6
53	2	2	1	1	1	0	A	15780.3675	1.8
54	3	2	2	2	1	1	A	18229.6342	1.8
55	3	2	2	2	1	1	E	18222.3467	−3.0
56	4	2	3	3	1	2	A	20476.4673	−2.4
57	4	2	2	3	2	1	A	11683.7160	0.3
58	4	2	2	3	2	1	E	11679.2230	0.6
59	5	2	3	4	2	2	A	14770.5321	−0.6
60	5	2	3	4	2	2	E	14768.4060	2.1
61	6	2	4	5	2	3	A	17908.4497	−0.1
62	6	2	4	5	2	3	E	17906.7389	0.8
63	7	2	5	6	2	4	A	21056.8707	−0.9
64	7	2	5	6	2	4	E	21055.1280	0.6
65	5	2	4	4	2	3	A	14151.7222	−0.8
66	5	2	4	4	2	3	E	14152.1608	0.9
67	6	2	5	5	2	4	A	16919.9837	1.7
68	6	2	5	5	2	4	E	16919.6260	1.1
69	7	2	6	6	2	5	A	19655.7944	0.4
70	7	2	6	6	2	5	E	19655.1250	−0.8
71	5	3	2	4	3	1	A	14365.7450	0.0
72	7	3	4	6	3	3	A	20319.0416	0.7
73	5	3	3	4	3	2	A	14327.2817	−1.5
74	5	3	3	4	3	2	E	14339.8422	3.3
75	6	3	4	5	3	3	A	17214.0787	−1.3
76	6	3	4	5	3	3	E	17227.9392	−0.3
77	7	3	5	6	3	4	A	20100.1021	−1.2
78	7	3	5	6	3	4	E	20106.6295	−2.9
79	5	4	2	4	4	1	A	14303.8897	−1.3
80	5	4	2	4	4	1	E	14303.5760	4.1
81	6	4	3	5	4	2	A	17188.9019	−1.5

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Table C.7g: Observed frequencies ν_{obs} of 40 rotational transitions of the $^{18}\text{O}(7)$ isotopologue (for atom numbering see Figure 5.1) of *anti*-2AF with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J upper level	K_a	K_c	J lower level	K_a	K_c	Species	ν_{obs} [MHz]	$\nu_{obs}-\nu_{calc}$ [kHz]
1	2	0	2	1	0	1	A	5541.3108	-0.7
2	2	0	2	1	0	1	E	5541.0093	-1.2
3	3	0	3	2	0	2	A	8228.4674	0.1
4	3	0	3	2	0	2	E	8228.0921	-0.5
5	4	0	4	3	0	3	A	10824.5971	-0.7
6	4	0	4	3	0	3	E	10824.2152	-0.5
7	5	0	5	4	0	4	A	13323.5124	0.8
8	5	0	5	4	0	4	E	13323.1706	0.1
9	6	0	6	5	0	5	A	15743.2734	0.6
10	6	0	6	5	0	5	E	15742.9871	-1.0
11	7	0	7	6	0	6	A	18117.0899	3.0
12	7	0	7	6	0	6	E	18116.8458	-1.0
13	6	0	6	5	1	5	A	14432.9859	-1.6
14	6	0	6	5	1	5	E	14432.4223	-2.4
15	2	1	2	1	1	1	A	5185.3272	-3.0
16	2	1	2	1	1	1	E	5185.5641	2.4
17	4	1	4	3	1	3	A	10307.7571	0.6
18	4	1	4	3	1	3	E	10307.5481	-1.3
19	5	1	5	4	1	4	A	12832.4969	0.4
20	5	1	5	4	1	4	E	12832.2439	-0.8
21	6	1	6	5	1	5	A	15330.9610	-1.8
22	6	1	6	5	1	5	E	15330.6911	-0.5
23	7	1	7	6	1	6	A	17804.7523	-0.6
24	7	1	7	6	1	6	E	17804.4769	-0.7
25	3	1	2	2	1	1	A	8925.8516	-0.4
26	3	1	2	2	1	1	E	8925.1323	-0.4
27	4	1	3	3	1	2	A	11856.8199	0.4
28	4	1	3	3	1	2	E	11855.9487	2.2
29	5	1	4	4	1	3	A	14744.1214	0.5
30	5	1	4	4	1	3	E	14743.0868	0.9
31	6	1	5	5	1	4	A	17570.2231	1.1
32	6	1	5	5	1	4	E	17569.0736	1.6
33	3	1	3	2	0	2	A	10546.6068	-2.1
34	3	1	3	2	0	2	E	10546.2482	0.1
35	4	1	4	3	0	3	A	12625.9022	4.0
36	4	1	4	3	0	3	E	12625.7062	1.3
37	5	1	5	4	0	4	A	14633.7980	1.1
38	5	1	5	4	0	4	E	14633.7335	-0.4
39	6	1	6	5	0	5	E	16641.2550	0.0

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40	2	2	1	1	1	0	A	15400.5522	−2.2

Table C.7h: Observed frequencies ν_{obs} of 82 rotational transitions of the $^{13}\text{C}(8)$ isotopologue (for atom numbering see Figure 5.1) of *anti*-2AF with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J upper level	K_a	K_c	J lower level	K_a	K_c	Species	ν_{obs} [MHz]	$\nu_{obs}-\nu_{calc}$ [kHz]
1	2	0	2	1	0	1	A	5608.9398	0.4
2	2	0	2	1	0	1	E	5608.6422	−1.7
3	3	0	3	2	0	2	A	8328.5902	−0.3
4	3	0	3	2	0	2	E	8328.2200	−0.8
5	4	0	4	3	0	3	A	10955.8258	0.0
6	4	0	4	3	0	3	E	10955.4448	−0.4
7	5	0	5	4	0	4	A	13484.4691	−0.5
8	5	0	5	4	0	4	E	13484.1256	0.7
9	6	0	6	5	0	5	A	15933.0079	−0.5
10	6	0	6	5	0	5	E	15932.7161	0.9
11	7	0	7	6	0	6	A	18335.2146	−0.8
12	7	0	7	6	0	6	E	18334.9656	1.6
13	8	0	8	7	0	7	A	20722.0355	7.8
14	8	0	8	7	0	7	E	20721.7933	−6.9
15	3	0	3	2	1	2	A	5512.0164	2.7
16	3	0	3	2	1	2	E	5511.9967	−0.5
17	4	0	4	3	1	3	A	8616.0457	−0.7
18	4	0	4	3	1	3	E	8615.7384	−0.6
19	5	0	5	4	1	4	A	11667.6582	−1.6
20	5	0	5	4	1	4	E	11667.2046	−0.3
21	6	0	6	5	1	5	A	14612.5978	−0.1
22	6	0	6	5	1	5	E	14612.0957	0.4
23	7	0	7	6	1	6	A	17431.1828	−0.1
24	7	0	7	6	1	6	E	17430.6970	0.8
25	8	0	8	7	1	7	A	20133.0349	−0.4
26	8	0	8	7	1	7	E	20132.5960	1.5
27	3	1	3	2	0	2	A	10668.3642	−5.8
28	3	1	3	2	0	2	E	10667.9268	−0.2
29	4	1	4	3	0	3	A	12772.6317	−4.0
30	4	1	4	3	0	3	E	12772.3660	0.9
31	5	1	5	4	0	4	A	14804.8820	1.8
32	5	1	5	4	0	4	E	14804.7458	1.0
33	6	1	6	5	0	5	A	16837.0408	−0.1
34	6	1	6	5	0	5	E	16836.9842	1.2
35	7	1	7	6	0	6	A	18924.2058	−2.0
36	7	1	7	6	0	6	E	18924.1716	1.9

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37	8	1	8	7	0	7	A	21091.0996	−3.3
38	8	1	8	7	0	7	E	21091.0480	1.8
39	3	1	2	2	1	1	A	9035.4394	1.0
40	3	1	2	2	1	1	E	9034.7174	1.9
41	4	1	3	3	1	2	A	12002.2176	0.6
42	4	1	3	3	1	2	E	12001.3522	−0.2
43	5	1	4	4	1	3	A	14924.6086	−0.2
44	5	1	4	4	1	3	E	14923.5863	−0.5
45	6	1	5	5	1	4	A	17784.7832	1.7
46	6	1	5	5	1	4	E	17783.6447	0.0
47	7	1	6	6	1	5	A	20562.4959	−0.3
48	8	1	7	7	1	6	A	23239.0920	0.5
49	8	1	7	7	1	6	E	23237.9472	−1.3
50	3	1	3	2	1	2	A	7851.7932	0.0
51	3	1	3	2	1	2	E	7851.7030	−0.4
52	4	1	4	3	1	3	A	10432.8557	−0.5
53	4	1	4	3	1	3	E	10432.6587	−0.3
54	5	1	5	4	1	4	A	12988.0694	−1.0
55	5	1	5	4	1	4	E	12987.8252	0.4
56	6	1	6	5	1	5	A	15516.6298	−0.6
57	6	1	6	5	1	5	E	15516.3631	0.0
58	8	1	8	7	1	7	A	20502.1097	−0.8
59	2	2	1	1	1	0	A	15570.1594	−2.3
60	2	2	1	1	1	0	E	15548.9478	2.9
61	3	2	2	2	1	1	A	17996.7457	−5.0
62	3	2	2	2	1	1	E	17989.3687	−4.2
63	4	2	3	3	1	2	A	20221.4421	6.2
64	5	2	4	4	1	3	A	22251.2089	4.7
65	4	2	2	3	2	1	A	11591.3123	0.2
66	5	2	3	4	2	2	A	14655.6870	0.7
67	6	2	4	5	2	3	A	17770.1849	0.5
68	7	2	5	6	2	4	A	20893.5477	2.0
69	5	2	4	4	2	3	A	14031.9849	−0.3
70	5	2	4	4	2	3	E	14032.4587	2.4
71	6	2	5	5	2	4	A	16775.6738	−0.3
72	6	2	5	5	2	4	E	16775.3468	0.1
73	5	3	2	4	3	1	A	14248.4945	−0.7
74	5	3	2	4	3	1	E	14234.1305	−2.2
75	6	3	3	5	3	2	A	17175.1082	−0.9
76	6	3	3	5	3	2	E	17159.1864	0.5
77	5	3	3	4	3	2	A	14209.1329	−1.5
78	5	3	3	4	3	2	E	14221.9623	3.5
79	6	3	4	5	3	3	A	17072.2206	−2.4
80	6	3	4	5	3	3	E	17086.2413	0.5
81	8	3	6	7	3	5	A	22787.5784	−2.3
82	8	3	6	7	3	5	E	22789.4576	0.0

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Table C.8a: Molecular parameters used for the *SFLAMS* fits of the A species of all assigned isotopologues of *anti*-2AF.

Par. ^a	Unit	¹² C	¹⁸ O(1)	¹³ C(2)	¹³ C(3)	¹³ C(4)
<i>A</i>	MHz	4852.41457(23)	4753.9836(14)	4851.56083(57)	4788.52039(39)	4836.3764(17)
<i>B</i>	MHz	1631.332542(91)	1625.94966(36)	1631.41692(55)	1626.71424(17)	1605.37265(24)
<i>C</i>	MHz	1230.594525(80)	1221.13733(26)	1.23058954(31)	1223.83430(12)	1214.75723(15)
<i>D_J</i>	kHz	0.06708(66)	0.0693(19)	-	0.0673(11)	0.0664(13)
<i>D_{JK}</i>	kHz	0.1347(28)	-	0.146(14)	0.116(14)	0.1242(79)
<i>D_K</i>	kHz	0.556(12)	-	0.641(67)	-	-
<i>d₁</i>	MHz	-0.02090(32)	-0.0197(21)	-0.0322(61)	-0.01724(78)	-0.01861(96)
<i>d₂</i>	kHz	-0.00312(16)	-	-	-	-
<i>N^b</i>		141	22	13	42	43
<i>σ^c</i>	kHz	3.0	1.9	1.7	2.1	2.0
Par. ^a	Unit	¹³ C(5)	¹³ C(6)	¹⁸ O(7)	¹³ C(8)	
<i>A</i>	MHz	4826.97136(39)	4851.91144(31)	4733.91205(51)	4785.62271(54)	
<i>B</i>	MHz	1609.61811(17)	1620.93355(14)	1588.87584(27)	1608.48166(21)	
<i>C</i>	MHz	1216.58876(11)	1224.636910(99)	1198.81877(14)	1213.29790(16)	
<i>D_J</i>	kHz	0.06599(89)	0.06738(73)	0.0628(24)	0.0654(12)	
<i>D_{JK}</i>	kHz	0.1216(96)	0.1262(56)	-	0.099(13)	
<i>D_K</i>	kHz	-	-	-	-	
<i>d₁</i>	MHz	-0.01912(86)	-0.01814(71)	-0.0157(17)	-0.0167(10)	
<i>d₂</i>	kHz	-0.00213(70)	-0.00185(53)	-	-	
<i>N^b</i>		48	43	20	45	
<i>σ^c</i>	kHz	1.8	1.4	1.5	2.5	

^a All parameters refer to the principal axis system. Watson's S reduction in the I^r representation was used.

^b Number of lines. ^c Standard deviation of the fit.

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Table C.8b: Molecular parameters used for the *SFLAMS* fits of the E species of all assigned isotopologues of *anti*-2AF.

Par. ^a	Unit	¹² C	¹⁸ O(1)	¹³ C(2)	¹³ C(3)	¹³ C(4)
<i>A</i>	MHz	4851.96489(11)	4753.5669(35)	4851.10469(87)	4788.0780(11)	4835.9213(30)
<i>B</i>	MHz	1631.182305(43)	1625.79848(68)	1631.27593(65)	1626.56601(16)	1605.22773(28)
<i>C</i>	MHz	1230.597772(38)	1221.14089(40)	1230.58438(89)	1223.837046(96)	1214.76020(19)
<i>D_J</i>	kHz	0.06697(32)	0.0636(41)	-	0.06726(75)	0.0677(17)
<i>D_{JK}</i>	kHz	0.0949(14)	-	0.244(35)	0.100(17)	-
<i>D_K</i>	kHz	0.5885(78)	-	-	-	-
<i>d₁</i>	MHz	-0.01926(17)	-0.0079(69)	-0.102(16)	-0.01854(64)	-0.0190(12)
<i>d₂</i>	kHz	-0.002532(97)	0.0210(82)	0.0218(68)	-	-
<i>q</i>	MHz	15.99805(26)	15.43(10)	15.9554(25)	15.9375(17)	16.1128(16)
<i>q_J</i>	kHz	-1.4905(62)	-	-1.54(18)	-1.538(48)	1.477(67)
<i>q_K</i>	kHz	-1.367(27)	-	-	-	-
<i>r</i>	MHz	9.565(11)	9.51(10)	-	9.355(46)	9.11(11)
<i>N</i> ^b		152	21	13	38	38
σ ^c	kHz	1.4	1.5	4.7	1.3	2.3
Par. ^a	Unit	¹³ C(5)	¹³ C(6)	¹⁸ O(7)	¹³ C(8)	
<i>A</i>	MHz	4826.53924(39)	4851.46501(51)	4733.5253(11)	4785.16351(82)	
<i>B</i>	MHz	1609.47067(12)	1620.78555(15)	1588.73006(26)	1608.33764(31)	
<i>C</i>	MHz	1216.591951(53)	1224.639825(83)	1198.82155(17)	1213.30129(14)	
<i>D_J</i>	kHz	0.06308(51)	0.06498(60)	0.0611(18)	0.0659(14)	
<i>D_{JK}</i>	kHz	0.1091(91)	0.142(11)	-	-	
<i>D_K</i>	kHz	-	-	-	-	
<i>d₁</i>	MHz	-0.01623(35)	-0.01824(66)	-0.0116(39)	-0.0147(13)	
<i>d₂</i>	kHz	-	-0.00365(54)	0.0122(70)	-	
<i>q</i>	MHz	15.6844(12)	15.9191(14)	14.908(12)	16.0839(14)	
<i>q_J</i>	kHz	-1.480(33)	-1.646(34)	-	-1.487(75)	
<i>q_K</i>	kHz	-	-	-	-	
<i>r</i>	MHz	9.599(28)	9.631(30)	9.348(46)	9.216(67)	
<i>N</i> ^b		33	38	20	37	
σ ^c	kHz	0.8	1.1	0.6	2.5	

^a All parameters refer to the principal axis system. Watson's S reduction in the I^r representation was used.

^b Number of lines. ^c Standard deviation of the fit.

Appendix C. 2-Acetylfuran

Table C.9: Rotational constants of 2-acetyl-5-methylfuran, furfural, and 5-methylfurfural calculated at the B3LYP-D3BJ/6-311G(d,p), B3LYP-D3BJ/6-311+G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels of theory.

Method/Basis Set	<i>A</i> / MHz	ΔA / MHz	<i>B</i> / MHz	ΔB / MHz	<i>C</i> / MHz	ΔC / MHz
<i>anti-furfural</i>						
B3LYP-D3BJ/6-311G(d,p)	8228.2	36.4	2045.7	−0.2	1638.4	1.2
B3LYP-D3BJ/6-311+G(d,p)	8233.9	42.1	2040.4	−5.5	1635.2	−2.0
B3LYP-D3BJ/6-311++G(d,p)	8234.1	42.3	2040.3	−5.6	1635.2	−2.0
Exp. X_0	8191.8		2045.9		1637.2	
<i>syn-furfural</i>						
B3LYP-D3BJ/6-311G(d,p)	8175.7	32.0	2095.4	−3.3	1667.9	−1.0
B3LYP-D3BJ/6-311+G(d,p)	8180.7	37.0	2091.2	−7.5	1665.5	−3.4
B3LYP-D3BJ/6-311++G(d,p)	8181.0	37.3	2091.0	−7.7	1665.3	−3.6
Exp. X_0	8143.7		2098.7		1668.9	
<i>anti-5-methylfurfural</i>						
B3LYP-D3BJ/6-311G(d,p)	6352.6	46.2	1312.1	−2.7	1094.9	−0.7
B3LYP-D3BJ/6-311+G(d,p)	6332.4	26.0	1311.1	−3.7	1093.6	−2.0
B3LYP-D3BJ/6-311++G(d,p)	6332.2	25.9	1311.1	−3.8	1093.6	−2.0
Exp. X_0	6306.4		1314.8		1095.6	
<i>syn-5-methylfurfural</i>						
B3LYP-D3BJ/6-311G(d,p)	4773.2	18.7	1494.0	−4.2	1145.9	−1.5
B3LYP-D3BJ/6-311+G(d,p)	4779.3	24.8	1490.5	−7.7	1144.3	−3.2
B3LYP-D3BJ/6-311++G(d,p)	4780.0	25.5	1490.3	−7.9	1144.2	−3.3
Exp. X_0	4754.5		1498.2		1147.5	
<i>anti-2-acetyl-5-methylfuran</i>						
B3LYP-D3BJ/6-311G(d,p)	3707.5	7.9	1124.9	−1.0	872.4	−0.5
B3LYP-D3BJ/6-311+G(d,p)	3704.8	5.1	1124.4	−1.6	871.9	−1.0
B3LYP-D3BJ/6-311++G(d,p)	3704.9	5.2	1124.4	−1.5	871.9	−1.0
Exp. X_0	3699.7		1126.0		872.9	
<i>syn-2-acetyl-5-methylfuran</i>						
B3LYP-D3BJ/6-311G(d,p)	3918.9	5.0	1094.4	−1.1	864.7	−0.8
B3LYP-D3BJ/6-311+G(d,p)	3922.1	8.3	1092.9	−2.7	863.9	−1.6
B3LYP-D3BJ/6-311++G(d,p)	3922.2	8.3	1092.9	−2.7	863.9	−1.6
Exp. X_0	3913.9		1095.6		865.5	

D. 2-Acetyl-3-Methylthiophene

Table D.1: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of 2A3MT given in Figure 6.2 calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V(\alpha) = \sum_{i=0}^8 a_i f_i$.

<i>i</i>	<i>f_i</i>	MP2		B3LYP-D3BJ	
		<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹
0	1	-743.5296272		-745.1200583	
1	cos(α)	0.0010598	232.6	0.0013472	295.7
2	cos(2α)	-0.0044989	-987.4	-0.0058456	-1283.0
3	cos(3α)	-0.0000149	-3.3	-0.0001805	-39.6
4	cos(4α)	0.0005535	121.5	0.0002997	65.8
5	cos(5α)	-0.0002058	-45.2	-0.0001860	-40.8
6	cos(6α)	0.0000561	12.3	-0.0000358	-7.9
7	cos(7α)	0.0000936	20.5	0.0000853	18.7
8	cos(8α)	0.0001091	23.9	0.0000612	13.4

Table D.2a: Nuclear coordinates in the principal axis system of *anti*-2A3MT and *syn*-2A3MT calculated at the MP2/6-311++G(d,p) level of theory (for atom numbering see Figure 6.1).

	<i>anti</i> -2A3MT			<i>syn</i> -2A3MT		
	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å
S1	-0.841539	-1.448454	-0.065242	0.909007	-1.405490	0.007198
C2	0.148677	-0.032597	-0.046452	-0.150511	-0.041480	-0.000018
C3	-0.624010	1.132452	0.031412	0.561367	1.167407	-0.003191
C4	-2.008265	0.830827	0.053256	1.960481	0.935271	0.000454
C5	-2.275691	-0.527084	0.008425	2.290522	-0.408483	0.007834
C6	1.625005	-0.113792	-0.030419	-1.599267	-0.343551	-0.003694
O7	2.308578	0.894542	-0.174023	-1.980531	-1.510411	-0.032827
C8	2.253897	-1.472975	0.207137	-2.590949	0.799201	0.037931
C9	-0.073243	2.530246	0.081855	-0.005747	2.564333	-0.021602
H10	-3.239909	-1.019292	-0.002366	3.280456	-0.847401	0.014117
H11	-2.786721	1.585498	0.105062	2.699211	1.730679	-0.001033
H12	0.428043	2.789160	-0.854560	-0.659973	2.754016	0.833453
H13	-0.883054	3.242953	0.260713	0.812111	3.288345	0.018339
H14	0.673821	2.631356	0.873258	-0.578953	2.761284	-0.932478
H15	2.029608	-1.813311	1.223371	-2.460539	1.386052	0.951555
H16	1.856820	-2.218243	-0.489267	-2.446718	1.468593	-0.814066
H17	3.334134	-1.390894	0.081248	-3.597653	0.380239	0.011856

Appendix D. 2-Acetyl-3-Methylthiophene

Table D.2b: Nuclear coordinates in the principal axis system of *anti*-2A3MT and *syn*-2A3MT calculated at the B3LYP-D3BJ/6-311++G(d,p) level of theory (for atom numbering see Figure 6.1).

	<i>anti</i> -2A3MT			<i>syn</i> -2A3MT		
	a / Å	b / Å	c / Å	a / Å	b / Å	c / Å
S1	−0.843054	−1.462033	0.000014	0.928793	−1.407204	−0.000063
C2	0.157538	−0.020727	−0.000002	−0.156598	−0.031977	0.000014
C3	−0.619512	1.128316	0.000013	0.542441	1.167688	0.000002
C4	−2.010582	0.825201	−0.000018	1.950627	0.952895	0.000022
C5	−2.280478	−0.516484	−0.000033	2.299052	−0.371017	0.000050
C6	1.625752	−0.103031	0.000001	−1.592668	−0.353642	0.000048
O7	2.309578	0.908881	−0.000046	−1.958690	−1.519142	0.000085
C8	2.265014	−1.478993	0.000020	−2.608518	0.769601	−0.000080
C9	−0.088719	2.531091	0.000038	−0.033525	2.557927	0.000009
H10	−3.244826	−1.001277	−0.000049	3.294314	−0.789583	0.000073
H11	−2.780940	1.585237	−0.000026	2.671016	1.760698	0.000041
H12	0.543225	2.711442	−0.871892	−0.652766	2.743972	0.880507
H13	−0.911764	3.248154	0.000096	0.772257	3.293084	0.000133
H14	0.543306	2.711376	0.871922	−0.652568	2.744060	−0.880611
H15	1.958359	−2.048863	0.881937	−2.489844	1.404546	0.881204
H16	1.958650	−2.048682	−0.882119	−2.489521	1.404703	−0.881200
H17	3.347466	−1.364807	0.000204	−3.604311	0.329719	−0.000285

Appendix D. 2-Acetyl-3-Methylthiophene

Table D.3: Rotational constants, the dihedral angle α and the predicted torsional barriers of *anti*-2A3MT optimized at various levels of theory. The deviations between the calculated and the experimental values of the rotational constants are given as ΔA , ΔB , and ΔC . $V_{3,1}$ is the barrier of the acetyl methyl and $V_{3,2}$ that of the ring methyl group. Θ is the tilt angle of the acetyl group out of the thiophene plane. All optimizations were performed under full geometry relaxation.

Method/Basis Set	$A /$ MHz	$\Delta A /$ MHz	$B /$ MHz	$\Delta B /$ MHz	$C /$ MHz	$\Delta C /$ MHz	$V_{3,1} /$ cm^{-1}	$\Delta V_{3,1} /$ cm^{-1}	$V_{3,2} /$ cm^{-1}	$\Delta V_{3,2} /$ cm^{-1}	$\alpha /$ $^\circ$	Planar	$\Theta /$ $^\circ$
B3LYP-D3/6-311G(2d,2p)	2002.7562	4.8	1406.0075	-6.0	834.4760	-1.8	283.7	22.5	289.8	32.0	179.98	Yes	0.02
B3LYP-D3/6-311+G(2d,2p)	1999.4253	1.4	1406.8265	-5.1	834.1922	-2.1	251.9	54.3	330.0	-8.2	179.99	Yes	0.01
B3LYP-D3/6-311++G(2d,2p)	1999.3824	1.4	1406.9156	-5.1	834.2164	-2.1	250.8	55.4	328.2	-6.4	179.97	Yes	0.03
B3LYP-D3/6-311G(2df,2pd)	2007.5745	9.6	1408.9040	-3.1	836.3291	0.0	281.5	24.7	308.4	13.4	179.99	Yes	0.01
B3LYP-D3/6-311+G(2df,2pd)	2004.0825	6.1	1409.3829	-2.6	835.8958	-0.4	252.0	54.2	336.9	-15.1	179.99	Yes	0.01
B3LYP-D3/6-311++G(2df,2pd)	2004.0704	6.1	1409.4280	-2.5	835.9100	-0.4	255.8	50.4	336.1	-14.3	179.98	Yes	0.02
B3LYP-D3/6-311G(3df,3pd)	2009.2155	11.2	1410.7673	-1.2	837.2723	1.0	272.9	33.3	330.9	-9.1	180.00	Yes	0.00
B3LYP-D3/6-311+G(3df,3pd)	2006.4720	8.5	1411.4624	-0.5	837.0448	0.8	257.4	48.8	328.3	-6.5	179.97	Yes	0.03
B3LYP-D3/6-311++G(3df,3pd)	2006.4625	8.5	1411.4423	-0.5	837.0356	0.7	258.6	47.6	328.4	-6.6	179.97	Yes	0.03
B3LYP-D3/6-311G(df,pd)	2001.6341	3.7	1405.3576	-6.6	834.0797	-2.2	248.1	58.1	289.9	31.9	179.96	Yes	0.04
B3LYP-D3/6-311+G(df,pd)	1998.5140	0.5	1405.5632	-6.4	833.6124	-2.7	223.2	83.0	325.2	-3.4	179.94	Yes	0.06
B3LYP-D3/6-311++G(df,pd)	1998.5126	0.5	1405.6433	-6.3	833.6390	-2.6	217.3	88.9	321.6	0.2	179.96	Yes	0.04
B3LYP-D3/6-311G(d,p)	1995.3479	-2.6	1401.2186	-10.7	831.5498	-4.7	258.4	47.8	264.4	57.4	180.01	Yes	-0.01
B3LYP-D3/6-311+G(d,p)	1992.0607	-5.9	1401.4298	-10.5	831.0581	-5.2	235.2	71.0	308.7	13.1	179.98	Yes	0.02
B3LYP-D3/6-311++G(d,p)	1992.0453	-5.9	1401.5310	-10.4	831.0911	-5.2	228.9	77.3	306.3	15.5	179.96	Yes	0.04
B3LYP-D3/6-31G(d,p)	1990.5429	-7.4	1398.6845	-13.3	829.8316	-6.5	306.1	0.1	253.6	68.2	179.99	Yes	0.01
B3LYP-D3/6-31+G(d,p)	1984.9254	-13.1	1397.2310	-14.7	828.3614	-7.9	243.8	62.4	334.6	-12.8	179.98	Yes	0.02
B3LYP-D3/6-31++G(d,p)	1985.0767	-12.9	1397.2922	-14.7	828.4097	-7.9	240.5	65.7	338.5	-16.7	179.97	Yes	0.03
B3LYP-D3/aug-cc-pVDZ	1981.7207	-16.3	1396.3122	-15.7	827.5401	-8.7	260.4	45.8	336.6	-14.8	179.98	Yes	0.02
B3LYP-D3/aug-cc-pVTZ	2002.7443	4.8	1408.8215	-3.1	835.4678	-0.8	255.8	50.4	331.3	-9.5	179.96	Yes	0.04
B3LYP-D3BJ/6-311G(2d,2p)	2001.1254	3.1	1411.5147	-0.5	836.1318	-0.2	237.3	68.9	241.3	80.5	180.00	Yes	0.00
B3LYP-D3BJ/6-311+G(2d,2p)	1997.6762	-0.3	1412.2869	0.3	835.8065	-0.5	204.7	101.5	287.5	34.3	179.99	Yes	0.01

Appendix D. 2-Acetyl-3-Methylthiophene

B3LYP-D3BJ/6-311++G(2d,2p)	1997.6437	-0.3	1412.3745	0.4	835.8317	-0.5	208.5	97.7	285.7	36.1	179.99	Yes	0.01
B3LYP-D3BJ/6-311G(2df,2pd)	2005.7422	7.8	1414.4533	2.5	837.9635	1.7	234.8	71.4	260.0	61.8	180.00	Yes	0.00
B3LYP-D3BJ/6-311+G(2df,2pd)	2002.2228	4.2	1414.8468	2.9	837.4927	1.2	204.8	101.4	294.6	27.2	180.00	Yes	0.00
B3LYP-D3BJ/6-311++G(2df,2pd)	2002.2076	4.2	1414.8985	2.9	837.5085	1.2	208.6	97.6	293.7	28.1	180.00	Yes	0.00
B3LYP-D3BJ/6-311G(3df,3pd)	2007.3432	9.4	1416.3203	4.4	838.9013	2.6	226.4	79.8	283.9	37.9	180.00	Yes	0.00
B3LYP-D3BJ/6-311+G(3df,3pd)	2004.5105	6.5	1416.9671	5.0	838.6376	2.3	209.8	96.4	285.2	36.6	180.00	Yes	0.00
B3LYP-D3BJ/6-311++G(3df,3pd)	2004.5158	6.5	1416.9491	5.0	838.6317	2.3	210.9	95.3	285.3	36.5	180.00	Yes	0.00
B3LYP-D3BJ/6-311G(df,pd)	2000.0432	2.1	1410.8775	-1.1	835.7468	-0.5	201.0	105.2	240.8	81.0	179.99	Yes	0.01
B3LYP-D3BJ/6-311+G(df,pd)	1996.7614	-1.2	1411.0030	-1.0	835.2201	-1.1	175.8	130.4	282.1	39.7	179.98	Yes	0.02
B3LYP-D3BJ/6-311++G(df,pd)	1996.7909	-1.2	1411.0942	-0.9	835.2559	-1.0	170.1	136.1	278.3	43.5	179.99	Yes	0.01
B3LYP-D3BJ/6-311G(d,p)	1993.9149	-4.1	1406.6604	-5.3	833.2169	-3.1	212.4	93.8	215.5	106.3	179.99	Yes	0.01
B3LYP-D3BJ/6-311+G(d,p)	1990.4953	-7.5	1406.7845	-5.2	832.6682	-3.6	188.8	117.4	265.9	55.9	179.97	Yes	0.03
B3LYP-D3BJ/6-311++G(d,p)	1990.4984	-7.5	1406.9541	-5.0	832.7281	-3.6	182.7	123.5	263.4	58.4	180.00	Yes	0.00
B3LYP-D3BJ/6-31G(d,p)	1989.3355	-8.6	1403.9340	-8.0	831.4701	-4.8	263.4	42.8	201.5	120.3	179.97	Yes	0.03
B3LYP-D3BJ/6-31+G(d,p)	1983.5530	-14.4	1402.5249	-9.4	829.9829	-6.3	200.3	105.9	291.5	30.3	179.99	Yes	0.01
B3LYP-D3BJ/6-31++G(d,p)	1983.5890	-14.4	1402.5097	-9.5	829.9838	-6.3	196.7	109.5	295.2	26.6	179.99	Yes	0.01
B3LYP-D3BJ/aug-cc-pVDZ	1980.2412	-17.7	1401.7828	-10.2	829.2029	-7.1	215.1	91.1	294.3	27.5	179.99	Yes	0.01
B3LYP-D3BJ/aug-cc-pVTZ	2000.8540	2.9	1414.3229	2.4	837.0719	0.8	209.0	97.2	289.1	32.7	179.99	Yes	0.01
B3LYP-D3BJ/cc-pVDZ	1983.7864	-14.2	1401.3538	-10.6	829.6832	-6.6	284.3	21.9	211.9	109.9	180.00	Yes	0.00
B3LYP-D3BJ/cc-pVTZ	2001.7832	3.8	1413.8759	1.9	837.0754	0.8	220.9	85.3	265.4	56.4	179.99	Yes	0.01
B3LYP-D3/cc-pVDZ	1985.0693	-12.9	1395.8512	-16.1	827.9715	-8.3	328.2	-22.0	264.5	57.3	179.95	Yes	0.05
B3LYP-D3/cc-pVTZ	2003.6075	5.6	1408.3749	-3.6	835.4580	-0.8	267.5	38.7	309.7	12.1	179.98	Yes	0.02
CAM-B3LYP-D3BJ/6-311G(d,p)	2013.3968	15.4	1415.7122	3.7	839.7808	3.5	232.3	73.9	208.4	113.4	179.99	Yes	0.01
CAM-B3LYP-D3BJ/6-311+G(d,p)	2009.8536	11.9	1415.8869	3.9	839.2304	2.9	209.6	96.6	260.5	61.3	180.01	Yes	-0.01
CAM-B3LYP-D3BJ/6-311++G(d,p)	2009.8346	11.9	1416.0094	4.0	839.2699	3.0	205.5	100.7	257.6	64.2	179.99	Yes	0.01
CAM-B3LYP-D3BJ/aug-cc-pVDZ	1999.5818	1.6	1410.6008	-1.4	835.6632	-0.6	230.6	75.6	277.5	44.3	179.99	Yes	0.01
CAM-B3LYP-D3BJ/aug-cc-pVTZ	2020.1182	22.1	1423.3993	11.4	843.6086	7.3	228.1	78.1	280.4	41.4	179.99	Yes	0.01
CAM-B3LYP-D3BJ/cc-pVDZ	2003.2950	5.3	1410.0786	-1.9	836.1384	-0.2	296.4	9.8	188.6	133.2	179.99	Yes	0.01
CAM-B3LYP-D3BJ/cc-pVTZ	2021.1858	23.2	1423.0308	11.1	843.6630	7.4	240.8	65.4	255.3	66.5	179.97	Yes	0.03
CCSD/cc-pVDZ	1970.5678	-27.4	1389.2197	-22.7	823.2340	-13.1	376.8	-70.6	335.8	-14.0	179.96	Yes	0.04

Appendix D. 2-Acetyl-3-Methylthiophene

M06-2X/6-311G(3df,3pd)	2021.5796	23.6	1424.1581	12.2	844.1515	7.9	344.0	-37.8	391.0	-69.2	179.96	Yes	0.04
M06-2X/6-311+G(3df,3pd)	2019.2558	21.3	1424.7666	12.8	843.9641	7.7	333.8	-27.6	386.4	-64.6	179.98	Yes	0.02
M06-2X/6-311++G(3df,3pd)	2019.2421	21.3	1424.7483	12.8	843.9546	7.7	335.4	-29.2	386.3	-64.5	179.98	Yes	0.02
M06-2X/6-311G(df,pd)	2014.7269	16.8	1419.2845	7.3	841.2772	5.0	292.2	14.0	358.7	-36.9	179.99	Yes	0.01
M06-2X/6-311+G(df,pd)	2012.0969	14.1	1419.2922	7.3	840.8209	4.5	279.0	27.2	382.8	-61.0	179.99	Yes	0.01
M06-2X/6-311++G(df,pd)	2012.0133	14.0	1419.3965	7.4	840.8423	4.6	274.8	31.4	379.2	-57.4	179.98	Yes	0.02
M06-2X/6-311G(d,p)	2009.6389	11.7	1415.9836	4.0	839.2501	3.0	305.1	1.1	340.8	-19.0	180.00	Yes	0.00
M06-2X/6-311+G(d,p)	2006.8048	8.8	1415.9801	4.0	838.7573	2.5	292.8	13.4	372.3	-50.5	179.98	Yes	0.02
M06-2X/6-311++G(d,p)	2006.7485	8.8	1416.1132	4.1	838.7948	2.5	288.4	17.8	369.8	-48.0	180.00	Yes	0.00
M06-2X/6-31G(d,p)	2006.5618	8.6	1413.6710	1.7	837.9107	1.6	332.9	-26.7	312.1	9.7	180.00	Yes	0.00
M06-2X/6-31+G(d,p)	2001.7245	3.7	1412.3014	0.3	836.6018	0.3	278.0	28.2	377.6	-55.8	179.99	Yes	0.01
M06-2X/6-31++G(d,p)	2001.6981	3.7	1412.3336	0.4	836.6083	0.3	274.5	31.7	381.4	-59.6	179.99	Yes	0.01
M06-2X/aug-cc-pVDZ	1999.9174	1.9	1411.4927	-0.5	836.0539	-0.2	308.1	-1.9	367.0	-45.2	180.00	Yes	0.00
M06-2X/aug-cc-pVTZ	2016.5849	18.6	1423.3360	11.4	842.9959	6.7	318.5	-12.3	383.7	-61.9	179.98	Yes	0.02
M06-2X/cc-pVDZ	2002.7737	4.8	1411.5358	-0.4	836.5816	0.3	347.1	-40.9	312.1	9.7	179.98	Yes	0.02
M06-2X/cc-pVTZ	2017.1889	19.2	1423.0174	11.1	842.9903	6.7	325.0	-18.8	364.4	-42.6	179.94	Yes	0.06
MP2/6-311G(2d,2p)	2000.1514	2.2	1416.5220	4.6	837.7125	1.4	301.0	5.2	358.8	-37.0	180.00	Yes	0.00
MP2/6-311+G(2d,2p)	1996.1020	-1.9	1417.2861	5.3	837.2749	1.0	279.7	26.5	423.5	-101.7	180.01	Yes	-0.01
MP2/6-311++G(2d,2p)	1996.0517	-1.9	1417.4463	5.5	837.3241	1.0	244.3	61.9	417.2	-95.4	180.01	Yes	-0.01
MP2/6-311G(2df,2pd)	2011.1884	13.2	1425.1979	13.2	842.6909	6.4	295.2	11.0	359.7	-37.9	179.93	Yes	0.07
MP2/6-311+G(2df,2pd)	2006.6522	8.7	1425.2066	13.2	841.9037	5.6	271.3	34.9	406.5	-84.7	180.00	Yes	0.00
MP2/6-311++G(2df,2pd)	2006.6585	8.7	1425.3283	13.4	841.9489	5.7	274.2	32.0	405.3	-83.5	180.00	Yes	0.00
MP2/6-311G(3df,3pd)	2010.2913	12.3	1425.6410	13.7	842.7080	6.4	303.1	3.1	382.2	-60.4	179.96	Yes	0.04
MP2/6-311+G(3df,3pd)	2006.8342	8.9	1425.8502	13.9	842.1781	5.9	266.5	39.7	389.4	-67.6	179.97	Yes	0.03
MP2/6-311++G(3df,3pd)	2006.8395	8.9	1425.8420	13.9	842.1758	5.9	273.7	32.5	389.2	-67.4	179.96	Yes	0.04
MP2/6-311G(df,pd)	2008.5029	10.5	1419.4563	7.5	840.5681	4.3	276.6	29.6	393.0	-71.2	177.91	No	2.09
MP2/6-311+G(df,pd)	2005.5448	7.6	1414.5150	2.5	842.3849	6.1	293.2	13.0	417.7	-95.9	171.16	No	8.84
MP2/6-311++G(df,pd)	2005.4402	7.5	1414.2446	2.3	843.0686	6.8	307.0	-0.8	404.8	-83.0	170.80	No	9.20
MP2/6-311G(d,p)	1994.1937	-3.8	1410.2776	-1.7	834.5987	-1.7	306.9	-0.7	410.8	-89.0	180.02	Yes	-0.02
MP2/6-311+G(d,p)	1991.4344	-6.5	1407.1605	-4.8	836.0273	-0.3	305.0	1.2	439.8	-118.0	172.58	No	7.42

Appendix D. 2-Acetyl-3-Methylthiophene

MP2/6-311++G(d,p)	1991.4877	-6.5	1406.2009	-5.8	836.8944	0.6	316.1	-9.9	424.8	-103.0	171.47	No	8.53
MP2/6-31G(d,p)	1998.0135	0.0	1411.1488	-0.8	835.4992	-0.8	365.0	-58.8	343.4	-21.6	180.01	Yes	0.01
MP2/6-31+G(d,p)	1991.4849	-6.5	1406.9802	-5.0	834.6421	-1.6	288.2	18.0	412.8	-91.0	174.06	No	5.94
MP2/6-31++G(d,p)	1991.3537	-6.6	1406.0562	-5.9	835.5509	-0.7	303.5	2.7	394.7	-72.9	173.11	No	6.89
MP2/aug-cc-pVDZ	1966.2899	-31.7	1398.5114	-13.5	825.7057	-10.6	271.7	34.5	400.0	-78.2	179.97	Yes	0.03
MP2/aug-cc-pVTZ	2001.9133	3.9	1422.6234	10.7	840.1936	3.9	^a		^a		180.00	Yes	0.00
MP2/cc-pVDZ	1975.7803	-22.2	1398.1949	-13.8	827.2509	-9.0	378.2	-72.0	332.7	-10.9	179.99	Yes	0.01
MP2/cc-pVTZ	2003.7456	5.8	1421.8441	9.9	840.2247	3.9	281.5	24.7	361.4	-39.6	179.96	Yes	0.04
ω B97X-D/6-311G(d,p)	2005.5701	7.6	1411.6054	-0.4	837.0132	0.7	232.4	73.8	285.7	36.1	180.00	Yes	0.00
ω B97X-D/6-311+G(d,p)	2005.5318	7.6	1411.7392	-0.2	837.0534	0.8	227.1	79.1	282.9	38.9	180.00	Yes	0.00
ω B97X-D/6-311++G(d,p)	2008.5172	10.5	1411.5709	-0.4	837.5148	1.2	248.9	57.3	243.9	77.9	179.69	Yes	0.31
ω B97X-D/aug-cc-pVDZ	1995.3205	-2.7	1406.4217	-5.5	833.4901	-2.8	268.1	38.1	290.9	30.9	179.68	Yes	0.32
ω B97X-D/aug-cc-pVTZ	2015.7562	17.8	1418.8771	6.9	841.2891	5.0	264.4	41.8	307.6	14.2	179.99	Yes	0.01
ω B97X-D/cc-pVDZ	1997.9542	0.0	1405.5094	-6.5	833.6362	-2.7	301.8	4.4	207.2	114.6	179.97	Yes	0.03
ω B97X-D/cc-pVTZ	2016.2760	18.3	1418.3646	6.4	841.1981	4.9	265.9	40.3	283.0	38.8	179.99	Yes	0.01
Experiment	1997.9755		1411.9663		836.2886		306.2		321.8				

^a Not done due to high quantum chemical cost.

