Determination of a High Potential Barrier Hindering Internal Rotation from the Ground State Spectrum

The Methylbarrier of Ethylchloride

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We present an analysis of the rotational spectrum of ethylchloride- ^{35}Cl in the ground state. The ^{35}Cl -hfs analysis was extended and the barrier to internal rotation determined from narrow splittings of high J -transitions.

Introduction

With the higher resolution of microwave Fourier transform (MWFT) spectroscopy it is possible to resolve fine structures, which could not be measured before [1–3].

We noticed that the barrier to internal rotation V_3 of ethylchloride, $\text{CH}_3\text{CH}_2\text{Cl}$, was determined [4, 5] from two splittings in the first torsional excited state. As there is in some molecules an interaction of the internal rotation and other vibrations [6] we thought it interesting to determine the barrier from ground state measurements.

Experimental

The sample was purchased from FLUKA with a 98% purity. The spectra were recorded by a conventional Starkspectrometer [7, 8] in the region of 8–40 GHz with temperatures from -30 to -45°C and pressures between 4 and 15 mTorr and for high resolution with a MWFT-Spectrometer from 8 to 18 GHz [1] with temperatures from -60 to -75°C and pressures between 0.3 and 1.5 mTorr. The measuring errors are 50 kHz and 10 kHz respectively.

Measurements and Analysis

As the barrier V_3 is rather high, splittings could only be observed for high J lines within the range of our MWFT spectrometer. For correct assignment a

centrifugal distortion and extended chlorine hfs analysis was necessary.

In Table 1 we give the lines measured by us and by other authors [5]. They are marked by *. With FT we indicate MWFT measurements. In Fig. 1 we give a multiplet pattern.

Fig. 1. A section of 1.5 MHz of the rotational spectrum of $\text{CH}_3\text{CH}_2^{35}\text{Cl}$ showing the $8_{17}-7_{26}$ line with ^{35}Cl -hfs and internal rotation (A, E-species) splitting. Pressure 0.4 mT, temperature -70°C . Transient emission signal was recorded with a sample interval of 50 ns and 1024 data points. Measuring time 3 min 256 000 averaging cycles. Prior to Fourier transformation the time domain signal was extended to 4096 points by zeros. Spectral point distance 5 kHz.

