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THE MICROWAVE SPECTRUM OF CHLOROACETYL CHLORIDE

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ABSTRACT

The microwave spectrum, rotational constants and centrifugal distortion parameters for $CH_2\,{}^{35}ClCO^{35}Cl$ are reported. The nuclear quadrupole coupling constants of the two non-equivalent Cl atoms were determined from partially resolved quadrupole splittings. The molecule is planar in the conformation studied here and both Cl atoms occupy the *trans* position as shown from their substitution coordinates.

INTRODUCTION

Several IR and Raman studies on chloroacetyl chloride have been published. It is generally agreed that two conformations exist in the gaseous state and that both Cl atoms occupy the *trans* position in the more stable form. However, for the other conformation dihedral angles of 150° [1], 120° [2] and 180° [3] are suggested. We have started an investigation of the microwave spectrum to obtain more information about the rotational barrier. The results reported here refer to the *trans* conformation.

EXPERIMENTAL

Chloroacetyl chloride was prepared from chloroacetic acid and PCl_3 and purified by repeated distillation. The fraction with boiling point 105—108 °C was collected.

We recorded the microwave spectrum (0.06 mm Hg, 18—40 GHz) at room temperature, using 10 kHz Stark modulation. For identification purposes double resonance modulation was sometimes used instead. Frequency measurements were made at a pressure of 0.02 mm Hg; the accuracy varied from 0.05 to 0.2 MHz, depending on the separation of quadrupole hyperfine components.

RESULTS

The spectrum was strong and dominated by Q-type transitions $J_{3,J-3} \rightarrow J_{4,J-4}$ ($J = 29$—36) and $J_{2,J-2} \rightarrow J_{3,J-3}$ ($J = 16$—32). The assignment of these lines was performed numerically [4] for the vibrational ground state of $CH_2{}^{35}ClCO^{35}Cl$; the same transitions were observed for torsionally excited states and for monosubstituted ^{37}Cl species.

The R-type lines were considerably weaker, and their identification was greatly facilitated by using the double resonance modulation technique. Indeed, especially for the ^{37}Cl species, where only three R-type lines were found, an assignment from the Stark spectrum alone would have been rather questionable.

Many lines showed quadrupole splitting due to the two Cl nuclei. For the calculation of the rotational constants we used the average frequencies of the quadrupole components; when the quadrupole splittings were calculated this was found to be a very good approximation except for low J values (see below).

The transitions were exclusively b-type; the measured frequencies are given in Tables 1 and 2, and the molecular parameters derived from them in Table 3. Since the molecule is planar except for two H atoms, only four centrifugal distortion parameters were derived. This was done for the $CH_2{}^{35}ClCO^{35}Cl$ ground state only and the resulting values were used for the other calculations where insufficient data were available to obtain reliable centrifugal distortion parameters. In this case the standard deviations calculated by the least squares procedure were multiplied by a factor of 5 to give the values shown in Table 3, since reasonable variations in the fixed parameters were found to cause this kind of effect.

To analyse the quadrupole splitting we used the formulas given by Robinson and Cornwell [5]. With approximate quadrupole coupling constants transferred from chloroacetic acid [6] and acetyl chloride [7], the 16-fold splitting of each energy level was calculated and energy differences were taken according to the selection rules $\Delta F = \Delta J$ and $\Delta \epsilon = 0$ (i.e., within the $\Delta F = \Delta J$ scheme we allowed a transition between the lowest energy levels, then one between the next higher levels and so on). We found that usually most of the 16 transitions thus calculated coincided in groups within the line widths of our measurements. Four common line profiles are shown in Fig. 1; for the observed lines ($J > 7$) the calculated splittings were symmetric with respect to the unsplit frequency within 0.05 MHz. These results were in agreement with the observed spectrum; the distinction between the various line profiles is somewhat artificial since it depends on the experimental conditions.