Appendix D. 2-Acetyl-3-Methylthiophene

Table D.4a: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of *anti*-2A3MT given in Figure 6.4 calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V = \sum_0^i a_i f_i$.

i	f_i	MP2				B3LYP-D3BJ			
		Acetyl methyl		Ring methyl		Acetyl methyl		Ring methyl	
		$a_i /$ Hartree	$a_i /$ cm^{-1}	$a_i /$ Hartree	$a_i /$ cm^{-1}	$a_i /$ Hartree	$a_i /$ cm^{-1}	$a_i /$ Hartree	$a_i /$ cm^{-1}
0	1	−743.5337240		−743.5336636		−745.1262725		−745.1260587	
1	$\cos(3\alpha)$	0.0007375	161.9	0.0008902	195.4	0.0004204	92.3	0.0005936	130.3
2	$\cos(6\alpha)$	0.0000779	17.1	0.0002188	48.0	0.0000505	11.1	0.0000185	4.1
3	$\cos(9\alpha)$	−0.0000231	−5.2	/	/	/	/	/	/
8	$\cos(12\alpha)$	0.0000204	4.5	/	/	/	/	/	/
9	$\cos(15\alpha)$	−0.0000131	−2.9	−0.0000679	−14.9	/	/	/	/
10	$\sin(3\alpha)$	/	/	0.0000260	5.7	/	/	/	/
11	$\sin(6\alpha)$	/	/	0.0000788	17.3	/	/	/	/
12	$\sin(9\alpha)$	/	/	0.0000953	20.9	/	/	/	/
13	$\sin(12\alpha)$	/	/	0.0000787	17.3	/	/	/	/
14	$\sin(15\alpha)$	/	/	0.0000467	10.2	/	/	/	/

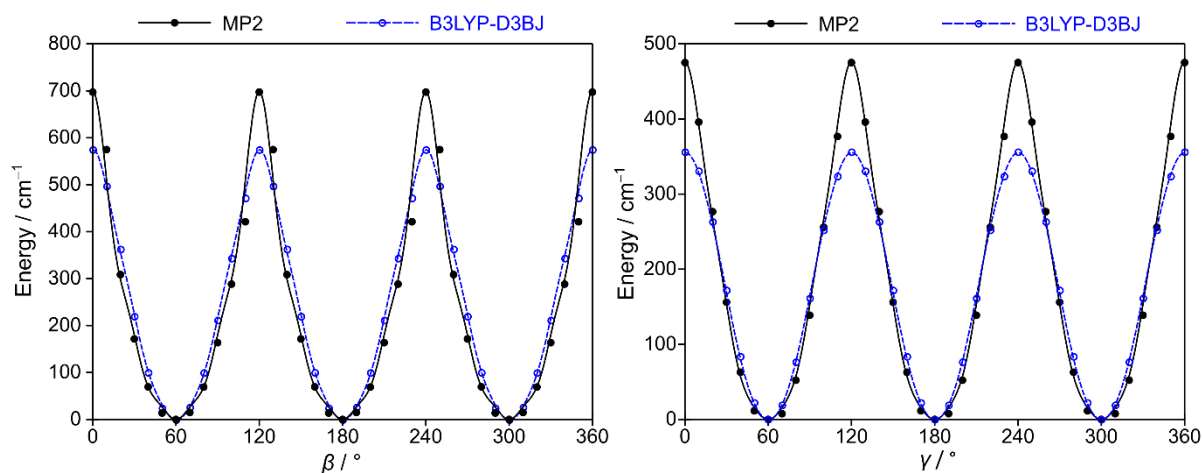


Figure D.1: Left hand side: The potential energy curves of *syn*-2A3MT obtained by rotating the acetyl methyl group about the C6–C8 bond by varying the dihedral angle β in steps of 10° . The relative energies are given in respect to the lowest energy with $E_{MP2} = -743.5325468$ Hartree and $E_{B3LYP-D3BJ} = -745.1245545$ Hartree. **Right hand side:** The potential energy curves of *syn*-2A3MT obtained by rotating the ring methyl group about the C3–C9 bond by varying the dihedral angle γ in steps of 10° . The relative energies are given in respect to the lowest energy with $E_{MP2} = -743.5325472$ Hartree and $E_{B3LYP-D3BJ} = -745.1245545$ Hartree. (Figure modified from Ref. [3])

Appendix D. 2-Acetyl-3-Methylthiophene

Table D.4b: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of *syn*-2A3MT given in Figure D.1 calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V = \sum_0^i a_i f_i$.

i	f_i	MP2				B3LYP-D3BJ			
		Acetyl methyl		Ring methyl		Acetyl methyl		Ring methyl	
		$a_i /$ Hartree	$a_i /$ cm^{-1}	$a_i /$ Hartree	$a_i /$ cm^{-1}	$a_i /$ Hartree	$a_i /$ cm^{-1}	$a_i /$ Hartree	$a_i /$ cm^{-1}
0	1	-743.5314862		-743.5317081		-745.1234391		-745.1237716	
1	$\cos 3\alpha$	0.0013406	294.2	0.0010149	222.7	0.0012334	270.7	0.0008083	177.4
2	$\cos 6\alpha$	0.0003855	84.6	0.0001921	42.2	0.0001516	33.3	0.0000247	5.4
3	$\cos 9\alpha$	0.0001822	40.0	0.0000443	9.7	0.0000527	11.6	/	/
4	$\cos 12\alpha$	0.0001168	25.6	0.0000384	8.4	0.0000327	7.2	/	/
5	$\cos 15\alpha$	0.0000682	15.0	0.0000242	5.3	0.0000253	5.6	/	/

Table D.5: Energies of *anti*-2A3MT calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) level of theory by varying the dihedral angles β and γ in a grid of 10° while all other geometry parameters were optimized. Due to symmetry, only data points in the range from 0° to 120° were calculated for both β and γ .

$\beta / ^\circ$	$\gamma / ^\circ$	$E_{\text{MP2}} / \text{Hartree}$	$E_{\text{B3LYP-D3BJ}} / \text{Hartree}$
0	0	-743.5308949	-745.1244108
0	10	-743.5310053	-745.1245229
0	20	-743.5313380	-745.1248478
0	30	-743.5318073	-745.1251934
0	40	-743.5322675	-745.1255164
0	50	-743.5325659	-745.1257406
0	60	-743.5325946	-745.1258082
0	70	-743.5323567	-745.1257017
0	80	-743.5317968	-745.1254578
0	90	-743.5314739	-745.1251398
0	100	-743.5313456	-745.1248188
0	110	-743.5310580	-745.1245226
0	120	-743.5309045	-745.1244121
10	0	-743.5313107	-745.1244953
10	10	-743.5314234	-745.1246035
10	20	-743.5317037	-745.1249227
10	30	-743.5320530	-745.1252658
10	40	-743.5324009	-745.1255879
10	50	-743.5323889	-745.1258127
10	60	-743.5323934	-745.1258816
10	70	-743.5321511	-745.1257770
10	80	-743.5326082	-745.1255354
10	90	-743.5321738	-745.1252197

Appendix D. 2-Acetyl-3-Methylthiophene

10	100	-743.5317405	-745.1249008
10	110	-743.5303962	-745.1246064
10	120	-743.5313112	-745.1244967
20	0	-743.5318274	-745.1247170
20	10	-743.5319422	-745.1248166
20	20	-743.5322217	-745.1251247
20	30	-743.5325631	-745.1254611
20	40	-743.5328849	-745.1257797
20	50	-743.5332053	-745.1260039
20	60	-743.5334138	-745.1260747
20	70	-743.5333698	-745.1259747
20	80	-743.5330873	-745.1257389
20	90	-743.5326723	-745.1254300
20	100	-743.5322518	-745.1251177
20	110	-743.5319446	-745.1248288
20	120	-743.5318282	-745.1247188
30	0	-743.5323321	-745.1249995
30	10	-743.5324519	-745.1250868
30	20	-743.5327370	-745.1253808
30	30	-743.5330768	-745.1257077
30	40	-743.5333728	-745.1260204
30	50	-743.5336499	-745.1262434
30	60	-743.5338534	-745.1263177
30	70	-743.5338286	-745.1262246
30	80	-743.5335706	-745.1259978
30	90	-743.5331749	-745.1256991
30	100	-743.5327613	-745.1253961
30	110	-743.5324513	-745.1251140
30	120	-743.5323321	-745.1250022
40	0	-743.5327074	-745.1252491
40	10	-743.5328338	-745.1253256
40	20	-743.5331319	-745.1255661
40	30	-743.5334806	-745.1258826
40	40	-743.5337606	-745.1262308
40	50	-743.5339874	-745.1264505
40	60	-743.5341824	-745.1265270
40	70	-743.5341796	-745.1264411
40	80	-743.5339477	-745.1262244
40	90	-743.5335695	-745.1259366
40	100	-743.5331598	-745.1256432
40	110	-743.5328377	-745.1253670
40	120	-743.5327077	-745.1252525
50	0	-743.5328880	-745.1253990
50	10	-743.5330208	-745.1254783
50	20	-743.5333397	-745.1257184
50	30	-743.5337150	-745.1260276

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50	40	-743.5340145	-745.1263235
50	50	-743.5341492	-745.1265346
50	60	-743.5343223	-745.1266068
50	70	-743.5343427	-745.1265642
50	80	-743.5341399	-745.1263089
50	90	-743.5337812	-745.1260281
50	100	-743.5333758	-745.1257426
50	110	-743.5330394	-745.1255152
50	120	-743.5328894	-745.1254022
60	0	-743.5329176	-745.1254399
60	10	-743.5330549	-745.1255429
60	20	-743.5333993	-745.1257901
60	30	-743.5338144	-745.1260952
60	40	-743.5341622	-745.1263811
60	50	-743.5343270	-745.1265800
60	60	-743.5342655	-745.1266401
60	70	-743.5343044	-745.1265453
60	80	-743.5341382	-745.1263283
60	90	-743.5338117	-745.1260462
60	100	-743.5334255	-745.1257623
60	110	-743.5330909	-745.1255405
60	120	-743.5329222	-745.1254412
70	0	-743.5328722	-745.1253933
70	10	-743.5329959	-745.1255106
70	20	-743.5333363	-745.1257625
70	30	-743.5337646	-745.1260688
70	40	-743.5341408	-745.1263977
70	50	-743.5343394	-745.1265903
70	60	-743.5343018	-745.1265984
70	70	-743.5341008	-745.1264921
70	80	-743.5339755	-745.1262642
70	90	-743.5337005	-745.1259741
70	100	-743.5333548	-745.1256875
70	110	-743.5330447	-745.1254730
70	120	-743.5328798	-745.1253919
80	0	-743.5326669	-745.1252425
80	10	-743.5327774	-745.1253593
80	20	-743.5331046	-745.1256598
80	30	-743.5335347	-745.1259748
80	40	-743.5339279	-745.1262669
80	50	-743.5341532	-745.1264652
80	60	-743.5341350	-745.1265162
80	70	-743.5339336	-745.1264055
80	80	-743.5337139	-745.1261701
80	90	-743.5334507	-745.1258293
80	100	-743.5331263	-745.1255373

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80	110	-743.5328340	-745.1253219
80	120	-743.5326759	-745.1252412
90	0	-743.5322813	-745.1250032
90	10	-743.5323867	-745.1251148
90	20	-743.5327049	-745.1254212
90	30	-743.5331379	-745.1257465
90	40	-743.5335474	-745.1260501
90	50	-743.5337964	-745.1262584
90	60	-743.5337962	-745.1263158
90	70	-743.5335830	-745.1262066
90	80	-743.5333190	-745.1259680
90	90	-743.5330418	-745.1256630
90	100	-743.5327244	-745.1253617
90	110	-743.5324429	-745.1250937
90	120	-743.5322906	-745.1250031
100	0	-743.5317882	-745.1247358
100	10	-743.5318936	-745.1248439
100	20	-743.5322108	-745.1251574
100	30	-743.5326519	-745.1254926
100	40	-743.5330797	-745.1258065
100	50	-743.5333514	-745.1260238
100	60	-743.5333665	-745.1260875
100	70	-743.5331448	-745.1259804
100	80	-743.5328418	-745.1257394
100	90	-743.5325430	-745.1254285
100	100	-743.5322236	-745.1251185
100	110	-743.5319459	-745.1248381
100	120	-743.5317973	-745.1247368
110	0	-743.5312945	-745.1245178
110	10	-743.5314023	-745.1246258
110	20	-743.5317252	-745.1249465
110	30	-743.5321792	-745.1252891
110	40	-743.5326258	-745.1256096
110	50	-743.5329156	-745.1258323
110	60	-743.5329415	-745.1258992
110	70	-743.5327119	-745.1257930
110	80	-743.5321598	-745.1255504
110	90	-743.5320588	-745.1252350
110	100	-743.5317320	-745.1249179
110	110	-743.5314521	-745.1246275
110	120	-743.5313034	-745.1245193
120	0	-743.5308996	-745.1244137
120	10	-743.5310101	-745.1245254
120	20	-743.5313440	-745.1248502
120	30	-743.5318140	-745.1251958
120	40	-743.5322738	-745.1255187

Appendix D. 2-Acetyl-3-Methylthiophene

120	50	-743.5325706	-745.1257429
120	60	-743.5325975	-745.1258106
120	70	-743.5323606	-745.1257043
120	80	-743.5318019	-745.1254605
120	90	-743.5314815	-745.1251425
120	100	-743.5313525	-745.1248221
120	110	-743.5310637	-745.1245262
120	120	-743.5309094	-745.1244154

Table D.6: Coefficients of the two-dimensional Fourier expansion for the potential energy surface calculated at the B3LYP-D3BJ/6-311++G(d,p) level of theory shown in Figure 6.5. Due to symmetry, only data points in the range from 0° to 120° were calculated for both β and γ . The potential is expanded as $V(\beta, \gamma) = \sum_i f_i V_i$. Max. dev. stands for maximum deviations between the fitted and the calculated values.

i	f_i	V_i / Hartree
1	1	-745.1256433
2	$\cos(3\beta)$	0.0004605
3	$\cos(3\gamma)$	-0.0006426
4	$\cos(6\beta)$	0.0000419
5	$\cos(6\gamma)$	0.0000294
6	$\cos(3\beta) \cdot \cos(3\gamma)$	-0.0000438
7	$\sin(3\beta) \cdot \sin(3\gamma)$	-0.0000276
Max. dev. (%)		4.7

Appendix D. 2-Acetyl-3-Methylthiophene

Table D.7: Observed frequencies ν_{obs} of 751 rotational transitions of *anti*-2A3MT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs} MHz	$\nu_{obs}-\nu_{calc}$ kHz
	upper level			lower level					
1	2	0	2	1	0	1	(00)	4232.2855	0.1
2	2	0	2	1	0	1	(01)	4232.1159	-1.4
3	2	0	2	1	0	1	(10)	4232.1482	-1.8
4	2	0	2	1	0	1	(11)	4231.9626	0.1
5	2	0	2	1	0	1	(12)	4232.0009	-0.2
6	5	0	5	4	0	4	(00)	9192.7136	1.7
7	5	0	5	4	0	4	(01)	9192.6138	0.0
8	5	0	5	4	0	4	(10)	9192.6462	-3.3
9	5	0	5	4	0	4	(11)	9192.5613	-0.3
10	5	0	5	4	0	4	(12)	9192.5398	-1.5
11	6	0	6	5	0	5	(00)	10857.2187	-0.5
12	6	0	6	5	0	5	(01)	10857.1174	-0.1
13	6	0	6	5	0	5	(10)	10857.1525	-0.2
14	6	0	6	5	0	5	(11)	10857.0554	0.4
15	6	0	6	5	0	5	(12)	10857.0462	-0.9
16	7	0	7	6	0	6	(00)	12527.4884	0.5
17	7	0	7	6	0	6	(01)	12527.3869	0.1
18	7	0	7	6	0	6	(10)	12527.4230	0.4
19	7	0	7	6	0	6	(12)	12527.3199	0.3
20	8	0	8	7	0	7	(00)	14199.3635	0.1
21	8	0	8	7	0	7	(01)	14199.2641	-0.4
22	8	0	8	7	0	7	(10)	14199.3013	0.0
23	8	0	8	7	0	7	(11)	14199.2028	-0.9
24	9	0	9	8	0	8	(01)	15871.5801	0.3
25	9	0	9	8	0	8	(10)	15871.6170	-0.6
26	9	0	9	8	0	8	(12)	15871.5207	0.1
27	10	0	10	9	0	9	(01)	17544.0280	2.9
28	10	0	10	9	0	9	(10)	17544.0661	2.1
29	10	0	10	9	0	9	(11)	17543.9731	1.6
30	11	0	11	10	0	10	(01)	19216.5161	-1.4
31	11	0	11	10	0	10	(10)	19216.5577	0.3
32	11	0	11	10	0	10	(12)	19216.4670	0.2
33	2	0	2	1	1	1	(00)	3646.3765	0.5
34	2	0	2	1	1	1	(01)	3646.1823	2.2
35	2	0	2	1	1	1	(10)	3646.1028	1.5
36	3	0	3	2	1	2	(00)	5649.4712	0.0
37	3	0	3	2	1	2	(01)	5649.2752	0.6
38	3	0	3	2	1	2	(10)	5649.2656	-0.7
39	4	0	4	3	1	3	(00)	7453.8340	-0.1
40	4	0	4	3	1	3	(01)	7453.6858	0.2

Appendix D. 2-Acetyl-3-Methylthiophene

41	4	0	4	3	1	3	(10)	7453.7036	0.1
42	5	0	5	4	1	4	(00)	9167.6079	0.3
43	5	0	5	4	1	4	(01)	9167.4870	0.1
44	5	0	5	4	1	4	(10)	9167.5160	0.4
45	5	0	5	4	1	4	(11)	9167.3900	1.1
46	5	0	5	4	1	4	(12)	9167.3999	−0.8
47	6	0	6	5	1	5	(00)	10851.0498	0.2
48	6	0	6	5	1	5	(01)	10850.9413	0.3
49	6	0	6	5	1	5	(10)	10850.9738	−0.3
50	6	0	6	5	1	5	(11)	10850.8655	0.1
51	7	0	7	6	1	6	(00)	12526.0686	0.0
52	7	0	7	6	1	6	(01)	12525.9661	0.5
53	7	0	7	6	1	6	(10)	12526.0020	1.2
54	7	0	7	6	1	6	(11)	12525.8986	−0.2
55	2	1	2	1	0	1	(01)	4506.8655	−2.6
56	2	1	2	1	0	1	(10)	4506.9444	−3.0
57	2	1	2	1	0	1	(11)	4507.0137	0.4
58	2	1	2	1	0	1	(12)	4506.7603	0.2
59	3	1	3	2	0	2	(00)	6015.8004	0.6
60	3	1	3	2	0	2	(01)	6015.7765	4.9
61	3	1	3	2	0	2	(10)	6015.8265	−3.5
62	3	1	3	2	0	2	(11)	6015.9079	0.5
63	3	1	3	2	0	2	(12)	6015.6960	−0.3
64	4	1	4	3	0	3	(00)	7570.6230	−0.5
65	4	1	4	3	0	3	(01)	7570.5589	0.1
66	4	1	4	3	0	3	(10)	7570.6034	−0.2
67	4	1	4	3	0	3	(11)	7570.5830	0.5
68	4	1	4	3	0	3	(12)	7570.4951	−0.2
69	5	1	5	4	0	4	(00)	9198.8813	−0.1
70	5	1	5	4	0	4	(01)	9198.7906	0.2
71	5	1	5	4	0	4	(10)	9198.8288	0.7
72	5	1	5	4	0	4	(11)	9198.7513	0.0
73	5	1	5	4	0	4	(12)	9198.7221	−0.8
74	6	1	6	5	0	5	(00)	10858.6386	0.1
75	6	1	6	5	0	5	(01)	10858.5388	0.1
76	6	1	6	5	0	5	(10)	10858.5746	0.1
77	6	1	6	5	0	5	(11)	10858.4802	0.5
78	6	1	6	5	0	5	(12)	10858.4694	−0.5
79	7	1	7	6	0	6	(00)	12527.8002	0.1
80	7	1	7	6	0	6	(01)	12527.6993	−0.2
81	7	1	7	6	0	6	(10)	12527.7355	0.0
82	7	1	7	6	0	6	(12)	12527.6340	1.3
83	6	1	5	6	0	6	(00)	8806.8396	−0.9
84	6	1	5	6	0	6	(01)	8805.3509	−6.7
85	6	1	5	6	0	6	(10)	8805.6374	−0.8
86	6	1	5	6	0	6	(12)	8804.2116	0.0

Appendix D. 2-Acetyl-3-Methylthiophene

87	3	1	3	2	1	2	(00)	5741.1574	0.9
88	3	1	3	2	1	2	(01)	5741.0203	−0.5
89	3	1	3	2	1	2	(10)	5741.0327	0.2
90	3	1	3	2	1	2	(11)	5740.8562	−0.3
91	3	1	3	2	1	2	(12)	5740.9371	−0.1
92	4	1	4	3	1	3	(00)	7478.9384	0.1
93	4	1	4	3	1	3	(01)	7478.8123	−0.3
94	4	1	4	3	1	3	(10)	7478.8371	−0.3
95	4	1	4	3	1	3	(11)	7478.6994	−0.1
96	4	1	4	3	1	3	(12)	7478.7242	0.2
97	5	1	5	4	1	4	(00)	9173.7781	0.9
98	5	1	5	4	1	4	(01)	9173.6632	−0.2
99	5	1	5	4	1	4	(10)	9173.6947	0.5
100	5	1	5	4	1	4	(11)	9173.5822	3.6
101	5	1	5	4	1	4	(12)	9173.5777	−4.6
102	6	1	6	5	1	5	(00)	10852.4686	−0.3
103	6	1	6	5	1	5	(01)	10852.3623	0.1
104	6	1	6	5	1	5	(10)	10852.3955	−0.4
105	6	1	6	5	1	5	(11)	10852.2892	−0.8
106	7	1	7	6	1	6	(00)	12526.3813	0.5
107	7	1	7	6	1	6	(01)	12526.2777	−0.6
108	7	1	7	6	1	6	(10)	12526.3134	−0.3
109	7	1	7	6	1	6	(11)	12526.2117	−0.7
110	8	1	8	7	1	7	(00)	14199.1142	−3.5
111	8	1	8	7	1	7	(01)	14199.0183	−0.1
112	8	1	8	7	1	7	(10)	14199.0554	0.3
113	8	1	8	7	1	7	(11)	14198.9537	−3.2
114	8	1	8	7	1	7	(12)	14198.9547	−0.1
115	9	1	9	8	1	8	(01)	15871.5274	0.4
116	9	1	9	8	1	8	(10)	15871.5646	−0.2
117	10	1	10	9	1	9	(00)	17544.1058	−1.4
118	10	1	10	9	1	9	(01)	17544.0125	−1.6
119	10	1	10	9	1	9	(10)	17544.0508	−2.1
120	10	1	10	9	1	9	(12)	17543.9566	−2.5
121	11	1	11	10	1	10	(00)	19216.6071	1.7
122	11	1	11	10	1	10	(01)	19216.5172	1.9
123	11	1	11	10	1	10	(10)	19216.5581	2.9
124	11	1	11	10	1	10	(11)	19216.4678	2.2
125	11	1	11	10	1	10	(12)	19216.4657	1.1
126	6	1	5	6	1	6	(00)	8805.4286	7.4
127	6	1	5	6	1	6	(01)	8803.9292	−7.2
128	6	1	5	6	1	6	(11)	8802.6739	−0.7
129	6	1	5	6	1	6	(12)	8802.7893	0.5
130	7	1	6	7	1	7	(00)	10477.1335	5.1
131	7	1	6	7	1	7	(01)	10475.4233	−4.4
132	7	1	6	7	1	7	(10)	10475.7747	2.9

Appendix D. 2-Acetyl-3-Methylthiophene

133	7	1	6	7	1	7	(11)	10474.0389	−0.1
134	7	1	6	7	1	7	(12)	10474.1050	1.5
135	2	1	1	1	1	0	(00)	5072.7073	−0.6
136	2	1	1	1	1	0	(01)	5072.1757	2.5
137	2	1	1	1	1	0	(10)	5072.2642	1.5
138	2	1	1	1	1	0	(11)	5071.6580	−0.2
139	2	1	1	1	1	0	(12)	5071.7979	−0.3
140	3	1	2	2	1	1	(00)	7382.5433	0.0
141	3	1	2	2	1	1	(01)	7381.9044	−1.1
142	3	1	2	2	1	1	(10)	7382.0010	0.9
143	3	1	2	2	1	1	(12)	7381.5952	−0.1
144	4	1	3	3	1	2	(00)	9353.7796	0.8
145	4	1	3	3	1	2	(01)	9353.3328	3.9
146	4	1	3	3	1	2	(10)	9353.4300	−0.9
147	4	1	3	3	1	2	(11)	9352.9611	0.4
148	4	1	3	3	1	2	(12)	9353.0008	−0.3
149	5	1	4	4	1	3	(00)	11007.0404	−0.3
150	5	1	4	4	1	3	(01)	11006.7565	3.3
151	5	1	4	4	1	3	(10)	11006.8630	−1.0
152	5	1	4	4	1	3	(11)	11006.6730	−0.3
153	5	1	4	4	1	3	(12)	11006.4798	0.2
154	6	1	5	5	1	4	(00)	12580.8663	0.3
155	6	1	5	5	1	4	(01)	12580.5785	−0.6
156	6	1	5	5	1	4	(11)	12580.4611	0.0
157	6	1	5	5	1	4	(12)	12580.3376	0.3
158	7	1	6	6	1	5	(00)	14198.0881	0.1
159	7	1	6	6	1	5	(01)	14197.7696	0.0
160	7	1	6	6	1	5	(10)	14197.8697	0.6
161	7	1	6	6	1	5	(11)	14197.5776	0.8
162	7	1	6	6	1	5	(12)	14197.5247	0.1
163	8	1	7	7	1	6	(00)	15849.5999	0.4
164	8	1	7	7	1	6	(01)	15849.2651	0.1
165	8	1	7	7	1	6	(10)	15849.3612	0.3
166	8	1	7	7	1	6	(11)	15849.0379	0.4
167	8	1	7	7	1	6	(12)	15849.0147	−0.5
168	9	1	8	8	1	7	(00)	17514.7589	0.2
169	9	1	8	8	1	7	(01)	17514.4191	−0.3
170	9	1	8	8	1	7	(10)	17514.5154	0.8
171	9	1	8	8	1	7	(11)	17514.1825	1.5
172	9	1	8	8	1	7	(12)	17514.1684	−1.1
173	10	1	9	9	1	8	(00)	19184.4635	−0.5
174	10	1	9	9	1	8	(01)	19184.1244	−0.2
175	10	1	9	9	1	8	(10)	19184.2215	1.2
176	11	1	10	10	1	9	(00)	20855.6698	−4.9
177	11	1	10	10	1	9	(01)	20855.3373	0.2
178	11	1	10	10	1	9	(10)	20855.4344	0.8

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179	11	1	10	10	1	9	(12)	20855.0894	−4.1
180	4	1	3	3	2	2	(00)	8233.3033	0.5
181	4	1	3	3	2	2	(01)	8232.6578	−2.7
182	4	1	3	3	2	2	(10)	8232.5161	0.1
183	4	1	3	3	2	2	(11)	8231.4335	4.4
184	4	1	3	3	2	2	(12)	8232.3191	0.1
185	5	1	4	4	2	3	(00)	10463.4999	0.9
186	5	1	4	4	2	3	(01)	10462.9248	1.5
187	5	1	4	4	2	3	(10)	10462.9158	−0.1
188	5	1	4	4	2	3	(11)	10462.1549	0.3
189	5	1	4	4	2	3	(12)	10462.5257	−0.3
190	6	1	5	5	2	4	(00)	12379.0813	0.0
191	6	1	5	5	2	4	(01)	12378.6276	0.4
192	6	1	5	5	2	4	(10)	12378.6807	0.6
193	6	1	5	5	2	4	(11)	12378.1659	0.3
194	6	1	5	5	2	4	(12)	12378.2863	0.0
195	7	1	6	6	2	5	(00)	14135.7792	0.4
196	7	1	6	6	2	5	(01)	14135.3932	0.3
197	7	1	6	6	2	5	(10)	14135.4726	0.7
198	7	1	6	6	2	5	(11)	14135.0727	0.5
199	7	1	6	6	2	5	(12)	14135.0998	0.1
200	8	1	7	7	2	6	(00)	15832.4178	0.0
201	8	1	7	7	2	6	(01)	15832.0606	0.0
202	8	1	7	7	2	6	(10)	15832.1503	0.5
203	8	1	7	7	2	6	(11)	15831.7927	0.1
204	9	1	8	8	2	7	(00)	17510.3611	0.3
205	9	1	8	8	2	7	(01)	17510.0152	0.6
206	9	1	8	8	2	7	(10)	17510.1089	1.0
207	9	1	8	8	2	7	(12)	17509.7575	−1.5
208	2	2	0	1	0	1	(00)	8256.7661	−2.0
209	2	2	0	1	0	1	(01)	8257.2698	−2.7
210	2	2	0	1	0	1	(10)	8256.9102	0.7
211	2	2	0	1	0	1	(12)	8257.9185	0.7
212	3	2	1	2	0	2	(00)	11590.9541	1.7
213	3	2	1	2	0	2	(01)	11590.3945	6.5
214	3	2	1	2	0	2	(10)	11590.4485	4.4
215	3	2	1	2	0	2	(11)	11590.1183	0.6
216	3	2	1	2	0	2	(12)	11589.6420	−0.1
217	4	2	2	3	0	3	(00)	15868.8791	−1.2
218	4	2	2	3	0	3	(11)	15866.0204	0.1
219	3	2	2	3	0	3	(11)	4580.5626	0.3
220	4	2	3	4	0	4	(00)	5812.4066	0.0
221	4	2	3	4	0	4	(01)	5811.5943	7.8
222	4	2	3	4	0	4	(10)	5811.8330	−5.4
223	4	2	3	4	0	4	(11)	5811.1012	0.9
224	4	2	3	4	0	4	(12)	5810.9371	0.4

Appendix D. 2-Acetyl-3-Methylthiophene

225	5	2	4	5	0	5	(00)	7284.9779	−0.4
226	5	2	4	5	0	5	(01)	7283.8554	7.4
227	5	2	4	5	0	5	(10)	7284.1061	−4.7
228	5	2	4	5	0	5	(11)	7282.9897	1.0
229	5	2	4	5	0	5	(12)	7282.9704	−2.0
230	6	2	5	6	0	6	(00)	8869.1493	−0.5
231	6	2	5	6	0	6	(01)	8867.7413	6.9
232	6	2	5	6	0	6	(10)	8868.0335	−1.9
233	6	2	5	6	0	6	(11)	8866.6031	−0.8
234	6	2	5	6	0	6	(12)	8866.6362	−0.3
235	7	2	6	7	0	7	(00)	10494.6229	0.5
236	7	2	6	7	0	7	(01)	10492.9422	−2.6
237	7	2	6	7	0	7	(10)	10493.2931	−2.7
238	7	2	6	7	0	7	(11)	10491.6008	3.2
239	7	2	6	7	0	7	(12)	10491.6372	−1.9
240	8	2	7	8	0	8	(00)	12132.0747	0.0
241	8	2	7	8	0	8	(01)	12130.1447	−0.9
242	8	2	7	8	0	8	(10)	12130.5509	−0.1
243	8	2	7	8	0	8	(11)	12128.6043	1.4
244	8	2	7	8	0	8	(12)	12128.6389	−2.3
245	9	2	8	9	0	9	(00)	13771.8310	3.9
246	9	2	8	9	0	9	(01)	13769.6543	4.5
247	9	2	8	9	0	9	(10)	13770.1152	4.0
248	9	2	8	9	0	9	(11)	13767.9216	4.0
249	9	2	8	9	0	9	(12)	13767.9506	0.0
250	10	2	9	10	0	10	(00)	15411.3562	1.9
251	10	2	9	10	0	10	(10)	15409.4466	−0.6
252	10	2	9	10	0	10	(11)	15407.0098	1.5
253	10	2	9	10	0	10	(12)	15407.0341	−2.5
254	11	2	10	11	0	11	(00)	17050.2288	0.0
255	11	2	10	11	0	11	(01)	17047.5551	−0.8
256	11	2	10	11	0	11	(10)	17048.1297	−0.5
257	11	2	10	11	0	11	(11)	17045.4492	3.8
258	11	2	10	11	0	11	(12)	17045.4696	−0.3
259	12	2	11	12	0	12	(00)	18688.5131	0.0
260	12	2	11	12	0	12	(01)	18685.5951	3.1
261	12	2	11	12	0	12	(10)	18686.2273	4.5
262	13	2	12	13	0	13	(00)	20326.3331	−3.8
263	13	2	12	13	0	13	(01)	20323.1639	−3.4
264	13	2	12	13	0	13	(10)	20323.8534	−1.1
265	2	2	0	1	1	1	(00)	7670.8636	4.9
266	2	2	0	1	1	1	(01)	7671.3366	1.3
267	2	2	0	1	1	1	(10)	7670.8637	2.8
268	2	2	0	1	1	1	(11)	7670.5892	0.5
269	2	2	0	1	1	1	(12)	7672.0824	1.0
270	3	2	1	2	1	2	(00)	11316.3074	−1.7