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K- K+	J' K-'K+	2F	2F'	ν_{exp}	ν_{ave}	$\Delta\nu_{\text{exp}}$	$\Delta\nu_{\text{calc}}$	J K- K+	J' K-'K+	2F	2F'	ν_{exp}	ν_{ave}	$\Delta\nu_{\text{exp}}$	$\Delta\nu_{\text{calc}}$
0 1	0 0 0	3 3	3	10446.081	10455.943	- 9.862	- 9.853	9 1 8	8 2 7	15 13	15	27279.737	27280.409	- 0.672	- 0.675
		5 3	5	10458.478		2.535	2.463			21 19	21	27280.091		- 0.318	- 0.324
		1 3	1	10468.191		12.248	12.317			17 15	17	27280.675		0.266	0.266
										19 17	19	27281.014		0.605	0.615
2 0	2 1 0 1	3 5	3	20891.45	20903.780	-12.330	-12.317	8 3 6	9 2 7	13 15	13		34435.945	- 1.007	- 1.066
		5 3	5	20892.41		-11.370	-11.300			19 21	19		34434.938		
				20904.87		1.090	1.044			15 17	15		34436.947		1.002
		7 5	7	20913.69		9.910	9.853			17 19	17				1.062
3 0	3 2 0 2	7 7	7	31323.373	31335.232	-11.859	-11.836	10 3 8	11 2 9	23 25	23	11372.841	11373.241	- 0.354	- 0.356
		3 1	3	31332.765		- 2.467	- 2.450			17 19	17	11372.898			
		7 5	7							21 23	21	11372.923			
				31335.786		0.554	0.576			19 21	19	11373.571			
		9 7	9	31341.571		6.339	6.346					11373.629		0.376	0.369
		3 3	3	31345.261		10.029	9.962					11373.651			
2 1	2 1 1 0	5 3	5	21433.79	21443.375	- 9.585	- 9.562	15 2 13	14 3 12	27 25	27	38559.908	38560.303	- 0.395	- 0.405
		3 3	3	21436.27		- 7.105	- 7.135			33 31	33				
		5 5	5	21442.73		- 0.645	- 0.644			29 27	29	38560.684		0.381	0.391
		7 5	7	21446.21		2.835	2.755			31 29	31				
		3 1	3	21452.27		8.895	8.918	23 6 18	24 5 19	43 45	43	34152.275	34152.633	- 0.358	- 0.367
		1 1	1	21455.62		12.245	12.317			49 51	49	34152.992		0.359	0.367
3 1	3 2 2 1 1	7 7	7	32154.405	32159.721	- 5.316	- 5.301			45 47	45				
		7 5	7	32157.814		- 1.907	- 1.902			47 49	47				
		5 3	5	32158.431		- 1.290	- 1.299								
		9 7	9	32160.906		1.185	1.161	25 6 20	26 5 21	47 49	47	12512.736	12513.054	- 0.285	- 0.283
		5 5	5	32161.484		1.763	1.797			53 55	53	12512.801			
		3 3	3	32164.935		5.214	5.196			49 51	49	12513.308		0.287	0.284
2 1	2 2 1 1 1	5 3	5	20371.50	20380.574	- 9.074	- 9.089	28 5 23	27 6 22	57 55	57	9350.536	9350.784	- 0.216	- 0.212
		5 5	5	20374.88		- 5.694	- 5.690			55 53	55	9350.600			
		3 3	3	20377.89		- 2.684	- 2.719			59 57	59	9350.967		0.215	0.211
		7 5	7	20383.79		3.216	3.228			53 51	53	9351.031			