To actually derive quadrupole coupling constants for the $CH_2{}^{35}ClCO^{35}Cl$ species from the measured frequency splittings we used a least squares procedure. The normal equations were rather ill-conditioned and we found it necessary to use not only the doublet splittings $\Delta\nu^{(1)}$ but also the subsplittings

TABLE 1

Observed and calculated transition frequencies and quadrupole splittings for the ground state of CH_2 $^{35}ClCO^{35}Cl$ (MHz)

Transition						ν_{obs}[a]	$\Delta\nu$[a]	Profile[c]	$\Delta\nu^{(1)}_{obs}$	$\Delta\nu^{(1)}_{calc}$	$\Delta\nu^{(2)}_{obs}$	$\Delta\nu^{(2)}_{calc}$[c]
8	2	6	8	3	5	37555.49[b]	−0.12	3	2.65	2.65		
8	0	8	9	1	9	28810.0	−0.03	1				
10	0	10	11	1	11	33020.7[b]	−0.21	1				
11	0	11	12	1	12	35154.9	−0.05	1				
11	1	11	12	0	12	29671.5	−0.04	1				
12	0	12	13	1	13	37325.0	+0.08	1				
12	1	12	13	0	13	32740.6	−0.04	1				
13	0	13	13	1	12	20276.94	+0.03	4	2.76	2.77	0.32	0.31
13	0	13	14	1	14	39538.7	+0.02	1				
13	1	13	14	0	14	35751.0[b]	+0.08	1				
14	1	14	15	0	15	38703.6[b]	−0.02	1				
14	2	13	15	1	14	29713.8	−0.17	1				
15	0	15	15	1	14	25004.01	+0.05	2	2.78	2.76	—	0.27
15	1	14	15	2	13	19907.02	+0.03	4	0.95	0.97	0.26	0.29
15	2	14	16	1	15	33614.8[b]	+0.17	1				
16	0	16	16	1	15	27605.15	+0.05	2	2.76	2.74	—	0.25
16	1	15	16	2	14	20571.04	−0.00	4	1.03	1.07	0.22	0.23
16	2	14	16	3	13	32667.4[b]	−0.01	1				
17	0	17	17	1	16	30329.82	−0.01	2	2.65	2.69	—	0.23
17	1	16	17	2	15	21462.07	−0.01	2	1.17	1.17	—	0.18
17	2	15	17	3	14	31847.4	+0.16	1				
18	0	18	18	1	17	33149.05	+0.04	2	2.62	2.63	—	0.21
18	1	17	18	2	16	22591.49	−0.03	2	1.33	1.28	—	0.14
18	2	16	18	3	15	31072.1	+0.25	1				
19	0	19	19	1	18	36034.29	+0.04	2	2.49	2.55	—	0.20
19	1	18	19	2	17	23967.30	−0.01	2	1.39	1.38	—	0.12
19	2	17	19	3	16	30377.4[b]	+0.10	1				
20	1	19	20	2	18	25593.30	+0.03	2	1.50	1.48	—	0.11
20	2	18	20	3	17	29798.2	−0.04	1				
21	6	16	20	7	13	39839.27[b]	−0.05	3	1.61	1.59		
21	6	15	20	7	14	39838.51[b]	−0.06	3	1.62	1.59		
21	1	20	21	2	19	27468.11	+0.03	2	1.63	1.57	—	0.11
21	2	19	21	3	18	29367.4	+0.14	1				
22	1	21	22	2	20	29584.21	+0.02	2	1.64	1.65	—	0.11
22	2	20	22	3	19	29115.9	+0.01	1				
23	1	22	23	2	21	31927.69	+0.02	2	1.68	1.72	—	0.11
23	2	21	23	3	20	29070.0	+0.03	1				
24	1	23	24	2	22	34478.61	−0.05	2	1.82	1.77	—	0.11
24	2	22	24	3	21	29252.9	+0.02	1				
25	1	24	25	2	23	37211.33	+0.01	2	1.83	1.80	—	0.11
25	2	23	25	3	22	29683.93	−0.03	2	0.51	0.57	—	0.15
26	1	25	26	2	24	40096.49	+0.00	2	1.93	1.82	—	0.10
26	2	24	26	3	23	30378.73	−0.02	2	0.62	0.68	—	0.11
27	2	25	27	3	24	31349.43	−0.03	2	0.79	0.78	—	0.08
28	2	26	28	3	25	32604.07	−0.03	2	0.89	0.89	—	0.06
29	2	27	29	3	26	34146.19	−0.07	2	0.99	0.99	—	0.05
29	3	26	29	4	25	40179.6[b]	+0.15	1				

TABLE 1 (continued)