Appendix D. 2-Acetyl-3-Methylthiophene

271	3	2	1	2	1	2	(01)	11315.6314	−5.7
272	3	2	1	2	1	2	(10)	11315.6523	5.7
273	3	2	1	2	1	2	(11)	11315.0661	−0.8
274	3	2	1	2	1	2	(12)	11314.8827	−0.4
275	4	2	2	3	1	3	(00)	15777.1930	−2.0
276	4	2	2	3	1	3	(10)	15775.7346	−4.8
277	4	2	2	3	1	3	(11)	15774.1345	−2.7
278	4	2	2	4	1	3	(10)	3054.1484	2.8
279	4	2	2	4	1	3	(11)	3054.0290	0.1
280	2	2	1	1	1	0	(00)	6830.4359	0.4
281	2	2	1	1	1	0	(01)	6829.2392	−5.1
282	2	2	1	1	1	0	(10)	6830.1026	−2.0
283	2	2	1	1	1	0	(11)	6829.7245	−0.2
284	2	2	1	1	1	0	(12)	6828.1058	−1.1
285	3	2	2	2	1	1	(00)	8503.0133	−6.0
286	3	2	2	2	1	1	(01)	8502.5707	−3.2
287	3	2	2	2	1	1	(10)	8502.9129	−2.2
288	3	2	2	2	1	1	(11)	8502.6618	0.4
289	3	2	2	2	1	1	(12)	8502.2781	0.7
290	4	2	3	3	1	2	(00)	9897.3207	0.2
291	4	2	3	3	1	2	(01)	9897.1662	7.4
292	4	2	3	3	1	2	(10)	9897.3756	−3.5
293	4	2	3	3	1	2	(12)	9896.9555	0.7
294	5	2	4	4	1	3	(01)	11208.7097	4.5
295	5	2	4	4	1	3	(10)	11208.8670	−3.0
296	5	2	4	4	1	3	(11)	11208.9694	0.6
297	5	2	4	4	1	3	(12)	11208.5307	0.1
298	6	2	5	5	1	4	(00)	12643.1754	0.1
299	6	2	5	5	1	4	(10)	12643.0835	0.2
300	6	2	5	5	1	4	(11)	12642.9657	0.0
301	6	2	5	5	1	4	(12)	12642.7622	0.0
302	7	2	6	6	1	5	(00)	14215.2700	0.3
303	7	2	6	6	1	5	(01)	14214.9732	−0.7
304	7	2	6	6	1	5	(10)	14215.0808	0.6
305	7	2	6	6	1	5	(11)	14214.8219	0.1
306	7	2	6	6	1	5	(12)	14214.7465	−0.6
307	8	2	7	7	1	6	(00)	15853.9970	−0.4
308	8	2	7	7	1	6	(01)	15853.6696	−0.1
309	8	2	7	7	1	6	(10)	15853.7682	0.6
310	8	2	7	7	1	6	(11)	15853.4542	0.2
311	8	2	7	7	1	6	(12)	15853.4261	0.3
312	9	2	8	8	1	7	(00)	17515.8253	−0.9
313	9	2	8	8	1	7	(01)	17515.4888	0.1
314	9	2	8	8	1	7	(10)	17515.5851	0.6
315	9	2	8	8	1	7	(11)	17515.2538	0.3
316	9	2	8	8	1	7	(12)	17515.2400	−0.6

Appendix D. 2-Acetyl-3-Methylthiophene

317	2	2	1	2	1	2	(00)	3485.2590	−2.0
318	2	2	1	2	1	2	(01)	3484.2986	−1.1
319	2	2	1	2	1	2	(10)	3485.0327	−4.5
320	2	2	1	2	1	2	(11)	3484.9411	0.2
321	3	2	2	3	1	3	(01)	4488.7770	−4.8
322	3	2	2	3	1	3	(10)	4489.0729	−5.0
323	3	2	2	3	1	3	(11)	4488.6789	−0.3
324	3	2	2	3	1	3	(12)	4488.2483	0.8
325	4	2	3	4	1	4	(00)	5787.3017	−0.6
326	4	2	3	4	1	4	(01)	5786.4630	3.4
327	4	2	3	4	1	4	(10)	5786.6977	−6.8
328	4	2	3	4	1	4	(11)	5785.9262	−1.3
329	4	2	3	4	1	4	(12)	5785.7951	−1.0
330	5	2	4	5	1	5	(00)	7278.8097	0.9
331	5	2	4	5	1	5	(01)	7277.6748	3.4
332	5	2	4	5	1	5	(10)	7277.9273	−4.9
333	5	2	4	5	1	5	(11)	7276.8008	1.8
334	6	2	5	6	1	6	(01)	8866.3187	5.6
335	8	2	7	8	1	8	(00)	12132.0079	−0.3
336	9	2	8	9	1	9	(00)	13771.8122	−1.1
337	9	2	8	9	1	9	(01)	13769.6288	−7.1
338	9	2	8	9	1	9	(10)	13770.0941	−3.3
339	3	2	1	2	2	0	(00)	7566.4702	0.4
340	3	2	1	2	2	0	(10)	7565.6872	2.6
341	3	2	1	2	2	0	(11)	7565.1756	0.1
342	3	2	1	2	2	0	(12)	7563.7260	0.6
343	4	2	2	3	2	1	(00)	10202.0421	−0.3
344	4	2	2	3	2	1	(01)	10200.9788	0.2
345	4	2	2	3	2	1	(10)	10201.1251	−0.2
346	4	2	2	3	2	1	(11)	10199.9262	−0.6
347	4	2	2	3	2	1	(12)	10200.1975	0.5
348	5	2	3	4	2	2	(00)	12551.7325	−0.2
349	5	2	3	4	2	2	(01)	12550.6702	−0.7
350	5	2	3	4	2	2	(10)	12550.8333	0.9
351	5	2	3	4	2	2	(11)	12549.4537	−0.6
352	5	2	3	4	2	2	(12)	12550.0887	1.4
353	6	2	4	5	2	3	(00)	14501.8876	0.5
354	6	2	4	5	2	3	(01)	14501.1652	−0.6
355	6	2	4	5	2	3	(10)	14501.3474	2.9
356	6	2	4	5	2	3	(11)	14500.5934	0.1
357	6	2	4	5	2	3	(12)	14500.6525	0.1
358	7	2	5	6	2	4	(00)	16109.8504	0.7
359	7	2	5	6	2	4	(01)	16109.3808	0.1
360	7	2	5	6	2	4	(10)	16109.5720	0.0
361	7	2	5	6	2	4	(11)	16109.2395	−0.1
362	7	2	5	6	2	4	(12)	16108.9659	−0.2

Appendix D. 2-Acetyl-3-Methylthiophene

363	8	2	6	7	2	5	(00)	17634.4113	−0.4
364	8	2	6	7	2	5	(01)	17633.9431	0.3
365	8	2	6	7	2	5	(10)	17634.1252	−0.2
366	8	2	6	7	2	5	(11)	17633.7532	0.6
367	8	2	6	7	2	5	(12)	17633.5606	0.1
368	9	2	7	8	2	6	(00)	19218.0156	−5.0
369	9	2	7	8	2	6	(01)	19217.4935	−0.6
370	9	2	7	8	2	6	(10)	19217.6624	0.7
371	9	2	7	8	2	6	(11)	19217.1791	0.2
372	9	2	7	8	2	6	(12)	19217.0915	−0.2
373	10	2	8	9	2	7	(00)	20852.5157	0.4
374	10	2	8	9	2	7	(01)	20851.9552	−0.1
375	10	2	8	9	2	7	(10)	20852.1140	−0.5
376	10	2	8	9	2	7	(11)	20851.5728	−1.1
377	10	2	8	9	2	7	(12)	20851.5370	1.8
378	11	2	9	10	2	8	(00)	22509.7142	−0.3
379	11	2	9	10	2	8	(01)	22509.1413	−0.1
380	11	2	9	10	2	8	(10)	22509.2976	0.1
381	11	2	9	10	2	8	(11)	22508.7348	0.4
382	11	2	9	10	2	8	(12)	22508.7141	−0.5
383	3	2	2	2	2	1	(00)	6745.2935	1.9
384	3	2	2	2	2	1	(01)	6745.5043	1.4
385	3	2	2	2	2	1	(10)	6745.0731	−0.1
386	3	2	2	2	2	1	(11)	6744.5951	0.2
387	3	2	2	2	2	1	(12)	6745.9681	−0.6
388	4	2	3	3	2	2	(00)	8776.8446	0.1
389	4	2	3	3	2	2	(01)	8776.4904	0.0
390	4	2	3	3	2	2	(10)	8776.4645	0.4
391	4	2	3	3	2	2	(11)	8775.9477	−0.1
392	4	2	3	3	2	2	(12)	8776.2728	0.2
393	5	2	4	4	2	3	(00)	10665.2843	0.7
394	5	2	4	4	2	3	(01)	10664.8755	0.3
395	5	2	4	4	2	3	(10)	10664.9219	0.1
396	5	2	4	4	2	3	(11)	10664.4500	−0.1
397	5	2	4	4	2	3	(12)	10664.5762	−0.8
398	6	2	5	5	2	4	(00)	12441.3907	0.1
399	6	2	5	5	2	4	(01)	12441.0041	0.2
400	6	2	5	5	2	4	(10)	12441.0777	0.3
401	6	2	5	5	2	4	(11)	12440.6723	2.1
402	6	2	5	5	2	4	(12)	12440.7097	−1.5
403	7	2	6	6	2	5	(00)	14152.9596	−0.9
404	7	2	6	6	2	5	(01)	14152.5968	−0.4
405	7	2	6	6	2	5	(10)	14152.6831	0.2
406	7	2	6	6	2	5	(11)	14152.3164	−0.8
407	7	2	6	6	2	5	(12)	14152.3228	0.6
408	8	2	7	7	2	6	(00)	15836.8161	0.4

Appendix D. 2-Acetyl-3-Methylthiophene

409	8	2	7	7	2	6	(01)	15836.4650	−0.3
410	8	2	7	7	2	6	(10)	15836.5561	−0.5
411	8	2	7	7	2	6	(11)	15836.2095	0.5
412	9	2	8	8	2	7	(00)	17511.4282	−0.1
413	9	2	8	8	2	7	(01)	17511.0841	0.1
414	9	2	8	8	2	7	(10)	17511.1785	0.7
415	10	2	9	9	2	8	(00)	19183.6437	−1.7
416	10	2	9	9	2	8	(01)	19183.3028	−1.9
417	10	2	9	9	2	8	(10)	19183.4003	0.4
418	10	2	9	9	2	8	(11)	19183.0638	1.6
419	10	2	9	9	2	8	(12)	19183.0549	−1.3
420	11	2	10	10	2	9	(00)	20855.4860	3.9
421	11	2	10	10	2	9	(01)	20855.1447	0.6
422	5	2	3	4	3	2	(00)	9973.1967	−0.8
423	5	2	3	4	3	2	(01)	9972.5784	−7.9
424	5	2	3	4	3	2	(10)	9971.7904	3.9
425	5	2	3	4	3	2	(11)	9969.9060	−0.8
426	5	2	3	4	3	2	(12)	9972.4448	0.6
427	6	2	4	5	3	3	(00)	12876.3128	1.1
428	6	2	4	5	3	3	(01)	12875.1335	0.6
429	6	2	4	5	3	3	(10)	12874.9042	−0.7
430	6	2	4	5	3	3	(11)	12873.1054	−0.2
431	6	2	4	5	3	3	(12)	12874.3476	−0.3
432	7	2	5	6	3	4	(00)	15296.9869	0.0
433	7	2	5	6	3	4	(01)	15295.9822	1.0
434	7	2	5	6	3	4	(10)	15295.9620	0.2
435	7	2	5	6	3	4	(11)	15294.6776	−0.4
436	7	2	5	6	3	4	(12)	15295.2353	1.1
437	8	2	6	7	3	5	(00)	17312.4490	0.9
438	8	2	6	7	3	5	(01)	17311.6628	−0.1
439	8	2	6	7	3	5	(10)	17311.7455	1.0
440	8	2	6	7	3	5	(11)	17310.8601	−1.7
441	8	2	6	7	3	5	(12)	17311.0581	1.3
442	9	2	7	8	3	6	(00)	19110.5861	−0.2
443	9	2	7	8	3	6	(01)	19109.9268	1.5
444	9	2	7	8	3	6	(10)	19110.0530	0.6
445	9	2	7	8	3	6	(11)	19109.3680	1.5
446	9	2	7	8	3	6	(12)	19109.4148	−1.5
447	10	2	8	9	3	7	(00)	20820.4574	0.6
448	10	2	8	9	3	7	(01)	20819.8491	0.2
449	10	2	8	9	3	7	(10)	20819.9938	−0.1
450	10	2	8	9	3	7	(12)	20819.3865	−1.1
451	3	3	0	2	1	1	(00)	13098.6875	−0.4
452	3	3	0	2	1	1	(10)	13100.2137	−1.9
453	3	3	0	2	1	1	(12)	13109.5481	−1.8
454	4	3	1	3	1	2	(00)	15501.4831	−0.1

Appendix D. 2-Acetyl-3-Methylthiophene

455	4	3	1	3	1	2	(01)	15501.7134	-2.2
456	4	3	1	3	1	2	(11)	15501.4072	0.7
457	4	3	1	3	1	2	(12)	15502.0388	1.1
458	5	3	2	4	1	3	(00)	18786.9059	0.5
459	5	3	2	4	1	3	(01)	18785.8595	-2.2
460	5	3	2	4	1	3	(10)	18785.9664	5.0
461	5	3	2	4	1	3	(11)	18785.3150	0.9
462	5	3	2	4	1	3	(12)	18784.5231	0.3
463	8	3	6	8	1	7	(00)	10324.2151	-2.3
464	8	3	6	8	1	7	(01)	10322.5180	3.0
465	8	3	6	8	1	7	(10)	10322.8504	1.3
466	8	3	6	8	1	7	(11)	10321.1355	2.9
467	8	3	6	8	1	7	(12)	10321.1595	-1.8
468	9	3	7	9	1	8	(00)	11952.1025	-0.9
469	9	3	7	9	1	8	(01)	11950.1289	1.6
470	9	3	7	9	1	8	(10)	11950.5055	-1.9
471	9	3	7	9	1	8	(11)	11948.5098	2.3
472	9	3	7	9	1	8	(12)	11948.5543	-1.4
473	10	3	8	10	1	9	(00)	13596.9537	-3.7
474	10	3	8	10	1	9	(01)	13594.7281	0.1
475	10	3	8	10	1	9	(10)	13595.1625	0.5
476	11	3	9	11	1	10	(00)	15244.4531	2.2
477	11	3	9	11	1	10	(01)	15241.9770	1.7
478	11	3	9	11	1	10	(10)	15242.4682	2.5
479	11	3	9	11	1	10	(11)	15239.9717	1.5
480	11	3	9	11	1	10	(12)	15240.0073	-3.4
481	3	3	0	2	2	1	(00)	11340.9598	-0.5
482	3	3	0	2	2	1	(01)	11346.4603	-2.7
483	3	3	0	2	2	1	(10)	11342.3747	1.1
484	3	3	0	2	2	1	(11)	11341.7012	1.0
485	3	3	0	2	2	1	(12)	11353.2430	1.8
486	4	3	1	3	2	2	(00)	14381.0133	6.1
487	4	3	1	3	2	2	(01)	14381.0392	-7.9
488	4	3	1	3	2	2	(10)	14380.5776	1.9
489	4	3	1	3	2	2	(11)	14379.8757	0.8
490	4	3	1	3	2	2	(12)	14381.3567	1.2
491	5	3	2	4	2	3	(00)	18243.3628	-0.9
492	5	3	2	4	2	3	(11)	18240.7955	0.1
493	5	3	2	4	2	3	(12)	18240.5724	3.2
494	3	3	0	2	2	0	(01)	11080.3554	-2.9
495	3	3	0	2	2	0	(10)	11077.4500	1.2
496	3	3	0	2	2	0	(12)	11085.3023	2.7
497	3	3	1	2	2	0	(00)	10990.2386	0.5
498	3	3	1	2	2	0	(01)	10983.6737	0.5
499	3	3	1	2	2	0	(10)	10988.4347	1.6
500	3	3	1	2	2	0	(11)	10988.0280	1.2

Appendix D. 2-Acetyl-3-Methylthiophene

501	3	3	1	2	2	0	(12)	10976.5202	−0.3
502	4	3	2	3	2	1	(00)	12780.5793	1.7
503	4	3	2	3	2	1	(01)	12779.0686	5.3
504	4	3	2	3	2	1	(10)	12780.1712	0.0
505	4	3	2	3	2	1	(11)	12779.4749	0.6
506	4	3	2	3	2	1	(12)	12777.8394	−0.7
507	5	3	3	4	2	2	(00)	14177.3107	2.6
508	5	3	3	4	2	2	(01)	14176.7074	3.6
509	5	3	3	4	2	2	(10)	14177.2729	0.9
510	5	3	3	4	2	2	(11)	14176.9412	−0.9
511	5	3	3	4	2	2	(12)	14176.3904	−1.4
512	6	3	4	5	2	3	(01)	15314.5709	5.6
513	6	3	4	5	2	3	(10)	15314.9515	−3.2
514	6	3	4	5	2	3	(11)	15315.1529	−2.1
515	6	3	4	5	2	3	(12)	15314.3830	−1.3
516	7	3	5	6	2	4	(01)	16431.6535	−7.2
517	7	3	5	6	2	4	(10)	16431.9514	−1.5
518	7	3	5	6	2	4	(11)	16432.1341	3.6
519	7	3	5	6	2	4	(12)	16431.4738	3.9
520	8	3	6	7	2	5	(00)	17741.8456	−0.4
521	8	3	6	7	2	5	(01)	17741.5105	−1.1
522	8	3	6	7	2	5	(10)	17741.7353	0.6
523	3	3	1	2	2	1	(01)	11249.7775	−0.4
524	3	3	1	2	2	1	(10)	11253.3592	1.3
525	3	3	1	2	2	1	(11)	11252.9777	0.4
526	3	3	1	2	2	1	(12)	11244.4618	−0.3
527	7	3	5	7	2	6	(00)	8736.7508	−2.0
528	7	3	5	7	2	6	(01)	8735.3428	−1.1
529	7	3	5	7	2	6	(11)	8734.2505	−0.4
530	7	3	5	7	2	6	(12)	8734.2237	1.7
531	8	3	6	8	2	7	(00)	10319.8187	−0.8
532	8	3	6	8	2	7	(01)	10318.1058	−4.4
533	8	3	6	8	2	7	(10)	10318.4425	0.1
534	8	3	6	8	2	7	(11)	10316.7164	0.3
535	8	3	6	8	2	7	(12)	10316.7514	0.7
536	9	3	7	9	2	8	(00)	11951.0340	−1.9
537	9	3	7	9	2	8	(01)	11949.0593	1.3
538	9	3	7	9	2	8	(10)	11949.4370	−0.5
539	9	3	7	9	2	8	(11)	11947.4347	−0.3
540	9	3	7	9	2	8	(12)	11947.4827	−1.9
541	10	3	8	10	2	9	(00)	13596.7117	3.3
542	10	3	8	10	2	9	(01)	13594.4785	−0.1
543	4	3	1	3	3	0	(00)	9785.3385	−0.1
544	4	3	1	3	3	0	(01)	9780.0828	−4.2
545	4	3	1	3	3	0	(10)	9783.2739	−1.3
546	4	3	1	3	3	0	(11)	9782.7683	−1.3

Appendix D. 2-Acetyl-3-Methylthiophene

547	4	3	1	3	3	0	(12)	9774.0841	1.1
548	5	3	2	4	3	1	(00)	12639.2005	−0.4
549	5	3	2	4	3	1	(01)	12637.4733	−1.8
550	5	3	2	4	3	1	(10)	12637.9016	0.0
551	5	3	2	4	3	1	(11)	12636.8689	0.7
552	5	3	2	4	3	1	(12)	12635.4860	−0.3
553	6	3	3	5	3	2	(00)	15365.3947	0.2
554	6	3	3	5	3	2	(01)	15363.7956	3.1
555	6	3	3	5	3	2	(10)	15363.9866	−0.7
556	6	3	3	5	3	2	(11)	15362.1949	1.4
557	6	3	3	5	3	2	(12)	15362.5798	1.4
558	7	3	4	6	3	3	(00)	17742.3367	−0.4
559	7	3	4	6	3	3	(01)	17740.8580	0.8
560	7	3	4	6	3	3	(10)	17741.0867	1.2
561	7	3	4	6	3	3	(11)	17739.2098	−0.5
562	7	3	4	6	3	3	(12)	17739.9995	−1.3
563	8	3	5	7	3	4	(00)	19669.3752	−0.2
564	8	3	5	7	3	4	(01)	19668.3964	0.8
565	8	3	5	7	3	4	(10)	19668.6582	1.4
566	8	3	5	7	3	4	(11)	19667.6326	0.1
567	8	3	5	7	3	4	(12)	19667.7207	0.6
568	9	3	6	8	3	5	(00)	21230.5187	0.4
569	9	3	6	8	3	5	(01)	21229.8858	0.0
570	9	3	6	8	3	5	(10)	21230.1644	−0.6
571	9	3	6	8	3	5	(11)	21229.7050	1.3
572	9	3	6	8	3	5	(12)	21229.3621	1.4
573	10	3	7	9	3	6	(00)	22704.8474	0.6
574	10	3	7	9	3	6	(10)	22704.4731	−5.5
575	10	3	7	9	3	6	(12)	22703.7114	−5.2
576	4	3	2	3	3	1	(00)	9356.8105	1.3
577	4	3	2	3	3	1	(01)	9360.6227	−0.1
578	4	3	2	3	3	1	(10)	9357.4222	−0.5
579	4	3	2	3	3	1	(11)	9356.6233	0.2
580	4	3	2	3	3	1	(12)	9365.0455	0.5
581	5	3	3	4	3	2	(00)	11598.7729	0.0
582	5	3	3	4	3	2	(01)	11598.6196	0.4
583	5	3	3	4	3	2	(10)	11598.2262	0.1
584	5	3	3	4	3	2	(11)	11597.3951	0.5
585	5	3	3	4	3	2	(12)	11598.7485	−0.2
586	6	3	4	5	3	3	(00)	13689.1748	0.3
587	6	3	4	5	3	3	(01)	13688.5332	0.7
588	6	3	4	5	3	3	(10)	13688.5151	−0.1
589	6	3	4	5	3	3	(11)	13687.6664	−0.8
590	6	3	4	5	3	3	(12)	13688.0795	−0.3
591	7	3	5	6	3	4	(00)	15618.9507	0.2
592	7	3	5	6	3	4	(01)	15618.2615	0.4

Appendix D. 2-Acetyl-3-Methylthiophene

593	7	3	5	6	3	4	(10)	15618.3427	0.0
594	7	3	5	6	3	4	(11)	15617.5687	−0.1
595	7	3	5	6	3	4	(12)	15617.7375	−0.5
596	8	3	6	7	3	5	(00)	17419.8824	0.0
597	8	3	6	7	3	5	(01)	17419.2318	0.1
598	8	3	6	7	3	5	(10)	17419.3545	0.6
599	8	3	6	7	3	5	(11)	17418.6738	−0.4
600	8	3	6	7	3	5	(12)	17418.7321	0.0
601	9	3	7	8	3	6	(00)	19142.6452	0.4
602	9	3	7	8	3	6	(01)	19142.0310	−0.8
603	9	3	7	8	3	6	(10)	19142.1777	4.8
604	9	3	7	8	3	6	(11)	19141.5551	−0.8
605	9	3	7	8	3	6	(12)	19141.5649	1.0
606	10	3	8	9	3	7	(00)	20829.3174	−0.5
607	10	3	8	9	3	7	(01)	20828.7243	−1.0
608	10	3	8	9	3	7	(10)	20828.8749	0.1
609	10	3	8	9	3	7	(11)	20828.2876	1.1
610	10	3	8	9	3	7	(12)	20828.2769	−1.0
611	11	3	9	10	3	8	(00)	22503.1692	0.9
612	11	3	9	10	3	8	(01)	22502.5841	−0.3
613	4	4	0	3	3	0	(01)	15138.0929	−3.6
614	4	4	0	3	3	0	(10)	15129.7573	−1.6
615	4	4	0	3	3	0	(11)	15128.5400	0.3
616	4	4	0	3	3	0	(12)	15146.3149	0.5
617	4	4	0	3	3	1	(00)	15210.0287	1.7
618	4	4	0	3	3	1	(01)	15234.7825	1.0
619	4	4	0	3	3	1	(10)	15218.7712	−3.4
620	4	4	0	3	3	1	(11)	15217.2560	−6.6
621	4	4	0	3	3	1	(12)	15255.0861	−7.4
622	5	4	1	4	3	2	(00)	17835.1800	0.1
623	5	4	1	4	3	2	(10)	17835.9356	2.1
624	5	4	1	4	3	2	(11)	17834.8994	−0.8
625	5	4	1	4	3	2	(12)	17844.7921	4.4
626	6	4	2	5	3	3	(00)	21026.0083	−2.2
627	6	4	2	5	3	3	(01)	21025.5887	−0.8
628	6	4	2	5	3	3	(10)	21025.0620	1.5
629	6	4	2	5	3	3	(11)	21023.8516	0.1
630	6	4	2	5	3	3	(12)	21025.4321	3.0
631	4	4	1	3	3	0	(00)	15100.8831	0.6
632	4	4	1	3	3	0	(01)	15074.7330	−3.6
633	4	4	1	3	3	0	(10)	15091.6796	−3.2
634	5	4	2	4	3	1	(00)	17134.5264	−2.1
635	5	4	2	4	3	1	(01)	17128.7100	−0.5
636	5	4	2	4	3	1	(10)	17132.9469	2.0
637	5	4	2	4	3	1	(11)	17132.1560	1.7
638	5	4	2	4	3	1	(12)	17122.3606	−3.7

Appendix D. 2-Acetyl-3-Methylthiophene

639	6	4	3	5	3	2	(00)	18713.3342	2.8
640	6	4	3	5	3	2	(01)	18711.5414	3.4
641	6	4	3	5	3	2	(10)	18712.9536	3.3
642	6	4	3	5	3	2	(11)	18712.0422	1.7
643	6	4	3	5	3	2	(12)	18710.2697	-2.2
644	7	4	4	6	3	3	(00)	19856.7345	-2.4
645	7	4	4	6	3	3	(01)	19856.0647	-3.7
646	7	4	4	6	3	3	(10)	19856.8829	-4.0
647	7	4	4	6	3	3	(11)	19856.5706	1.7
648	7	4	4	6	3	3	(12)	19855.8647	-0.5
649	8	4	5	7	3	4	(11)	20753.5887	0.8
650	8	4	5	7	3	4	(12)	20752.5895	2.0
651	4	4	1	3	3	1	(01)	15171.4226	1.0
652	4	4	1	3	3	1	(10)	15180.7002	1.7
653	4	4	1	3	3	1	(12)	15162.7660	-0.6
654	5	4	1	4	4	0	(00)	11981.9640	1.9
655	5	4	1	4	4	0	(01)	11965.0642	0.2
656	5	4	1	4	4	0	(10)	11974.5836	2.1
657	5	4	1	4	4	0	(11)	11974.2610	0.3
658	5	4	1	4	4	0	(12)	11954.7415	2.3
659	6	4	2	5	4	1	(00)	14789.6038	0.3
660	6	4	2	5	4	1	(01)	14784.9868	0.9
661	6	4	2	5	4	1	(10)	14787.3516	-1.5
662	6	4	2	5	4	1	(11)	14786.3457	-0.3
663	6	4	2	5	4	1	(12)	14779.3875	-2.7
664	7	4	3	6	4	2	(00)	17749.5854	-0.1
665	7	4	3	6	4	2	(01)	17747.2810	2.4
666	7	4	3	6	4	2	(10)	17747.7160	0.6
667	7	4	3	6	4	2	(11)	17746.1255	1.1
668	7	4	3	6	4	2	(12)	17744.6945	-0.2
669	8	4	4	7	4	3	(00)	20549.1618	-0.4
670	8	4	4	7	4	3	(01)	20547.0144	1.1
671	8	4	4	7	4	3	(10)	20547.2495	-0.4
672	8	4	4	7	4	3	(11)	20544.8571	-0.2
673	8	4	4	7	4	3	(12)	20545.3421	-3.9
674	5	4	1	4	4	1	(10)	12012.6550	-2.6
675	5	4	1	4	4	1	(11)	12011.0132	0.8
676	5	4	1	4	4	1	(12)	12047.0634	-2.7
677	5	4	2	4	4	0	(01)	11770.6982	-2.8
678	5	4	2	4	4	0	(10)	11786.4586	-2.6
679	5	4	2	4	4	0	(11)	11786.3796	-4.6
680	5	4	2	4	4	0	(12)	11750.1271	-5.9
681	5	4	2	4	4	1	(00)	11818.9862	1.6
682	5	4	2	4	4	1	(01)	11834.0581	-2.9
683	5	4	2	4	4	1	(10)	11824.5328	-4.5
684	5	4	2	4	4	1	(11)	11823.1322	-3.7

Appendix D. 2-Acetyl-3-Methylthiophene

685	5	4	2	4	4	1	(12)	11842.4587	-1.1
686	6	4	3	5	4	2	(00)	14218.0049	1.1
687	6	4	3	5	4	2	(01)	14220.3030	0.5
688	6	4	3	5	4	2	(10)	14217.9063	-0.7
689	6	4	3	5	4	2	(11)	14216.7544	0.0
690	6	4	3	5	4	2	(12)	14223.3955	1.6
691	7	4	4	6	4	3	(00)	16508.7994	-0.7
692	7	4	4	6	4	3	(01)	16508.3236	0.7
693	7	4	4	6	4	3	(10)	16507.9249	1.0
694	7	4	4	6	4	3	(11)	16506.7206	-1.3
695	7	4	4	6	4	3	(12)	16508.1713	-0.4
696	8	4	5	7	4	4	(00)	18638.3655	-0.4
697	8	4	5	7	4	4	(01)	18637.4243	0.2
698	8	4	5	7	4	4	(11)	18636.2308	1.4
699	8	4	5	7	4	4	(12)	18636.7261	2.9
700	9	4	6	8	4	5	(00)	20596.3053	0.7
701	9	4	6	8	4	5	(01)	20595.3287	-0.9
702	9	4	6	8	4	5	(10)	20595.4474	0.8
703	9	4	6	8	4	5	(11)	20594.3684	1.4
704	9	4	6	8	4	5	(12)	20594.5764	0.0
705	10	4	7	9	4	6	(00)	22414.1583	-0.1
706	10	4	7	9	4	6	(01)	22413.2428	0.1
707	10	4	7	9	4	6	(10)	22413.4136	-0.5
708	10	4	7	9	4	6	(11)	22412.4612	0.3
709	10	4	7	9	4	6	(12)	22412.5366	0.5
710	9	5	5	9	3	6	(00)	9302.9814	1.1
711	9	5	5	9	3	6	(01)	9302.2475	-1.0
712	9	5	5	9	3	6	(10)	9302.9816	0.2
713	9	5	5	9	3	6	(12)	9301.5774	-1.3
714	10	5	6	10	3	7	(00)	10212.3452	3.2
715	6	5	1	5	5	0	(00)	14252.9005	2.3
716	6	5	1	5	5	0	(01)	14235.1287	2.4
717	6	5	1	5	5	0	(10)	14240.9131	4.2
718	6	5	1	5	5	0	(11)	14240.3400	-4.5
719	6	5	1	5	5	0	(12)	14230.7255	6.8
720	7	5	2	6	5	1	(00)	16921.5029	-1.7
721	7	5	2	6	5	1	(01)	16906.4054	5.2
722	7	5	2	6	5	1	(10)	16915.5034	-3.1
723	7	5	2	6	5	1	(11)	16914.6442	2.2
724	7	5	2	6	5	1	(12)	16894.0945	-4.3
725	8	5	3	7	5	2	(00)	19831.5481	0.1
726	8	5	3	7	5	2	(01)	19826.7126	3.4
727	8	5	3	7	5	2	(10)	19828.8103	-4.0
728	8	5	3	7	5	2	(11)	19827.2889	2.1
729	8	5	3	7	5	2	(12)	19820.8096	-5.9
730	9	5	4	8	5	3	(00)	22883.3479	-0.9

Appendix D. 2-Acetyl-3-Methylthiophene

731	9	5	4	8	5	3	(01)	22880.4230	0.8
732	9	5	4	8	5	3	(10)	22880.8689	−2.1
733	9	5	4	8	5	3	(11)	22878.6954	−0.3
734	9	5	4	8	5	3	(12)	22877.1935	−1.7
735	6	5	2	5	5	1	(00)	14202.4779	−0.9
736	6	5	2	5	5	1	(10)	14212.2941	−8.0
737	6	5	2	5	5	1	(11)	14210.7651	3.6
738	7	5	3	6	5	2	(00)	16686.0017	−0.5
739	7	5	3	6	5	2	(01)	16698.4040	−4.6
740	7	5	3	6	5	2	(10)	16689.2796	2.3
741	7	5	3	6	5	2	(11)	16687.5658	−2.5
742	7	5	3	6	5	2	(12)	16707.8690	4.1
743	8	5	4	7	5	3	(00)	19128.3284	−0.9
744	8	5	4	7	5	3	(01)	19129.9141	0.4
745	8	5	4	7	5	3	(10)	19127.7564	0.3
746	8	5	4	7	5	3	(11)	19126.2088	−2.0
747	8	5	4	7	5	3	(12)	19132.3246	2.8
748	9	5	5	8	5	4	(00)	21455.6126	−0.5
749	9	5	5	8	5	4	(01)	21454.8137	0.4
750	9	5	5	8	5	4	(10)	21454.4010	1.1
751	9	5	5	8	5	4	(11)	21452.8214	3.9

Table D.8: Molecular parameters obtained from the *SFLAMS* fits of all five torsional species of *anti*-2A3MT.

Par. ^a	Unit	(00)	(01)	(10)	(11)	(12)
<i>A</i>	MHz	1998.04828(11)	1997.96225(17)	1998.02819(16)	1997.94242(15)	1997.94197(11)
<i>B</i>	MHz	1412.138846(51)	1412.00742(11)	1412.015281(71)	1411.884072(78)	1411.884172(50)
<i>C</i>	MHz	836.293865(32)	836.295439(65)	836.295993(43)	836.297513(60)	836.297561(31)
Δ_J	kHz	0.03742(36)	0.03484(78)	0.03594(47)	0.03447(63)	0.03576(34)
Δ_{JK}	kHz	0.1214(24)	0.1183(45)	0.1302(35)	0.1187(42)	0.1185(25)
Δ_K	kHz	−0.0284(71)	−0.0284 ^b	−0.0514(99)	−0.0284 ^b	−0.0225(72)
δ_J	kHz	−0.01937(21)	−0.01748(42)	−0.01864(27)	−0.01747(34)	−0.01796(19)
δ_K	kHz	−0.006614(76)	−0.00604(14)	−0.00670(12)	−0.00618(15)	−0.006116(88)
<i>q</i>	MHz		7.48011(88)	3.84031(22)	3.62793(31)	11.32004(45)
<i>q_J</i>	kHz		−0.536(39)			−0.858(20)
<i>q_K</i>	kHz					0.660(38)
<i>r</i>	MHz		9.619(17)	8.430(14)	18.0516(73)	1.333(58)
<i>N</i> ^c		155	158	159	139	140
σ ^d	kHz	1.7	3.5	2.2	2.8	1.5

^a All parameters refer to the principal axis system. Watson's A reduction in the I' representation was used.

^b Fixed to the value of the (00) species. ^c Number of lines. ^d Standard deviation of the fit.

E. 2-Acetyl-4-Methylthiophene

Table E.1: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of 2A4MT given in Figure 7.2 calculated at the MP2/6-311++G(d,p), MP2/6-31G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^i a_i f_i$.

i	f_i	MP2/6-311++G(d,p)		MP2/6-31G(d,p)		B3LYP-D3BJ/6-311++G(d,p)	
		a_i / Hartree	a_i / cm^{-1}	a_i / Hartree	a_i / cm^{-1}	a_i / Hartree	a_i / cm^{-1}
0	1	-743.5299671		-743.3606074		-745.12043	
1	$\cos 1\alpha$	-0.0005539	-121.6	-0.0006459	-141.8	-0.000139498	-30.6
2	$\cos 2\alpha$	-0.0055912	-1227.1	-0.0065075	-1428.2	-0.006604286	-1449.5
3	$\cos 3\alpha$	-0.0001370	-30.1	-0.0002760	-60.6	-0.000232022	-50.9
4	$\cos 4\alpha$	0.0006534	143.4	0.0004387	96.3	0.000485160	106.5
5	$\cos 5\alpha$	-0.0001200	-26.3	-0.0000683	-15.0	-0.000081316	-17.8
6	$\cos 6\alpha$	-0.0000285	-6.2	-0.0000616	-13.5	-0.000067455	-14.8
7	$\cos 7\alpha$	0.0000237	5.2	/	/	/	/
8	$\cos 8\alpha$	0.0000746	16.4	/	/	/	/

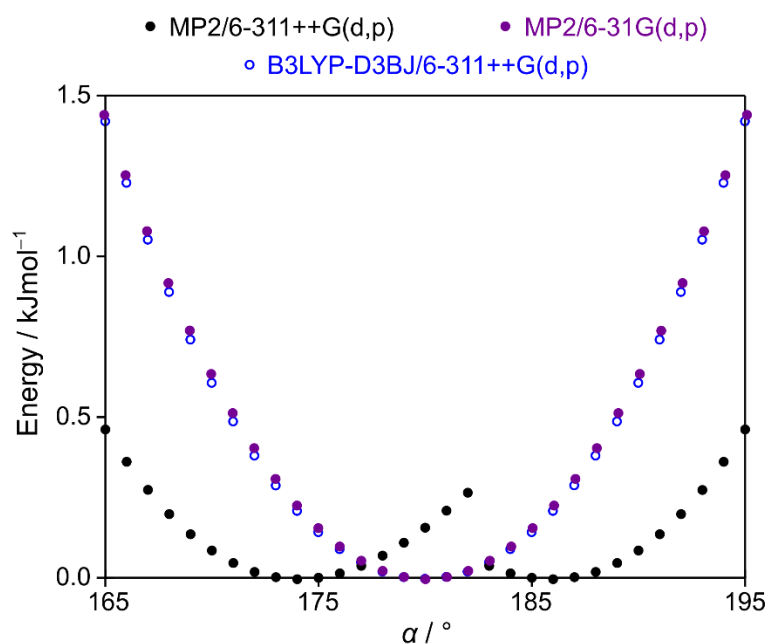


Figure E.1: The portion between 165° and 195° of the potential energy curves shown in Figure 7.2 where the dihedral angle α was varied in a grid of 1°. The relative energies are given in respect to the lowest energy points with $E_{\text{MP2/6-311++G(d,p)}} = -743.5340615$ Hartree, $E_{\text{MP2/6-31G(d,p)}} = -743.3657427$ Hartree, and $E_{\text{B3LYP-D3BJ}} = -745.1261434$ Hartree.