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J	K-	K+	J'	K-'	K+'	2F	2F'	γ_{exp}	γ_{ave}	$\Delta\gamma_{\text{exp}}$	$\Delta\gamma_{\text{calc}}$	J	K-	K+	J'	K-'	K+'	2F	2F'	γ_{exp}	γ_{ave}	$\Delta\gamma_{\text{exp}}$	$\Delta\gamma_{\text{calc}}$				
18	5	14	19	4	15	33	35	34567.094	34567.569	- 0.475	- 0.479	19	2	17	19	2	18	35	35	36811.091	36812.794	- 1.703	- 1.712				
						39	41					41	41	36811.315		- 1.479	- 1.467										
						35	37					37	37	36814.260		1.466	1.455										
												39	39	36814.485		1.691	1.699										
						37	39	34568.044		0.475	0.480	21	3	18	21	3	19	39	39	9194.088	9194.671	- 0.583	- 0.587				
20	5	16	21	4	17	37	39	12785.549	12785.923	- 0.339	- 0.337	FT						45	45	9194.168		- 0.503	- 0.511				
						43	45					41	41	9195.172		0.501	0.507										
						39	41					43	43	9195.254		0.583	0.584										
												41	43	12786.301													
						41	43	12786.223		0.339	0.338	22	3	19	22	3	20	47	47	11794.266	11794.935	- 0.669	- 0.674				
												FT						43	43	11795.516		0.581	0.586				
																		45	45	11795.605		0.670	0.670				
23	4	19	22	5	18	45	43	9379.723	9379.982	- 0.226	- 0.218	23	3	20	23	3	21	43	43	14894.911	14895.700	- 0.789	- 0.762				
						47	45					49	49	14895.005		- 0.695	- 0.671										
						43	41					45	45	14896.318		0.618	0.667										
						49	47						47	14896.432		0.732	0.758										
								9380.176		0.225	0.217																
								9380.238				26	3	23	26	3	24	49	49		27548.381	- 0.963	- 0.967				
25	4	21	24	5	20	53	51	32083.373	32083.373	0.000	0.000							55	55		27547.418						
						51	49														51	51		27549.339		0.958	0.963
						49	47														53	53					
						47	45																				
28	7	22	29	6	23	53	55	33688.454	33688.745	- 0.291	- 0.294	27	3	24	27	3	25	51	51		32953.738	32954.743	- 1.005	- 1.044			
						59	61														57	57					
						55	57														53	53					
																					55	55		32955.744		1.001	1.040
						57	59	33689.035		0.290	0.294																
30	7	24	31	6	25	57	59	12108.675	12108.942	- 0.241	- 0.238	28	3	25	28	3	26	53	53		38967.028	38968.128	- 1.100	- 1.116			
						63	65														59	59					
						59	61														55	55					
																					57	57		38969.224		1.096	1.112
						61	63	12109.158		0.241	0.238																
								12109.207				30	4	26	30	4	27	57	57		9248.896		- 0.336	- 0.363			
33	6	27	32	7	26	67	65	9625.805	9626.016	- 0.193	- 0.190							63	63		9248.560						
						65	63														59	59					
						69	67														61	61		9249.230		0.334	0.361
						63	61	9626.188		0.192	0.190																
								9626.228																			
35	6	29	34	7	28	69	67	31548.998	31549.128	- 0.130	- 0.147	2	1	1	2	0	2	3	1		26902.164	26914.546	-12.382	-12.371			
						71	69														1	1		26905.600		- 8.946	- 8.972
						67	65														5	7		26908.573		- 5.973	- 5.962
																					7	7					
						73	71	31549.258		0.130	0.147							5	3		26911.998		- 2.548	- 2.496			
																		1	3		26914.537		- 0.009	- 0.000			
6	1	5	6	1	6	9	9	11148.060	11151.550	- 3.490	- 3.507							3	3		26917.990		3.444	3.399			
						15	15	11149.344		- 2.206	- 2.204							5	5		26920.980		6.434	6.409			
						11	11	11153.556		2.006	2.004							7	5		26924.354		9.808	9.808			
						13	13	11154.840		3.290	3.306																
7	1	6	7	1	7	11	11	14856.973	14860.330	- 3.357	- 3.386	3	1	2	3	0	3	3	3		27734.266	27739.045	- 4.779	- 4.766			
FT						17	17	14858.038		- 2.292	- 2.266							9	9		27737.065		- 1.980	- 1.986			
						13	13	14862.423		2.093	2.116							5	5		27740.235		1.190	1.192			
						15	15	14863.586		3.256	3.237							7	7		27743.026		3.981	3.972			
10	1	9	10	1	10	17	17	29080.392	29083.540	- 3.148	- 3.154	4	1	3	4	0	4	5	5		28863.026	28866.470	- 3.444	- 3.434			
						23	23	29081.167		- 2.373	- 2.369							11	11		28864.730		- 1.740	- 1.748			
						19	19	29085.829		2.289	2.294							7	7		28867.833		1.363	1.374			
						21	21	29086.620		3.080	3.080							9	9		28869.544		3.074	3.059			
11	1	10	11	1	11	19	19	34827.626	34825.308	- 3.085	- 3.095	5	1	4	5	0	5	7	7		30317.435	30320.298	- 2.863	- 2.861			
						25	25	34822.928		- 2.380	- 2.383							13	13		30318.654		- 1.644	- 1.651			
						21	21	34822.223		2.318	2.321							9	9		30321.733		1.435	1.430			
						23	23	34828.332		3.024	3.033							11	11		30322.928		2.630	2.641			
13	2	11	13	2	12	23	23	10167.254	10167.254	- 1.062	- 1.051	6	1	5	6	0	6	9	9		32126.446	32129.027	- 2.581	- 2.581			
						29	29														15	15		32127.413		- 1.614	- 1.622
						27	27														11	11		32130.497		1.470	1.475
																					13	13		32131.458		2.431	2.434
						25	25	10168.298		1.044	1.034																
14	2	12	14	2	13	25	25	13233.806	13235.092	- 1.286	- 1.282	7	1	6	7	0	7	11	11		34322.750	34325.171	- 2.421	- 2.442			
FT						31	31	13234.057		- 1.035	- 1.042							17	17		34323.512		- 1.659	- 1.634			
						27	27	13236.111		1.019	1.026							13	13		34326.695		1.524	1.526			
						29	29	13236.361		1.269	1.266							15	15		34327.510		2.339	2.334			
15	2	13	15	2	14	27	27	16837.853	16839.240	- 1.387	- 1.386	8	1	7	8	0	8	13	13		36941.240	36943.615	- 2.375	- 2.378			
						33	33	16838.099		- 1.141	- 1.144							19	19		36941.932		- 1.683	- 1.669			
						29	29	16840.364		1.124	1.126							15	15		36945.206		1.591	1.586			
						31	31	16840.611		1.371	1.370							17	17		36945.917		2.302	2.295			
18	2	16	18	2	17	33	33	30984.938	30986.574	- 1.636	- 1.647	9	1	8	9	0	9	15	15		40017.463	40019.818	- 2.355				
						39	39	30985.162		- 1.412	- 1.400							21	21		40018.083		- 1.735				
						35	35	30987.958		1.384	1.387							17	17		40021.465		1.647				
						37	37	30988.211		1.637	1.634							19	19		40022.096		2.278				

