

# Hyperfine Structure in the Rotational Spectrum of Chloroacetonitrile

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In continuation of previous studies on substituted acetonitriles, the chloroacetonitriles  $\text{CH}_2^{35}\text{ClCN}$  and  $\text{CH}_2^{37}\text{ClCN}$  are investigated. Substituted acetonitriles have earlier been studied in our laboratory [1]. The rotational spectra of the  $^{35}\text{Cl}$ - and  $^{37}\text{Cl}$ -species of chloroacetonitrile were investigated by Graybeal [2] and by Wada, Kikuchi, Matsumura, Hirota and Morino [3], with some controversy. The latter authors investigated also the deuterated species  $\text{CD}_2^{35}\text{ClCN}$  and  $\text{CD}_2^{37}\text{ClCN}$ . The main object of the present investigation was the analysis of the nitrogen hyperfine structure (hfs), which had not been analyzed before.

We used microwave Fourier transform (MWFT) spectroscopy [4] in the range from 8 to 26.4 GHz [5–7] to resolve the hfs patterns of the rotational transitions produced by N- and Cl-hfs.

The substance was purchased from Aldrich Chemie, Steinheim, and used without further purification. The spectra were taken at temperatures varying from  $-15^\circ\text{C}$  to  $-50^\circ\text{C}$  and pressures between 0.3 and 2 mTorr (0.04 to 0.26 Pa). A sample of the measurements is given in Figure 1. A part of the measured lines is given in Tables 1 a and 1 b. The complete list has been deposited under number TNA 9 at the Universitätsbibliothek of the University of Kiel\*.

The given frequencies resulted from a line contour analysis of the measured multiplets [8, 9].

The analysis of the spectra was performed in an iterative way. The hfs multiplets were analyzed by first order approximation [10–12] using the rotational and the  $^{35}\text{Cl}$ -coupling constants of [3] as starting values. After refinement of the  $^{35}\text{Cl}$ -coupling constants and determination of the  $^{37}\text{Cl}$  and  $^{14}\text{N}$ -coupling constants the frequencies of the hypothetical unsplit lines were calculated. These frequencies were the input data for a fourth order centrifugal distortion analysis with Watson's S-reduction [13, 14], which provided improved rotational and centrifugal distortion constants. By iteration

we got the values given in Table 2 together with the correlation matrices for the  $^{37}\text{Cl}$ -species which are representative also for the  $^{35}\text{Cl}$ -species.

As only limited numbers of transitions were used the centrifugal distortion constants may change when a larger set of transitions is available. The main intention was to check the consistency of the assignment, which is mainly based on the hfs analysis.

It should be mentioned that our rotational constant  $A$  is closer to that of [3]. As a consequence of the higher resolution of MWFT spectroscopy our rotational constants are more precise. In comparison to [1] the  $\chi_{\text{gg}}(\text{N})$  show a larger error. This we think is a consequence of the more complicated multiplet patterns caused by two coupling nuclei.

The off diagonal elements  $\chi_{\text{gg}}$  could not be determined from the measurements. We checked that the molecular structure cannot be determined with high precision from the known 12 rotational constants (compare [3] and Table 2). Therefore we desisted from calculating the principal coupling tensor components. The measurement of more isotopic species may help.

As the molecules have a symmetry plane, the  $\chi_{\text{cc}}$  can be compared. The  $\chi_{\text{cc}}(\text{N})$  agree within the error limits. Further  $\chi_{\text{cc}}(^{35}\text{Cl})/\chi_{\text{cc}}(^{37}\text{Cl}) = 1.2684(32)$  agrees within the error limit with the quotient of the quadrupole moments  $^{35}\text{Q}/^{37}\text{Q} = 1.26878(15)$  [15].