Appendix E. 2-Acetyl-4-Methylthiophene

Table E.2a: Nuclear coordinates in the principal axis system of *syn-* and *anti*-2A4MT calculated at the MP2/6-311++G(d,p) level of theory (for atom numbering see Figure 7.1).

	<i>syn</i> -2A4MT			<i>anti</i> -2A4MT		
	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å
S1	−0.171311	−1.510635	0.000871	−0.124555	−1.491887	−0.059736
C2	0.452085	0.094722	0.001979	0.442609	0.137329	−0.037287
C3	−0.576338	1.033852	0.000784	−0.621831	1.030330	0.017853
C4	−1.867862	0.450744	−0.000280	−1.888069	0.397302	0.025398
C5	−1.781169	−0.935475	−0.000529	−1.756852	−0.985422	−0.010473
C6	1.911311	0.315028	−0.000137	1.878294	0.505945	−0.011861
O7	2.692690	−0.630321	−0.002626	2.215454	1.679459	−0.105990
C8	2.388987	1.753157	0.000810	2.888309	−0.608230	0.170303
C9	−3.158050	1.224248	−0.001329	−3.206686	1.119905	0.068485
H10	−2.605983	−1.638760	−0.000606	−2.552119	−1.721390	−0.025983
H11	−4.017021	0.548150	0.004574	−4.040050	0.412562	0.081684
H12	−3.232527	1.859204	−0.889704	−3.323237	1.767540	−0.805892
H13	−3.227880	1.868912	0.880368	−3.277472	1.746551	0.962787
H14	−0.398669	2.105189	0.000898	−0.459454	2.103360	0.046651
H15	2.014233	2.277199	−0.883635	2.706570	−1.422800	−0.537650
H16	2.015432	2.275648	0.886681	3.892830	−0.209086	0.025677
H17	3.479408	1.762686	0.000009	2.803183	−1.019691	1.181606

Table E.2b: Nuclear coordinates in the principal axis system of *syn-* and *anti*-2A4MT calculated at the MP2/6-31G(d,p) level of theory (for atom numbering see Figure 7.1).

	<i>syn</i> -2A4MT			<i>anti</i> -2A4MT		
	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å
S1	−0.164963	−1.506112	−0.000004	−0.130709	−1.502268	0.000070
C2	0.448251	0.106908	−0.000021	0.443132	0.129056	0.000291
C3	−0.580924	1.035895	−0.000032	−0.613524	1.022947	0.000199
C4	−1.868276	0.446527	−0.000005	−1.882732	0.398706	0.000013
C5	−1.778725	−0.934251	0.000065	−1.762542	−0.979579	−0.000119
C6	1.903228	0.319388	0.000001	1.872431	0.503316	0.000031
O7	2.681931	−0.637973	−0.000031	2.197918	1.691793	−0.000032
C8	2.397143	1.748672	0.000047	2.901967	−0.603559	−0.000242
C9	−3.157289	1.215340	−0.000017	−3.192415	1.131739	−0.000194
H10	−2.599160	−1.635939	0.000093	−2.560442	−1.706444	−0.000039
H11	−4.011429	0.540389	0.000131	−4.029133	0.435256	0.000294
H12	−3.233157	1.853569	−0.880423	−3.282765	1.767789	−0.880556
H13	−3.233027	1.853789	0.880240	−3.282506	1.768728	0.879509
H14	−0.410111	2.104529	−0.000089	−0.443380	2.090955	0.000364
H15	2.033197	2.276773	−0.880935	2.782595	−1.235018	−0.881030
H16	2.033114	2.276713	0.881036	3.893273	−0.160029	−0.000006

Appendix E. 2-Acetyl-4-Methylthiophene

H17	3.483094	1.740083	0.000093	2.782448	-1.235722	0.880006

Table E.2c: Nuclear coordinates in the principal axis system of *syn*- and *anti*-2A4MT calculated at the B3LYP-D3BJ/6-311++G(d,p) level of theory (for atom numbering see Figure 7.1).

	<i>syn</i>-2A4MT			<i>anti</i>-2A4MT		
	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å
S1	-0.178651	-1.523715	0.000026	0.128091	-1.508068	0.000027
C2	0.453090	0.102430	0.000000	-0.444061	0.144929	0.000042
C3	-0.565307	1.028504	-0.000075	0.613014	1.022898	0.000051
C4	-1.866587	0.450679	0.000004	1.888621	0.392541	-0.000016
C5	-1.795697	-0.921083	0.000095	1.770549	-0.975716	-0.000047
C6	1.908551	0.312648	-0.000006	-1.875009	0.512444	0.000014
O7	2.681863	-0.629691	-0.000136	-2.207486	1.684347	-0.000012
C8	2.403273	1.746079	0.000131	-2.898197	-0.604576	-0.000046
C9	-3.142764	1.243757	-0.000061	3.194880	1.134715	-0.000025
H10	-2.624111	-1.614393	0.000164	2.568069	-1.703956	-0.000084
H11	-4.014040	0.586869	0.000431	4.041231	0.445968	-0.000150
H12	-3.207402	1.887281	-0.882394	3.280951	1.776255	0.881618
H13	-3.206998	1.888074	0.881718	3.280839	1.776436	-0.881546
H14	-0.391156	2.096874	-0.000137	0.456419	2.093534	0.000084
H15	2.039485	2.278955	-0.882605	-2.773554	-1.239761	-0.881972
H16	2.039366	2.278813	0.882909	-2.773350	-1.240132	0.881570
H17	3.491783	1.742340	0.000210	-3.897695	-0.173682	0.000132

Appendix E. 2-Acetyl-4-Methylthiophene

Table E.3: Rotational constants and the dihedral angle α of *syn*-2A4MT optimized at various levels of theory. The deviations between the calculated and the experimental values of the rotational constants are given as ΔA , ΔB and ΔC . $V_{3,1}$ is the barrier of the acetyl methyl and $V_{3,2}$ that of the ring methyl group. Θ is the tilt angle of the acetyl group out of the thiophene plane. All optimizations were performed under full-symmetry relaxation.

Method/Basis Set	$A /$ MHz	$\Delta A /$ MHz	$B /$ MHz	$\Delta B /$ MHz	$C /$ MHz	$\Delta C /$ MHz	$V_{3,1} /$ cm^{-1}	$\Delta V_{3,1} /$ cm^{-1}	$V_{3,2} /$ cm^{-1}	$\Delta V_{3,2} /$ cm^{-1}	$\alpha /$ $^{\circ}$	Planar	$\Theta /$ $^{\circ}$
B3LYP-D3/6-311G(2d,2p)	2619.2060	-25.7	1008.0091	1.8	734.4795	-1.3	316.0	8.9	194.5	16.2	0.00	Yes	0.00
B3LYP-D3/6-311+G(2d,2p)	2612.8810	-32.0	1008.3118	2.1	734.1448	-1.6	264.9	60.0	193.0	17.7	0.01	Yes	0.01
B3LYP-D3/6-311++G(2d,2p)	2612.9388	-32.0	1008.3026	2.1	734.1445	-1.6	267.7	57.2	191.6	19.1	0.01	Yes	0.01
B3LYP-D3/6-311G(2df,2pd)	2626.7024	-18.2	1009.6178	3.4	735.9201	0.1	320.1	4.8	189.9	20.8	0.00	Yes	0.00
B3LYP-D3/6-311+G(2df,2pd)	2620.3221	-24.6	1009.7213	3.5	735.4757	-0.3	268.5	56.4	189.6	21.1	0.01	Yes	0.01
B3LYP-D3/6-311++G(2df,2pd)	2620.3391	-24.6	1009.7076	3.5	735.4699	-0.3	271.2	53.7	187.2	23.5	0.01	Yes	0.01
B3LYP-D3/6-311G(3df,3pd)	2631.2874	-13.6	1009.9583	3.7	736.4635	0.7	304.5	20.4	186.1	24.6	0.01	Yes	0.01
B3LYP-D3/6-311+G(3df,3pd)	2626.1748	-18.8	1010.3115	4.1	736.2511	0.5	279.0	45.9	187.6	23.1	0.01	Yes	0.01
B3LYP-D3/6-311++G(3df,3pd)	2626.1571	-18.8	1010.3074	4.1	736.2472	0.5	278.3	46.6	186.5	24.2	0.01	Yes	0.01
B3LYP-D3/6-311G(df,pd)	2613.8997	-31.0	1008.0801	1.8	734.1254	-1.7	287.5	37.4	203.0	7.7	0.00	Yes	0.00
B3LYP-D3/6-311+G(df,pd)	2606.6722	-38.3	1008.0817	1.8	733.5557	-2.2	246.4	78.5	204.7	6.0	0.01	Yes	0.01
B3LYP-D3/6-311++G(df,pd)	2606.6226	-38.3	1008.0911	1.9	733.5556	-2.2	251.3	73.6	201.7	9.0	0.01	Yes	0.01
B3LYP-D3/6-311G(d,p)	2607.2534	-37.7	1005.0833	-1.2	732.0281	-3.8	298.1	26.8	206.3	4.4	0.02	Yes	0.02
B3LYP-D3/6-311+G(d,p)	2599.5519	-45.4	1004.9105	-1.3	731.3305	-4.5	255.6	69.3	206.5	4.2	0.02	Yes	0.02
B3LYP-D3/6-311++G(d,p)	2599.4792	-45.4	1004.9117	-1.3	731.3251	-4.5	257.1	67.8	203.1	7.6	0.02	Yes	0.02
B3LYP-D3/6-31G(d,p)	2601.4782	-43.4	1002.7369	-3.5	730.3342	-5.5	307.4	17.5	214.1	-3.4	0.01	Yes	0.01
B3LYP-D3/6-31+G(d,p)	2591.2296	-53.7	1001.5151	-4.7	728.8929	-6.9	244.8	80.1	198.2	12.5	0.01	Yes	0.01
B3LYP-D3/6-31++G(d,p)	2591.3320	-53.6	1001.4868	-4.7	728.8861	-6.9	243.4	81.5	200.3	10.4	0.01	Yes	0.01
B3LYP-D3/aug-cc-pVDZ	2585.1179	-59.8	1000.7469	-5.5	728.0478	-7.7	266.7	58.2	206.8	3.9	0.01	Yes	0.01
B3LYP-D3/aug-cc-pVTZ	2617.2079	-27.7	1009.5244	3.3	735.1275	-0.7	265.1	59.8	194.5	16.2	0.01	Yes	0.01
B3LYP-D3BJ/6-311G(2d,2p)	2630.3615	-14.6	1008.9671	2.7	735.8633	0.1	282.9	42.0	196.5	14.2	0.02	Yes	0.02
B3LYP-D3BJ/6-311+G(2d,2p)	2623.9337	-21.0	1009.3067	3.1	735.5415	-0.2	229.5	95.4	194.9	15.8	0.00	Yes	0.00
B3LYP-D3BJ/6-311++G(2d,2p)	2623.9948	-20.9	1009.2975	3.1	735.5415	-0.2	232.3	92.6	193.6	17.1	0.00	Yes	0.00

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B3LYP-D3BJ/6-311G(2df,2pd)	2637.7344	-7.2	1010.5188	4.3	737.2615	1.5	286.2	38.7	191.9	18.8	0.00	Yes	0.00
B3LYP-D3BJ/6-311+G(2df,2pd)	2631.0756	-13.9	1010.7070	4.5	736.8427	1.1	232.8	92.1	191.4	19.3	0.00	Yes	0.00
B3LYP-D3BJ/6-311++G(2df,2pd)	2631.0962	-13.8	1010.6930	4.5	736.8370	1.0	235.5	89.4	189.1	21.6	0.00	Yes	0.00
B3LYP-D3BJ/6-311G(3df,3pd)	2642.2993	-2.6	1010.8504	4.6	737.7972	2.0	270.7	54.2	188.1	22.6	0.00	Yes	0.00
B3LYP-D3BJ/6-311+G(3df,3pd)	2636.8637	-8.1	1011.2921	5.1	737.6087	1.8	243.1	81.8	189.5	21.2	0.00	Yes	0.00
B3LYP-D3BJ/6-311++G(3df,3pd)	2636.8489	-8.1	1011.2878	5.1	737.6050	1.8	242.4	82.5	188.4	22.3	0.00	Yes	0.00
B3LYP-D3BJ/6-311G(df,pd)	2624.7854	-20.1	1009.0603	2.8	735.5007	-0.3	253.0	71.9	204.9	5.8	0.00	Yes	0.00
B3LYP-D3BJ/6-311+G(df,pd)	2617.4033	-27.5	1009.1352	2.9	734.9602	-0.8	210.0	114.9	206.6	4.1	0.00	Yes	0.00
B3LYP-D3BJ/6-311++G(df,pd)	2617.3557	-27.6	1009.1443	2.9	734.9601	-0.8	214.9	110.0	203.6	7.1	0.00	Yes	0.00
B3LYP-D3BJ/6-311G(d,p)	2618.3454	-26.6	1006.0078	-0.2	733.3895	-2.4	264.4	60.5	208.3	2.4	0.02	Yes	0.02
B3LYP-D3BJ/6-311+G(d,p)	2610.5933	-34.3	1006.0068	-0.2	732.7816	-3.0	219.9	105.0	208.4	2.3	0.01	Yes	0.01
B3LYP-D3BJ/6-311++G(d,p)	2610.5255	-34.4	1006.0075	-0.2	732.7764	-3.0	221.4	103.5	205.0	5.7	0.01	Yes	0.01
B3LYP-D3BJ/6-31G(d,p)	2612.8340	-32.1	1003.6541	-2.6	731.7123	-4.1	273.8	51.1	216.0	-5.3	0.01	Yes	0.01
B3LYP-D3BJ/6-31+G(d,p)	2602.3153	-42.6	1002.5002	-3.7	730.2883	-5.5	209.8	115.1	200.2	10.5	0.01	Yes	0.01
B3LYP-D3BJ/6-31++G(d,p)	2602.4267	-42.5	1002.4709	-3.8	730.2817	-5.5	208.4	116.5	202.4	8.3	0.01	Yes	0.01
B3LYP-D3BJ/aug-cc-pVDZ	2596.2485	-48.7	1001.5802	-4.7	729.3670	-6.4	229.1	95.8	208.8	1.9	0.02	Yes	0.02
B3LYP-D3BJ/aug-cc-pVTZ	2628.0400	-16.9	1010.5210	4.3	736.5073	0.7	229.1	95.8	196.4	14.3	0.00	Yes	0.00
B3LYP-D3BJ/cc-pVDZ	2607.2897	-37.6	1001.2629	-5.0	730.0814	-5.7	327.9	-3.0	223.1	-12.4	0.02	Yes	0.02
B3LYP-D3BJ/cc-pVTZ	2630.0196	-14.9	1010.3374	4.1	736.5644	0.8	244.4	80.5	198.5	12.2	0.00	Yes	0.00
B3LYP-D3/cc-pVDZ	2595.6788	-49.2	1000.2675	-6.0	728.6418	-7.1	361.8	-36.9	221.2	-10.5	0.03	Yes	0.03
B3LYP-D3/cc-pVTZ	2619.1081	-25.8	1009.3731	3.1	735.1963	-0.6	279.6	45.3	196.6	14.1	0.01	Yes	0.01
CAM-B3LYP-D3BJ/6-311G(d,p)	2645.0327	0.1	1012.3437	6.1	738.8379	3.0	289.0	35.9	220.1	-9.4	0.00	Yes	0.00
CAM-B3LYP-D3BJ/6-311+G(d,p)	2636.7089	-8.2	1012.4586	6.2	738.2510	2.5	245.9	79.0	223.0	-12.3	0.01	Yes	0.01
CAM-B3LYP-D3BJ/6-311++G(d,p)	2636.6305	-8.3	1012.4620	6.2	738.2466	2.5	248.3	76.6	220.0	-9.3	0.01	Yes	0.01
CAM-B3LYP-D3BJ/aug-cc-pVDZ	2622.2020	-22.7	1007.9473	1.7	734.7802	-1.0	251.8	73.1	229.9	-19.2	0.01	Yes	0.01
CAM-B3LYP-D3BJ/aug-cc-pVTZ	2653.3824	8.5	1017.0339	10.8	741.9462	6.2	254.9	70.0	215.6	-4.9	0.02	Yes	0.02
CAM-B3LYP-D3BJ/cc-pVDZ	2634.6978	-10.2	1007.3015	1.1	735.4288	-0.4	343.6	-18.7	237.4	-26.7	0.01	Yes	0.01
CAM-B3LYP-D3BJ/cc-pVTZ	2655.7364	10.8	1016.8809	10.6	742.0484	6.3	269.5	55.4	215.6	-4.9	0.01	Yes	0.01
CCSD-cc-pVDZ	2589.7646	-55.2	992.8722	-13.4	724.3161	-11.5	416.8	-91.9	181.7	29.0	0.01	Yes	0.01
M06-2X/6-311G(3df,3pd)	2657.3824	12.5	1015.3633	9.1	741.3826	5.6	385.4	-60.5	208.7	2.0	0.02	Yes	0.02

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M06-2X/6-311+G(3df,3pd)	2653.2325	8.3	1015.7277	9.5	741.2544	5.5	367.6	-42.7	210.6	0.1	0.02	Yes	0.02
M06-2X/6-311++G(3df,3pd)	2653.2271	8.3	1015.7186	9.5	741.2488	5.5	367.2	-42.3	209.7	1.0	0.02	Yes	0.02
M06-2X/6-311G(df,pd)	2642.4006	-2.5	1013.7400	7.5	739.3770	3.6	348.6	-23.7	211.7	-1.0	0.01	Yes	0.01
M06-2X/6-311+G(df,pd)	2636.3481	-8.6	1013.6732	7.4	738.8661	3.1	321.3	3.6	217.6	-6.9	0.01	Yes	0.01
M06-2X/6-311++G(df,pd)	2636.2790	-8.6	1013.6931	7.5	738.8705	3.1	327.1	-2.2	214.3	-3.6	0.01	Yes	0.01
M06-2X/6-311G(d,p)	2637.7788	-7.1	1011.3133	5.1	737.7395	1.9	362.7	-37.8	216.9	-6.2	0.02	Yes	0.02
M06-2X/6-311+G(d,p)	2631.4442	-13.5	1011.1984	5.0	737.1835	1.4	333.8	-8.9	221.6	-10.9	0.00	Yes	0.00
M06-2X/6-311++G(d,p)	2631.3433	-13.6	1011.2132	5.0	737.1836	1.4	335.3	-10.4	217.8	-7.1	0.00	Yes	0.00
M06-2X/6-31G(d,p)	2635.9870	-8.9	1009.0625	2.8	736.4066	0.6	355.9	-31.0	226.3	-15.6	0.01	Yes	0.01
M06-2X/6-31+G(d,p)	2627.7528	-17.2	1007.8931	1.7	735.1554	-0.6	303.6	21.3	215.9	-5.2	0.01	Yes	0.01
M06-2X/6-31++G(d,p)	2627.8255	-17.1	1007.8828	1.6	735.1559	-0.6	302.4	22.5	218.0	-7.3	0.01	Yes	0.01
M06-2X/aug-cc-pVDZ	2621.4279	-23.5	1007.5902	1.4	734.5411	-1.2	325.5	-0.6	232.2	-21.5	0.00	Yes	0.00
M06-2X/aug-cc-pVTZ	2646.0467	1.1	1015.7707	9.5	740.7156	4.9	341.2	-16.3	215.3	-4.6	0.02	Yes	0.02
M06-2X/cc-pVDZ	2632.8818	-12.0	1007.0152	0.8	735.1449	-0.6	386.6	-61.7	231.0	-20.3	0.01	Yes	0.01
M06-2X/cc-pVTZ	2647.5473	2.6	1015.6045	9.4	740.7453	5.0	348.4	-23.5	213.6	-2.9	0.01	Yes	0.01
MP2/6-311G(2d,2p)	2635.6490	-9.3	1009.4822	3.2	736.5367	0.7	355.2	-30.3	156.4	54.3	0.02	Yes	0.02
MP2/6-311+G(2d,2p)	2628.5531	-16.4	1009.7794	3.5	736.1437	0.4	303.7	21.2	153.6	57.1	0.01	Yes	0.01
MP2/6-311++G(2d,2p)	2628.6870	-16.2	1009.7233	3.5	736.1260	0.3	307.2	17.7	151.7	59.0	0.01	Yes	0.01
MP2/6-311G(2df,2pd)	2660.6414	15.7	1013.3557	7.1	740.5544	4.8	350.8	-25.9	143.5	67.2	0.01	Yes	0.01
MP2/6-311+G(2df,2pd)	2652.4601	7.5	1013.2104	7.0	739.8459	4.1	295.4	29.5	144.4	66.3	0.01	Yes	0.01
MP2/6-311++G(2df,2pd)	2652.3683	7.4	1013.2005	7.0	739.8344	4.0	301.0	23.9	141.2	69.5	0.02	Yes	0.02
MP2/6-311G(3df,3pd)	2666.0479	21.1	1011.9974	5.8	740.2604	4.5	353.9	-29.0	137.5	73.2	0.01	Yes	0.01
MP2/6-311+G(3df,3pd)	2659.9035	15.0	1012.1462	5.9	739.8668	4.1	311.3	13.6	141.1	69.6	0.01	Yes	0.01
MP2/6-311++G(3df,3pd)	2659.9087	15.0	1012.1573	5.9	739.8733	4.1	311.0	13.9	140.6	70.1	0.01	Yes	0.01
MP2/6-311G(df,pd)	2654.3153	9.4	1010.4405	4.2	738.5643	2.8	334.9	-10.0	161.8	48.9	0.00	Yes	0.00
MP2/6-311+G(df,pd)	2644.8388	-0.1	1009.9215	3.7	737.5579	1.8	286.0	38.9	167.1	43.6	-0.03	Yes	-0.03
MP2/6-311++G(df,pd)	2644.5603	-0.4	1009.8853	3.7	737.5160	1.7	289.6	35.3	162.5	48.2	-0.12	Yes	-0.12
MP2/6-311G(d,p)	2635.1569	-9.8	1004.6614	-1.6	734.0230	-1.8	352.6	-27.7	164.8	45.9	0.04	Yes	0.04
MP2/6-311+G(d,p)	2625.8529	-19.1	1004.4667	-1.8	733.2009	-2.6	311.4	13.5	172.3	38.4	0.00	Yes	0.00
MP2/6-311++G(d,p)	2625.8529	-19.1	1004.4667	-1.8	733.2009	-2.6	314.3	10.6	165.7	45.0	0.00	Yes	0.00

Appendix E. 2-Acetyl-4-Methylthiophene

MP2/6-31G(d,p)	2638.4658	-6.5	1006.2736	0.0	735.0768	-0.7	370.2	-45.3	184.2	26.5	0.00	Yes	0.00
MP2/6-31+G(d,p)	2627.0088	-17.9	1004.5288	-1.7	733.2786	-2.5	285.2	39.7	176.2	34.5	0.01	Yes	0.01
MP2/6-31++G(d,p)	2626.8646	-18.1	1004.4746	-1.8	733.2406	-2.6	349.7	-24.8	182.3	28.4	-0.06	Yes	-0.06
MP2/aug-cc-pVDZ	2597.4151	-47.5	994.5343	-11.7	725.7778	-10.0	290.1	34.8	166.0	44.7	0.00	Yes	0.00
MP2/aug-cc-pVTZ	2648.3007	3.4	1011.2585	5.0	738.4997	2.7	^a		^a		0.01	Yes	0.01
MP2/cc-pVDZ	2613.4345	-31.5	995.3465	-10.9	727.4509	-8.3	418.0	-93.1	184.3	26.4	0.00	Yes	0.00
MP2/cc-pVTZ	2650.9636	6.0	1011.1248	4.9	738.6209	2.8	308.6	16.3	153.5	57.2	0.00	Yes	0.00
ωB97X-D /6-311G(d,p)	2629.8921	-15.0	1010.8145	4.6	736.8607	1.1	290.7	34.2	210.2	0.5	0.00	Yes	0.00
ωB97X-D /6-311+G(d,p)	2629.7781	-15.2	1010.8188	4.6	736.8538	1.1	293.9	31.0	206.8	3.9	0.00	Yes	0.00
ωB97X-D /6-311++G(d,p)	2636.7931	-8.1	1010.8193	4.6	737.4018	1.6	320.4	4.5	206.1	4.6	0.00	Yes	0.00
ωB97X-D /aug-cc-pVDZ	2616.6259	-28.3	1005.9957	-0.2	733.3220	-2.5	310.2	14.7	221.8	-11.1	0.01	Yes	0.01
ωB97X-D /aug-cc-pVTZ	2646.6516	1.7	1015.1397	8.9	740.4266	4.6	308.3	16.6	202.9	7.8	0.01	Yes	0.01
ωB97X-D /cc-pVDZ	2628.3348	-16.6	1005.1752	-1.1	733.8127	-2.0	358.4	-33.5	222.0	-11.3	0.02	Yes	0.02
ωB97X-D /cc-pVTZ	2648.4300	3.5	1014.8613	8.6	740.4173	4.6	312.4	12.5	202.0	8.7	0.01	Yes	0.01
Experiment	2644.9282		1006.2336		735.7908		324.9		210.7				

^a Not done due to high quantum chemical cost.

Appendix E. 2-Acetyl-4-Methylthiophene

Table E.4: Rotational constants of *anti*-2A4MT optimized at various levels of theory. The deviations between the calculated and the experimental values of the rotational constants are given as ΔA , ΔB and ΔC . $V_{3,1}$ is the barrier of the acetyl methyl and $V_{3,2}$ that of the ring methyl group. Θ is the tilt angle of the acetyl group out of the thiophene plane. All optimizations were performed under full-symmetry relaxation.

Method/Basis Set	$A /$ MHz	$\Delta A /$ MHz	$B /$ MHz	$\Delta B /$ MHz	$C /$ MHz	$\Delta C /$ MHz	$V_{3,1} /$ cm^{-1}	$\Delta V_{3,1} /$ cm^{-1}	$V_{3,2} /$ cm^{-1}	$\Delta V_{3,2} /$ cm^{-1}	$\alpha /$ $^\circ$	Planar	$\Theta /$ $^\circ$
B3LYP-D3/6-311G(2d,2p)	2698.0544	-32.5	993.1695	1.7	732.5025	-1.8	276.4	4.8	200.9	12.1	-179.99	Yes	-0.01
B3LYP-D3/6-311+G(2d,2p)	2702.5715	-28.0	992.4287	1.0	732.4325	-1.8	234.5	46.7	200.4	12.6	180.01	Yes	0.01
B3LYP-D3/6-311++G(2d,2p)	2702.6846	-27.9	992.4343	1.0	732.4441	-1.8	239.2	42.0	198.6	14.4	180.01	Yes	0.01
B3LYP-D3/6-311G(2df,2pd)	2706.7202	-23.9	994.8561	3.4	734.0552	-0.2	271.4	9.8	196.8	16.2	180.01	Yes	0.01
B3LYP-D3/6-311+G(2df,2pd)	2711.6058	-19.0	993.8990	2.4	733.8926	-0.4	234.5	46.7	196.7	16.3	180.01	Yes	0.01
B3LYP-D3/6-311++G(2df,2pd)	2711.6608	-18.9	993.8964	2.4	733.8956	-0.4	238.6	42.6	194.1	18.9	180.01	Yes	0.01
B3LYP-D3/6-311G(3df,3pd)	2715.7476	-14.8	995.1724	3.7	734.8911	0.6	254.6	26.6	188.5	24.5	-179.98	Yes	-0.02
B3LYP-D3/6-311+G(3df,3pd)	2718.0482	-12.5	994.6161	3.2	734.7565	0.5	240.9	40.3	193.7	19.3	180.01	Yes	0.01
B3LYP-D3/6-311++G(3df,3pd)	2718.0005	-12.6	994.5847	3.1	734.7356	0.5	239.8	41.4	192.5	20.5	180.00	Yes	0.00
B3LYP-D3/6-311G(df,pd)	2690.6927	-39.9	993.7649	2.3	732.3055	-2.0	239.7	41.5	220.5	-7.5	-179.96	Yes	-0.04
B3LYP-D3/6-311+G(df,pd)	2695.4562	-35.1	992.5417	1.1	731.9909	-2.3	207.9	73.3	219.3	-6.3	-179.99	Yes	-0.01
B3LYP-D3/6-311++G(df,pd)	2695.4669	-35.1	992.5676	1.1	732.0049	-2.3	213.4	67.8	214.8	-1.8	180.00	Yes	0.00
B3LYP-D3/6-311G(d,p)	2682.3126	-48.3	990.6725	-0.8	730.0208	-4.3	251.3	29.9	224.3	-11.3	-179.99	Yes	-0.01
B3LYP-D3/6-311+G(d,p)	2686.9337	-43.6	989.4651	-2.0	729.7072	-4.6	220.2	61.0	220.6	-7.6	-179.99	Yes	-0.01
B3LYP-D3/6-311++G(d,p)	2686.9523	-43.6	989.4849	-2.0	729.7195	-4.6	223.6	57.6	216.2	-3.2	180.01	Yes	0.01
B3LYP-D3/6-31G(d,p)	2673.5389	-57.0	988.7175	-2.7	728.3155	-6.0	293.4	-12.2	234.3	-21.3	179.98	Yes	-0.02
B3LYP-D3/6-31+G(d,p)	2677.1494	-53.4	986.1828	-5.3	727.2193	-7.1	221.0	60.2	215.6	-2.6	-179.97	Yes	-0.03
B3LYP-D3/6-31++G(d,p)	2677.3617	-53.2	986.1525	-5.3	727.2187	-7.1	215.3	65.9	216.4	-3.4	-179.99	Yes	-0.01
B3LYP-D3/aug-cc-pVDZ	2674.4695	-56.1	984.9770	-6.5	726.4110	-7.9	236.1	45.1	209.5	3.5	180.01	Yes	0.01
B3LYP-D3/aug-cc-pVTZ	2707.5402	-23.0	993.9172	2.5	733.6058	-0.7	237.3	43.9	200.6	12.4	180.01	Yes	0.01
B3LYP-D3BJ/6-311G(2d,2p)	2708.6540	-21.9	994.2569	2.8	733.8718	-0.4	235.3	45.9	202.3	10.7	180.03	Yes	0.03
B3LYP-D3BJ/6-311+G(2d,2p)	2713.5010	-17.1	993.4740	2.0	733.8009	-0.5	191.8	89.4	201.7	11.3	-179.98	Yes	-0.02
B3LYP-D3BJ/6-311++G(2d,2p)	2713.5976	-17.0	993.4957	2.0	733.8201	-0.5	196.7	84.5	199.9	13.1	-179.98	Yes	-0.02

Appendix E. 2-Acetyl-4-Methylthiophene

B3LYP-D3BJ/6-311G(2df,2pd)	2717.2634	-13.3	995.9366	4.5	735.4154	1.1	229.6	51.6	198.3	14.7	180.03	Yes	0.03
B3LYP-D3BJ/6-311+G(2df,2pd)	2722.4213	-8.2	994.9458	3.5	735.2518	1.0	191.5	89.7	197.9	15.1	-179.99	Yes	-0.01
B3LYP-D3BJ/6-311++G(2df,2pd)	2722.4917	-8.1	994.9462	3.5	735.2575	1.0	195.6	85.6	195.4	17.6	-179.99	Yes	-0.01
B3LYP-D3BJ/6-311G(3df,3pd)	2726.3224	-4.3	996.2316	4.8	736.2396	2.0	212.7	68.5	190.0	23.0	-179.97	Yes	-0.03
B3LYP-D3BJ/6-311+G(3df,3pd)	2728.8828	-1.7	995.6649	4.2	736.1168	1.8	197.1	84.1	195.0	18.0	-179.99	Yes	-0.01
B3LYP-D3BJ/6-311++G(3df,3pd)	2728.8540	-1.7	995.6462	4.2	736.1042	1.8	196.0	85.2	193.9	19.1	-179.99	Yes	-0.01
B3LYP-D3BJ/6-311G(df,pd)	2701.0908	-29.5	994.8229	3.4	733.6465	-0.6	197.9	83.3	222.2	-9.2	180.00	Yes	0.00
B3LYP-D3BJ/6-311+G(df,pd)	2706.2617	-24.3	993.6018	2.1	733.3608	-0.9	165.2	116.0	220.8	-7.8	179.96	Yes	-0.04
B3LYP-D3BJ/6-311++G(df,pd)	2706.3329	-24.2	993.6205	2.2	733.3752	-0.9	170.6	110.6	216.2	-3.2	179.99	Yes	-0.01
B3LYP-D3BJ/6-311G(d,p)	2692.7856	-37.8	991.7359	0.3	731.3705	-2.9	211.0	70.2	226.0	-13.0	180.01	Yes	0.01
B3LYP-D3BJ/6-311+G(d,p)	2697.7977	-32.8	990.5326	-0.9	731.0855	-3.2	178.8	102.4	222.0	-9.0	179.99	Yes	-0.01
B3LYP-D3BJ/6-311++G(d,p)	2697.8456	-32.7	990.5528	-0.9	731.1000	-3.2	182.3	98.9	217.7	-4.7	179.99	Yes	-0.01
B3LYP-D3BJ/6-31G(d,p)	2683.6800	-46.9	989.8207	-1.6	729.6631	-4.6	257.1	24.1	235.8	-22.8	179.99	Yes	-0.01
B3LYP-D3BJ/6-31+G(d,p)	2687.9700	-42.6	987.2505	-4.2	728.5947	-5.7	182.9	98.3	217.1	-4.1	-179.96	Yes	-0.04
B3LYP-D3BJ/6-31++G(d,p)	2688.1636	-42.4	987.1791	-4.3	728.5702	-5.7	176.9	104.3	217.9	-4.9	180.02	Yes	0.02
B3LYP-D3BJ/aug-cc-pVDZ	2685.6086	-45.0	986.1277	-5.3	727.8551	-6.4	195.6	85.6	210.9	2.1	-179.97	Yes	-0.03
B3LYP-D3BJ/aug-cc-pVTZ	2718.4714	-12.1	994.9671	3.5	734.9763	0.7	194.7	86.5	201.9	11.1	-179.99	Yes	-0.01
B3LYP-D3BJ/cc-pVDZ	2675.1523	-55.4	987.9894	-3.5	728.1135	-6.2	285.3	-4.1	239.2	-26.2	179.99	Yes	-0.01
B3LYP-D3BJ/cc-pVTZ	2716.2177	-14.4	995.2439	3.8	734.9621	0.7	210.5	70.7	206.8	6.2	-179.97	Yes	-0.03
B3LYP-D3/cc-pVDZ	2664.4117	-66.2	986.8474	-4.6	726.6988	-7.6	323.5	-42.3	237.8	-24.8	179.99	Yes	-0.01
B3LYP-D3/cc-pVTZ	2705.5037	-25.1	994.1679	2.7	733.5924	-0.7	252.8	28.4	205.5	7.5	-179.97	Yes	-0.03
CAM-B3LYP-D3BJ/6-311G(d,p)	2716.7748	-13.8	998.6185	7.2	736.8736	2.6	230.6	50.6	240.0	-27.0	180.00	Yes	0.00
CAM-B3LYP-D3BJ/6-311+G(d,p)	2722.1944	-8.4	997.3387	5.9	736.5744	2.3	199.7	81.5	239.9	-26.9	179.98	Yes	-0.02
CAM-B3LYP-D3BJ/6-311++G(d,p)	2722.2625	-8.3	997.3623	5.9	736.5923	2.3	204.3	76.9	235.3	-22.3	180.00	Yes	0.00
CAM-B3LYP-D3BJ/aug-cc-pVDZ	2709.9589	-20.6	992.7073	1.3	733.2164	-1.1	213.6	67.6	234.4	-21.4	-179.98	Yes	-0.02
CAM-B3LYP-D3BJ/aug-cc-pVTZ	2743.2407	12.7	1001.7193	10.3	740.4609	6.2	215.6	65.6	224.1	-11.1	-179.98	Yes	-0.02
CAM-B3LYP-D3BJ/cc-pVDZ	2698.9992	-31.6	994.6806	3.2	733.5039	-0.8	299.3	-18.1	256.7	-43.7	180.02	Yes	0.02
CAM-B3LYP-D3BJ/cc-pVTZ	2740.8239	10.2	1002.0625	10.6	740.4722	6.2	231.5	49.7	226.6	-13.6	-179.97	Yes	-0.03
CCSD-cc-pVDZ	2659.9505	-70.6	979.3844	-12.1	722.3826	-11.9	366.6	-85.4	193.0	20.0	-179.95	Yes	-0.05
M06-2X/6-311G(3df,3pd)	2751.5364	21.0	999.9629	8.5	740.1171	5.8	320.9	-39.7	211.3	1.7	180.01	Yes	0.01