Table 2. Rotational [MHz] and centrifugal distortion [kHz] constants according to Watson's S-reduction. $|(a, b)|$: highest correlation, σ : standard deviation of the fit [kHz].

A	31337.406 (34)	$\mathfrak{A}$	31337.413 (34)
B	5493.699 (6)	$\mathfrak{B}$	5493.682 (6)
C	4962.276 (6)	$\mathfrak{C}$	4962.261 (6)
D_J	3.40 (5)	τ_{aaaa}	−999 (4)
D_{JK}	−22.3 (8)	τ_{bbbb}	18.1 (2)
D_K	268 (2)	τ_{cccc}	−9.4 (2)
d_1	−0.540 (2)	τ_1	49 (4)
d_2	−0.018 (1)	τ_2	−87 (23)
σ	142		
$ (D_J, D_{JK}) $	0.999		

The centrifugal distortion and hfs analysis were made independently. For the centrifugal distortion analysis unsplit lines ν_{ave} corrected for hfs were used. For the hfs analysis it was assumed that the components of one transition are equally shifted by centrifugal distortion. In Table 2 we give the rotational and centrifugal distortion constants according to the fourth order Hamiltonian of Watson's S-reduction [9]. The standard deviation of the fit is 142 kHz, the highest correlation is $|(D_J, D_{JK})| = 0.999$.

Table 3. Chlorine hfs coupling constants [MHz] of $\text{CH}_3\text{CH}_2^{35}\text{Cl}$ calculated with different selections of lines (column 1 J to 23 and column 2 J to 3) and first order approximation. Column 3 gives values from lines up to $J = 3$ calculated with diagonalisation [10]. Standard errors are given. $|\chi^+, \chi^-|$ correlation coefficient. Column 4 is calculated from [5].

χ^+	49.267 (52)	49.21 (12)	49.241 (47)	49.20 (10)
χ^-	−22.078 (30)	−22.09 (18)	−22.100 (72)	−22.04 (21)
$ \chi^+, \chi^- $	0.014	0.203	0.375	—
χ_{aa}	−49.267 (52)	−49.21 (12)	−49.241 (47)	−49.20 (10)
χ_{bb}	13.595 (41)	13.56 (15)	13.570 (60)	13.58 (16)
χ_{cc}	35.673 (41)	35.65 (15)	35.670 (60)	35.62 (16)

Table 4. Internal Rotation splittings [kHz] of $\text{CH}_3\text{CH}_2^{35}\text{Cl}$ averaged over hfs components.