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Table 1a. Selection of measured rotational transitions of  $^{35}\text{Cl}$ -Chloroacetonitrile showing  $^{35}\text{Cl}$  ( $F_1$  quantum numbers) and  $^{14}\text{N}$  ( $F$  quantum numbers) hyperfine structure.  $F$  and  $F_1$ : quantum numbers multiplied by 2,  $\nu$ : measured and improved frequencies,  $\Delta\nu_{\text{hfs}}$ : splittings referred to the strongest component,  $\nu_0$ : hypothetical unsplit lines,  $\delta_{\text{hfs}} = \Delta\nu_{\text{hfs}} - \Delta\nu_{\text{calc}}$ : deviations of the splittings,  $\Delta\nu_{\text{calc}}$ : splittings calculated with the constants of Table 2,  $\delta$ : deviation from the spectrum calculated with the rotational and centrifugal distortion constants of Table 2.

$J$	$K_-$	$K_+ - J'$	$K'_-$	$K'_+$	$F_1$	$F - F'_1$ *2	$F'$	$\nu$ [MHz]	$\Delta\nu_{\text{hfs}}$ [MHz]	$\delta_{\text{hfs}}$ [kHz]	$\nu_0$ [MHz]	$\delta$ [kHz]							
1	1	0 - 1	0	1	5	3 - 5	3	22 417.869	-9.386	-14	22 422.295	-34							
					5	7 - 5	7	22 418.258	-8.997	-17									
					1	3 - 3	3	22 418.645	-8.610	9									
					1	1 - 3	3												
					5	3 - 5	5												
					1	3 - 3	5												
					5	5 - 5	5	22 419.110	-8.145	-6									
					1	1 - 3	1	22 419.220	-8.035	-15									
					1	1 - 3	1	22 419.560	-7.695	-11									
					3	5 - 1	3	22 421.788	-5.467	-10									
					3	1 - 1	1	22 422.166	-5.089	-13									
					5	5 - 3	3	22 427.152	-0.103	-3									
					5	7 - 3	5	22 427.255											
					5	3 - 3	1	22 427.497	0.224	-32									
					3	5 - 5	7	22 428.704	1.449	-10									
					3	1 - 5	3	22 428.801	1.546	2									
					3	3 - 5	5	22 428.896	1.641	2									
2	1	1 - 1	1	0	3	5 - 3	5	12 292.625	-10.027	15	12 300.882	-38							
					5	3 - 3	1	12 293.436	-9.216	-28									
					5	7 - 3	5	12 293.697	-8.955	-23									
					5	5 - 3	3	12 293.996	-8.656	-31									
					7	7 - 5	5	12 302.028	-0.624	-6									
					7	9 - 5	7	12 302.652											
					7	5 - 5	3	12 302.852	0.200	1									
					1	3 - 1	1	12 309.589	6.937	-20									
					1	1 - 1	3												
					1	3 - 1	3												
					3	3 - 1	1												
					3	5 - 1	3	12 311.146	8.494	17									
					3	5 - 1	3	12 311.214	8.562	27									
					1	1	1 - 2	0	2	1			3 - 1	1	10 117.436	-4.800	27	10 124.695	-4
										1			1 - 1	3					
										1			3 - 1	3					
										5			3 - 7	5					
5	7 - 7	9	10 121.912	-0.324						13									
5	5 - 7	7	10 122.236																
1	3 - 3	5	10 123.154	0.918						12									
3	5 - 5	7	10 126.289	4.053						45									
5	7 - 5	7	10 129.722	7.486						27									
5	7 - 5	7	10 131.185	8.949	15														
3	0	3 - 2	0	2	3	3 - 1	1	17 983.047	-0.458	10	17 985.163	45							
					5	5 - 3	3												
					5	7 - 3	5												
					7	7 - 5	5												
					9	9 - 7	7	17 985.299	1.794	2									
					7	9 - 5	7						17 985.562	2.057	-19				
					9	7 - 7	5												
					7	5 - 3	5												
					9	11 - 7	9	17 985.657	2.152	9									
4	2	2 - 3	2	1	9	9 - 7	7	24 024.158	-3.642	20	24 026.496	-7							
					9	11 - 7	9	24 024.431	-3.369	1									
					9	7 - 7	5	24 024.485	-3.315	11									
					7	7 - 5	5	24 025.389	-2.411	6									
					7	9 - 5	7	24 025.617	-2.183	-7									
					7	5 - 5	3	24 025.691	-2.109	4									
					11	11 - 9	9	24 027.474	-0.326	18									
					11	13 - 9	11	24 027.800											
					11	9 - 9	7	24 027.878	0.078	10									
					5	5 - 3	3	24 028.695	0.895	7									
					5	7 - 3	5	24 028.958	1.158	-12									