Appendix E. 2-Acetyl-4-Methylthiophene

M06-2X/6-311+G(3df,3pd)	2753.6205	23.0	999.5225	8.1	740.0272	5.8	314.2	-33.0	216.3	-3.3	-179.98	Yes	-0.02
M06-2X/6-311++G(3df,3pd)	2753.5907	23.0	999.5047	8.1	740.0150	5.7	313.0	-31.8	215.3	-2.3	-179.98	Yes	-0.02
M06-2X/6-311G(df,pd)	2727.5835	-3.0	998.9027	7.5	737.8219	3.5	276.6	4.6	229.6	-16.6	-179.96	Yes	-0.04
M06-2X/6-311+G(df,pd)	2732.3101	1.7	997.7455	6.3	737.5321	3.3	259.1	22.1	232.6	-19.6	180.00	Yes	0.00
M06-2X/6-311++G(df,pd)	2732.4539	1.9	997.7724	6.3	737.5570	3.3	266.1	15.1	227.4	-14.4	180.00	Yes	0.00
M06-2X/6-311G(d,p)	2720.5492	-10.0	996.5336	5.1	736.0299	1.8	292.3	-11.1	235.2	-22.2	-179.98	Yes	-0.02
M06-2X/6-311+G(d,p)	2725.3481	-5.2	995.3236	3.9	735.7194	1.4	274.4	6.8	236.2	-23.2	-179.98	Yes	-0.02
M06-2X/6-311++G(d,p)	2725.4583	-5.1	995.3539	3.9	735.7445	1.5	279.0	2.2	231.0	-18.0	-179.98	Yes	-0.02
M06-2X/6-31G(d,p)	2713.0282	-17.6	995.0118	3.6	734.6556	0.4	320.2	-39.0	247.0	-34.0	-180.00	Yes	0.00
M06-2X/6-31+G(d,p)	2716.6462	-13.9	992.6814	1.2	733.6610	-0.6	256.7	24.5	233.7	-20.7	180.01	Yes	0.01
M06-2X/6-31++G(d,p)	2716.7567	-13.8	992.6909	1.2	733.6747	-0.6	250.9	30.3	233.7	-20.7	180.00	Yes	0.00
M06-2X/aug-cc-pVDZ	2716.0771	-14.5	991.6555	0.2	733.1005	-1.2	286.3	-5.1	233.5	-20.5	-179.99	Yes	-0.01
M06-2X/aug-cc-pVTZ	2745.6248	15.0	999.4736	8.0	739.4220	5.1	297.2	-16.0	221.4	-8.4	-179.97	Yes	-0.03
M06-2X/cc-pVDZ	2706.2011	-24.4	993.5869	2.1	733.4492	-0.8	340.9	-59.7	248.6	-35.6	-179.99	Yes	-0.01
M06-2X/cc-pVTZ	2742.9568	12.4	999.7467	8.3	739.3785	5.1	305.5	-24.3	222.6	-9.6	180.01	Yes	0.01
MP2/6-311G(2d,2p)	2717.9579	-12.6	994.3983	2.9	734.6183	0.3	290.0	-8.8	159.1	53.9	-179.98	Yes	-0.02
MP2/6-311+G(2d,2p)	2722.9976	-7.6	993.4229	2.0	734.4538	0.2	256.5	24.7	156.2	56.8	180.01	Yes	0.01
MP2/6-311++G(2d,2p)	2723.4295	-7.2	993.3735	1.9	734.4604	0.2	257.9	23.3	155.4	57.6	180.01	Yes	0.01
MP2/6-311G(2df,2pd)	2742.1858	11.6	998.8556	7.4	738.8272	4.6	280.6	0.6	148.0	65.0	-179.99	Yes	-0.01
MP2/6-311+G(2df,2pd)	2747.4517	16.9	997.3091	5.9	738.3627	4.1	246.9	34.3	147.9	65.1	180.00	Yes	0.00
MP2/6-311++G(2df,2pd)	2747.5992	17.0	997.3011	5.8	738.3705	4.1	249.4	31.8	145.9	67.1	180.01	Yes	0.00
MP2/6-311G(3df,3pd)	2752.9610	22.4	997.3915	5.9	738.8151	4.5	274.8	6.4	138.5	74.5	-179.99	Yes	-0.01
MP2/6-311+G(3df,3pd)	2755.1990	24.6	996.4282	5.0	738.4483	4.2	247.7	33.5	144.5	68.5	180.02	Yes	0.02
MP2/6-311++G(3df,3pd)	2755.2768	24.7	996.3739	4.9	738.4242	4.1	243.8	37.4	142.6	70.4	180.02	Yes	0.02
MP2/6-311G(df,pd)	2734.1347	3.6	996.3579	4.9	736.9312	2.7	264.6	16.6	173.3	39.7	-179.98	Yes	-0.02
MP2/6-311+G(df,pd)	2732.7276	2.1	993.8389	2.4	737.4365	3.2	253.2	28.0	173.7	39.3	173.67	No	-6.33
MP2/6-311++G(df,pd)	2730.7259	0.1	993.8610	2.4	737.8011	3.5	254.3	26.9	170.1	42.9	173.28	No	-6.72
MP2/6-311G(d,p)	2711.9214	-18.7	990.3318	-1.1	732.0507	-2.2	295.8	-14.6	177.3	35.7	180.00	Yes	0.00
MP2/6-311+G(d,p)	2714.3525	-16.2	988.2229	-3.2	732.2135	-2.1	269.9	11.3	176.8	36.2	175.10	No	-4.90
MP2/6-311++G(d,p)	2712.0149	-18.6	988.1640	-3.3	732.7234	-1.6	266.4	14.8	172.3	40.7	174.08	No	-5.92

Appendix E. 2-Acetyl-4-Methylthiophene

MP2/6-31G(d,p)	2703.1755	-27.4	993.2393	1.8	732.9337	-1.3	341.4	-60.2	197.7	15.3	180.01	Yes	0.01
MP2/6-31+G(d,p)	2706.1712	-24.4	989.2247	-2.2	731.8120	-2.5	253.9	27.3	188.2	24.8	175.23	No	-4.77
MP2/6-31++G(d,p)	2703.0127	-27.6	989.3621	-2.1	732.3712	-1.9	252.6	28.6	191.0	22.0	174.93	No	-5.07
MP2/aug-cc-pVDZ	2690.2845	-40.3	978.5267	-12.9	724.1102	-10.2	248.6	32.6	163.0	50.0	180.00	Yes	0.00
MP2/aug-cc-pVTZ	2740.5904	10.0	995.6018	4.1	736.9496	2.7	366.4	-85.2	193.7	19.3	180.02	Yes	0.02
MP2/cc-pVDZ	2678.4668	-52.1	982.6398	-8.8	725.4915	-8.8	260.1	21.1	159.1	53.9	180.01	Yes	0.01
MP2/cc-pVTZ	2738.3196	7.7	996.0755	4.6	737.0309	2.8	^a		^a		-179.99	Yes	-0.01
ω B97X-D /6-311G(d,p)	2719.1353	-11.4	994.6788	3.2	734.9196	0.6	221.5	59.7	226.6	-13.6	180.00	Yes	0.00
ω B97X-D /6-311+G(d,p)	2719.1954	-11.4	994.6938	3.2	734.9322	0.7	226.4	54.8	221.8	-8.8	179.99	Yes	-0.01
ω B97X-D /6-311++G(d,p)	2714.7557	-15.8	995.7710	4.3	735.1950	0.9	244.8	36.4	225.5	-12.5	-179.99	Yes	-0.01
ω B97X-D /aug-cc-pVDZ	2707.7899	-22.8	989.9923	-1.5	731.5950	-2.7	250.8	30.4	226.2	-13.2	-179.99	Yes	-0.01
ω B97X-D /aug-cc-pVTZ	2741.1694	10.6	998.7434	7.3	738.7002	4.4	249.5	31.7	210.2	2.8	-179.97	Yes	-0.03
ω B97X-D /cc-pVDZ	2697.0119	-33.6	991.5958	0.1	731.6937	-2.6	300.3	-19.1	240.2	-27.2	180.00	Yes	0.00
ω B97X-D /cc-pVTZ	2738.9395	8.4	998.8403	7.4	738.5911	4.3	253.9	27.3	211.6	1.4	-179.97	Yes	-0.03
Experiment	2730.5803		991.4523		734.2752		281.2		213.0				

^a Not done due to high quantum chemical cost.

Appendix E. 2-Acetyl-4-Methylthiophene

Table E.5: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of *syn*-2A4MT given in Figure 7.3 calculated at the MP2/6-311++G(d,p), MP2/6-31G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^2 a_i f_i$.

Acetyl Methyl				Ring Methyl	
<i>i</i>	f_i	a_i / Hartree	a_i / cm⁻¹	a_i / Hartree	a_i / cm⁻¹
MP2/6-311++G(d,p)					
0	1	-743.5350082		-743.5353640	
1	cos 3α	0.0007082	155.4	-0.0003717	-81.6
2	cos 6α	0.0000536	11.8	0.0000733	16.1
MP2/6-31G(d,p)					
0	1	-743.366885		-743.3673266	
1	cos 3α	0.0008349	183.2	-0.000415580	-91.2
2	cos 6α	0.0000263	5.8	0.000047612	10.4
B3LYP-D3BJ/6-311++G(d,p)					
0	1	-745.1265504		-745.1265922	
1	cos 3α	0.0005004	109.8	-0.0004663	-102.3
2	cos 6α	0.0000122	2.7	0.0000193	4.2

Appendix E. 2-Acetyl-4-Methylthiophene

Table E.6: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of *anti*-2A4MT given in Figure 7.4 calculated at the MP2/6-311++G(d,p), MP2/6-31G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^i a_i f_i$.

Acetyl Methyl				Ring Methyl	
<i>i</i>	<i>f_i</i>	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹
MP2/6-311++G(d,p)					
0	1	−743.5335740		−743.5337235	
1	cos 3α	0.0006057	132.9	−0.0003891	−85.4
2	cos 6α	0.0001297	28.5	0.0000539	11.8
3	cos 9α	−0.0000223	−4.9	/	/
4	cos 12α	0.000021	4.6	/	/
5	sin 3α	−0.000036	−7.9	/	/
6	sin 6α	−0.000024	−5.2	/	/
MP2/6-31G(d,p)					
0	1	−743.3650273		−743.36533997	
1	cos 3α	0.0007736	169.8	−0.00044619	−97.9
2	cos 6α	0.0000618	13.6	0.00004698	10.3
B3LYP-D3BJ/6-311++G(d,p)					
0	1	−745.1257696		−745.1256652	
1	cos 3α	0.0004185	91.9	−0.0004949	−108.6
2	cos 6α	0.00004068	8.9	0.0000181	4.0

Table E.7: Coefficients of the two-dimensional Fourier expansion for the potential energy surfaces calculated at the MP2/6-31G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels of theory for *syn*- and *anti*-2A4MT shown in Figure 7.5. Due to symmetry, only data points in the range from 0° to 120° were calculated for both β and γ. The potential is expanded as $V(\beta, \gamma) = \sum_i f_i V_i$. Max. dev. stands for maximum deviations between the fitted and the calculated values.

<i>i</i>	<i>f_i</i>	<i>syn</i> -2A4MT		<i>anti</i> -2A4MT	
		MP2 <i>V_i</i> / Hartree	B3LYP-D3BJ <i>V_i</i> / Hartree	MP2 <i>V_i</i> / Hartree	B3LYP-D3BJ <i>V_i</i> / Hartree
1	1	−743.3665195	−745.1261071	−743.364623	−745.1253020
2	cos(3β)	0.0008304	0.0004964	−0.0007674	−0.0004082
3	cos(3γ)	−0.0004088	−0.0004612	−0.0004395	−0.0004845
4	cos(6β)	0.0000274	0.0000127	0.0000616	0.0000413
5	cos(6γ)	0.0000466	0.0000190	0.0000463	0.0000173
	Max. dev. (%)	1.4	0.9	2.8	2.4

Appendix E. 2-Acetyl-4-Methylthiophene

Table E.8: Observed frequencies ν_{obs} of 890 rotational transitions of *syn*-2A4MT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J upper level	K_a	K_c	J lower level	K_a	K_c	Species	ν_{obs} MHz	$\nu_{obs}-\nu_{calc}$ kHz
1	2	0	2	1	0	1	(00)	3453.4733	-0.3
2	2	0	2	1	0	1	(01)	3453.3522	-1.7
3	2	0	2	1	0	1	(10)	3453.0365	0.2
4	2	0	2	1	0	1	(12)	3453.0536	-0.2
5	3	0	3	2	0	2	(00)	5105.7940	-0.5
6	3	0	3	2	0	2	(01)	5105.6605	0.8
7	3	0	3	2	0	2	(10)	5105.2556	-1.0
8	3	0	3	2	0	2	(12)	5105.2160	-0.6
9	4	0	4	3	0	3	(00)	6681.9767	0.8
10	4	0	4	3	0	3	(01)	6681.8556	-0.3
11	4	0	4	3	0	3	(10)	6681.3734	0.5
12	4	0	4	3	0	3	(12)	6681.2677	-0.4
13	4	0	4	3	0	3	(11)	6681.2383	0.5
14	5	0	5	4	0	4	(00)	8187.2986	0.7
15	5	0	5	4	0	4	(01)	8187.2046	-0.1
16	5	0	5	4	0	4	(10)	8186.6428	-0.2
17	5	0	5	4	0	4	(12)	8186.5037	-0.9
18	5	0	5	4	0	4	(11)	8186.5953	0.2
19	6	0	6	5	0	5	(00)	9647.9521	-0.3
20	6	0	6	5	0	5	(01)	9647.8808	0.5
21	6	0	6	5	0	5	(10)	9647.2831	3.7
22	7	0	7	6	0	6	(00)	11092.9049	0.3
23	7	0	7	6	0	6	(01)	11092.8419	-0.5
24	7	0	7	6	0	6	(10)	11092.2508	-4.5
25	8	0	8	7	0	7	(00)	12539.3332	0.2
26	8	0	8	7	0	7	(01)	12539.2740	1.1
27	8	0	8	7	0	7	(10)	12538.7283	-0.1
28	8	0	8	7	0	7	(12)	12538.6284	-0.2
29	9	0	9	8	0	8	(00)	13992.6570	1.4
30	9	0	9	8	0	8	(01)	13992.5950	0.3
31	9	0	9	8	0	8	(10)	13992.0942	-1.0
32	9	0	9	8	0	8	(11)	13992.0662	6.3
33	10	0	10	9	0	9	(00)	15452.5171	-0.6
34	10	0	10	9	0	9	(01)	15452.4559	0.1
35	10	0	10	9	0	9	(10)	15451.9916	0.2
36	10	0	10	9	0	9	(12)	15451.9129	-0.7
37	10	0	10	9	0	9	(11)	15451.9462	0.9
38	11	0	11	10	0	10	(00)	16917.0405	-2.2
39	11	0	11	10	0	10	(01)	16916.9802	-0.1
40	11	0	11	10	0	10	(10)	16916.5383	-1.2

Appendix E. 2-Acetyl-4-Methylthiophene

41	12	0	12	11	0	11	(00)	18384.5096	0.3
42	12	0	12	11	0	11	(01)	18384.4493	2.0
43	12	0	12	11	0	11	(10)	18384.0198	-1.4
44	13	0	13	12	0	12	(00)	19853.7183	0.6
45	13	0	13	12	0	12	(01)	19853.6559	-0.7
46	13	0	13	12	0	12	(10)	19853.2394	0.4
47	13	0	13	12	0	12	(12)	19853.1752	1.3
48	13	0	13	12	0	12	(11)	19853.1752	-6.7
49	14	0	14	13	0	13	(00)	21323.9211	-0.5
50	14	0	14	13	0	13	(01)	21323.8606	-1.2
51	14	0	14	13	0	13	(10)	21323.4484	-0.5
52	14	0	14	13	0	13	(12)	21323.3828	-3.6
53	14	0	14	13	0	13	(11)	21323.3828	-9.1
54	15	0	15	14	0	14	(00)	22794.6833	-0.4
55	15	0	15	14	0	14	(01)	22794.6230	-2.6
56	15	0	15	14	0	14	(10)	22794.2146	-0.4
57	16	0	16	15	0	15	(00)	24265.7667	10.3
58	16	0	16	15	0	15	(01)	24265.6990	-1.2
59	3	0	3	2	1	2	(00)	3705.6354	-3.6
60	3	0	3	2	1	2	(01)	3705.4976	-1.3
61	3	0	3	2	1	2	(10)	3713.2008	0.7
62	4	0	4	3	1	3	(00)	5585.2915	-1.5
63	4	0	4	3	1	3	(01)	5585.0882	-0.2
64	4	0	4	3	1	3	(10)	5589.1354	-0.3
65	5	0	5	4	1	4	(00)	7400.6538	-0.5
66	5	0	5	4	1	4	(01)	7400.4381	-0.3
67	5	0	5	4	1	4	(10)	7402.7926	-0.9
68	6	0	6	5	1	5	(00)	9127.9931	0.1
69	6	0	6	5	1	5	(01)	9127.7962	-0.3
70	6	0	6	5	1	5	(10)	9129.1432	-1.1
71	7	0	7	6	1	6	(00)	10771.8400	-0.1
72	7	0	7	6	1	6	(01)	10771.6740	-0.2
73	7	0	7	6	1	6	(10)	10772.3658	0.2
74	8	0	8	7	1	7	(00)	12351.1578	-2.6
75	8	0	8	7	1	7	(01)	12351.0236	-0.7
76	8	0	8	7	1	7	(10)	12351.2859	-1.4
77	9	0	9	8	1	8	(00)	13886.5487	1.8
78	9	0	9	8	1	8	(01)	13886.4354	0.5
79	9	0	9	8	1	8	(10)	13886.4258	-0.2
80	9	0	9	8	1	8	(12)	13886.3836	7.0
81	9	0	9	8	1	8	(11)	13886.2535	1.7
82	10	0	10	9	1	9	(00)	15394.3799	0.1
83	10	0	10	9	1	9	(01)	15394.2880	2.7
84	10	0	10	9	1	9	(10)	15394.1078	-1.7
85	11	0	11	10	1	10	(00)	16885.8801	-0.4
86	11	0	11	10	1	10	(01)	16885.7986	0.3

Appendix E. 2-Acetyl-4-Methylthiophene

87	11	0	11	10	1	10	(10)	16885.5230	0.1
88	12	0	12	11	1	11	(00)	18368.0926	0.0
89	12	0	12	11	1	11	(01)	18368.0199	1.0
90	12	0	12	11	1	11	(10)	18367.6860	0.5
91	13	0	13	12	1	12	(00)	19845.1895	0.2
92	13	0	13	12	1	12	(01)	19845.1201	-1.4
93	13	0	13	12	1	12	(10)	19844.7570	2.1
94	14	0	14	13	1	13	(00)	21319.5418	-0.2
95	14	0	14	13	1	13	(01)	21319.4797	1.2
96	14	0	14	13	1	13	(10)	21319.0933	0.0
97	15	0	15	14	1	14	(00)	22792.4567	0.3
98	15	0	15	14	1	14	(01)	22792.3957	-0.5
99	15	0	15	14	1	14	(10)	22792.0001	-0.4
100	1	1	1	0	0	0	(00)	3382.0361	-3.1
101	1	1	1	0	0	0	(01)	3381.8212	0.5
102	1	1	1	0	0	0	(10)	3361.0713	-4.6
103	2	1	2	1	0	1	(00)	4853.6252	-3.9
104	2	1	2	1	0	1	(01)	4853.5148	0.1
105	2	1	2	1	0	1	(10)	4845.0880	-4.8
106	3	1	3	2	0	2	(00)	6202.4806	3.1
107	3	1	3	2	0	2	(01)	6202.4266	-0.6
108	3	1	3	2	0	2	(10)	6197.5004	6.6
109	3	1	3	2	0	2	(12)	6196.7200	0.8
110	4	1	4	3	0	3	(00)	7468.6226	3.1
111	4	1	4	3	0	3	(10)	7465.2243	1.9
112	4	1	4	3	0	3	(12)	7464.6608	0.3
113	4	1	4	3	0	3	(11)	7465.7901	1.3
114	5	1	5	4	0	4	(00)	8707.2616	4.2
115	5	1	5	4	0	4	(01)	8707.2884	-0.2
116	5	1	5	4	0	4	(10)	8704.7783	0.3
117	5	1	5	4	0	4	(12)	8704.3642	-1.5
118	5	1	5	4	0	4	(11)	8705.2536	1.5
119	6	1	6	5	0	5	(00)	9969.0190	2.0
120	6	1	6	5	0	5	(01)	9969.0469	-1.5
121	6	1	6	5	0	5	(10)	9967.1700	1.1
122	6	1	6	5	0	5	(12)	9966.8796	-1.1
123	6	1	6	5	0	5	(11)	9967.5204	0.8
124	7	1	7	6	0	6	(00)	11281.0762	-1.1
125	7	1	7	6	0	6	(01)	11281.0923	1.3
126	7	1	7	6	0	6	(10)	11279.6964	0.0
127	7	1	7	6	0	6	(12)	11279.5003	-0.2
128	7	1	7	6	0	6	(11)	11279.9213	1.9
129	8	1	8	7	0	7	(00)	12645.4442	2.6
130	8	1	8	7	0	7	(01)	12645.4307	-2.0
131	8	1	8	7	0	7	(10)	12644.4007	3.1
132	9	1	9	8	0	8	(00)	14050.7898	-3.7

Appendix E. 2-Acetyl-4-Methylthiophene

133	9	1	9	8	0	8	(01)	14050.7653	0.2
134	9	1	9	8	0	8	(10)	14049.9777	0.7
135	9	1	9	8	0	8	(12)	14049.8741	0.0
136	10	1	10	9	0	9	(00)	15483.6758	-4.1
137	10	1	10	9	0	9	(01)	15483.6380	0.2
138	10	1	10	9	0	9	(10)	15483.0083	0.3
139	10	1	10	9	0	9	(12)	15482.9235	-0.1
140	11	1	11	10	0	10	(00)	16933.4594	0.0
141	11	1	11	10	0	10	(01)	16933.4095	0.9
142	11	1	11	10	0	10	(10)	16932.8754	0.2
143	11	1	11	10	0	10	(12)	16932.7946	-6.1
144	12	1	12	11	0	11	(00)	18393.0373	-0.5
145	12	1	12	11	0	11	(01)	18392.9835	1.1
146	12	1	12	11	0	11	(10)	18392.5044	-0.8
147	12	1	12	11	0	11	(12)	18392.4359	-0.5
148	12	1	12	11	0	11	(11)	18392.4676	4.4
149	13	1	13	12	0	12	(00)	19858.0955	-1.8
150	13	1	13	12	0	12	(01)	19858.0400	0.0
151	13	1	13	12	0	12	(10)	19857.5952	0.6
152	14	1	14	13	0	13	(00)	21326.1453	-3.6
153	14	1	14	13	0	13	(01)	21326.0908	-0.4
154	14	1	14	13	0	13	(10)	21325.6693	5.9
155	14	1	14	13	0	13	(11)	21325.6059	-4.5
156	15	1	15	14	0	14	(00)	22795.8072	0.2
157	15	1	15	14	0	14	(01)	22795.7481	-2.0
158	3	1	2	3	0	3	(00)	2717.7244	0.5
159	3	1	2	3	0	3	(01)	2717.5596	0.6
160	3	1	2	3	0	3	(10)	2719.9356	0.8
161	4	1	3	4	0	4	(00)	3476.7148	-2.8
162	4	1	3	4	0	4	(01)	3476.3390	-0.5
163	6	1	5	6	0	6	(00)	5825.7102	10.5
164	6	1	5	6	0	6	(01)	5824.6834	-2.3
165	6	1	5	6	0	6	(10)	5824.0611	8.6
166	7	1	6	7	0	7	(00)	7340.0383	6.5
167	7	1	6	7	0	7	(01)	7338.6922	-2.0
168	7	1	6	7	0	7	(10)	7337.2164	8.2
169	7	1	6	7	0	7	(12)	7336.3798	1.3
170	7	1	6	7	0	7	(11)	7335.3621	-2.7
171	8	1	7	8	0	8	(01)	8971.6872	-0.8
172	8	1	7	8	0	8	(10)	8969.2222	8.6
173	8	1	7	8	0	8	(12)	8968.1563	0.2
174	8	1	7	8	0	8	(11)	8967.0603	-0.1
175	9	1	8	9	0	9	(00)	10641.2112	5.6
176	9	1	8	9	0	9	(01)	10639.3953	2.4
177	9	1	8	9	0	9	(10)	10635.7875	9.3
178	9	1	8	9	0	9	(12)	10634.4509	0.6

Appendix E. 2-Acetyl-4-Methylthiophene

179	9	1	8	9	0	9	(11)	10633.4841	0.5
180	10	1	9	10	0	10	(00)	12286.5017	3.8
181	10	1	9	10	0	10	(01)	12284.5282	4.6
182	10	1	9	10	0	10	(10)	12279.6832	4.0
183	11	1	10	11	0	11	(00)	13885.3630	0.9
184	11	1	10	11	0	11	(01)	13883.2425	-2.4
185	11	1	10	11	0	11	(10)	13877.1809	3.3
186	12	1	11	12	0	12	(00)	15437.6109	-8.3
187	12	1	11	12	0	12	(01)	15435.3638	3.9
188	12	1	11	12	0	12	(10)	15428.1378	-5.5
189	2	1	1	1	1	0	(00)	3754.8129	7.9
190	2	1	1	1	1	0	(01)	3754.5594	-3.1
191	2	1	1	1	1	0	(10)	3742.3304	0.9
192	2	1	1	1	1	0	(12)	3740.1950	-4.2
193	2	1	1	1	1	0	(11)	3744.0581	2.1
194	3	1	2	2	1	1	(00)	5611.7380	-0.3
195	3	1	2	2	1	1	(01)	5611.4742	-2.0
196	3	1	2	2	1	1	(10)	5607.9643	-0.6
197	3	1	2	2	1	1	(12)	5607.1573	0.6
198	3	1	2	2	1	1	(11)	5608.2528	1.1
199	4	1	3	3	1	2	(00)	7440.9682	-1.3
200	4	1	3	3	1	2	(01)	7440.6364	0.0
201	4	1	3	3	1	2	(10)	7438.8190	-1.7
202	4	1	3	3	1	2	(12)	7438.3961	-0.2
203	4	1	3	3	1	2	(11)	7438.5791	-0.1
204	5	1	4	4	1	3	(00)	9228.1921	-1.5
205	5	1	4	4	1	3	(01)	9227.8043	1.4
206	5	1	4	4	1	3	(10)	9226.3589	-1.0
207	5	1	4	4	1	3	(12)	9226.0931	0.5
208	5	1	4	4	1	3	(11)	9225.8459	-0.3
209	6	1	5	5	1	4	(00)	10956.0387	-0.2
210	6	1	5	5	1	4	(01)	10955.6288	0.3
211	6	1	5	5	1	4	(10)	10954.2333	1.0
212	6	1	5	5	1	4	(12)	10954.0040	1.2
213	6	1	5	5	1	4	(11)	10953.6434	1.9
214	7	1	6	6	1	5	(00)	12607.2337	-3.0
215	7	1	6	6	1	5	(01)	12606.8490	-1.8
216	7	1	6	6	1	5	(10)	12605.4106	-0.4
217	7	1	6	6	1	5	(12)	12605.1424	0.4
218	7	1	6	6	1	5	(11)	12604.9101	1.2
219	8	1	7	7	1	6	(00)	14172.5971	1.3
220	8	1	7	7	1	6	(01)	14172.2656	-1.1
221	8	1	7	7	1	6	(10)	14170.7348	1.0
222	9	1	8	8	1	7	(00)	15660.5656	-1.0
223	9	1	8	8	1	7	(01)	15660.2980	-1.6
224	9	1	8	8	1	7	(10)	15658.6623	2.4

Appendix E. 2-Acetyl-4-Methylthiophene

225	9	1	8	8	1	7	(11)	15658.4850	1.9
226	10	1	9	9	1	8	(00)	17097.8089	-1.1
227	10	1	9	9	1	8	(01)	17097.5860	-0.5
228	10	1	9	9	1	8	(10)	17095.8930	0.7
229	10	1	9	9	1	8	(12)	17095.5441	-0.6
230	10	1	9	9	1	8	(11)	17095.7945	1.4
231	11	1	10	10	1	9	(00)	18515.9051	-1.8
232	11	1	10	10	1	9	(01)	18515.6999	-1.7
233	11	1	10	10	1	9	(10)	18514.0387	0.7
234	11	1	10	10	1	9	(12)	18513.7195	0.7
235	12	1	11	11	1	10	(00)	19936.7664	-0.1
236	12	1	11	11	1	10	(01)	19936.5626	0.4
237	12	1	11	11	1	10	(10)	19934.9871	0.3
238	13	1	12	12	1	11	(00)	21369.1988	3.1
239	13	1	12	12	1	11	(01)	21368.9839	-1.2
240	13	1	12	12	1	11	(10)	21367.5119	0.8
241	14	1	13	13	1	12	(00)	22813.6671	1.0
242	14	1	13	13	1	12	(01)	22813.4476	-0.7
243	14	1	13	13	1	12	(10)	22812.0620	1.2
244	2	1	2	1	1	1	(00)	3213.7246	2.6
245	2	1	2	1	1	1	(01)	3213.7532	-2.2
246	2	1	2	1	1	1	(10)	3225.8951	1.6
247	3	1	3	2	1	2	(00)	4802.3222	0.2
248	3	1	3	2	1	2	(01)	4802.2664	0.0
249	3	1	3	2	1	2	(10)	4805.4379	0.5
250	3	1	3	2	1	2	(12)	4805.9607	1.4
251	4	1	4	3	1	3	(00)	6371.9365	-0.1
252	4	1	4	3	1	3	(01)	6371.8543	-0.4
253	4	1	4	3	1	3	(10)	6372.9854	0.2
254	4	1	4	3	1	3	(12)	6373.1579	0.0
255	4	1	4	3	1	3	(11)	6372.6491	0.1
256	5	1	5	4	1	4	(00)	7920.6137	-0.1
257	5	1	5	4	1	4	(01)	7920.5223	0.0
258	5	1	5	4	1	4	(10)	7920.9281	-0.5
259	6	1	6	5	1	5	(00)	9449.0571	-0.3
260	6	1	6	5	1	5	(01)	9448.9650	0.5
261	6	1	6	5	1	5	(10)	9449.0369	3.1
262	7	1	7	6	1	6	(00)	10960.0123	-0.4
263	7	1	7	6	1	6	(01)	10959.9290	6.2
264	7	1	7	6	1	6	(10)	10959.8081	1.2
265	8	1	8	7	1	7	(00)	12457.2686	-0.4
266	8	1	8	7	1	7	(01)	12457.1838	-0.3
267	8	1	8	7	1	7	(10)	12456.9573	0.9
268	8	1	8	7	1	7	(12)	12456.8986	1.3
269	8	1	8	7	1	7	(11)	12456.8453	-0.7
270	9	1	9	8	1	8	(00)	13944.6856	0.7

Appendix E. 2-Acetyl-4-Methylthiophene

271	9	1	9	8	1	8	(01)	13944.6044	-1.0
272	9	1	9	8	1	8	(10)	13944.3058	-2.0
273	9	1	9	8	1	8	(11)	13944.2158	1.1
274	10	1	10	9	1	9	(00)	15425.5420	0.0
275	10	1	10	9	1	9	(01)	15425.4673	0.0
276	10	1	10	9	1	9	(10)	15425.1266	0.4
277	10	1	10	9	1	9	(11)	15425.0416	-3.4
278	11	1	11	10	1	10	(00)	16902.3014	4.2
279	11	1	11	10	1	10	(01)	16902.2227	-3.9
280	11	1	11	10	1	10	(10)	16901.8595	1.0
281	12	1	12	11	1	11	(00)	18376.6220	0.9
282	12	1	12	11	1	11	(01)	18376.5508	-3.2
283	12	1	12	11	1	11	(10)	18376.1697	0.1
284	12	1	12	11	1	11	(12)	18376.1023	-0.9
285	13	1	13	12	1	12	(00)	19849.5677	-1.2
286	13	1	13	12	1	12	(01)	19849.5034	-1.4
287	13	1	13	12	1	12	(10)	19849.1104	-0.2
288	13	1	13	12	1	12	(12)	19849.0468	0.7
289	13	1	13	12	1	12	(11)	19849.0468	-0.2
290	14	1	14	13	1	13	(00)	21321.7682	-1.1
291	14	1	14	13	1	13	(01)	21321.7079	0.1
292	14	1	14	13	1	13	(10)	21321.3081	0.3
293	14	1	14	13	1	13	(12)	21321.2455	0.0
294	14	1	14	13	1	13	(11)	21321.2455	-1.8
295	15	1	15	14	1	14	(00)	22793.5798	0.1
296	15	1	15	14	1	14	(01)	22793.5200	-0.7
297	15	1	15	14	1	14	(10)	22793.1190	1.9
298	4	1	3	4	1	4	(01)	2689.5712	-1.9
299	4	1	3	4	1	4	(10)	2693.5324	-0.7
300	6	1	5	6	1	6	(00)	5504.6323	-2.9
301	6	1	5	6	1	6	(01)	5503.5150	-2.6
302	6	1	5	6	1	6	(10)	5504.1726	9.8
303	9	1	8	9	1	9	(00)	10583.0655	-2.2
304	5	1	4	4	2	3	(00)	5190.3003	5.0
305	5	1	4	4	2	3	(01)	5190.1520	-1.4
306	6	1	5	5	2	4	(00)	7504.0339	3.8
307	6	1	5	5	2	4	(01)	7503.5440	-1.9
308	7	1	6	6	2	5	(00)	9795.7993	-1.3
309	7	1	6	6	2	5	(01)	9795.1459	2.6
310	7	1	6	6	2	5	(10)	9808.8835	-0.5
311	8	1	7	7	2	6	(00)	12007.7844	-2.4
312	8	1	7	7	2	6	(01)	12007.0714	0.5
313	8	1	7	7	2	6	(10)	12015.3797	-4.3
314	9	1	8	8	2	7	(00)	14092.5214	-0.3
315	9	1	8	8	2	7	(01)	14091.8336	0.2
316	9	1	8	8	2	7	(10)	14096.9477	-0.5

Appendix E. 2-Acetyl-4-Methylthiophene

317	10	1	9	9	2	8	(00)	16029.2264	−3.5
318	10	1	9	9	2	8	(01)	16028.6226	3.4
319	10	1	9	9	2	8	(10)	16031.6180	−1.1
320	11	1	10	10	2	9	(00)	17826.7676	−1.6
321	11	1	10	10	2	9	(01)	17826.2522	1.7
322	11	1	10	10	2	9	(10)	17827.7884	0.6
323	12	1	11	11	2	10	(00)	19512.2890	1.6
324	12	1	11	11	2	10	(01)	19511.8523	0.0
325	12	1	11	11	2	10	(10)	19512.3837	−2.9
326	13	1	12	12	2	11	(00)	21117.1095	−2.6
327	13	1	12	12	2	11	(01)	21116.7466	3.6
328	13	1	12	12	2	11	(10)	21116.6061	−4.0
329	2	2	0	1	1	1	(00)	8975.8527	2.0
330	2	2	0	1	1	1	(01)	8979.8942	0.4
331	2	2	0	1	1	1	(10)	9122.8505	−15.3
332	2	2	0	1	1	1	(12)	9137.6486	12.7
333	3	2	1	2	1	2	(00)	11109.1223	0.6
334	3	2	1	2	1	2	(01)	11109.6721	2.9
335	3	2	1	2	1	2	(10)	11199.8003	0.6
336	3	2	1	2	1	2	(12)	11211.1702	−10.8
337	3	2	1	2	1	2	(11)	11187.8181	−1.6
338	4	2	2	3	1	3	(00)	13537.7173	4.3
339	4	2	2	3	1	3	(01)	13537.3861	−1.3
340	4	2	2	3	1	3	(10)	13578.8503	6.2
341	4	2	2	3	1	3	(12)	13585.2100	−0.2
342	4	2	2	3	1	3	(11)	13571.5875	0.4
343	5	2	3	4	1	4	(00)	16330.3954	7.5
344	5	2	3	4	1	4	(01)	16329.5588	−2.3
345	5	2	3	4	1	4	(10)	16347.0725	12.0
346	5	2	3	4	1	4	(12)	16349.3695	−3.8
347	5	2	3	4	1	4	(11)	16343.0734	−4.0
348	6	2	4	5	1	5	(00)	19525.4209	8.6
349	6	2	4	5	1	5	(01)	19524.0985	−4.0
350	6	2	4	5	1	5	(12)	19531.6738	−2.3
351	6	2	4	5	1	5	(11)	19528.8920	−0.7
352	2	2	0	2	1	1	(00)	4950.5053	1.3
353	2	2	0	2	1	1	(01)	4954.5603	3.7
354	3	2	1	3	1	2	(01)	4686.6129	1.6
355	3	2	1	3	1	2	(10)	4766.6687	4.0
356	4	2	2	4	1	3	(00)	4475.7032	0.7
357	4	2	2	4	1	3	(01)	4475.9603	0.7
358	5	2	3	5	1	4	(10)	4427.1680	0.4
359	6	2	4	6	1	5	(00)	4571.7180	−1.7
360	7	2	5	7	1	6	(10)	5015.0380	0.2
361	8	2	6	8	1	7	(00)	5771.9248	−6.4
362	8	2	6	8	1	7	(01)	5771.2171	−1.5

Appendix E. 2-Acetyl-4-Methylthiophene

363	8	2	6	8	1	7	(10)	5773.2950	-6.9
364	2	2	0	1	1	0	(10)	8814.1319	0.1
365	3	2	1	2	1	1	(01)	10298.0872	-0.3
366	3	2	1	2	1	1	(10)	10374.6345	4.9
367	5	2	3	4	1	3	(10)	13653.5272	-0.2
368	3	2	1	3	1	3	(10)	6394.3614	-0.9
369	4	2	2	4	1	4	(10)	7205.8681	9.2
370	2	2	1	1	1	0	(00)	8674.5264	7.3
371	2	2	1	1	1	0	(01)	8669.9116	1.0
372	2	2	1	1	1	0	(12)	8500.7102	0.1
373	2	2	1	1	1	0	(11)	8530.6066	-7.3
374	3	2	2	2	1	1	(00)	10146.1032	-4.8
375	3	2	2	2	1	1	(01)	10144.8425	1.3
376	3	2	2	2	1	1	(10)	10043.8427	-0.5
377	3	2	2	2	1	1	(12)	10031.7612	-5.6
378	3	2	2	2	1	1	(11)	10055.0849	4.8
379	4	2	3	3	1	2	(00)	11478.8743	6.5
380	4	2	3	3	1	2	(01)	11478.2860	0.1
381	4	2	3	3	1	2	(10)	11426.3171	4.5
382	4	2	3	3	1	2	(12)	11418.9517	0.5
383	4	2	3	3	1	2	(11)	11432.7493	-1.0
384	5	2	4	4	1	3	(00)	12680.2106	8.3
385	5	2	4	4	1	3	(01)	12679.8858	0.5
386	5	2	4	4	1	3	(10)	12652.5434	7.9
387	5	2	4	4	1	3	(12)	12648.7427	0.2
388	5	2	4	4	1	3	(11)	12655.7128	1.2
389	6	2	5	5	1	4	(00)	13767.4741	-0.9
390	6	2	5	5	1	4	(01)	13767.3382	2.2
391	6	2	5	5	1	4	(10)	13750.7634	4.1
392	6	2	5	5	1	4	(12)	13748.6033	0.3
393	6	2	5	5	1	4	(11)	13752.6350	1.0
394	7	2	6	6	1	5	(00)	14772.0493	3.6
395	7	2	6	6	1	5	(01)	14772.0439	-2.8
396	7	2	6	6	1	5	(10)	14760.7658	5.0
397	7	2	6	6	1	5	(12)	14759.3327	-0.6
398	7	2	6	6	1	5	(11)	14762.1880	1.9
399	8	2	7	7	1	6	(00)	15740.6432	2.5
400	8	2	7	7	1	6	(01)	15740.7337	0.8
401	8	2	7	7	1	6	(10)	15732.4479	2.4
402	9	2	8	8	1	7	(00)	16729.1461	-0.6
403	9	2	8	8	1	7	(01)	16729.2658	-1.1
404	9	2	8	8	1	7	(10)	16722.9336	0.5
405	10	2	9	9	1	8	(00)	17786.9518	4.2
406	10	2	9	9	1	8	(01)	17787.0405	2.9
407	10	2	9	9	1	8	(10)	17782.1429	0.4
408	11	2	10	10	1	9	(00)	18940.3849	-1.0