J	K^-	K^+	J'	K'^-	K'^+	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$
8	1	7	7	2	6	40	36.3
10	3	8	11	2	9	69	63.7
15	4	12	16	3	13	75	76.4
18	3	15	17	4	14	68	69.8
20	5	16	21	4	17	74	76.4
23	4	19	22	5	18	67	69.2
25	6	20	26	5	21	65	65.7
28	5	23	27	6	22	64	57.9
30	7	24	31	6	25	51	47.9
33	6	27	32	7	26	38	40.0
35	8	28	36	7	29	30	28.0

We also tried sixth order centrifugal distortion analysis, which improves the fit. But the constants are poorly determined, and many correlation coefficients are high.

The hfs analysis was based on lines with J up to 23. We omitted lines split by internal rotation. In Table 3 we give the quadrupole coupling constants χ_{gg} , $g = a, b, c$, calculated with first order theory. A mean shift of 3.14 MHz was fitted with a standard deviation of 0.027 MHz. To check the influence of centrifugal distortion we give also the χ_{gg} determined from lines with J up to 3. The approximation

Table 5. Internal rotation parameters of $\text{CH}_3\text{CH}_2^{35}\text{Cl}$. Standard errors in brackets. Assumptions in square brackets.

w_1 (s)	$-6.05 (11) \cdot 10^{-7}$	$-5.88 (14) \cdot 10^{-7}$	$-5.87 (15) \cdot 10^{-7}$	—
λ_a	[0.7317]	[0.7317]	[0.7317]	[0.7317]
λ_b	[0.6816]	[0.6816]	[0.6816]	[0.6816]
I_x [amuÅ ²]	3.246 (15)	[3.1613]	[3.155]	[3.1613]
$ (w_1(s), I_x) $	0.383	—	—	—
$\Delta\nu_{\text{exp}}$ [kHz]	58.3	58.3	58.3	—
σ [kHz]	3.5	5.0	5.1	—
s	91.84 (19)	92.14 (25)	92.16 (24)	94.43
V_3 [cal/mole]	3529 (8)	3595 (10)	3602 (10)	3685 (12)
F [GHz]	179.1	181.9	182.17	181.9
$\star(a, i)$ [°]	[42.97]	[42.97]	[42.97]	[42.97]
$\star(b, i)$ [°]	[47.03]	[47.03]	[47.03]	[47.03]

of first order was controlled by a program [10] using diagonalisation of Hamiltonian matrices for lines up to $J = 3$. The values are given also in Table 3. The measured splittings are not sensitive to χ_{ab} .

A comparison of the values of Table 3 shows agreement within the error limits. So the first order analysis is sufficient up to higher J values.

The torsional analysis was based on the mean values of the splittings of the hfs components as given in Table 4. Thus we neglected interaction. We used a program by Woods [11–14] based on the internal axis method.

We tried to fit $w_1(s)$, with s the reduced barrier, I_x the moment of inertia of the methyl group and $\angle(a, i)$ the angle between the a axis and the internal rotation axis. The fit converged, but the correlation is high. In a next step we assumed the angle $\angle(a, i)$ from the structure [5], taking the C–C-bond colinear to the internal rotation axis. A rather high value for I_x resulted (Tab. 5, column 1). For comparison with literature we finally present in Table 5

two fits with I_x fixed to $3.1613 \text{ amu}\text{\AA}^2$ [5] and $3.155 \text{ amu}\text{\AA}^2$ and $\angle(a, i) = \theta_m = 42.97^\circ$ [5]. The value $I_x = 3.155 \text{ amu}\text{\AA}^2$ was determined by a torsion analysis of ethylfluoride [15]. In Table 5 column 4 we repeat the values of [5] for convenience. We favour the values of column 3, as a comparison with $\text{CH}_3\text{CH}_2\text{F}$ is possible. The last column of Table 4 is calculated with the first set of Table 5. The numbers vary slightly with the other sets.

It may be noticed that the s and V_3 values are lower than in [5]. To our knowledge the barrier is the highest determined from an analysis of splittings of torsion ground state transitions. The errors indicate that we are near the limit of the MWFT-technique.

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