Table 1 a (continued)

$J$	$K_-$	$K_+ - J'$	$K'_-$	$K'_+$	$F_1$	$F - F'_1$ *2	$F'$	$\nu$ [MHz]	$\Delta \nu_{\text{hfs}}$ [MHz]	$\delta_{\text{hfs}}$ [kHz]	$\nu_0$ [MHz]	$\delta$ [kHz]								
5	0	5-4	1	4	7	5-	5	3	9 131.487	-2.109	31	9 134.894	-18							
					7	7-	5	5	9 131.522	-2.074	31									
					7	9-	5	7	9 131.576	-2.020	32									
					13	11-	11	9	9 133.552	-0.044	-5									
					13	15-	11	13	9 133.596											
					13	13-	11	11												
					9	9-	7	7	9 135.569	1.973	-9									
					9	7-	7	5	9 135.613	2.017	3									
					9	11-	7	9	9 135.646	2.050	5									
					11	11-	9	9	9 137.680	4.084	19									
					11	9-	9	7												
					11	13-	9	11	9137.723	4.127	23									
6	0	6-5	1	5	9	7-	7	5	15 791.214	-4.410	12	15 794.457	9							
					9	11-	7	9	15 791.297	-4.327	26									
					9	9-	7	7	15 791.317	-4.307	19									
					15	13-	13	11	15 792.873	-2.751	-8									
					15	17-	13	15	15 792.910	-2.714	-2									
					15	15-	13	13	15 792.982	-2.642	3									
					11	9-	9	7	15 795.573	-0.051	-6									
					11	13-	9	11	15 795.624											
					11	11-	9	9												
					13	11-	11	9	15 797.233	1.609	8									
					13	15-	11	13	15 797.278	1.654	11									
					13	13-	11	11	15 797.305	1.681	11									
					7	2	6-8	1	7	15	13-			17	15	13 485.671	-4.289	-7	13 488.243	0
										15	15-			17	17	13 485.758	-4.202	0		
15	17-	17	19																	
13	15-	15	17	13 486.672						-3.288	-18									
13	11-	15	13																	
17	17-	19	19	13 489.920						-0.040	-2									
17	19-	19	21	13 489.960																
17	15-	19	17																	
11	11-	13	13	13 490.836						0.876	-10									
11	13-	13	15	13 490.859						0.899	-11									
11	9-	13	11	13 490.888						0.928	-7									

Table 1 b. Selection of measured rotational transitions of  $^{37}\text{Cl}$ -Chloroacetonitrile. See also Table 1 a.

$J$	$K_-$	$K_+ - J'$	$K'_-$	$K'_+$	$F_1$	$F - F'_1$ *2	$F'$	$\nu$ [MHz]	$\Delta\nu_{\text{hfs}}$ [MHz]	$\delta_{\text{hfs}}$ [kHz]	$\nu_0$ [MHz]	$\delta$ [kHz]
1	1	0-1	0	1	5	3-5	3	22 329.088	-3.101	2	22 332.710	-7
					5	7-5	7	22 329.462	-2.727	-2		
					1	3-3	3	22 329.842	-2.347	8		
					5	3-5	5					
					1	1-3	3					
					5	5-5	7					
					1	3-3	5	22 330.294	-1.895	3		
					5	5-5	5	22 330.414	-1.775	12		
					1	1-3	1	22 330.741	-1.448	-1		
					3	5-1	3	22 332.189				
					5	5-3	3	22 336.603	4.414	-12		
					5	7-3	5	22 336.715	4.526	12		
					5	3-3	1	22 336.948	4.759	-5		
					3	5-5	7	22 337.727	5.538	-5		

Table 1 b (continued)