Appendix E. 2-Acetyl-4-Methylthiophene

409	11	2	10	10	1	9	(01)	18940.4104	-1.1
410	12	2	11	11	1	10	(00)	20188.8488	-1.3
411	12	2	11	11	1	10	(01)	20188.8062	1.9
412	12	2	11	11	1	10	(10)	20185.8859	-1.9
413	13	2	12	12	1	11	(00)	21514.6555	-2.7
414	13	2	12	12	1	11	(01)	21514.5511	0.2
415	2	2	1	1	1	1	(10)	8824.7540	-4.3
416	3	2	2	2	1	2	(10)	10869.0078	-5.4
417	2	2	1	2	1	2	(00)	5731.3352	-3.6
418	2	2	1	2	1	2	(01)	5726.9226	-7.3
419	3	2	2	3	1	3	(00)	6155.4108	0.1
420	3	2	2	3	1	3	(10)	6063.5711	-4.7
421	6	2	5	6	1	6	(00)	8316.0794	8.2
422	6	2	5	6	1	6	(01)	8315.2279	2.7
423	6	2	5	6	1	6	(10)	8300.6916	1.8
424	7	2	6	7	1	7	(00)	9316.6638	-4.3
425	7	2	6	7	1	7	(01)	9315.6428	1.4
426	7	2	6	7	1	7	(10)	9305.1131	-3.7
427	7	2	6	7	1	7	(12)	9303.2032	-3.1
428	7	2	6	7	1	7	(11)	9304.9723	0.6
429	8	2	7	8	1	8	(00)	10435.2360	5.1
430	8	2	7	8	1	8	(01)	10433.9912	-3.1
431	8	2	7	8	1	8	(10)	10425.2492	-6.9
432	8	2	7	8	1	8	(12)	10423.5193	-1.5
433	8	2	7	8	1	8	(11)	10424.5191	1.8
434	9	2	8	9	1	9	(00)	11651.6503	2.5
435	9	2	8	9	1	9	(01)	11650.1892	-0.5
436	9	2	8	9	1	9	(10)	11642.1660	-3.6
437	9	2	8	9	1	9	(12)	11640.4347	-1.1
438	9	2	8	9	1	9	(11)	11640.9865	-0.8
439	10	2	9	10	1	10	(00)	12944.4781	4.8
440	10	2	9	10	1	10	(01)	12942.7918	-0.9
441	10	2	9	10	1	10	(10)	12934.9151	2.4
442	10	2	9	10	1	10	(12)	12933.0919	0.4
443	10	2	9	10	1	10	(11)	12933.3719	-1.7
444	11	2	10	11	1	11	(00)	14293.4198	-4.6
445	11	2	10	11	1	11	(01)	14291.5273	0.8
446	11	2	10	11	1	11	(10)	14283.4409	-1.3
447	11	2	10	11	1	11	(12)	14281.4848	-1.2
448	11	2	10	11	1	11	(11)	14281.6034	-0.7
449	12	2	11	12	1	12	(00)	15681.1678	-6.6
450	12	2	11	12	1	12	(01)	15679.0711	4.2
451	12	2	11	12	1	12	(10)	15670.5526	-7.6
452	3	2	1	2	2	0	(00)	5346.9932	0.2
453	3	2	1	2	2	0	(10)	5302.8315	4.1
454	4	2	2	3	2	1	(00)	7230.9125	-0.8

Appendix E. 2-Acetyl-4-Methylthiophene

455	4	2	2	3	2	1	(01)	7229.9816	−3.1
456	4	2	2	3	2	1	(10)	7184.4839	2.2
457	4	2	2	3	2	1	(12)	7179.9874	−1.2
458	4	2	2	3	2	1	(11)	7188.5732	3.9
459	5	2	3	4	2	2	(00)	9164.6113	−0.1
460	5	2	3	4	2	2	(01)	9164.0265	−1.8
461	5	2	3	4	2	2	(10)	9141.1985	−3.1
462	5	2	3	4	2	2	(12)	9137.3215	0.5
463	5	2	3	4	2	2	(11)	9144.1391	−0.1
464	6	2	4	5	2	3	(00)	11115.6374	−0.8
465	6	2	4	5	2	3	(01)	11115.0632	−0.5
466	6	2	4	5	2	3	(10)	11105.4595	−0.9
467	6	2	4	5	2	3	(12)	11103.2755	−0.4
468	6	2	4	5	2	3	(11)	11106.5163	−0.1
469	7	2	5	6	2	4	(00)	13047.3603	−0.3
470	7	2	5	6	2	4	(01)	13046.7273	0.2
471	7	2	5	6	2	4	(10)	13042.0527	−0.4
472	7	2	5	6	2	4	(12)	13040.7559	−1.9
473	7	2	5	6	2	4	(11)	13042.0809	−2.1
474	8	2	6	7	2	5	(00)	14932.6822	−1.1
475	8	2	6	7	2	5	(01)	14931.9893	0.6
476	8	2	6	7	2	5	(10)	14928.9978	−0.1
477	8	2	6	7	2	5	(12)	14928.1686	2.3
478	8	2	6	7	2	5	(11)	14928.4416	1.1
479	9	2	7	8	2	6	(00)	16753.3783	−1.1
480	9	2	7	8	2	6	(01)	16752.6534	0.0
481	9	2	7	8	2	6	(10)	16750.1479	−0.4
482	9	2	7	8	2	6	(12)	16749.5689	0.9
483	9	2	7	8	2	6	(11)	16749.2788	1.5
484	10	2	8	9	2	7	(00)	18494.5853	−4.0
485	10	2	8	9	2	7	(01)	18493.8829	0.8
486	10	2	8	9	2	7	(10)	18491.4424	0.0
487	10	2	8	9	2	7	(12)	18490.9621	1.3
488	10	2	8	9	2	7	(11)	18490.5112	0.6
489	11	2	9	10	2	8	(00)	20143.8569	−2.0
490	11	2	9	10	2	8	(01)	20143.2223	−1.0
491	11	2	9	10	2	8	(10)	20140.7009	−0.6
492	11	2	9	10	2	8	(12)	20140.2167	2.7
493	11	2	9	10	2	8	(11)	20139.9176	−1.3
494	12	2	10	11	2	9	(00)	21696.7685	0.8
495	12	2	10	11	2	9	(01)	21696.2372	0.5
496	12	2	10	11	2	9	(10)	21693.5663	1.5
497	12	2	10	11	2	9	(12)	21693.0359	0.5
498	12	2	10	11	2	9	(11)	21693.0359	2.7
499	13	2	11	12	2	10	(00)	23164.9668	3.8
500	13	2	11	12	2	10	(01)	23164.5369	2.7

Appendix E. 2-Acetyl-4-Methylthiophene

501	3	2	2	2	2	1	(00)	5226.3926	-1.2
502	3	2	2	2	2	1	(01)	5229.4889	-4.2
503	3	2	2	2	2	1	(10)	5270.1437	-4.7
504	3	2	2	2	2	1	(12)	5271.2459	-10.0
505	3	2	2	2	2	1	(11)	5268.5221	0.0
506	4	2	3	3	2	2	(00)	6944.4963	-1.8
507	4	2	3	3	2	2	(01)	6944.9220	1.2
508	4	2	3	3	2	2	(10)	6990.4311	-3.3
509	4	2	3	3	2	2	(12)	6994.3442	3.2
510	4	2	3	3	2	2	(11)	6985.9197	-2.2
511	5	2	4	4	2	3	(00)	8642.3037	-0.4
512	5	2	4	4	2	3	(01)	8642.2357	-0.2
513	5	2	4	4	2	3	(10)	8665.0441	0.5
514	5	2	4	4	2	3	(12)	8668.1874	-0.3
515	5	2	4	4	2	3	(11)	8661.5406	0.1
516	6	2	5	5	2	4	(00)	10315.4645	-1.7
517	6	2	5	5	2	4	(01)	10315.2534	-0.1
518	6	2	5	5	2	4	(10)	10324.5783	-5.1
519	6	2	5	5	2	4	(12)	10325.9540	1.0
520	6	2	5	5	2	4	(11)	10322.7675	-1.2
521	7	2	6	6	2	5	(00)	11960.6081	-1.5
522	7	2	6	6	2	5	(01)	11960.3393	0.2
523	7	2	6	6	2	5	(10)	11964.2337	-0.3
524	7	2	6	6	2	5	(12)	11964.7331	0.0
525	7	2	6	6	2	5	(11)	11963.1927	-0.8
526	8	2	7	7	2	6	(00)	13575.8332	1.5
527	8	2	7	7	2	6	(01)	13575.5355	-1.6
528	8	2	7	7	2	6	(10)	13577.0907	-4.9
529	8	2	7	7	2	6	(12)	13577.2112	-0.6
530	8	2	7	7	2	6	(11)	13576.3910	-0.6
531	9	2	8	8	2	7	(00)	15161.1014	-0.4
532	9	2	8	8	2	7	(01)	15160.8007	0.0
533	9	2	8	8	2	7	(10)	15161.2216	0.3
534	9	2	8	8	2	7	(11)	15160.6846	-0.2
535	10	2	9	9	2	8	(00)	16718.3667	-0.8
536	10	2	9	9	2	8	(01)	16718.0681	-2.2
537	10	2	9	9	2	8	(11)	16717.4300	-1.3
538	11	2	10	10	2	9	(00)	18251.2470	-1.3
539	11	2	10	10	2	9	(01)	18250.9595	-0.9
540	11	2	10	10	2	9	(10)	18250.3891	1.1
541	11	2	10	10	2	9	(11)	18250.0139	-2.0
542	12	2	11	11	2	10	(00)	19764.3717	0.6
543	12	2	11	11	2	10	(01)	19764.0949	0.4
544	12	2	11	11	2	10	(10)	19763.2912	3.6
545	12	2	11	11	2	10	(11)	19762.9613	-0.8
546	13	2	12	12	2	11	(00)	21262.5783	3.8

Appendix E. 2-Acetyl-4-Methylthiophene

547	13	2	12	12	2	11	(01)	21262.3102	1.5
548	13	2	12	12	2	11	(10)	21261.3495	−0.8
549	13	2	12	12	2	11	(11)	21261.0595	1.7
550	14	2	13	13	2	12	(00)	22750.2407	0.3
551	14	2	13	13	2	12	(01)	22749.9858	1.8
552	14	2	13	13	2	12	(10)	22748.9249	−2.6
553	14	2	13	13	2	12	(11)	22748.6626	4.5
554	3	3	0	2	2	1	(00)	14122.7144	0.7
555	3	3	0	2	2	1	(01)	14143.6265	−16.6
556	4	3	1	3	2	2	(00)	15933.4768	0.4
557	4	3	1	3	2	2	(01)	15945.9535	−5.7
558	4	3	1	3	2	2	(10)	16227.7680	−10.9
559	4	3	1	3	2	2	(12)	16256.2373	15.7
560	4	3	1	3	2	2	(11)	16198.4932	−6.8
561	3	3	1	2	2	0	(00)	14089.7171	0.6
562	3	3	1	2	2	0	(01)	14067.9132	12.0
563	4	3	2	3	2	1	(00)	15766.7515	1.5
564	5	3	2	4	2	3	(00)	17829.3945	0.3
565	5	3	2	4	2	3	(01)	17834.0617	2.3
566	5	3	2	4	2	3	(10)	18055.3929	14.0
567	5	3	2	4	2	3	(12)	18079.3256	6.3
568	5	3	2	4	2	3	(11)	18030.5982	−11.8
569	6	3	3	5	2	4	(00)	19870.7327	−0.8
570	6	3	3	5	2	4	(01)	19871.8486	−4.1
571	6	3	3	5	2	4	(10)	20028.2209	9.3
572	6	3	3	5	2	4	(12)	20047.2985	2.3
573	6	3	3	5	2	4	(11)	20008.0166	−4.4
574	7	3	4	6	2	5	(00)	22135.3458	−0.9
575	7	3	4	6	2	5	(01)	22135.0881	1.3
576	7	3	4	6	2	5	(10)	22225.9506	−0.5
577	7	3	4	6	2	5	(11)	22211.3851	0.2
578	8	3	5	7	2	6	(00)	24709.3549	−1.1
579	8	3	5	7	2	6	(01)	24708.3168	0.6
580	3	3	0	3	2	1	(00)	8744.9240	−6.8
581	3	3	0	3	2	1	(10)	8867.2886	−7.5
582	3	3	0	3	2	1	(12)	8874.5269	−5.8
583	3	3	0	3	2	1	(11)	8859.3649	−5.2
584	4	3	1	4	2	2	(00)	8551.1667	−7.4
585	4	3	1	4	2	2	(10)	8712.5110	0.3
586	4	3	1	4	2	2	(12)	8723.9175	1.1
587	4	3	1	4	2	2	(11)	8700.3463	2.0
588	5	3	2	5	2	3	(00)	8226.9764	−2.1
589	5	3	2	5	2	3	(01)	8231.7209	0.0
590	5	3	2	5	2	3	(10)	8389.3433	−0.1
591	5	3	2	5	2	3	(12)	8404.0326	−1.5
592	5	3	2	5	2	3	(11)	8374.2372	0.3

Appendix E. 2-Acetyl-4-Methylthiophene

593	7	3	4	7	2	5	(00)	7327.7026	0.1
594	7	3	4	7	2	5	(01)	7328.4442	-2.7
595	7	3	4	7	2	5	(10)	7402.0446	15.3
596	7	3	4	7	2	5	(12)	7413.9385	-3.5
597	7	3	4	7	2	5	(11)	7390.7207	-0.9
598	8	3	5	8	2	6	(00)	6929.6422	4.1
599	8	3	5	8	2	6	(01)	6930.0242	-2.5
600	8	3	5	8	2	6	(10)	6965.2411	-0.1
601	3	3	1	3	2	2	(00)	8894.1161	3.5
602	3	3	1	3	2	2	(01)	8877.6251	8.5
603	3	3	1	3	2	2	(10)	8753.0980	4.4
604	3	3	1	3	2	2	(12)	8745.3978	0.4
605	3	3	1	3	2	2	(11)	8760.4293	-3.6
606	4	3	2	4	2	3	(00)	8973.6373	-3.7
607	4	3	2	4	2	3	(01)	8961.5999	9.6
608	4	3	2	4	2	3	(10)	8793.4677	4.6
609	4	3	2	4	2	3	(12)	8781.6706	-4.0
610	4	3	2	4	2	3	(11)	8805.0152	-4.2
611	5	3	3	5	2	4	(00)	9126.6434	4.7
612	5	3	3	5	2	4	(01)	9121.4342	4.5
613	5	3	3	5	2	4	(10)	8945.2980	3.7
614	5	3	3	5	2	4	(12)	8930.2892	-3.8
615	5	3	3	5	2	4	(11)	8959.7730	-5.5
616	6	3	4	6	2	5	(00)	9378.6317	1.3
617	6	3	4	6	2	5	(01)	9376.4701	-0.7
618	6	3	4	6	2	5	(10)	9233.0452	5.1
619	6	3	4	6	2	5	(12)	9217.5443	2.1
620	6	3	4	6	2	5	(11)	9247.5494	1.5
621	7	3	5	7	2	6	(00)	9751.9374	1.3
622	7	3	5	7	2	6	(01)	9750.6936	3.4
623	7	3	5	7	2	6	(10)	9659.5249	-4.8
624	7	3	5	7	2	6	(11)	9670.4045	-0.8
625	8	3	6	8	2	7	(00)	10263.2624	-0.3
626	8	3	6	8	2	7	(01)	10262.2370	1.5
627	8	3	6	8	2	7	(10)	10210.9714	-5.5
628	9	3	7	9	2	8	(00)	10922.0247	-4.8
629	10	3	8	10	2	9	(00)	11729.4940	1.2
630	10	3	8	10	2	9	(01)	11728.2553	-9.1
631	11	3	9	11	2	10	(00)	12678.7801	-2.6
632	11	3	9	11	2	10	(01)	12677.3337	-1.1
633	11	3	9	11	2	10	(10)	12663.0545	-2.8
634	3	3	0	2	2	0	(01)	14104.4308	-3.9
635	3	3	0	2	2	0	(10)	14170.1181	-5.3
636	4	3	1	3	2	1	(01)	15792.7146	1.7
637	4	3	1	3	2	1	(10)	15896.9885	-4.0
638	6	3	3	5	2	3	(10)	19027.2230	3.2

Appendix E. 2-Acetyl-4-Methylthiophene

639	3	3	1	2	2	1	(01)	14107.1160	6.3
640	3	3	1	2	2	1	(10)	14023.2396	-2.4
641	4	3	2	3	2	2	(01)	15906.5127	1.6
642	4	3	2	3	2	2	(10)	15783.8955	-2.0
643	5	3	3	4	2	3	(10)	17610.3324	-5.5
644	6	3	4	5	2	4	(10)	19557.6136	-10.0
645	5	3	3	4	2	2	(00)	17331.1364	-2.1
646	5	3	3	4	2	2	(01)	17325.3556	0.1
647	5	3	3	4	2	2	(10)	17085.4992	-4.9
648	5	3	3	4	2	2	(12)	17060.5117	-4.8
649	5	3	3	4	2	2	(11)	17109.0887	3.6
650	6	3	4	5	2	3	(00)	18733.9901	5.1
651	6	3	4	5	2	3	(01)	18731.6212	-0.4
652	6	3	4	5	2	3	(10)	18556.6252	-6.6
653	6	3	4	5	2	3	(12)	18536.3987	1.0
654	6	3	4	5	2	3	(11)	18575.4840	0.0
655	7	3	5	6	2	4	(00)	19952.2642	2.2
656	7	3	5	6	2	4	(01)	19951.1142	-2.3
657	7	3	5	6	2	4	(10)	19841.8841	-10.8
658	7	3	5	6	2	4	(12)	19827.3617	4.0
659	7	3	5	6	2	4	(11)	19855.0187	0.2
660	8	3	6	7	2	5	(00)	20992.0689	9.2
661	8	3	6	7	2	5	(01)	20991.4708	-0.9
662	8	3	6	7	2	5	(10)	20928.3883	3.7
663	8	3	6	7	2	5	(12)	20919.8386	-0.3
664	8	3	6	7	2	5	(11)	20935.8832	0.4
665	9	3	7	8	2	6	(00)	21879.2460	1.0
666	9	3	7	8	2	6	(01)	21879.0121	3.1
667	9	3	7	8	2	6	(10)	21840.5520	0.9
668	9	3	7	8	2	6	(12)	21835.8145	0.1
669	9	3	7	8	2	6	(11)	21844.8182	0.8
670	10	3	8	9	2	7	(00)	22651.7048	8.4
671	10	3	8	9	2	7	(01)	22651.7287	-0.9
672	10	3	8	9	2	7	(10)	22626.0463	2.1
673	11	3	9	10	2	8	(00)	23357.6413	-4.1
674	11	3	9	10	2	8	(01)	23357.8747	-3.6
675	12	3	10	11	2	9	(00)	24055.3339	-5.6
676	4	3	2	3	3	1	(00)	7024.0318	5.3
677	5	3	3	4	3	2	(00)	8795.3002	-1.5
678	5	3	3	4	3	2	(01)	8802.0703	-5.0
679	5	3	3	4	3	2	(10)	8816.8747	-0.1
680	5	3	3	4	3	2	(12)	8816.8035	-2.6
681	5	3	3	4	3	2	(11)	8816.2994	-0.2
682	6	3	4	5	3	3	(00)	10567.4575	-0.5
683	6	3	4	5	3	3	(01)	10570.2959	1.4
684	6	3	4	5	3	3	(10)	10612.3275	-1.8

Appendix E. 2-Acetyl-4-Methylthiophene

685	6	3	4	5	3	3	(12)	10613.2017	−0.5
686	7	3	5	6	3	4	(00)	12333.9172	1.9
687	7	3	5	6	3	4	(01)	12334.5606	2.0
688	7	3	5	6	3	4	(10)	12390.7308	7.3
689	7	3	5	6	3	4	(12)	12394.2367	0.8
690	7	3	5	6	3	4	(11)	12386.0506	−0.3
691	8	3	6	7	3	5	(00)	14087.1569	−1.4
692	8	3	6	7	3	5	(01)	14087.0818	−0.5
693	8	3	6	7	3	5	(10)	14128.5471	4.2
694	8	3	6	7	3	5	(12)	14133.2361	−2.9
695	9	3	7	8	3	6	(00)	15819.8671	−1.6
696	9	3	7	8	3	6	(01)	15819.5272	1.2
697	9	3	7	8	3	6	(10)	15841.1657	1.3
698	10	3	8	9	3	7	(00)	17525.8309	0.1
699	10	3	8	9	3	7	(01)	17525.3748	0.8
700	10	3	8	9	3	7	(10)	17535.6421	0.7
701	11	3	9	10	3	8	(00)	19200.5393	1.1
702	11	3	9	10	3	8	(01)	19200.0310	0.3
703	12	3	10	11	3	9	(00)	20841.5517	−1.3
704	12	3	10	11	3	9	(01)	20841.0327	4.9
705	13	3	11	12	3	10	(00)	22448.6591	−2.9
706	5	3	2	4	3	1	(00)	8840.4148	−1.1
707	5	3	2	4	3	1	(01)	8833.0199	−1.1
708	5	3	2	4	3	1	(10)	8818.0334	−0.9
709	5	3	2	4	3	1	(12)	8817.4367	−2.1
710	6	3	3	5	3	2	(00)	10683.6394	−3.9
711	6	3	3	5	3	2	(01)	10680.0351	5.9
712	6	3	3	5	3	2	(10)	10637.8752	−1.1
713	6	3	3	5	3	2	(12)	10636.1646	0.0
714	6	3	3	5	3	2	(11)	10638.9529	1.4
715	7	3	4	6	3	3	(00)	12580.0786	−0.8
716	7	3	4	6	3	3	(01)	12578.4852	−2.3
717	7	3	4	6	3	3	(10)	12522.3196	−3.4
718	7	3	4	6	3	3	(12)	12517.7773	0.3
719	8	3	5	7	3	4	(00)	14534.6190	0.1
720	8	3	5	7	3	4	(01)	14533.5696	1.1
721	8	3	5	7	3	4	(10)	14492.2150	5.2
722	8	3	5	7	3	4	(12)	14486.2846	2.3
723	8	3	5	7	3	4	(11)	14496.7862	1.6
724	9	3	6	8	3	5	(00)	16533.9704	−0.5
725	9	3	6	8	3	5	(01)	16533.0167	−1.1
726	9	3	6	8	3	5	(10)	16511.4132	−1.2
727	9	3	6	8	3	5	(12)	16507.0512	0.7
728	9	3	6	8	3	5	(11)	16514.0019	2.0
729	10	3	7	9	3	6	(00)	18545.6427	−1.6
730	11	3	8	10	3	7	(00)	20530.6182	0.4

Appendix E. 2-Acetyl-4-Methylthiophene

731	12	3	9	11	3	8	(00)	22457.2298	1.2
732	13	3	10	12	3	9	(00)	24304.1947	3.4
733	4	4	0	3	3	1	(00)	19400.5596	0.4
734	5	4	1	4	3	2	(00)	21156.5686	0.1
735	6	4	2	5	3	3	(00)	22921.9245	-0.5
736	7	4	3	6	3	4	(00)	24712.1484	0.0
737	4	4	0	3	3	0	(01)	19404.8291	2.6
738	5	4	1	4	3	1	(01)	21152.1935	1.1
739	4	4	1	3	3	0	(00)	19398.2214	0.6
740	5	4	2	4	3	1	(00)	21140.0574	0.2
741	6	4	3	5	3	2	(00)	22855.6517	-1.3
742	4	4	1	3	3	1	(01)	19392.7401	2.3
743	5	4	2	4	3	2	(01)	21143.0980	-4.0
744	4	4	0	4	3	1	(00)	12361.1909	-4.4
745	4	4	0	4	3	1	(01)	12373.0193	1.8
746	4	4	0	4	3	1	(10)	12430.3389	-4.1
747	4	4	0	4	3	1	(12)	12436.1308	-7.5
748	4	4	0	4	3	1	(11)	12423.8027	-6.3
749	5	4	1	5	3	2	(00)	12300.8099	-5.4
750	5	4	1	5	3	2	(01)	12319.1692	-2.1
751	5	4	1	5	3	2	(10)	12390.8491	-4.8
752	5	4	1	5	3	2	(12)	12396.8808	-7.5
753	5	4	1	5	3	2	(11)	12384.0784	-5.9
754	6	4	2	6	3	3	(00)	12177.8292	-1.0
755	6	4	2	6	3	3	(01)	12197.1988	0.6
756	6	4	2	6	3	3	(10)	12309.9042	-5.1
757	7	4	3	7	3	4	(00)	11955.4330	0.9
758	7	4	3	7	3	4	(01)	11970.2361	-1.6
759	7	4	3	7	3	4	(10)	12135.8045	-4.1
760	7	4	3	7	3	4	(12)	12147.0399	-6.8
761	8	4	4	8	3	5	(00)	11598.6976	1.6
762	8	4	4	8	3	5	(01)	11606.4277	-0.6
763	8	4	4	8	3	5	(10)	11799.7129	1.6
764	9	4	5	9	3	6	(00)	11095.6003	1.0
765	10	4	6	10	3	7	(00)	10478.5117	1.0
766	4	4	1	4	3	2	(00)	12376.3933	-8.3
767	4	4	1	4	3	2	(01)	12363.8447	1.4
768	4	4	1	4	3	2	(10)	12281.3350	1.6
769	4	4	1	4	3	2	(12)	12274.8338	-2.2
770	4	4	1	4	3	2	(11)	12287.1003	3.2
771	5	4	2	5	3	3	(00)	12360.0918	-1.0
772	5	4	2	5	3	3	(01)	12341.0235	-3.1
773	5	4	2	5	3	3	(10)	12244.0461	1.3
774	5	4	2	5	3	3	(12)	12237.3614	4.5
775	5	4	2	5	3	3	(11)	12250.0536	5.9
776	6	4	3	6	3	4	(00)	12348.6458	-0.8

Appendix E. 2-Acetyl-4-Methylthiophene

777	6	4	3	6	3	4	(01)	12328.6176	3.2
778	6	4	3	6	3	4	(10)	12190.4024	2.3
779	6	4	3	6	3	4	(11)	12197.7649	4.5
780	7	4	4	7	3	5	(00)	12357.1858	4.1
781	7	4	4	7	3	5	(01)	12341.7843	1.6
782	7	4	4	7	3	5	(10)	12150.3942	0.9
783	7	4	4	7	3	5	(12)	12138.7079	4.5
784	7	4	4	7	3	5	(11)	12161.8676	3.9
785	8	4	5	8	3	6	(00)	12407.1144	2.1
786	8	4	5	8	3	6	(01)	12398.8747	-1.5
787	8	4	5	8	3	6	(10)	12179.4015	0.0
788	8	4	5	8	3	6	(12)	12162.7788	5.4
789	8	4	5	8	3	6	(11)	12195.6593	3.4
790	9	4	6	9	3	7	(00)	12524.0587	-2.9
791	9	4	6	9	3	7	(01)	12520.2428	0.1
792	9	4	6	9	3	7	(10)	12315.8581	1.5
793	10	4	7	10	3	8	(00)	12734.7743	-0.6
794	10	4	7	10	3	8	(01)	12732.7250	0.4
795	5	4	1	4	4	0	(00)	8780.0300	-5.9
796	5	4	1	4	4	0	(01)	8779.1785	3.5
797	5	4	1	4	4	0	(10)	8778.5451	-0.1
798	5	4	1	4	4	0	(12)	8778.1858	-2.9
799	5	4	1	4	4	0	(11)	8778.3065	-0.7
800	6	4	2	5	4	1	(00)	10560.6538	-4.3
801	6	4	2	5	4	1	(01)	10558.0591	2.9
802	6	4	2	5	4	1	(10)	10556.9318	0.0
803	6	4	2	5	4	1	(12)	10556.4703	-1.5
804	6	4	2	5	4	1	(11)	10556.6633	2.1
805	7	4	3	6	4	2	(00)	12357.6782	-3.1
806	7	4	3	6	4	2	(01)	12351.5266	-0.3
807	7	4	3	6	4	2	(10)	12348.2244	2.2
808	7	4	3	6	4	2	(11)	12347.9450	3.5
809	8	4	4	7	4	3	(00)	14177.8854	2.6
810	8	4	4	7	4	3	(10)	14156.1040	-8.6
811	8	4	4	7	4	3	(12)	14155.2699	-3.0
812	9	4	5	8	4	4	(00)	16030.8731	-1.1
813	9	4	5	8	4	4	(01)	16025.5894	0.4
814	9	4	5	8	4	4	(10)	15988.6852	-0.3
815	9	4	5	8	4	4	(12)	15987.1200	-0.9
816	9	4	5	8	4	4	(11)	15989.1324	4.5
817	10	4	6	9	4	5	(00)	17928.5538	-1.9
818	10	4	6	9	4	5	(01)	17925.8438	0.7
819	10	4	6	9	4	5	(10)	17866.0686	-1.2
820	10	4	6	9	4	5	(12)	17862.3996	0.0
821	10	4	6	9	4	5	(11)	17868.5765	1.9
822	11	4	7	10	4	6	(00)	19881.7188	-2.4

Appendix E. 2-Acetyl-4-Methylthiophene

823	11	4	7	10	4	6	(10)	19818.9941	3.1
824	12	4	8	11	4	7	(00)	21892.5674	−0.9
825	12	4	8	11	4	7	(01)	21891.1488	1.5
826	12	4	8	11	4	7	(10)	21849.7678	0.9
827	13	4	9	12	4	8	(00)	23946.0014	1.4
828	5	4	2	4	4	1	(00)	8778.9994	6.5
829	5	4	2	4	4	1	(10)	8779.5862	0.0
830	6	4	3	5	4	2	(00)	10556.0093	−2.5
831	6	4	3	5	4	2	(01)	10557.8864	4.2
832	6	4	3	5	4	2	(10)	10558.6835	−1.1
833	6	4	3	5	4	2	(12)	10558.3874	0.9
834	7	4	4	6	4	3	(00)	12342.4485	−2.0
835	7	4	4	6	4	3	(01)	12347.7261	−0.8
836	7	4	4	6	4	3	(10)	12350.7156	−1.0
837	7	4	4	6	4	3	(12)	12350.3993	1.1
838	7	4	4	6	4	3	(11)	12350.1505	−3.8
839	8	4	5	7	4	4	(00)	14137.0876	−1.3
840	8	4	5	7	4	4	(01)	14144.1705	−5.3
841	8	4	5	7	4	4	(10)	14157.5492	−1.9
842	8	4	5	7	4	4	(12)	14157.3112	2.2
843	8	4	5	7	4	4	(11)	14156.7406	1.1
844	9	4	6	8	4	5	(00)	15936.8173	−0.6
845	9	4	6	8	4	5	(01)	15940.8925	0.0
846	9	4	6	8	4	5	(10)	15977.6178	−1.7
847	9	4	6	8	4	5	(12)	15977.9104	−2.7
848	10	4	7	9	4	6	(00)	17736.5444	0.2
849	11	4	8	10	4	7	(00)	19529.5365	−0.7
850	11	4	8	10	4	7	(01)	19529.6476	2.1
851	12	4	9	11	4	8	(00)	21308.1797	−1.5
852	5	5	1	4	4	0	(00)	24691.8962	−6.2
853	6	5	2	6	4	3	(00)	15887.2080	−2.0
854	6	5	2	6	4	3	(01)	15877.8940	−2.8
855	6	5	2	6	4	3	(12)	15786.5084	8.6
856	6	5	2	6	4	3	(11)	15798.7768	7.9
857	7	5	3	7	4	4	(00)	15849.4802	0.3
858	7	5	3	7	4	4	(01)	15834.7261	−1.7
859	7	5	3	7	4	4	(10)	15747.3845	7.4
860	8	5	4	8	4	5	(00)	15800.4793	−0.4
861	8	5	4	8	4	5	(01)	15778.9867	−1.8
862	8	5	4	8	4	5	(10)	15679.0186	4.8
863	8	5	4	8	4	5	(12)	15672.2115	4.9
864	9	5	5	9	4	6	(00)	15744.8034	−2.0
865	9	5	5	9	4	6	(01)	15721.0526	−1.6
866	9	5	5	9	4	6	(12)	15578.1197	5.6
867	6	5	1	5	5	0	(00)	10530.2440	−7.2
868	6	5	1	5	5	0	(01)	10529.8167	3.2

Appendix E. 2-Acetyl-4-Methylthiophene

869	6	5	1	5	5	0	(10)	10529.2068	−0.2
870	6	5	1	5	5	0	(12)	10528.7976	0.7
871	6	5	1	5	5	0	(11)	10528.9067	−0.1
872	6	5	2	5	5	1	(00)	10530.1838	2.7
873	6	5	2	5	5	1	(01)	10529.9051	−2.7
874	6	5	2	5	5	1	(10)	10530.1287	−1.9
875	6	5	2	5	5	1	(12)	10529.8178	3.5
876	6	5	2	5	5	1	(11)	10529.7326	−3.3
877	8	5	4	7	5	3	(00)	14088.0883	−0.5
878	8	5	4	7	5	3	(01)	14088.4360	−0.5
879	9	5	5	8	5	4	(00)	15881.1433	−0.3
880	9	5	5	8	5	4	(01)	15882.9564	−1.9
881	9	5	5	8	5	4	(10)	15884.2630	−2.3
882	9	5	5	8	5	4	(12)	15883.8219	1.3
883	9	5	5	8	5	4	(11)	15883.5790	4.0
884	10	5	6	9	5	5	(00)	17684.1930	−3.6
885	10	5	6	9	5	5	(01)	17688.9191	1.4
886	10	5	6	9	5	5	(10)	17691.9300	−1.5
887	11	5	7	10	5	6	(00)	19496.6471	−2.0
888	11	5	7	10	5	6	(01)	19504.0196	0.9
889	11	5	7	10	5	6	(10)	19513.8374	0.9
890	6	6	1	6	5	2	(01)	19447.4432	−3.3

Table E.9: Observed frequencies ν_{obs} of 359 rotational transitions of *anti*-2A4MT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs} MHz	$\nu_{obs}-\nu_{calc}$ kHz
	upper level			lower level					
1	5	0	5	4	0	4	(00)	8169.9379	1.2
2	5	0	5	4	0	4	(01)	8169.7490	0.0
3	5	0	5	4	0	4	(10)	8169.3074	−1.0
4	5	0	5	4	0	4	(11)	8169.0659	0.3
5	5	0	5	4	0	4	(12)	8169.1770	0.4
6	6	0	6	5	0	5	(00)	9636.7798	0.1
7	6	0	6	5	0	5	(01)	9636.6034	−0.3
8	6	0	6	5	0	5	(10)	9636.1083	−0.6
9	6	0	6	5	0	5	(11)	9635.9047	−0.1
10	6	0	6	5	0	5	(12)	9635.9613	−0.4
11	7	0	7	6	0	6	(00)	11082.6178	0.0
12	7	0	7	6	0	6	(01)	11082.4540	0.9
13	7	0	7	6	0	6	(10)	11081.9541	0.7
14	7	0	7	6	0	6	(11)	11081.7727	0.0
15	7	0	7	6	0	6	(12)	11081.8054	0.1
16	8	0	8	7	0	7	(00)	12525.9971	−0.1

Appendix E. 2-Acetyl-4-Methylthiophene

17	8	0	8	7	0	7	(01)	12525.8418	−0.6
18	8	0	8	7	0	7	(10)	12525.3696	−1.9
19	9	0	9	8	0	8	(00)	13974.6726	−1.2
20	9	0	9	8	0	8	(01)	13974.5284	1.2
21	9	0	9	8	0	8	(10)	13974.0933	−1.3
22	9	0	9	8	0	8	(11)	13973.9524	8.8
23	9	0	9	8	0	8	(12)	13973.9524	−0.4
24	10	0	10	9	0	9	(00)	15429.7597	−0.3
25	10	0	10	9	0	9	(01)	15429.6194	−0.7
26	10	0	10	9	0	9	(10)	15429.2198	−0.7
27	10	0	10	9	0	9	(11)	15429.0816	2.0
28	10	0	10	9	0	9	(12)	15429.0816	−0.6
29	11	0	11	10	0	10	(00)	16889.9356	−1.2
30	11	0	11	10	0	10	(01)	16889.8021	−0.5
31	11	0	11	10	0	10	(10)	16889.4271	0.4
32	11	0	11	10	0	10	(11)	16889.2919	−1.5
33	11	0	11	10	0	10	(12)	16889.2919	0.0
34	5	0	5	4	1	4	(00)	7271.3532	−0.1
35	5	0	5	4	1	4	(01)	7271.4753	−1.6
36	5	0	5	4	1	4	(10)	7273.9946	1.7
37	5	0	5	4	1	4	(11)	7274.9362	−1.4
38	5	0	5	4	1	4	(12)	7273.2935	6.1
39	6	0	6	5	1	5	(00)	9019.1604	−2.9
40	6	0	6	5	1	5	(01)	9019.1781	1.9
41	6	0	6	5	1	5	(10)	9020.7099	2.2
42	6	0	6	5	1	5	(11)	9021.1576	−0.2
43	6	0	6	5	1	5	(12)	9020.2807	1.8
44	7	0	7	6	1	6	(01)	10684.8506	−0.8
45	7	0	7	6	1	6	(10)	10685.7253	−1.1
46	7	0	7	6	1	6	(11)	10685.9158	−0.7
47	7	0	7	6	1	6	(12)	10685.4326	1.4
48	8	0	8	7	1	7	(00)	12282.7528	0.3
49	8	0	8	7	1	7	(01)	12282.6630	−1.4
50	8	0	8	7	1	7	(10)	12283.0961	0.6
51	8	0	8	7	1	7	(11)	12283.1425	−0.4
52	8	0	8	7	1	7	(12)	12282.8707	0.3
53	9	0	9	8	1	8	(00)	13831.5846	−0.3
54	9	0	9	8	1	8	(01)	13831.4779	1.1
55	9	0	9	8	1	8	(10)	13831.6133	−1.2
56	9	0	9	8	1	8	(12)	13831.4280	−0.8
57	10	0	10	9	1	9	(00)	15348.0122	−1.6
58	10	0	10	9	1	9	(01)	15347.8945	−1.1
59	10	0	10	9	1	9	(10)	15347.8474	2.1
60	10	0	10	9	1	9	(11)	15347.7705	−0.6
61	10	0	10	9	1	9	(12)	15347.6878	5.0
62	11	0	11	10	1	10	(00)	16844.2680	−0.9