Transition						ν_{obs}[a]	$\Delta\nu$[a]	Profile[c]	$\Delta\nu^{(1)}_{obs}$	$\Delta\nu^{(1)}_{calc}$	$\Delta\nu^{(2)}_{obs}$	$\Delta\nu^{(2)}_{calc}$[c]
30	2	28	30	3	27	35973.89	—0.04	2	1.07	1.08	—	0.05
30	3	27	30	4	26	39412.1[b]	—0.29	1				
31	2	29	31	3	28	38079.54	—0.11	2	1.14	1.17	—	0.06
31	3	28	31	4	27	38834.9	+0.03	1				
32	3	29	32	4	28	38481.3	—0.10	1				
33	3	30	33	4	29	38378.6	—0.11	1				
34	3	31	34	4	30	38550.2	—0.01	1				
35	3	32	35	4	31	39015.1	+0.12	1				
36	3	33	36	4	32	39787.8	+0.15	1				
36	5	31	37	4	34	29946.29[b]	—0.02	2	0.90	1.00	—	0.15
41	6	35	42	5	38	35636.25[b]	+0.19	2	0.48	0.55	—	0.20
42	6	36	43	5	39	37677.4[b]	—0.15	1				
43	10	34	42	11	31	37978.43[b]	+0.03	3	0.55	0.57		

[a] Average values of quadrupole components; $\Delta\nu = \nu_{calc} - \nu_{obs}$.
[b] Measured with double resonance modulation.
[c] See Fig. 1 for identification of line profiles and definition of $\Delta\nu^{(1)}$ and $\Delta\nu^{(2)}$.

$\Delta\nu^{(2)}$ (Fig. 1). The latter were generally unobservable, but they had to be introduced as zero (with a smaller statistical weight than the actually measured splittings) in order to make the least squares procedure converge and to obtain quadrupole coupling constants with acceptable standard deviations. The resulting agreement between observed and calculated splittings was satisfactory (Table 1); the derived quadrupole coupling constants appear in Table 4, together with values for some related molecules. For each molecule the constants are also given in the coordinate system $\alpha\beta c$ where α coincides with the C—Cl bond, on the assumption that this is the quadrupole principal axis system.

DISCUSSION

From the $I_a + I_b - I_c$ values (Table 3) and the smooth curves of inertial moments versus torsional quantum number v, we deduced that the molecule has a plane of symmetry.

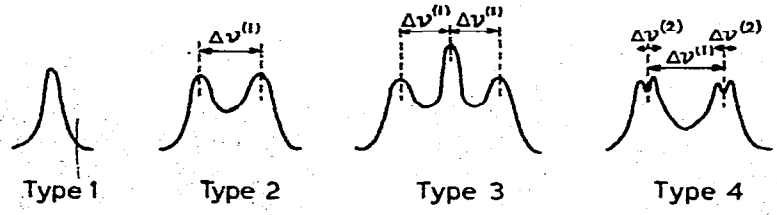

Fig. 1. Line profiles in the microwave spectrum of chloroacetyl chloride.

TABLE 2

Observed and calculated transition frequencies[a] for other species of chloroacetyl chloride

