Hyperfine Structure in the Rotational Spectrum of Chloroacetonitrile

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In continuation of previous studies on substituted acetonitriles, the chloroacetonitriles $CH_2{}^{35}ClCN$ and $CH_2{}^{37}ClCN$ are investigated. Substituted acetonitriles have earlier been studied in our laboratory [1]. The rotational spectra of the ^{35}Cl- and ^{37}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 $CD_2{}^{35}ClCN$ and $CD_2{}^{37}ClCN$. 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 °C to −50 °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}Cl-coupling constants of [3] as starting values. After refinement of the ^{35}Cl-coupling constants and determination of the ^{37}Cl and ^{14}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}Cl-species which are representative also for the ^{35}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 χ_{gg} (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 χ_{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 χ_{cc} can be compared. The χ_{cc} (N) agree within the error limits. Further $\chi_{cc}(^{35}Cl)/\chi_{cc}(^{37}Cl) = 1.2684(32)$ agrees within the error limit with the quotient of the quadrupole moments $^{35}Q/^{37}Q = 1.26878(15)$ [15].

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Table 1 a. Selection of measured rotational transitions of ^{35}Cl-Chloroacetonitrile showing ^{35}Cl (F_1 quantum numbers) and ^{14}N (F quantum numbers) hyperfine structure. F and F_1: quantum numbers multiplied by 2, ν: measured and improved frequencies, $\Delta\nu_{\mathrm{hfs}}$: splittings referred to the strongest component, ν_0: hypothetical unsplit lines, $\delta_{\mathrm{hfs}} = \Delta\nu_{\mathrm{hfs}} - \Delta\nu_{\mathrm{calc}}$: deviations of the splittings, $\Delta\nu_{\mathrm{calc}}$: splittings calculated with the constants of Table 2, δ: 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'	ν [MHz]	$\Delta\nu_{\mathrm{hfs}}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]	δ [kHz]
1	1	0 − 1	0	1	5	3 − 5	3	22 417.869	−9.386	−14		
					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	22 419.110	−8.145	−6		
					5	5 − 5	5	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			22 422.295	−34
					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		
					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			12 300.882	−38
					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	12 309.612	6.960	−21		
					3	3 − 1	1	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		
					1	1 − 1	3					
					1	3 − 1	3					
					5	3 − 7	5	10 121.912	−0.324	13		
					5	7 − 7	9	10 122.236			10 124.695	−4
					5	5 − 7	7	10 123.154	0.918	12		
					1	3 − 3	5	10 126.289	4.053	45		
					3	5 − 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		
					5	5 − 3	3					
					5	7 − 3	5	17 983.505			17 985.163	45
					7	7 − 5	5	17 985.299	1.794	2		
					9	9 − 7	7	17 985.562	2.057	−19		
					7	9 − 5	7					
					9	7 − 7	5					
					7	5 − 3	5	17 985.657	2.152	9		
					9	11 − 7	9					
4	2	2 − 3	2	1	9	9 − 7	7	24 024.158	−3.642	20		
					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			24 026.496	−7
					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'	ν [MHz]	$\Delta\nu_{hfs}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]	δ [kHz]
5 0 5 − 4 1 4	7	5 − 5	3	9 131.487	−2.109	31		
	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			9 134.894	−18
	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		
	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			15 794.457	9
	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		
	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			13 488.243	0
	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}Cl-Chloroacetonitrile. See also Table 1 a.

J K_- K_+ − J' K'_- K'_+	F_1	$F - F'_1$ *2	F'	ν [MHz]	$\Delta\nu_{hfs}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]	δ [kHz]
1 1 0 − 1 0 1	5	3 − 5	3	22 329.088	−3.101	2		
	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			22 332.710	−7
	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'	ν [MHz]	$\Delta\nu_{\mathrm{hfs}}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]	δ [kHz]
	3	1 − 5	3	22 337.852	5.663	30		
	3	3 − 5	5	22 337.935	5.746	29		
3 0 3 − 2 0 2	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			17 599.772	7
	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		
	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			17 172.579	1
	9	7 − 7	5					
4 2 2 − 3 2 1	9	9 − 7	7	23 507.718	−2.983	13		
	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			23 509.638	−1
	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		
	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	23 480.279	−1.828	25		
	5	7 − 5	5					
	7	5 − 7	5					
	11	11 − 9	11	23 481.695	−0.412	−3		
	11	11 − 9	9					
	11	13 − 9	11	23 482.026	−0.081	−13		
	11	9 − 9	7	23 482.107			23 480.930	−1
	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'	ν [MHz]	$\Delta\nu_{hfs}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]	δ [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	8528.701	−1.628	−18		
					11	11 − 9	9	8530.283	−0.046	−6		
					11	9 − 9	7					
					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}Cl and ^{37}Cl, CH_2ClCN. Correlation matrices are given for ^{37}Cl. Watson's S-Reduction is used. Single standard errors in brackets. N, N_{comp}: number of lines and components, σ: standard deviation of the fit (kHz), $\overline{\Delta\nu}$: mean deviation (MHz) of hyperfinestructure component to the reference component.