Appendix E. 2-Acetyl-4-Methylthiophene

63	11	0	11	10	1	10	(01)	16844.1481	1.4
64	11	0	11	10	1	10	(10)	16843.9796	0.7
65	11	0	11	10	1	10	(11)	16843.8810	−1.4
66	11	0	11	10	1	10	(12)	16843.8292	−1.8
67	12	0	12	11	1	11	(00)	18328.4954	−0.1
68	12	0	12	11	1	11	(01)	18328.3722	−0.5
69	12	0	12	11	1	11	(10)	18328.1336	0.4
70	12	0	12	11	1	11	(12)	18327.9957	0.5
71	3	1	3	2	0	2	(00)	6286.9885	0.4
72	3	1	3	2	0	2	(01)	6286.2825	0.9
73	3	1	3	2	0	2	(10)	6281.4806	−1.9
74	3	1	3	2	0	2	(11)	6278.8586	2.8
75	3	1	3	2	0	2	(12)	6282.7123	−2.0
76	4	1	4	3	0	3	(00)	7554.4982	−0.1
77	5	1	5	4	0	4	(00)	8787.5533	0.2
78	5	1	5	4	0	4	(01)	8787.1772	0.7
79	5	1	5	4	0	4	(10)	8784.7066	−3.0
80	5	1	5	4	0	4	(11)	8783.8144	1.8
81	5	1	5	4	0	4	(12)	8784.8556	−3.7
82	6	1	6	5	0	5	(00)	10034.4961	1.2
83	6	1	6	5	0	5	(01)	10034.2051	−0.2
84	6	1	6	5	0	5	(10)	10032.3312	−4.6
85	7	1	7	6	0	6	(00)	11325.8628	0.2
86	7	1	7	6	0	6	(01)	11325.6309	−0.1
87	7	1	7	6	0	6	(10)	11324.2279	−1.5
88	7	1	7	6	0	6	(11)	11323.8376	0.3
89	7	1	7	6	0	6	(12)	11324.1592	−2.1
90	8	1	8	7	0	7	(00)	12669.0874	1.3
91	8	1	8	7	0	7	(01)	12668.8943	1.6
92	8	1	8	7	0	7	(10)	12667.8527	1.1
93	8	1	8	7	0	7	(11)	12667.5692	1.3
94	8	1	8	7	0	7	(12)	12667.7496	−0.9
95	9	1	9	8	0	8	(00)	14056.4178	−2.2
96	9	1	9	8	0	8	(01)	14056.2523	0.7
97	9	1	9	8	0	8	(10)	14055.4708	0.9
98	9	1	9	8	0	8	(11)	14055.2534	1.2
99	9	1	9	8	0	8	(12)	14055.3508	−1.4
100	10	1	10	9	0	9	(00)	15475.4294	1.5
101	10	1	10	9	0	9	(01)	15475.2755	−0.5
102	10	1	10	9	0	9	(10)	15474.6695	1.2
103	11	1	11	10	0	10	(00)	16915.0053	0.5
104	11	1	11	10	0	10	(01)	16914.8639	−0.1
105	11	1	11	10	0	10	(10)	16914.3671	0.5
106	11	1	11	10	0	10	(11)	16914.2131	−0.3
107	11	1	11	10	0	10	(12)	16914.2392	0.4
108	12	1	12	11	0	11	(00)	18367.1313	1.3

Appendix E. 2-Acetyl-4-Methylthiophene

109	12	1	12	11	0	11	(01)	18366.9976	0.5
110	12	1	12	11	0	11	(10)	18366.5646	-1.9
111	4	1	4	3	1	3	(00)	6342.4576	-3.3
112	4	1	4	3	1	3	(01)	6342.4712	-0.6
113	5	1	5	4	1	4	(00)	7888.9706	0.9
114	5	1	5	4	1	4	(01)	7888.9034	-1.0
115	5	1	5	4	1	4	(10)	7889.3929	-1.2
116	5	1	5	4	1	4	(11)	7889.6853	0.7
117	6	1	6	5	1	5	(00)	9416.8770	-1.5
118	6	1	6	5	1	5	(01)	9416.7770	-0.9
119	6	1	6	5	1	5	(10)	9416.9348	0.2
120	6	1	6	5	1	5	(11)	9417.0136	-0.4
121	6	1	6	5	1	5	(12)	9416.6530	-0.1
122	7	1	7	6	1	6	(00)	10928.1496	2.1
123	7	1	7	6	1	6	(01)	10928.0314	2.0
124	7	1	7	6	1	6	(10)	10928.0031	0.6
125	7	1	7	6	1	6	(11)	10927.9847	3.7
126	7	1	7	6	1	6	(12)	10927.7888	1.6
127	8	1	8	7	1	7	(00)	12425.8406	-0.7
128	8	1	8	7	1	7	(01)	12425.7185	3.7
129	8	1	8	7	1	7	(10)	12425.5763	0.7
130	8	1	8	7	1	7	(11)	12425.5045	1.1
131	8	1	8	7	1	7	(12)	12425.3958	1.3
132	9	1	9	8	1	8	(00)	13913.3330	1.9
133	9	1	9	8	1	8	(01)	13913.2002	-1.0
134	9	1	9	8	1	8	(11)	13912.8936	1.9
135	9	1	9	8	1	8	(12)	13912.8287	0.5
136	10	1	10	9	1	9	(00)	15393.6816	-0.1
137	10	1	10	9	1	9	(01)	15393.5523	0.8
138	10	1	10	9	1	9	(10)	15393.2924	-0.6
139	10	1	10	9	1	9	(11)	15393.1831	0.9
140	11	1	11	10	1	10	(00)	16869.3372	0.3
141	11	1	11	10	1	10	(01)	16869.2086	0.5
142	11	1	11	10	1	10	(10)	16868.9175	-1.4
143	11	1	11	10	1	10	(11)	16868.8035	1.1
144	11	1	11	10	1	10	(12)	16868.7753	-2.7
145	12	1	12	11	1	11	(00)	18342.0616	-0.4
146	12	1	12	11	1	11	(01)	18341.9351	-0.6
147	12	1	12	11	1	11	(10)	18341.6273	0.7
148	12	1	12	11	1	11	(12)	18341.4885	-3.8
149	3	1	2	2	1	1	(00)	5547.6571	1.3
150	3	1	2	2	1	1	(10)	5543.6705	-1.9
151	3	1	2	2	1	1	(11)	5541.1160	-0.2
152	3	1	2	2	1	1	(12)	5545.1643	-0.5
153	4	1	3	3	1	2	(00)	7361.7769	1.2
154	4	1	3	3	1	2	(01)	7361.2780	0.0

Appendix E. 2-Acetyl-4-Methylthiophene

155	4	1	3	3	1	2	(10)	7359.6721	-0.9
156	4	1	3	3	1	2	(11)	7358.2188	0.1
157	4	1	3	3	1	2	(12)	7360.1422	1.6
158	5	1	4	4	1	3	(00)	9140.6576	0.3
159	5	1	4	4	1	3	(01)	9140.1118	-2.2
160	5	1	4	4	1	3	(10)	9138.9824	2.6
161	5	1	4	4	1	3	(11)	9137.7525	1.3
162	5	1	4	4	1	3	(12)	9139.1260	2.8
163	6	1	5	5	1	4	(00)	10869.8101	-2.0
164	6	1	5	5	1	4	(01)	10869.2193	-2.3
165	6	1	5	5	1	4	(10)	10868.1886	1.8
166	6	1	5	5	1	4	(11)	10867.0289	-2.0
167	6	1	5	5	1	4	(12)	10868.1648	3.0
168	7	1	6	6	1	5	(00)	12533.8159	-1.8
169	7	1	6	6	1	5	(01)	12533.2083	-1.4
170	7	1	6	6	1	5	(10)	12532.1475	-0.2
171	7	1	6	6	1	5	(11)	12531.1062	-2.9
172	8	1	7	7	1	6	(00)	14121.5207	0.3
173	8	1	7	7	1	6	(01)	14120.9241	0.3
174	8	1	7	7	1	6	(10)	14119.7710	0.5
175	8	1	7	7	1	6	(11)	14118.8993	-0.2
176	8	1	7	7	1	6	(12)	14119.4504	1.3
177	9	1	8	8	1	7	(00)	15633.9123	0.0
178	9	1	8	8	1	7	(01)	15633.3433	2.1
179	9	1	8	8	1	7	(10)	15632.0676	0.2
180	9	1	8	8	1	7	(11)	15631.3494	-3.9
181	9	1	8	8	1	7	(12)	15631.6387	-2.1
182	10	1	9	9	1	8	(00)	17088.3416	1.7
183	10	1	9	9	1	8	(01)	17087.7956	0.5
184	10	1	9	9	1	8	(10)	17086.4265	-1.9
185	11	1	10	10	1	9	(00)	18512.0624	1.4
186	11	1	10	10	1	9	(01)	18511.5386	0.6
187	11	1	10	10	1	9	(10)	18510.1518	0.3
188	11	1	10	10	1	9	(11)	18509.5987	-2.0
189	11	1	10	10	1	9	(12)	18509.6587	0.4
190	12	1	11	11	1	10	(00)	19929.3289	-3.1
191	12	1	11	11	1	10	(01)	19928.8272	0.9
192	2	2	0	1	1	1	(00)	9215.9540	2.5
193	2	2	0	1	1	1	(01)	9248.6545	-3.6
194	3	2	1	2	1	2	(00)	11303.8211	3.4
195	3	2	1	2	1	2	(01)	11315.8845	-2.3
196	3	2	1	2	1	2	(10)	11403.4831	1.1
197	3	2	1	2	1	2	(12)	11359.5493	0.1
198	4	2	2	3	1	3	(00)	13660.8012	0.7
199	4	2	2	3	1	3	(01)	13664.0629	2.2
200	4	2	2	3	1	3	(10)	13709.2726	0.9

Appendix E. 2-Acetyl-4-Methylthiophene

201	4	2	2	3	1	3	(12)	13681.6994	−2.0
202	5	2	3	4	1	4	(00)	16352.4460	1.8
203	5	2	3	4	1	4	(01)	16352.6678	−2.6
204	5	2	3	4	1	4	(10)	16372.8996	0.9
205	5	2	3	4	1	4	(12)	16357.4099	−7.9
206	6	2	4	5	1	5	(00)	19421.4021	−1.0
207	6	2	4	5	1	5	(01)	19420.2258	2.9
208	2	2	1	1	1	0	(00)	8932.0854	1.2
209	2	2	1	1	1	0	(01)	8896.3940	1.5
210	2	2	1	1	1	0	(10)	8766.6831	6.8
211	2	2	1	1	1	0	(12)	8818.4876	−3.1
212	3	2	2	2	1	1	(00)	10401.0574	−1.9
213	3	2	2	2	1	1	(01)	10385.8640	−1.9
214	3	2	2	2	1	1	(10)	10288.9770	2.8
215	3	2	2	2	1	1	(12)	10329.7902	−0.4
216	4	2	3	3	1	2	(00)	11738.1834	0.1
217	4	2	3	3	1	2	(01)	11731.6601	−4.7
218	4	2	3	3	1	2	(10)	11677.4331	3.2
219	4	2	3	3	1	2	(12)	11701.5691	1.9
220	5	2	4	4	1	3	(00)	12949.3963	2.0
221	5	2	4	4	1	3	(01)	12945.7703	−4.2
222	5	2	4	4	1	3	(10)	12917.0517	3.3
223	5	2	4	4	1	3	(12)	12928.5747	2.2
224	6	2	5	5	1	4	(00)	14048.5766	1.0
225	6	2	5	5	1	4	(01)	14046.1841	−3.8
226	6	2	5	5	1	4	(10)	14029.0454	0.6
227	6	2	5	5	1	4	(11)	14018.9537	7.8
228	6	2	5	5	1	4	(12)	14034.4954	−1.8
229	7	2	6	6	1	5	(00)	15060.9389	1.5
230	7	2	6	6	1	5	(01)	15059.2192	−0.6
231	7	2	6	6	1	5	(10)	15047.6994	−1.5
232	7	2	6	6	1	5	(11)	15041.7847	4.9
233	7	2	6	6	1	5	(12)	15050.2249	−3.9
234	8	2	7	7	1	6	(00)	16025.0353	−0.6
235	8	2	7	7	1	6	(01)	16023.7455	1.2
236	8	2	7	7	1	6	(10)	16015.3287	−4.2
237	8	2	7	7	1	6	(11)	16011.7412	4.6
238	8	2	7	7	1	6	(12)	16016.3595	−8.4
239	9	2	8	8	1	7	(00)	16989.9424	1.2
240	9	2	8	8	1	7	(01)	16988.9360	0.7
241	9	2	8	8	1	7	(10)	16982.4891	−3.7
242	9	2	8	8	1	7	(11)	16980.2305	3.7
243	9	2	8	8	1	7	(12)	16982.7552	−6.6
244	10	2	9	9	1	8	(00)	18004.7146	2.4
245	10	2	9	9	1	8	(01)	18003.8981	0.7
246	10	2	9	9	1	8	(10)	17998.8763	−3.2

Appendix E. 2-Acetyl-4-Methylthiophene

247	10	2	9	9	1	8	(11)	17997.3715	2.4
248	11	2	10	10	1	9	(00)	19103.5604	0.4
249	11	2	10	10	1	9	(10)	19098.9743	-1.9
250	11	2	10	10	1	9	(11)	19097.8957	0.7
251	6	2	5	6	1	6	(00)	8445.2859	5.2
252	6	2	5	6	1	6	(01)	8442.3461	-0.9
253	6	2	5	6	1	6	(10)	8427.5929	2.3
254	6	2	5	6	1	6	(11)	8418.6348	8.4
255	6	2	5	6	1	6	(12)	8430.8072	-3.6
256	7	2	6	7	1	7	(00)	9399.3062	-0.9
257	7	2	6	7	1	7	(01)	9396.5710	-0.2
258	8	2	7	8	1	8	(00)	10471.3834	1.5
259	8	2	7	8	1	8	(01)	10468.5915	1.0
260	8	2	7	8	1	8	(11)	10456.0736	0.8
261	9	2	8	9	1	9	(00)	11644.4770	0.4
262	9	2	8	9	1	9	(01)	11641.5034	-0.8
263	9	2	8	9	1	9	(10)	11634.5725	-3.3
264	9	2	8	9	1	9	(11)	11630.5702	-0.6
265	9	2	8	9	1	9	(12)	11632.6479	0.9
266	10	2	9	10	1	10	(01)	12896.2562	0.3
267	10	2	9	10	1	10	(10)	12889.7399	3.0
268	11	2	10	11	1	11	(00)	14217.3258	-3.2
269	4	2	2	3	2	1	(00)	7134.2059	0.3
270	5	2	3	4	2	2	(00)	9034.1051	0.5
271	5	2	3	4	2	2	(01)	9031.0843	2.8
272	5	2	3	4	2	2	(10)	9007.3043	-3.4
273	5	2	3	4	2	2	(12)	9018.6201	-5.0
274	6	2	4	5	2	3	(00)	10957.9297	1.2
275	6	2	4	5	2	3	(01)	10956.4593	2.4
276	6	2	4	5	2	3	(10)	10946.0264	-2.6
277	6	2	4	5	2	3	(11)	10938.6611	4.1
278	6	2	4	5	2	3	(12)	10951.0053	-3.7
279	7	2	5	6	2	4	(01)	12872.2505	0.4
280	7	2	5	6	2	4	(10)	12867.3843	-1.9
281	7	2	5	6	2	4	(11)	12863.4119	3.3
282	7	2	5	6	2	4	(12)	12869.3661	1.4
283	8	2	6	7	2	5	(00)	14753.8007	-0.6
284	8	2	6	7	2	5	(10)	14750.0786	-0.3
285	8	2	6	7	2	5	(11)	14747.4206	1.1
286	8	2	6	7	2	5	(12)	14750.8305	2.7
287	9	2	7	8	2	6	(00)	16581.6026	-0.6
288	9	2	7	8	2	6	(01)	16580.6067	-2.3
289	9	2	7	8	2	6	(10)	16578.5922	3.4
290	9	2	7	8	2	6	(11)	16576.3831	-1.2
291	9	2	7	8	2	6	(12)	16578.8122	2.9
292	10	2	8	9	2	7	(00)	18343.1630	-1.1

Appendix E. 2-Acetyl-4-Methylthiophene

293	10	2	8	9	2	7	(01)	18342.1287	-2.2
294	10	2	8	9	2	7	(10)	18340.3061	2.7
295	10	2	8	9	2	7	(11)	18338.3084	-0.5
296	10	2	8	9	2	7	(12)	18340.2375	5.1
297	11	2	9	10	2	8	(00)	20026.5088	0.4
298	11	2	9	10	2	8	(01)	20025.4640	-2.8
299	11	2	9	10	2	8	(10)	20023.6120	3.0
300	6	2	5	5	2	4	(00)	10239.8359	-2.6
301	6	2	5	5	2	4	(01)	10240.5281	0.7
302	6	2	5	5	2	4	(10)	10250.9773	1.1
303	6	2	5	5	2	4	(11)	10257.7237	-6.8
304	7	2	6	6	2	5	(00)	11882.1751	1.2
305	7	2	6	6	2	5	(01)	11882.2555	1.9
306	7	2	6	6	2	5	(10)	11886.8444	1.4
307	7	2	6	6	2	5	(11)	11889.8606	-4.2
308	7	2	6	6	2	5	(12)	11883.8956	2.2
309	8	2	7	7	2	6	(00)	13497.9177	1.6
310	8	2	7	7	2	6	(01)	13497.7346	0.4
311	8	2	7	7	2	6	(10)	13499.7791	-0.5
312	8	2	7	7	2	6	(11)	13501.0634	-2.5
313	8	2	7	7	2	6	(12)	13498.1091	-0.5
314	9	2	8	8	2	7	(00)	15086.4258	0.1
315	9	2	8	8	2	7	(01)	15086.1143	-0.6
316	9	2	8	8	2	7	(10)	15086.9314	1.0
317	9	2	8	8	2	7	(11)	15087.3906	0.9
318	10	2	9	9	2	8	(00)	16648.6872	3.9
319	10	2	9	9	2	8	(01)	16648.3037	0.4
320	10	2	9	9	2	8	(10)	16648.4531	-1.0
321	10	2	9	9	2	8	(12)	16647.6507	0.7
322	3	3	1	2	2	0	(00)	14515.1104	2.1
323	3	3	1	2	2	0	(01)	14415.6231	-6.4
324	4	3	2	3	2	1	(00)	16185.5467	0.3
325	4	3	2	3	2	1	(01)	16110.3106	-2.3
326	4	3	2	3	2	1	(10)	15856.2551	-6.2
327	4	3	2	3	2	1	(12)	15957.6162	-7.5
328	5	3	3	4	2	2	(00)	17757.5460	0.9
329	5	3	3	4	2	2	(01)	17704.6658	-0.6
330	5	3	3	4	2	2	(10)	17493.2452	2.4
331	5	3	3	4	2	2	(12)	17578.9249	-3.5
332	6	3	4	5	2	3	(00)	19184.1766	0.2
333	6	3	4	5	2	3	(01)	19154.1832	-3.8
334	6	3	4	5	2	3	(10)	18984.6739	-0.7
335	6	3	4	5	2	3	(12)	19054.5888	2.2
336	7	3	5	6	2	4	(00)	20438.2176	1.6
337	7	3	5	6	2	4	(01)	20422.9462	-7.3
338	7	3	5	6	2	4	(10)	20305.4750	7.5

Appendix E. 2-Acetyl-4-Methylthiophene

339	7	3	5	6	2	4	(12)	20356.7386	3.9
340	8	3	6	7	2	5	(00)	21518.5134	−3.7
341	8	3	6	7	2	5	(10)	21439.1170	7.1
342	8	3	6	7	2	5	(12)	21469.5037	1.8
343	3	3	0	2	2	1	(00)	14543.3078	0.8
344	4	3	1	3	2	2	(00)	16328.0859	1.7
345	8	3	5	7	3	4	(00)	14315.9866	−0.4
346	8	3	5	7	3	4	(01)	14309.2850	3.0
347	8	3	5	7	3	4	(10)	14267.7975	−3.9
348	8	3	5	7	3	4	(12)	14285.4221	−1.8
349	9	3	6	8	3	5	(00)	16271.8990	−1.3
350	9	3	6	8	3	5	(01)	16268.5728	2.6
351	9	3	6	8	3	5	(10)	16243.6279	−5.7
352	9	3	6	8	3	5	(12)	16255.6158	−3.2
353	10	3	7	9	3	6	(00)	18253.4945	−0.5
354	10	3	7	9	3	6	(10)	18238.8192	−5.5
355	11	3	8	10	3	7	(00)	20227.8145	−2.3
356	11	3	8	10	3	7	(01)	20226.2612	1.2
357	11	3	8	10	3	7	(10)	20219.7230	5.3
358	4	4	0	3	3	1	(00)	19995.7770	1.9
359	5	4	1	4	3	2	(00)	21733.4540	0.5

F. 2-Acetyl-5-Methylthiophene

Table F.1: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of 2A4MT given in Figure 8.2 calculated at the MP2/6-31G(d,p) level of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^5 a_i f_i$.

i	f_i	a_i / Hartree	a_i / cm^{-1}
0	1	-743.36102813	
1	$\cos 1\alpha$	-0.000721750	-158.4
2	$\cos 2\alpha$	-0.006602747	-1449.2
3	$\cos 3\alpha$	-0.000293569	-64.4
4	$\cos 4\alpha$	0.000439625	96.5
5	$\cos 5\alpha$	-0.000066190	-14.5

Table F.2: Nuclear coordinates in the principal axis system of *syn*-2A5MT and *anti*-2A5MT calculated at the MP2/6-311++G(d,p) level of theory (for atom numbering see Figure 8.1).

	<i>syn</i> -2A5MT			<i>anti</i> -2A5MT		
	a / Å	b / Å	c / Å	a / Å	b / Å	c / Å
S1	0.633959	-1.010491	-0.000088	-0.611102	-1.015933	0.000059
C2	-0.564937	0.232994	0.000042	0.561539	0.257459	0.000013
C3	0.017715	1.490700	-0.000031	-0.057695	1.494956	0.000063
C4	1.427528	1.433507	-0.000095	-1.464250	1.401443	0.000048
C5	1.917932	0.140589	-0.000129	-1.928946	0.099237	-0.000006
C6	-1.985912	-0.141843	0.000042	2.022440	0.038248	-0.000003
O7	-2.327220	-1.327833	0.000011	2.790051	1.001974	-0.000086
C8	-3.000748	0.979643	0.000083	2.532029	-1.385022	-0.000014
C9	3.352687	-0.286808	0.000227	-3.350664	-0.368558	-0.000118
H10	3.596419	-0.878304	0.882748	-3.579192	-0.967367	-0.881844
H11	3.992378	0.594172	-0.002335	-4.012277	0.496066	0.000136
H12	3.595536	-0.882770	-0.879514	-3.579165	-0.967860	0.881278
H13	2.073683	2.300829	-0.000153	-2.132887	2.251577	0.000055
H14	-0.554664	2.407808	-0.000048	0.515442	2.410700	0.000086
H15	-2.873377	1.608201	0.881088	2.173164	-1.918592	0.880557
H16	-3.996135	0.545438	0.000143	3.617934	-1.368476	-0.000193
H17	-2.873474	1.608169	-0.880959	2.172869	-1.918714	-0.880389

Appendix F. 2-Acetyl-5-Methylthiophene

Table F.3: Rotational constants and the dihedral angle α of *syn*-2A5MT optimized at various levels of theory. The deviations between the calculated and the experimental values of the rotational constants are given as ΔA , ΔB and ΔC . $V_{3,1}$ is the barrier of the acetyl methyl and $V_{3,2}$ that of the ring methyl group. All optimizations were performed under full-symmetry relaxation.

Method/Basis Set	$A /$ MHz	$\Delta A /$ MHz	$B /$ MHz	$\Delta B /$ MHz	$C /$ MHz	$\Delta C /$ MHz	$V_{3,1} /$ cm^{-1}	$\Delta V_{3,1} /$ cm^{-1}	$V_{3,2} /$ cm^{-1}	$\Delta V_{3,2} /$ cm^{-1}	$\alpha /$ $^\circ$	Planar
B3LYP-D3/6-311G(2d,2p)	3448.4943	0.9	922.4506	-4.6	734.3722	-3.2	292.3	9.5	168.3	-11.0	0.04	Yes
B3LYP-D3/6-311+G(2d,2p)	3447.3820	-0.2	921.5052	-5.5	733.7264	-3.8	237.2	64.6	170.4	-13.1	0.00	Yes
B3LYP-D3/6-311++G(2d,2p)	3447.2525	-0.4	921.5282	-5.5	733.7355	-3.8	239.6	62.2	174.1	-16.8	0.00	Yes
B3LYP-D3/6-311G(2df,2pd)	3456.8451	9.2	924.3065	-2.7	735.9243	-1.6	295.9	5.9	155.5	1.8	0.02	Yes
B3LYP-D3/6-311+G(2df,2pd)	3455.7159	8.1	923.0726	-3.9	735.0944	-2.4	241.2	60.6	158.2	-0.9	0.00	Yes
B3LYP-D3/6-311++G(2df,2pd)	3455.6563	8.0	923.0699	-4.0	735.0905	-2.4	243.8	58.0	163.1	-5.8	0.00	Yes
B3LYP-D3/6-311G(3df,3pd)	3461.6822	14.1	924.7836	-2.2	736.4519	-1.1	279.8	22.0	149.2	8.1	0.00	Yes
B3LYP-D3/6-311+G(3df,3pd)	3459.5610	11.9	924.3036	-2.7	736.0521	-1.5	251.7	50.1	156.8	0.5	0.00	Yes
B3LYP-D3/6-311++G(3df,3pd)	3459.5068	11.9	924.3083	-2.7	736.0523	-1.5	251.2	50.6	157.0	0.3	0.00	Yes
B3LYP-D3/6-311G(df,pd)	3443.4749	-4.1	921.9676	-5.1	733.8649	-3.7	262.7	39.1	194.9	-37.6	-0.04	Yes
B3LYP-D3/6-311+G(df,pd)	3443.1506	-4.5	920.5616	-6.5	732.9595	-4.6	217.8	84.0	192.9	-35.6	-0.04	Yes
B3LYP-D3/6-311++G(df,pd)	3443.2000	-4.4	920.5383	-6.5	732.9462	-4.6	212.2	89.6	198.1	-40.8	-0.04	Yes
B3LYP-D3/6-311G(d,p)	3431.1657	-16.5	919.7186	-7.3	731.8976	-5.6	272.9	28.9	196.3	-39.0	0.03	Yes
B3LYP-D3/6-311+G(d,p)	3430.6772	-16.9	918.1648	-8.9	730.8941	-6.6	227.2	74.6	197.2	-39.9	-0.04	Yes
B3LYP-D3/6-311++G(d,p)	3430.6089	-17.0	918.1501	-8.9	730.8818	-6.7	227.1	74.7	209.4	-52.1	-0.04	Yes
B3LYP-D3/6-31G(d,p)	3418.3619	-29.3	918.3812	-8.6	730.4766	-7.1	282.5	19.3	219.5	-62.2	0.03	Yes
B3LYP-D3/6-31+G(d,p)	3415.9261	-31.7	915.4731	-11.5	728.5392	-9.0	216.6	85.2	214.7	-57.4	0.00	Yes
B3LYP-D3/6-31++G(d,p)	3415.9593	-31.7	915.4634	-11.6	728.5349	-9.0	214.9	86.9	215.3	-58.0	0.00	Yes
B3LYP-D3/aug-cc-pVDZ	3408.6021	-39.0	914.5675	-12.5	727.6775	-9.9	236.0	65.8	195.1	-37.8	0.00	Yes
B3LYP-D3/aug-cc-pVTZ	3452.6106	5.0	922.5850	-4.4	734.6462	-2.9	238.0	63.8	169.2	-11.9	0.00	Yes
B3LYP-D3BJ/6-311G(2d,2p)	3448.6950	1.1	926.0056	-1.0	736.6312	-0.9	259.3	42.5	147.8	9.5	-0.01	Yes
B3LYP-D3BJ/6-311+G(2d,2p)	3447.5436	-0.1	925.0572	-2.0	735.9810	-1.6	201.9	99.9	149.7	7.6	-0.01	Yes
B3LYP-D3BJ/6-311++G(2d,2p)	3447.4083	-0.2	925.0767	-1.9	735.9877	-1.5	204.4	97.4	153.4	3.9	-0.01	Yes

Appendix F. 2-Acetyl-5-Methylthiophene

B3LYP-D3BJ/6-311G(2df,2pd)	3456.3326	8.7	927.7737	0.8	738.0961	0.6	262.2	39.6	134.7	22.6	0.00	Yes
B3LYP-D3BJ/6-311+G(2df,2pd)	3455.4266	7.8	926.6364	-0.4	737.3373	-0.2	205.7	96.1	137.3	20.0	0.00	Yes
B3LYP-D3BJ/6-311++G(2df,2pd)	3455.3680	7.7	926.6342	-0.4	737.3337	-0.2	208.2	93.6	142.2	15.1	0.00	Yes
B3LYP-D3BJ/6-311G(3df,3pd)	3461.3764	13.8	928.3088	1.3	738.6696	1.1	246.2	55.6	128.3	29.0	0.00	Yes
B3LYP-D3BJ/6-311+G(3df,3pd)	3459.0805	11.5	927.8741	0.9	738.2903	0.8	215.8	86.0	136.0	21.3	0.00	Yes
B3LYP-D3BJ/6-311++G(3df,3pd)	3459.0250	11.4	927.8789	0.9	738.2906	0.8	215.4	86.4	136.1	21.2	0.00	Yes
B3LYP-D3BJ/6-311G(df,pd)	3443.5927	-4.0	925.3976	-1.6	736.0399	-1.5	228.3	73.5	174.9	-17.6	0.00	Yes
B3LYP-D3BJ/6-311+G(df,pd)	3443.3558	-4.3	924.0092	-3.0	735.1515	-2.4	181.6	120.2	173.0	-15.7	0.02	Yes
B3LYP-D3BJ/6-311++G(df,pd)	3443.3907	-4.2	923.9910	-3.0	735.1409	-2.4	176.0	125.8	178.0	-20.7	0.02	Yes
B3LYP-D3BJ/6-311G(d,p)	3432.3884	-15.2	923.1190	-3.9	734.1031	-3.4	239.4	62.4	176.5	-19.2	0.02	Yes
B3LYP-D3BJ/6-311+G(d,p)	3431.3484	-16.3	921.6454	-5.4	733.1266	-4.4	191.6	110.2	177.4	-20.1	0.00	Yes
B3LYP-D3BJ/6-311++G(d,p)	3431.3484	-16.3	921.6454	-5.4	733.1266	-4.4	191.5	110.3	189.6	-32.3	0.00	Yes
B3LYP-D3BJ/6-31G(d,p)	3418.6813	-28.9	921.8194	-5.2	732.6629	-4.9	249.0	52.8	200.4	-43.1	0.00	Yes
B3LYP-D3BJ/6-31+G(d,p)	3416.6542	-31.0	918.9596	-8.1	730.7763	-6.8	181.7	120.1	196.0	-38.7	0.00	Yes
B3LYP-D3BJ/6-31++G(d,p)	3416.6880	-30.9	918.9506	-8.1	730.7725	-6.8	179.8	122.0	196.5	-39.2	0.00	Yes
B3LYP-D3BJ/aug-cc-pVDZ	3409.4634	-38.2	918.1520	-8.9	729.9816	-7.6	198.6	103.2	175.0	-17.7	0.01	Yes
B3LYP-D3BJ/aug-cc-pVTZ	3452.2999	4.7	926.1371	-0.9	736.8804	-0.7	202.1	99.7	148.3	9.0	0.00	Yes
B3LYP-D3BJ/cc-pVDZ	3406.3694	-41.3	920.2583	-6.8	731.1857	-6.3	301.3	0.5	176.0	-18.7	0.00	Yes
B3LYP-D3BJ/cc-pVTZ	3452.0427	4.4	926.4325	-0.6	737.0548	-0.5	219.3	82.5	151.4	5.9	0.00	Yes
B3LYP-D3/cc-pVDZ	3405.5805	-42.0	916.6983	-10.3	728.9029	-8.6	334.9	-33.1	195.7	-38.4	0.00	Yes
B3LYP-D3/cc-pVTZ	3452.1936	4.6	922.9304	-4.1	734.8454	-2.7	254.4	47.4	172.1	-14.8	0.00	Yes
CAM-B3LYP-D3BJ/6-311G(d,p)	3469.6977	22.1	929.1899	2.2	739.6393	2.1	264.9	36.9	178.0	-20.7	0.00	Yes
CAM-B3LYP-D3BJ/6-311+G(d,p)	3469.4404	21.8	927.6204	0.6	738.6353	1.1	217.9	83.9	181.3	-24.0	0.00	Yes
CAM-B3LYP-D3BJ/6-311++G(d,p)	3469.3630	21.7	927.6105	0.6	738.6258	1.1	218.5	83.3	193.3	-36.0	0.00	Yes
CAM-B3LYP-D3BJ/aug-cc-pVDZ	3447.3200	-0.3	923.9464	-3.1	735.3687	-2.2	221.8	80.0	182.1	-24.8	0.01	Yes
CAM-B3LYP-D3BJ/aug-cc-pVTZ	3489.8800	42.3	932.0109	5.0	742.3022	4.8	228.3	73.5	156.0	1.3	0.00	Yes
CAM-B3LYP-D3BJ/cc-pVDZ	3444.2266	-3.4	926.1504	-0.9	736.6390	-0.9	318.5	-16.7	182.2	-24.9	0.00	Yes
CAM-B3LYP-D3BJ/cc-pVTZ	3489.6607	42.0	932.4014	5.4	742.5390	5.0	244.8	57.0	157.1	0.2	0.00	Yes
CCSD/cc-pVDZ	3391.1934	-56.4	912.0127	-15.0	725.3503	-12.2	403.7	-101.9	161.3	-4.0	0.01	Yes
M06-2X/6-311G(3df,3pd)	3484.9651	37.3	932.2561	5.2	742.2514	4.7	363.3	-61.5	153.3	4.0	0.00	Yes

Appendix F. 2-Acetyl-5-Methylthiophene

M06-2X/6-311+G(3df,3pd)	3483.0253	35.4	931.9722	4.9	741.9841	4.5	343.2	-41.4	160.2	-2.9	0.01	Yes
M06-2X/6-311++G(3df,3pd)	3482.9696	35.3	931.9736	5.0	741.9821	4.4	343.4	-41.6	160.5	-3.2	0.00	Yes
M06-2X/6-311G(df,pd)	3468.7535	21.1	929.9338	2.9	740.0689	2.5	326.2	-24.4	188.4	-31.1	0.00	Yes
M06-2X/6-311+G(df,pd)	3469.1235	21.5	928.6382	1.6	739.2640	1.7	294.0	7.8	190.6	-33.3	0.00	Yes
M06-2X/6-311++G(df,pd)	3469.1104	21.5	928.6307	1.6	739.2586	1.7	288.0	13.8	196.3	-39.0	0.01	Yes
M06-2X/6-311G(d,p)	3458.5736	11.0	928.3073	1.3	738.5914	1.1	340.2	-38.4	188.4	-31.1	0.01	Yes
M06-2X/6-311+G(d,p)	3458.7617	11.1	926.9316	-0.1	737.7305	0.2	306.3	-4.5	193.8	-36.5	0.00	Yes
M06-2X/6-311++G(d,p)	3458.6776	11.1	926.9272	-0.1	737.7245	0.2	306.6	-4.8	207.2	-49.9	0.00	Yes
M06-2X/6-31G(d,p)	3448.3181	0.7	927.4369	0.4	737.5813	0.0	335.3	-33.5	205.7	-48.4	0.00	Yes
M06-2X/6-31+G(d,p)	3446.9602	-0.7	925.1120	-1.9	736.0613	-1.5	278.3	23.5	202.3	-45.0	0.00	Yes
M06-2X/6-31++G(d,p)	3446.9427	-0.7	925.1195	-1.9	736.0658	-1.5	277.3	24.5	204.0	-46.7	0.00	Yes
M06-2X/aug-cc-pVDZ	3441.3354	-6.3	924.1893	-2.8	735.2623	-2.3	297.3	4.5	188.9	-31.6	0.00	Yes
M06-2X/aug-cc-pVTZ	3477.5311	29.9	931.0761	4.1	741.1666	3.6	316.5	-14.7	169.3	-12.0	0.00	Yes
M06-2X/cc-pVDZ	3438.5948	-9.0	926.2620	-0.8	736.4632	-1.1	362.8	-61.0	186.8	-29.5	0.00	Yes
M06-2X/cc-pVTZ	3476.6829	29.1	931.3229	4.3	741.2847	3.8	324.6	-22.8	167.3	-10.0	0.00	Yes
MP2/6-311G(2d,2p)	3433.9215	-13.7	928.9467	1.9	737.8014	0.3	340.8	-39.0	132.4	24.9	0.04	Yes
MP2/6-311+G(2d,2p)	3432.7451	-14.9	927.7451	0.7	736.9930	-0.5	283.3	18.5	137.0	20.3	0.03	Yes
MP2/6-311++G(2d,2p)	3432.5457	-15.1	927.7467	0.7	736.9867	-0.5	287.9	13.9	138.6	18.7	0.03	Yes
MP2/6-311G(2df,2pd)	3450.7935	3.2	934.6498	7.6	742.1877	4.7	335.8	-34.0	116.8	40.5	0.00	Yes
MP2/6-311+G(2df,2pd)	3448.8603	1.2	933.0737	6.1	741.1090	3.6	277.5	24.3	123.8	33.5	0.00	Yes
MP2/6-311++G(2df,2pd)	3448.7951	1.2	933.0566	6.0	741.0965	3.6	281.6	20.2	127.9	29.4	0.00	Yes
MP2/6-311G(3df,3pd)	3454.6254	7.0	934.2892	7.3	742.1542	4.6	339.2	-37.4	97.4	59.9	-0.03	Yes
MP2/6-311+G(3df,3pd)	3451.4295	3.8	933.6344	6.6	741.5942	4.1	295.2	6.6	108.1	49.2	-0.03	Yes
MP2/6-311++G(3df,3pd)	3451.3235	3.7	933.6862	6.7	741.6214	4.1	294.6	7.2	109.2	48.1	0.00	Yes
MP2/6-311G(df,pd)	3448.7375	1.1	931.6314	4.6	740.2461	2.7	326.7	-24.9	177.2	-19.9	-0.01	Yes
MP2/6-311+G(df,pd)	3445.5305	-2.1	929.8089	2.8	738.9522	1.4	272.0	29.8	168.3	-11.0	-0.02	Yes
MP2/6-311++G(df,pd)	3445.7387	-1.9	929.8698	2.8	739.0695	1.5	270.6	31.2	194.2	-36.9	-3.18	No
MP2/6-311G(d,p)	3422.6439	-25.0	926.4466	-0.6	735.8002	-1.7	347.3	-45.5	172.8	-15.5	-0.01	Yes
MP2/6-311+G(d,p)	3421.5236	-26.1	924.5314	-2.5	734.5427	-3.0	295.6	6.2	165.0	-7.7	-0.01	Yes
MP2/6-311++G(d,p)	3421.4884	-26.1	924.5102	-2.5	734.5289	-3.0	290.8	11.0	202.1	-44.8	-0.02	Yes

Appendix F. 2-Acetyl-5-Methylthiophene

MP2/6-31G(d,p)	3425.2312	-22.4	927.6229	0.6	736.5991	-0.9	359.0	-57.2	165.5	-8.2	-0.01	Yes
MP2/6-31+G(d,p)	3419.5932	-28.0	924.9485	-2.1	734.6713	-2.9	266.6	35.2	185.4	-28.1	0.01	Yes
MP2/6-31++G(d,p)	3419.4941	-28.1	924.9131	-2.1	734.6466	-2.9	262.2	39.6	194.2	-36.9	0.01	Yes
MP2/aug-cc-pVDZ	3373.8306	-73.8	916.4477	-10.6	727.3270	-10.2	271.2	30.6	152.0	5.3	0.00	Yes
MP2/cc-pVDZ	3382.8111	-64.8	919.1623	-7.9	729.4494	-8.1	406.3	-104.5	166.8	-9.5	0.00	Yes
MP2/cc-pVTZ	3441.6008	-6.0	931.9170	4.9	740.0479	2.5	293.6	8.2	137.9	19.4	0.00	Yes
ω B97X-D/6-311G(d,p)	3462.6795	15.1	925.5488	-1.5	737.0348	-0.5	262.7	39.1	183.4	-26.1	0.00	Yes
ω B97X-D/6-311+G(d,p)	3462.5874	15.0	925.5358	-1.5	737.0225	-0.5	263.8	38.0	195.7	-38.4	0.00	Yes
ω B97X-D/6-311++G(d,p)	3462.5550	14.9	926.9501	-0.1	737.9157	0.4	296.4	5.4	179.8	-22.5	0.00	Yes
ω B97X-D/aug-cc-pVDZ	3441.0349	-6.6	921.8369	-5.2	733.7647	-3.8	280.4	21.4	174.6	-17.3	0.02	Yes
ω B97X-D/aug-cc-pVTZ	3483.3105	35.7	929.6988	2.7	740.5541	3.0	283.1	18.7	154.5	2.8	0.00	Yes
ω B97X-D/cc-pVDZ	3438.4941	-9.1	923.6269	-3.4	734.7946	-2.7	334.4	-32.6	176.5	-19.2	0.00	Yes
ω B97X-D/cc-pVTZ	3482.9519	35.3	929.8956	2.9	740.6620	3.1	288.8	13.0	154.9	2.4	0.00	Yes
Experiment	3447.6227		927.0222		737.5335		301.8		157.3			

Table F.4: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of *syn*- and *anti*-2A5MT given in Figure 8.3 and Figure F.1 calculated at the MP2/6-31G(d,p), level of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^2 a_i f_i$.