$J$	$K_-$	$K_+ - J'$	$K'_-$	$K'_+$	$F_1$	$F - F'_1$ *2	$F'$	$\nu$ [MHz]	$\Delta\nu_{\text{hfs}}$ [MHz]	$\delta_{\text{hfs}}$ [kHz]	$\nu_0$ [MHz]	$\delta$ [kHz]							
3	0	3-2	0	2	3	1-5	3	22 337.852	5.663	30	17 599.772	7							
					3	3-5	5	22 337.935	5.746	29									
					3	3-1	1	17 598.030	-1.852	19									
					5	5-3	3												
					5	7-3	5	17 598.480	-1.375	1									
					3	5-1	3	17 598.528	-1.327	-17									
					7	7-5	5	17 599.855											
					9	9-7	7	17 600.073	0.218	40									
9	7-7	5																	
7	9-5	7																	
3	1	3-2	1	2	5	5-3	3	17 170.293	-3.334	6	17 172.579	1							
					5	7-3	5	17 170.712	-2.915	-6									
					5	3-3	1	17 170.915	2.712	23									
					7	7-5	5	17 171.530	-2.097	10									
					7	9-5	7	17 171.875	-1.752	0									
					7	5-5	3	17 171.940	-1.687	4									
					3	3-1	3	17 171.985	-1.642	33									
					3	5-1	3	17 172.463	-1.164	-6									
					3	1-1	1	17 172.882	-0.745	26									
					9	9-7	7	17 173.362	-0.265	3									
					9	11-7	9	17 173.627											
					9	7-7	5												
					4	2	2-3	2	1	9			9-7	7	23 507.718	-2.983	13	23 509.638	-1
										9			11-7	9	23 507.997	-2.704	5		
7	7-5	5	23 508.738	-1.963						18									
7	9-5	7	23 508.937	-1.764						-14									
7	5-5	3	23 509.018	-1.683						9									
11	11-9	9	23 510.375	-0.326						10									
11	13-9	11	23 510.701																
11	9-9	7	23 510.785	0.084						17									
5	5-3	3	23 511.361	0.660						1									
5	5-3	5																	
5	7-3	5	23 511.627	0.926						-7									
4	2	3-3	2	2						9	9-9	9	23 478.928	-3.179	9	23 480.930	-1		
										9	9-7	7							
										9	9-7	9							
					9	11-9	11	23 479.210	-2.897	-1									
					9	11-7	9												
					9	7-9	7	23 479.263	-2.844	13									
					9	7-7	5												
					9	7-7	7												
					7	7-5	7	23 479.969	-2.138	13									
					7	7-5	5												
					7	7-7	7												
					7	9-5	7	23 480.202	-1.905	8									
					7	9-7	9												
					5	7-5	3												
					5	7-5	5	23 480.279	-1.828	25									
					7	5-7	5												
					11	11-9	11												
					11	11-9	9	23 481.695	-0.412	-3									
					11	13-9	11	23 482.026	-0.081	-13									
					11	9-9	7	23 482.107											
					11	9-9	9												
					5	5-3	5	23 482.741	0.634	25									
5	5-3	3																	
5	5-5	5																	
5	7-3	5	23 483.006	0.899	9														
5	7-5	7																	

Table 1 b (continued)

$J$	$K_-$	$K_+ - J'$	$K'_-$	$K'_+$	$F_1$	$F - F'_1$ *2	$F'$	$\nu$ [MHz]	$\Delta\nu_{\text{hfs}}$ [MHz]	$\delta_{\text{hfs}}$ [kHz]	$\nu_0$ [MHz]	$\delta$ [kHz]
5	0	5-4	1	4	7	7-5	5	8525.491	-4.838	-3		
					7	9-5	7	8525.563	-4.766	22		
					13	11-11	9	8527.081	-3.248	-22		
					13	15-11	13	8527.128	-3.201	-17		
					13	13-11	11					
					9	9-7	7	8528.658	-1.671	-20		
					9	7-7	5					
					9	11-7	9					
					11	11-9	9	8528.701	-1.628	-18		
					11	9-9	7	8530.283	-0.046	-6		
					11	13-9	11					
								8530.329			8528.127	-9
6	0	6-5	1	5	9	7-7	5	15 035.711	-4.991	-13		
					9	11-7	9	15 035.800	-4.702	7		
					9	9-7	7	15 035.827	-4.675	3		
					15	13-13	11	15 037.030	-3.472	-13		
					15	17-13	15	15 037.068	-3.434	-7		
					15	15-13	13	15 037.146	-3.356	1		
					11	9-9	7	15 039.127	-1.375	-14		
					11	13-9	11	15 039.165	-1.337	-12		
					11	11-9	9	15 039.200	-1.302	-9		
					13	11-11	9	15 040.401	-0.101	-20		
					13	15-11	13	15 404.469	-0.033	-2		
					13	13-11	11	15 040.502			15 038.264	5