	$^{35}Cl-CH_2-CN$	$^{37}Cl-CH_2-CN$		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	1.00
N	12	11									
σ	38	9									
				χ_{aa}(Cl)	χ_{bb}(Cl)	χ_{aa}(N)	χ_{bb}(N)				
χ_{aa}(Cl)	−34.873(20)	−27.918(30)	χ_{aa}(Cl)	1.00							
χ_{bb}(Cl)	−6.145(15)	−4.421(19)	χ_{bb}(Cl)	−0.73	1.00						
χ_{aa}(N)	−2.721(22)	−2.667(16)	χ_{aa}(N)	0.01	0.08	1.00					
χ_{bb}(N)	0.760(15)	0.730(14)	χ_{bb}(N)	−0.04	−0.06	−0.55	1.00				
χ_{cc}(Cl)	41.018(35)	32.339(49)									
χ_{cc}(N)	1.961(37)	1.937(30)									
$\overline{\Delta\nu}$	3.247	2.550									
N_{comp}	99	104									
σ	16	14									

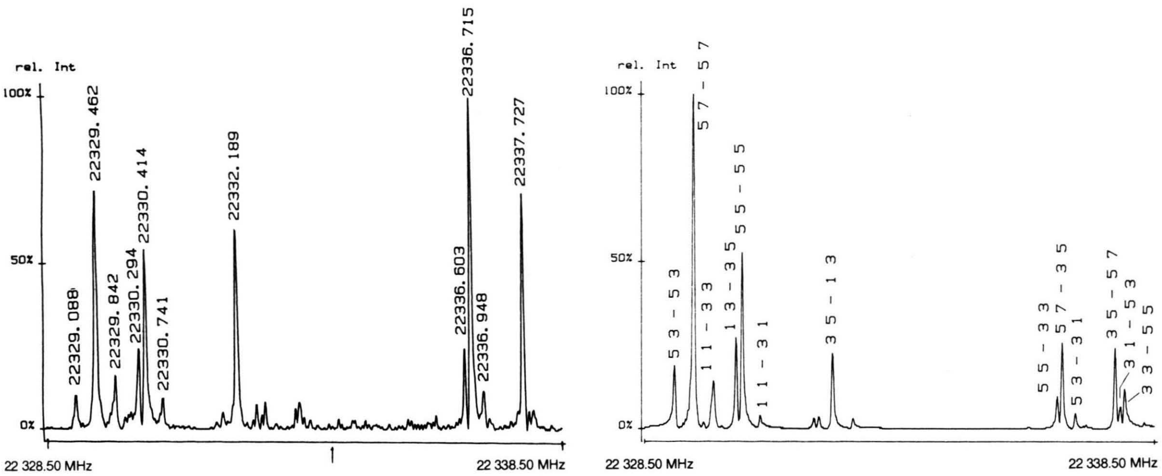

Fig. 1. 10 MHz section out of a 25 MHz range of the power spectrum showing the $J\,K_-K_+ - J'\,K'_-K'_+ = 1_{10} - 1_{01}$ transition of $CH_2{}^{37}ClCN$ with chlorine and nitrogen hfs. Frequencies (MHz) and quantum numbers $2F_1$ and $2F$ are given. Sample interval 20 ns, 10^8 averaging cycles, 1024 data points supplemented by 3072 zeros before Fourier transformation, temperature −48 °C, pressure 0.5 mTorr (0.06 Pa), polarizing frequency 22334.000 MHz (↑). Lower trace: simulated spectrum calculated with the constants of Table 2. The difference in intensities reflects the varying polarization conditions.

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