<i>i</i>	<i>f_i</i>	<i>syn</i>				<i>anti</i>			
		Acetyl Methyl		Ring Methyl		Acetyl Methyl		Ring Methyl	
		<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹	<i>a_i</i> / Hartree	<i>a_i</i> / cm ⁻¹
0	1	-743.3675393		-743.3679628		-743.3654078		-743.3658014	
1	cos 3α	-0.0008114	-178.1	0.0003787	83.1	0.0007944	174.3	0.0004014	88.1
2	cos 6α	-0.0000496	-10.9	0.0000325	7.1	0.0000360	7.9	0.0000329	7.2

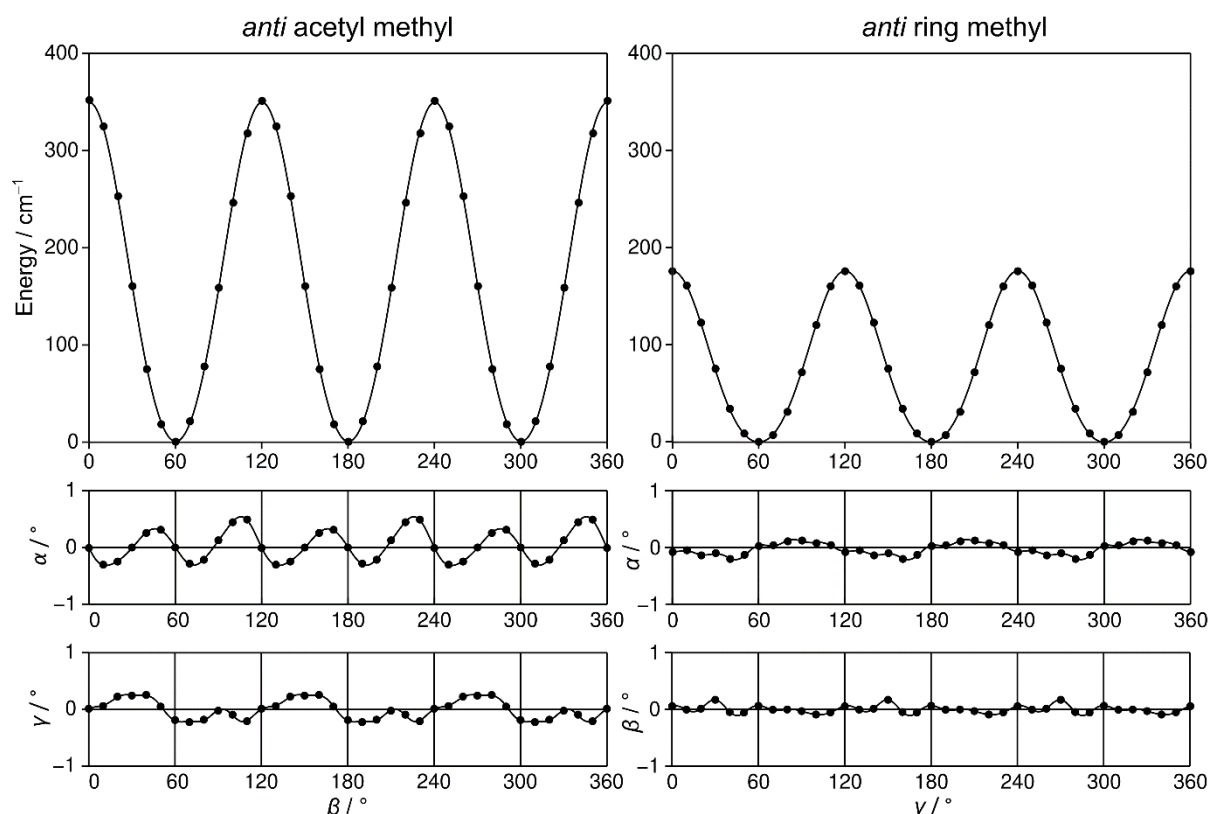


Figure F.1: Left hand side: The potential energy curve of *anti*-2A5MT obtained at the MP2/6-31G(d,p) level of theory by rotating the acetyl methyl group about the C6–C8 bond by varying the dihedral angle β in steps of 10°. The energies are given relative to the lowest energy with $E = -743.3661677$ Hartree. The calculated barrier height is 351.6 cm⁻¹. The middle trace visualizes the oscillation of the acetyl group upon the acetyl methyl rotation and the lowest trace that of the ring methyl group. The deviations of the dihedral angles α and γ are given relative to the values of the fully optimized geometries, which are 180.00° for α and 179.98° for γ . **Right hand side:** The potential energy curve of *syn*-2A5MT obtained by rotating the ring methyl group about the C3–C9 bond by varying the dihedral angle γ in steps of 10°. The energies are given relative to the lowest energy with $E = -743.3661678$ Hartree. The calculated barrier height is 175.5 cm⁻¹. The middle trace visualizes the oscillation of the acetyl group upon the ring methyl rotation and the lowest trace that of the acetyl methyl group. The deviations of the dihedral angles α and β are given relative to the values of the fully optimized geometries, which are 180.00° for α and 0.00° for β .

Appendix F. 2-Acetyl-5-Methylthiophene

Table F.5: Coefficients of the two-dimensional Fourier expansion for the potential energy surface calculated at the MP2/6-31G(d,p) level of theory shown in Figure 8.4. Due to symmetry, only data points in the range from 0° to 120° were calculated for both β and γ . The potential is expanded as $V(\beta, \gamma) = \sum_i f_i V_i$. Max. dev. stands for maximum deviations between the fitted and the calculated values.

i	f_i	V_i / Hartree
1	1	-743.3673255
2	$\cos(3\beta)$	0.0007590
3	$\cos(3\gamma)$	0.0003762
4	$\cos(6\beta)$	0.0001384
5	$\cos(6\gamma)$	0.0000323
Max. dev. (%)		8.0

Table F.6: Observed frequencies ν_{obs} of 427 rotational transitions of *syn*-2A5MT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program XIAM.

No.	J upper level	K_a	K_c	J lower level	K_a	K_c	Species	ν_{obs} MHz	$\nu_{obs}-\nu_{calc}$ kHz
1	4	0	4	3	0	3	(00)	6557.6150	0.1
2	4	0	4	3	0	3	(01)	6557.4625	-0.5
3	4	0	4	3	0	3	(10)	6556.4996	0.3
4	4	0	4	3	0	3	(11)	6556.1676	2.1
5	4	0	4	3	0	3	(12)	6556.5281	-0.3
6	5	0	5	4	0	4	(00)	8126.3405	-0.8
7	5	0	5	4	0	4	(01)	8126.1754	-0.3
8	5	0	5	4	0	4	(10)	8124.7950	1.1
9	5	0	5	4	0	4	(11)	8124.4691	-0.7
10	5	0	5	4	0	4	(12)	8124.7950	7.8
11	6	0	6	5	0	5	(00)	9657.5524	-1.3
12	6	0	6	5	0	5	(01)	9657.3814	-1.2
13	6	0	6	5	0	5	(10)	9655.5293	-1.2
14	6	0	6	5	0	5	(11)	9655.2258	-0.7
15	6	0	6	5	0	5	(12)	9655.4940	0.6
16	7	0	7	6	0	6	(00)	11155.6346	-1.5
17	7	0	7	6	0	6	(01)	11155.4632	-2.0
18	7	0	7	6	0	6	(10)	11153.1946	-1.6
19	7	0	7	6	0	6	(11)	11152.9114	-0.7
20	7	0	7	6	0	6	(12)	11153.1397	-0.3

Appendix F. 2-Acetyl-5-Methylthiophene

21	8	0	8	7	0	7	(00)	12629.7351	−2.4
22	8	0	8	7	0	7	(01)	12629.5681	−1.9
23	8	0	8	7	0	7	(10)	12627.0447	0.3
24	8	0	8	7	0	7	(11)	12626.7765	−2.5
25	9	0	9	8	0	8	(00)	14090.3852	−0.1
26	9	0	9	8	0	8	(01)	14090.2212	−1.8
27	9	0	9	8	0	8	(10)	14087.6369	−2.0
28	9	0	9	8	0	8	(11)	14087.3919	−1.5
29	9	0	9	8	0	8	(12)	14087.5598	−2.1
30	10	0	10	9	0	9	(00)	15546.2084	−1.0
31	10	0	10	9	0	9	(01)	15546.0510	−1.8
32	10	0	10	9	0	9	(10)	15543.5683	−0.5
33	10	0	10	9	0	9	(11)	15543.3444	−0.5
34	11	0	11	10	0	10	(00)	17002.5530	1.6
35	11	0	11	10	0	10	(01)	17002.3983	−2.1
36	11	0	11	10	0	10	(10)	17000.1034	2.0
37	11	0	11	10	0	10	(11)	16999.8980	−1.2
38	12	0	12	11	0	11	(00)	18461.8418	0.4
39	12	0	12	11	0	11	(01)	18461.6951	−0.2
40	12	0	12	11	0	11	(10)	18459.6003	−1.8
41	12	0	12	11	0	11	(11)	18459.4195	0.2
42	12	0	12	11	0	11	(12)	18459.4962	1.7
43	13	0	13	12	0	12	(00)	19924.6580	−1.2
44	13	0	13	12	0	12	(01)	19924.5179	0.4
45	13	0	13	12	0	12	(10)	19922.6094	−2.4
46	13	0	13	12	0	12	(11)	19922.4457	0.5
47	13	0	13	12	0	12	(12)	19922.4959	−0.5
48	15	0	15	14	0	14	(00)	22859.2859	1.9
49	15	0	15	14	0	14	(01)	22859.1452	−3.6
50	6	0	6	5	1	5	(00)	8175.0415	−1.0
51	6	0	6	5	1	5	(01)	8175.3098	−0.1
52	6	0	6	5	1	5	(10)	8206.9829	2.5
53	6	0	6	5	1	5	(11)	8210.5275	3.1
54	6	0	6	5	1	5	(12)	8203.9260	0.1
55	7	0	7	6	1	6	(00)	9984.4456	−0.2
56	7	0	7	6	1	6	(01)	9984.5986	−2.0
57	7	0	7	6	1	6	(10)	10007.2031	2.6
58	7	0	7	6	1	6	(11)	10009.5094	3.7
59	7	0	7	6	1	6	(12)	10005.1763	−0.9
60	8	0	8	7	1	7	(00)	11739.5480	−0.8
61	8	0	8	7	1	7	(01)	11739.6208	0.2
62	8	0	8	7	1	7	(10)	11755.8016	0.1
63	8	0	8	7	1	7	(11)	11757.3152	3.1
64	8	0	8	7	1	7	(12)	11754.4157	−0.4
65	9	0	9	8	1	8	(00)	13436.6391	−6.9
66	9	0	9	8	1	8	(01)	13436.6569	0.1

Appendix F. 2-Acetyl-5-Methylthiophene

67	9	0	9	8	1	8	(10)	13448.0691	−0.1
68	9	0	9	8	1	8	(11)	13449.0485	−1.2
69	9	0	9	8	1	8	(12)	13447.0967	−0.8
70	10	0	10	9	1	9	(00)	15079.9323	−7.2
71	10	0	10	9	1	9	(01)	15079.9066	0.7
72	10	0	10	9	1	9	(10)	15087.7347	−0.5
73	10	0	10	9	1	9	(11)	15088.3555	0.5
74	10	0	10	9	1	9	(12)	15087.0368	−2.6
75	11	0	11	10	1	10	(00)	16677.9040	4.0
76	11	0	11	10	1	10	(01)	16677.8320	−2.9
77	11	0	11	10	1	10	(10)	16682.9896	−5.0
78	11	0	11	10	1	10	(11)	16683.3675	−0.3
79	11	0	11	10	1	10	(12)	16682.4849	−0.3
80	12	0	12	11	1	11	(00)	18240.1688	−2.1
81	12	0	12	11	1	11	(01)	18240.0824	−1.5
82	12	0	12	11	1	11	(10)	18243.2871	0.0
83	12	0	12	11	1	11	(11)	18243.4949	2.5
84	13	0	13	12	1	12	(00)	19775.6876	−0.2
85	13	0	13	12	1	12	(01)	19775.5860	0.0
86	13	0	13	12	1	12	(10)	19777.3793	−0.7
87	13	0	13	12	1	12	(11)	19777.4690	−3.3
88	14	0	14	13	1	13	(00)	21291.8609	−2.0
89	14	0	14	13	1	13	(01)	21291.7539	2.3
90	14	0	14	13	1	13	(10)	21292.5444	−2.9
91	3	1	3	2	0	2	(00)	7051.7346	−0.8
92	3	1	3	2	0	2	(01)	7050.7847	−1.6
93	3	1	3	2	0	2	(10)	6978.4485	−4.5
94	3	1	3	2	0	2	(11)	6968.7094	1.2
95	3	1	3	2	0	2	(12)	6986.5604	0.0
96	4	1	4	3	0	3	(00)	8358.6082	−0.1
97	4	1	4	3	0	3	(01)	8357.8640	−1.6
98	4	1	4	3	0	3	(10)	8309.7424	−3.6
99	4	1	4	3	0	3	(11)	8303.5045	−0.3
100	4	1	4	3	0	3	(12)	8314.5922	−0.7
101	5	1	5	4	0	4	(00)	9608.8518	−0.7
102	5	1	5	4	0	4	(01)	9608.2478	−0.7
103	5	1	5	4	0	4	(10)	9573.3398	−4.2
104	5	1	5	4	0	4	(11)	9569.1702	−1.6
105	5	1	5	4	0	4	(12)	9576.3520	−2.7
106	6	1	6	5	0	5	(00)	10828.7436	−0.5
107	6	1	6	5	0	5	(01)	10828.2453	−1.9
108	6	1	6	5	0	5	(10)	10801.5221	−4.0
109	6	1	6	5	0	5	(11)	10798.6281	−4.7
110	6	1	6	5	0	5	(12)	10803.4546	−1.6
111	7	1	7	6	0	6	(00)	12045.8262	1.3
112	7	1	7	6	0	6	(01)	12045.4120	−2.5

Appendix F. 2-Acetyl-5-Methylthiophene

113	7	1	7	6	0	6	(10)	12024.4350	−4.0
114	7	1	7	6	0	6	(11)	12022.3755	−3.5
115	7	1	7	6	0	6	(12)	12025.6992	−1.4
116	8	1	8	7	0	7	(00)	13283.4759	−1.0
117	8	1	8	7	0	7	(01)	13283.1345	−1.7
118	8	1	8	7	0	7	(10)	13266.6123	−1.7
119	8	1	8	7	0	7	(11)	13265.1194	−3.3
120	8	1	8	7	0	7	(12)	13267.4391	−2.1
121	9	1	9	8	0	8	(00)	14556.6558	0.6
122	9	1	9	8	0	8	(01)	14556.3703	0.4
123	9	1	9	8	0	8	(10)	14543.4708	−1.7
124	9	1	9	8	0	8	(11)	14542.3823	−1.1
125	9	1	9	8	0	8	(12)	14544.0031	−1.0
126	10	1	10	9	0	9	(00)	15870.8658	5.0
127	10	1	10	9	0	9	(01)	15870.6179	−0.4
128	10	1	10	9	0	9	(10)	15860.6720	−3.6
129	10	1	10	9	0	9	(11)	15859.8720	−4.3
130	10	1	10	9	0	9	(12)	15860.9997	−0.2
131	11	1	11	10	0	10	(00)	17224.2229	1.1
132	11	1	11	10	0	10	(01)	17224.0117	−0.1
133	11	1	11	10	0	10	(10)	17216.4154	−1.0
134	11	1	11	10	0	10	(11)	17215.8247	−1.4
135	12	1	12	11	0	11	(00)	18610.8160	3.2
136	12	1	12	11	0	11	(01)	18610.6271	0.3
137	12	1	12	11	0	11	(10)	18604.8322	−1.6
138	12	1	12	11	0	11	(11)	18604.3937	1.5
139	12	1	12	11	0	11	(12)	18604.9140	5.1
140	13	1	13	12	0	12	(00)	20023.4811	1.4
141	13	1	13	12	0	12	(01)	20023.3128	1.7
142	13	1	13	12	0	12	(10)	20018.8587	1.1
143	13	1	13	12	0	12	(11)	20018.5205	0.4
144	14	1	14	13	0	13	(00)	21455.5323	1.0
145	14	1	14	13	0	13	(01)	21455.3761	0.8
146	8	1	7	8	0	8	(00)	7321.6212	−3.4
147	8	1	7	8	0	8	(01)	7320.1696	−0.8
148	5	1	5	4	1	4	(00)	7807.8578	−1.3
149	6	1	6	5	1	5	(00)	9346.2336	0.8
150	6	1	6	5	1	5	(01)	9346.1733	−1.2
151	6	1	6	5	1	5	(10)	9352.9761	0.1
152	6	1	6	5	1	5	(11)	9353.9304	−0.3
153	6	1	6	5	1	5	(12)	9351.8885	−0.2
154	7	1	7	6	1	6	(00)	10874.6336	−0.9
155	7	1	7	6	1	6	(01)	10874.5433	−6.6
156	7	1	7	6	1	6	(10)	10878.4439	0.6
157	7	1	7	6	1	6	(11)	10878.9722	−0.5
158	7	1	7	6	1	6	(12)	10877.7370	−0.9

Appendix F. 2-Acetyl-5-Methylthiophene

159	8	1	8	7	1	7	(00)	12393.2883	0.2
160	8	1	8	7	1	7	(01)	12393.1861	−0.8
161	8	1	8	7	1	7	(10)	12395.3720	0.8
162	8	1	8	7	1	7	(11)	12395.6557	−0.1
163	8	1	8	7	1	7	(12)	12394.8807	0.2
164	9	1	9	8	1	8	(00)	13902.9158	−0.1
165	9	1	9	8	1	8	(01)	13902.8020	−1.7
166	9	1	9	8	1	8	(10)	13903.9021	−0.7
167	9	1	9	8	1	8	(11)	13904.0393	−0.4
168	9	1	9	8	1	8	(12)	13903.5395	−0.2
169	10	1	10	9	1	9	(00)	15404.5896	−1.3
170	10	1	10	9	1	9	(01)	15404.4698	−1.6
171	10	1	10	9	1	9	(10)	15404.8413	−0.7
172	10	1	10	9	1	9	(11)	15404.8841	−2.2
173	11	1	11	10	1	10	(00)	16899.5698	−0.6
174	11	1	11	10	1	10	(01)	16899.4470	0.8
175	11	1	11	10	1	10	(10)	16899.3091	−0.5
176	12	1	12	11	1	11	(00)	18389.1410	−1.4
177	12	1	12	11	1	11	(01)	18389.0137	−1.7
178	12	1	12	11	1	11	(10)	18388.5181	−0.7
179	12	1	12	11	1	11	(11)	18388.4652	−0.1
180	12	1	12	11	1	11	(12)	18388.3168	−1.5
181	5	1	4	4	1	3	(00)	8748.2981	−0.4
182	5	1	4	4	1	3	(01)	8747.9334	−0.8
183	5	1	4	4	1	3	(10)	8734.8292	−0.6
184	5	1	4	4	1	3	(11)	8732.5953	0.5
185	5	1	4	4	1	3	(12)	8736.3795	−0.9
186	6	1	5	5	1	4	(00)	10464.2402	−1.8
187	6	1	5	5	1	4	(01)	10463.8449	−2.0
188	6	1	5	5	1	4	(10)	10455.6184	0.3
189	6	1	5	5	1	4	(11)	10453.9683	1.8
190	6	1	5	5	1	4	(12)	10456.4924	−1.0
191	7	1	6	6	1	5	(00)	12158.6604	−0.5
192	7	1	6	6	1	5	(01)	12158.2245	−1.0
193	7	1	6	6	1	5	(10)	12152.2409	0.5
194	7	1	6	6	1	5	(11)	12150.8515	2.1
195	7	1	6	6	1	5	(12)	12152.7654	0.0
196	8	1	7	7	1	6	(00)	13825.7137	−1.2
197	8	1	7	7	1	6	(01)	13825.2410	−2.1
198	8	1	7	7	1	6	(10)	13820.2302	0.9
199	8	1	7	7	1	6	(11)	13818.9794	1.4
200	8	1	7	7	1	6	(12)	13820.5395	1.0
201	9	1	8	8	1	7	(00)	15459.3203	−0.7
202	9	1	8	8	1	7	(01)	15458.8198	−2.9
203	9	1	8	8	1	7	(10)	15454.0766	−1.5
204	9	1	8	8	1	7	(11)	15452.9399	1.2

Appendix F. 2-Acetyl-5-Methylthiophene

205	9	1	8	8	1	7	(12)	15454.2201	-1.8
206	10	1	9	9	1	8	(00)	17054.1776	-1.3
207	10	1	9	9	1	8	(01)	17053.6655	0.0
208	10	1	9	9	1	8	(10)	17048.7473	-0.2
209	11	1	10	10	1	9	(00)	18607.3727	-2.0
210	11	1	10	10	1	9	(01)	18606.8577	1.3
211	11	1	10	10	1	9	(10)	18601.4806	-1.5
212	11	1	10	10	1	9	(11)	18600.5700	0.2
213	11	1	10	10	1	9	(12)	18601.3596	-1.2
214	4	2	2	3	1	3	(00)	15244.7807	2.7
215	4	2	2	3	1	3	(01)	15253.7595	-3.7
216	4	2	2	3	1	3	(12)	15703.8532	3.4
217	5	2	3	4	1	4	(00)	17481.8957	4.5
218	5	2	3	4	1	4	(01)	17484.7595	-3.0
219	5	2	3	4	1	4	(12)	17841.7554	2.2
220	4	2	3	3	1	3	(01)	15080.5163	-3.2
221	2	2	1	1	1	0	(00)	11101.8884	0.8
222	2	2	1	1	1	0	(01)	11060.7186	-5.8
223	3	2	2	2	1	1	(00)	12576.9674	-0.4
224	3	2	2	2	1	1	(01)	12550.9348	-5.1
225	3	2	2	2	1	1	(12)	11963.1193	-4.1
226	4	2	3	3	1	2	(00)	13955.8834	-1.3
227	4	2	3	3	1	2	(01)	13943.0319	-2.8
228	4	2	3	3	1	2	(10)	13384.6547	-4.9
229	4	2	3	3	1	2	(12)	13432.9934	0.2
230	5	2	4	4	1	3	(00)	15240.2237	-0.6
231	5	2	4	4	1	3	(01)	15233.3890	-1.6
232	5	2	4	4	1	3	(10)	14774.2798	-3.1
233	5	2	4	4	1	3	(12)	14817.3896	2.6
234	6	2	5	5	1	4	(00)	16433.5593	1.0
235	6	2	5	5	1	4	(01)	16429.2475	-1.3
236	6	2	5	5	1	4	(10)	16082.0018	-1.0
237	6	2	5	5	1	4	(12)	16118.1409	2.3
238	7	2	6	6	1	5	(00)	17542.2279	1.2
239	7	2	6	6	1	5	(01)	17539.1338	-0.6
240	7	2	6	6	1	5	(10)	17292.6300	-1.5
241	7	2	6	6	1	5	(12)	17319.7174	3.9
242	8	2	7	7	1	6	(00)	18576.2726	1.5
243	8	2	7	7	1	6	(01)	18573.8688	-0.3
244	8	2	7	7	1	6	(10)	18400.8544	-0.8
245	8	2	7	7	1	6	(12)	18419.4213	3.2
246	9	2	8	8	1	7	(00)	19550.3480	4.2
247	9	2	8	8	1	7	(01)	19548.3978	2.8
248	9	2	8	8	1	7	(11)	19407.6975	7.4
249	9	2	8	8	1	7	(12)	19435.8104	3.7
250	10	2	9	9	1	8	(00)	20484.2381	2.8

Appendix F. 2-Acetyl-5-Methylthiophene

251	10	2	9	9	1	8	(01)	20482.6209	2.9
252	10	2	9	9	1	8	(10)	20388.9186	2.8
253	10	2	9	9	1	8	(11)	20377.8167	4.2
254	10	2	9	9	1	8	(12)	20396.9345	4.0
255	11	2	10	10	1	9	(01)	21401.0981	4.8
256	11	2	10	10	1	9	(10)	21328.2621	1.8
257	11	2	10	10	1	9	(11)	21320.4017	9.8
258	11	2	10	10	1	9	(12)	21333.5073	4.6
259	2	2	1	2	1	2	(00)	8151.7294	6.2
260	2	2	1	2	1	2	(10)	7687.1121	-1.0
261	2	2	1	2	1	2	(12)	7712.8350	-1.8
262	4	2	3	4	1	4	(00)	8832.9001	-1.5
263	4	2	3	4	1	4	(01)	8820.5540	-1.7
264	4	2	3	4	1	4	(10)	8365.6140	0.1
265	4	2	3	4	1	4	(12)	8398.9048	1.7
266	5	2	4	5	1	5	(00)	9325.3494	0.6
267	5	2	4	5	1	5	(01)	9318.6528	-3.5
268	5	2	4	5	1	5	(10)	8926.7637	5.2
269	5	2	4	5	1	5	(12)	8959.5405	-0.8
270	6	2	5	6	1	6	(00)	9920.7550	6.6
271	6	2	5	6	1	6	(01)	9916.2765	2.2
272	6	2	5	6	1	6	(10)	9616.3320	-0.3
273	6	2	5	6	1	6	(12)	9644.7861	1.5
274	7	2	6	7	1	7	(00)	10619.0277	3.4
275	7	2	6	7	1	7	(01)	10615.4562	-0.6
276	7	2	6	7	1	7	(10)	10404.1299	-5.9
277	7	2	6	7	1	7	(11)	10377.7589	10.0
278	7	2	6	7	1	7	(12)	10425.1169	1.8
279	8	2	7	8	1	8	(00)	11418.4458	4.4
280	8	2	7	8	1	8	(01)	11415.2297	-0.5
281	8	2	7	8	1	8	(10)	11269.2239	-4.8
282	8	2	7	8	1	8	(12)	11282.7084	3.9
283	5	2	3	4	2	2	(00)	8496.9987	0.1
284	5	2	3	4	2	2	(01)	8490.9627	-0.4
285	5	2	3	4	2	2	(10)	8416.4825	-1.4
286	5	2	3	4	2	2	(11)	8414.5496	-0.4
287	5	2	3	4	2	2	(12)	8418.2337	-1.5
288	6	2	4	5	2	3	(00)	10271.4562	0.0
289	6	2	4	5	2	3	(01)	10268.8126	0.5
290	6	2	4	5	2	3	(10)	10171.2451	-0.4
291	7	2	5	6	2	4	(00)	12068.4516	1.4
292	7	2	5	6	2	4	(01)	12067.0519	2.3
293	7	2	5	6	2	4	(10)	11975.9092	-3.2
294	6	2	5	5	2	4	(00)	9941.6318	-0.7
295	6	2	5	5	2	4	(01)	9943.7931	0.7
296	6	2	5	5	2	4	(10)	10042.5508	1.0

Appendix F. 2-Acetyl-5-Methylthiophene

297	6	2	5	5	2	4	(11)	10047.0351	-2.0
298	6	2	5	5	2	4	(12)	10037.1327	0.6
299	7	2	6	6	2	5	(00)	11572.9107	0.3
300	7	2	6	6	2	5	(01)	11573.7327	0.2
301	7	2	6	6	2	5	(10)	11666.2480	1.2
302	7	2	6	6	2	5	(11)	11673.5155	-4.3
303	7	2	6	6	2	5	(12)	11658.0685	0.2
304	8	2	7	7	2	6	(00)	13192.7059	0.7
305	8	2	7	7	2	6	(01)	13192.9604	0.1
306	8	2	7	7	2	6	(10)	13260.4653	1.2
307	8	2	7	7	2	6	(11)	13267.8829	-3.9
308	8	2	7	7	2	6	(12)	13252.4694	-0.5
309	9	2	8	8	2	7	(00)	14799.7883	0.6
310	9	2	8	8	2	7	(01)	14799.7642	-4.8
311	9	2	8	8	2	7	(10)	14842.9312	1.5
312	9	2	8	8	2	7	(11)	14848.5052	-2.1
313	9	2	8	8	2	7	(12)	14836.9263	-0.9
314	10	2	9	9	2	8	(00)	16393.2112	-1.2
315	10	2	9	9	2	8	(01)	16393.0461	0.4
316	10	2	9	9	2	8	(10)	16419.4386	0.2
317	10	2	9	9	2	8	(11)	16423.0586	-2.5
318	10	2	9	9	2	8	(12)	16415.3452	-0.4
319	11	2	10	10	2	9	(00)	17972.3952	-0.5
320	11	2	10	10	2	9	(01)	17972.1412	0.4
321	11	2	10	10	2	9	(10)	17988.0908	-1.2
322	11	2	10	10	2	9	(11)	17990.2991	-2.4
323	11	2	10	10	2	9	(12)	17985.3208	0.8
324	3	3	1	2	2	0	(00)	18102.1494	-2.2
325	4	3	2	3	2	1	(00)	19745.4348	-1.4
326	5	3	3	4	2	2	(00)	21348.9383	-0.3
327	3	3	0	2	2	1	(00)	18112.7617	-2.4
328	4	3	1	3	2	2	(00)	19798.9903	-1.2
329	5	3	2	4	2	3	(00)	21510.6267	-0.4
330	6	3	3	5	2	4	(00)	23264.4563	1.2
331	3	3	0	3	2	1	(00)	13067.7714	0.6
332	3	3	0	3	2	1	(01)	13104.0048	5.7
333	3	3	0	3	2	1	(10)	13318.1201	-9.3
334	4	3	1	4	2	2	(00)	12996.4916	-7.0
335	4	3	1	4	2	2	(01)	13044.4298	-7.0
336	4	3	1	4	2	2	(10)	13293.2651	-5.2
337	4	3	1	4	2	2	(12)	13268.8990	-8.3
338	5	3	2	5	2	3	(00)	12861.6355	-2.0
339	5	3	2	5	2	3	(01)	12911.8650	-2.6
340	5	3	2	5	2	3	(10)	13234.0452	-1.9
341	5	3	2	5	2	3	(12)	13207.8057	-6.7
342	6	3	3	6	2	4	(00)	12644.3159	0.2

Appendix F. 2-Acetyl-5-Methylthiophene

343	6	3	3	6	2	4	(01)	12688.6471	−1.2
344	6	3	3	6	2	4	(10)	13105.4014	1.0
345	6	3	3	6	2	4	(12)	13074.3549	−4.6
346	7	3	4	7	2	5	(00)	12335.8003	4.5
347	7	3	4	7	2	5	(01)	12367.5601	−3.0
348	7	3	4	7	2	5	(10)	12865.5908	6.2
349	7	3	4	7	2	5	(12)	12827.1842	0.2
350	8	3	5	8	2	6	(00)	11943.1300	5.1
351	8	3	5	8	2	6	(01)	11961.1336	−0.8
352	8	3	5	8	2	6	(10)	12496.5742	10.8
353	8	3	5	8	2	6	(12)	12451.3147	1.7
354	6	3	4	6	2	4	(01)	12560.4294	−1.2
355	3	3	1	3	2	2	(00)	13118.5457	−0.3
356	3	3	1	3	2	2	(01)	13076.4492	4.0
357	4	3	2	4	2	3	(00)	13146.0467	−10.7
358	4	3	2	4	2	3	(01)	13092.2471	−2.3
359	5	3	3	5	2	4	(00)	13200.6245	1.2
360	5	3	3	5	2	4	(01)	13144.5275	−2.5
361	6	3	4	6	2	5	(00)	13293.8937	0.4
362	6	3	4	6	2	5	(01)	13243.7099	−0.7
363	7	3	5	7	2	6	(00)	13438.1755	2.8
364	7	3	5	7	2	6	(01)	13400.5763	−1.3
365	8	3	6	8	2	7	(00)	13645.6944	1.9
366	8	3	6	8	2	7	(01)	13621.8919	2.1
367	5	3	3	4	2	2	(00)	21348.9381	−0.5
368	5	3	3	4	2	2	(01)	21277.2348	1.9
369	6	3	4	5	2	3	(00)	22886.8430	0.6
370	6	3	4	5	2	3	(01)	22829.2407	−2.0
371	5	3	3	4	3	2	(00)	8354.8742	2.0
372	6	3	4	5	3	3	(00)	10034.9051	2.7
373	6	3	4	5	3	3	(01)	10042.9756	2.7
374	6	3	4	5	3	3	(10)	10046.2123	−0.5
375	6	3	4	5	3	3	(11)	10046.1744	2.1
376	6	3	4	5	3	3	(12)	10045.7794	−1.0
377	7	3	5	6	3	4	(00)	11717.1916	1.8
378	6	3	3	5	3	2	(00)	10054.1375	3.2
379	6	3	3	5	3	2	(01)	10045.5930	0.3
380	6	3	3	5	3	2	(10)	10042.5993	0.6
381	4	4	0	4	3	1	(00)	18336.8924	1.2
382	4	4	0	4	3	1	(01)	18354.8502	3.6
383	4	4	1	4	3	2	(00)	18339.3122	−1.4
384	4	4	1	4	3	2	(01)	18313.1564	6.7
385	5	4	2	5	3	3	(00)	18330.3416	−8.1
386	5	4	2	5	3	3	(01)	18300.7197	−3.2
387	6	4	3	6	3	4	(00)	18317.9510	−4.5
388	6	4	3	6	3	4	(01)	18280.2716	−0.5

Appendix F. 2-Acetyl-5-Methylthiophene

389	7	4	4	7	3	5	(00)	18303.7482	−0.7
390	7	4	4	7	3	5	(01)	18253.0651	−2.4
391	8	4	5	8	3	6	(00)	18291.2675	7.0
392	8	4	5	8	3	6	(01)	18227.9332	1.9
393	9	4	6	9	3	7	(00)	18286.2245	6.2
394	9	4	6	9	3	7	(01)	18216.9769	3.3
395	6	4	2	5	4	1	(00)	10022.8666	7.2
396	6	4	2	5	4	1	(01)	10022.3802	−1.3
397	6	4	2	5	4	1	(10)	10021.6967	1.2
398	6	4	2	5	4	1	(11)	10021.4084	4.0
399	6	4	2	5	4	1	(12)	10021.5244	2.1
400	7	4	3	6	4	2	(00)	11704.1500	0.8
401	7	4	3	6	4	2	(01)	11703.1996	7.3
402	7	4	3	6	4	2	(10)	11702.1573	2.6
403	7	4	3	6	4	2	(11)	11701.7957	3.6
404	7	4	3	6	4	2	(12)	11701.9728	0.9
405	8	4	4	7	4	3	(00)	13390.9302	5.0
406	8	4	4	7	4	3	(01)	13388.8996	2.2
407	8	4	4	7	4	3	(10)	13387.3739	0.9
408	8	4	4	7	4	3	(11)	13386.9303	2.4
409	8	4	4	7	4	3	(12)	13387.1931	3.2
410	9	4	5	8	4	4	(00)	15084.5591	5.0
411	9	4	5	8	4	4	(10)	15078.1214	5.9
412	6	4	3	5	4	2	(01)	10022.5244	2.3
413	6	4	3	5	4	2	(10)	10023.1795	0.6
414	6	4	3	5	4	2	(11)	10023.0299	−0.1
415	7	4	4	6	4	3	(00)	11702.9854	2.2
416	7	4	4	6	4	3	(01)	11703.3984	3.5
417	7	4	4	6	4	3	(10)	11704.4884	3.4
418	7	4	4	6	4	3	(11)	11704.3353	1.7
419	7	4	4	6	4	3	(12)	11704.0945	4.1
420	8	4	5	7	4	4	(00)	13387.7405	3.9
421	8	4	5	7	4	4	(01)	13389.1385	2.3
422	8	4	5	7	4	4	(10)	13390.8384	1.0
423	8	4	5	7	4	4	(11)	13390.6908	−4.0
424	8	4	5	7	4	4	(12)	13390.3521	1.1
425	9	4	6	8	4	5	(00)	15076.9689	4.3
426	9	4	6	8	4	5	(10)	15083.0464	3.1
427	9	4	6	8	4	5	(11)	15082.9237	0.1