Table 2. Rotational (MHz), centrifugal distortion (kHz) and quadrupole coupling constants (MHz) of chloroacetonitrile  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ ,  $\text{CH}_2\text{ClCN}$ . Correlation matrices are given for  $^{37}\text{Cl}$ . Watson's S-Reduction is used. Single standard errors in brackets.  $N$ ,  $N_{\text{comp}}$ : number of lines and components,  $\sigma$ : standard deviation of the fit (kHz),  $\bar{\Delta\nu}$ : mean deviation (MHz) of hyperfinestructure component to the reference component.

	$^{35}\text{Cl}-\text{CH}_2-\text{CN}$	$^{37}\text{Cl}-\text{CH}_2-\text{CN}$	$A$	$B$	$C$	$D_J$	$D_{JK}$	$D_K$	$d_1$	$d_2$
$A$	25 271.408(37)	25 122.826(10)	$A$	1.00						
$B$	3 150.6869(87)	3 080.9891(17)	$B$	0.30	1.00					
$C$	2 848.440(11)	2 789.4927(22)	$C$	0.06	-0.06	1.00				
$D_J$	1.52(16)	1.667(25)	$D_J$	-0.06	0.57	0.66	1.00			
$D_{JK}$	-51.6(13)	-52.09(25)	$D_{JK}$	0.36	0.39	0.63	0.71	1.00		
$D_K$	758(10)	733.0(48)	$D_K$	0.54	0.17	-0.49	-0.36	-0.33	1.00	
$d_1$	-0.344(26)	-0.303(21)	$d_1$	-0.25	-0.48	0.86	0.40	0.39	-0.60	1.00
$d_2$	-0.071(23)	0.014(27)	$d_2$	-0.36	-0.04	0.03	0.00	0.00	-0.77	0.07
$N$	12	11								
$\sigma$	38	9								
$\chi_{aa}(\text{Cl})$	-34.873(20)	-27.918(30)	$\chi_{aa}(\text{Cl})$	$\chi_{aa}(\text{Cl})$	$\chi_{bb}(\text{Cl})$	$\chi_{aa}(\text{N})$	$\chi_{bb}(\text{N})$			
$\chi_{bb}(\text{Cl})$	-6.145(15)	-4.421(19)	$\chi_{bb}(\text{Cl})$	1.00						
$\chi_{aa}(\text{N})$	-2.721(22)	-2.667(16)	$\chi_{aa}(\text{N})$	-0.73	1.00					
$\chi_{bb}(\text{N})$	0.760(15)	0.730(14)	$\chi_{bb}(\text{N})$	0.01	0.08	1.00				
$\chi_{cc}(\text{Cl})$	41.018(35)	32.339(49)		-0.04	-0.06	-0.55	1.00			
$\chi_{cc}(\text{N})$	1.961(37)	1.937(30)								
$\bar{\Delta\nu}$	3.247	2.550								
$N_{\text{comp}}$	99	104								
$\sigma$	16	14								

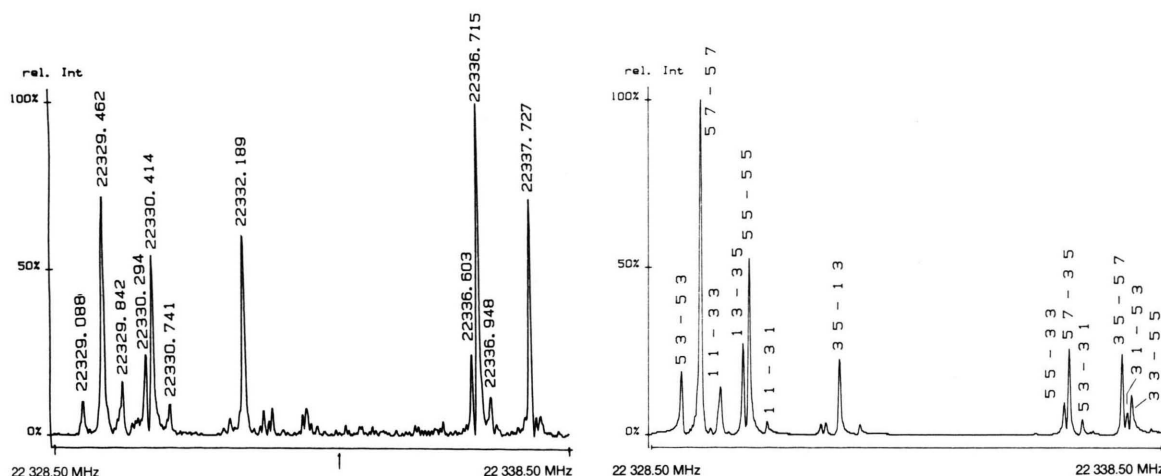


Fig. 1. 10 MHz section out of a 25 MHz range of the power spectrum showing the  $J K_+ K_- - J' K'_+ K'_- = 1_{10} - 1_{01}$  transition of  $\text{CH}_2^{37}\text{ClCN}$  with chlorine and nitrogen hfs. Frequencies (MHz) and quantum numbers  $2F_1$  and  $2F$  are given. Sample interval 20 ns,  $10^8$  averaging cycles, 1024 data points supplemented by 3072 zeros before Fourier transformation, temperature  $-48^\circ\text{C}$ , pressure 0.5 mTorr (0.06 Pa), polarizing frequency 22 334.000 MHz (↑). Lower trace: simulated spectrum calculated with the constants of Table 2. The difference in intensities reflects the varying polarization conditions.

- [1] W. Kasten, H. Dreizler, B. E. Job, and J. Sheridan, *Z. Naturforsch.* **38 a**, 1015 (1983).
- [2] J. D. Graybeal, *J. Chem. Phys.* **32**, 1258 (1960).
- [3] K. Wada, Y. Kikuchi, Ch. Matsumura, E. Hirota, and Y. Morino, *Bull. Chem. Soc. Japan* **34**, 337 (1961).
- [4] H. Dreizler, *J. Mol. Phys.* **59**, 1 (1986).
- [5] G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, *Z. Naturforsch.* **35 a**, 392 (1980).
- [6] G. Bestmann and H. Dreizler, *Z. Naturforsch.* **37 a**, 58 (1982).
- [7] W. Stahl, G. Bestmann, H. Dreizler, U. Andresen, and R. Schwarz, *Rev. Sci. Instrum.* **56**, 1759 (1985).
- [8] E. Fliege and H. Dreizler, *Z. Naturforsch.* **39 a**, 630 (1984).
- [9] I. Merke, Diplomarbeit Kiel, 1986.
- [10] Authors: H. Günter, Tübingen, and R. Reinstädler, Giessen. Program Q2SIM.
- [11] Authors: D. Hübner and W. Stolze, Kiel, Program Q2FIT.
- [12] W. Gordy and R. L. Cook, *Microwave Molecular Spectra*; J. Wiley, New York, Chapter IX.
- [13] J. K. G. Watson, "Aspects of Quartic and Sextic Centrifugal Effects on Rotational Energy Levels", in *Vibrational Spectra and Structure*, J. R. Durig ed., Vol. 6, Marcel Dekker, New York, p. 36.
- [14] Author: V. Typke, Ulm, Program ZFAP4.
- [15] l.c. 12, p. 861.