Transition						$CH_2{}^{35}ClCO^{35}Cl$[c]		$CH_2{}^{35}ClCO^{35}Cl$[d]		$CH_2{}^{37}ClCO^{35}Cl$[e]		$CH_2{}^{35}ClCO^{37}Cl$[e]	
						ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$
10	0	10	11	1	11			33012.6[b]	+0.18				
11	0	11	12	1	12	35158.9	+0.19	35167.8	+0.05				
11	1	11	12	0	12	29773.3	−0.03	29877.0	−0.01				
12	0	12	13	1	13	37339.7	+0.06	37359.0	+0.05				
12	1	12	13	0	13			32944.6	+0.05				
13	1	13	14	0	14	35851.5[b]	−0.18	35954.6[b]	−0.36				
14	1	14	15	0	15	38803.6[b]	−0.06	38906.5[b]	+0.07				
14	2	13	15	1	14	29968.4	−0.29						
15	2	14	16	1	15	33863.3[b]	−0.01	34111.4	+0.01	31922.5[b]	−0.21	32153.5[b]	−0.09
16	2	14	16	3	13	32250.2	−0.13						
16	2	15	17	1	16	37732.6	+0.31			35716.7[b]	−0.11	35951.2[b]	−0.03
17	2	16	18	1	17					39478.2[b]	+0.29	39714.4[b]	+0.11
18	2	16	18	3	15	30673.3	+0.09	30286.5	+0.15				
19	2	17	19	3	16	29990.1	+0.04	29614.5	+0.34				
20	2	18	20	3	17	29423.7	+0.12	29061.2	+0.22				
21	2	19	21	3	18	29007.3	+0.12	28658.9	+0.23				
22	2	20	22	3	19	28770.8	+0.11	28437.5	+0.18				
23	2	21	23	3	20	28740.7	+0.05	28423.0	+0.21				
24	2	22	24	3	21	28939.5	+0.13	28638.1	+0.01				
25	2	23	25	3	22	29386.5	+0.07	29101.0	+0.10	29478.0	+0.08	29404.2	+0.06
26	2	24	26	3	23	30096.9	+0.10	29827.1	+0.17	29972.3	+0.01	29936.8	+0.15
27	2	25	27	3	24	31082.6	+0.03	30827.9	+0.13	30720.9	−0.29	30727.3	+0.09
28	2	26	28	3	25	32351.1	+0.06	32110.6	+0.08			31785.2	+0.14
29	2	27	29	3	26	33905.6	+0.05	33677.7	+0.16			33116.7	+0.04
29	3	26	29	4	25	39641.7	+0.09	39121.0	−0.13				
30	2	28	30	3	27			35526.6	+0.15			34723.1	−0.00
30	3	27	30	4	26	38896.4	−0.04	38397.7	+0.17			39884.2	+0.14
31	2	29	31	3	28	37857.2	+0.06	37648.3	+0.14	36399.6	+0.28	36600.9	−0.08
31	3	28	31	4	27	38344.4	−0.28	37870.4	−0.18	39480.3	+0.14		

TABLE 2 (continued)

Transition	$CH_2{}^{35}ClCO^{35}Cl$[c]		$CH_2{}^{35}ClCO^{35}Cl$[d]		$CH_2{}^{37}ClCO^{35}Cl$[e]		$CH_2{}^{35}ClCO^{37}Cl$[e]	
	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$
32 2 30 32 3 29			40027.5	+0.08				
32 3 29 32 4 28	38016.7	−0.00	37569.3	−0.23	38943.2	−0.03	38691.5	−0.04
33 3 30 33 4 29	37941.5	−0.04	37521.5	−0.19			38413.4	−0.07
34 3 31 34 4 30	38141.5	−0.19	37749.7	−0.36			38382.1	−0.18
35 3 32 35 4 31	38634.6	+0.04	38271.4	−0.39	38719.3	+0.10		
36 3 33 36 4 32	39435.6	−0.31	39100.3	−0.62	39178.6	−0.09	39138.4	−0.15
37 3 34 37 4 33					39930.1	−0.22		

[a] Average values of quadrupole components in MHz; $\Delta\nu = \nu_{calc} - \nu_{obs}$.
[b] Measured with double resonance modulation.
[c] Torsional quantum number $v = 1$.
[d] $v = 2$.
[e] $v = 0$.

TABLE 3

Rotational constants (MHz), principal moments of inertia (u.A^2, conversion factor 505376 MHz. u.A^2) and centrifugal distortion parameters (kHz) of chloroacetyl chloride

Parameter	$CH_2{}^{35}ClCO^{35}Cl$			$CH_2{}^{37}ClCO^{35}Cl$	$CH_2{}^{35}ClCO^{37}Cl$
	$v = 0$	$v = 1$	$v = 2$	$v = 0$	$v = 0$
A	9030.255 ± 0.007	8944.60 ± 0.04	8861.89 ± 0.06	9024.64 ± 0.10	8993.09 ± 0.05
B	1503.976 ± 0.001	1505.48 ± 0.01	1507.16 ± 0.02	1462.53 ± 0.02	1465.67 ± 0.01
C	1299.588 ± 0.001	1302.19 ± 0.01	1304.91 ± 0.02	1268.41 ± 0.02	1270.14 ± 0.01
I_a	55.9648	56.5007	57.0280	55.9996	56.1960
I_b	336.0266	335.692	335.318	345.548	344.808
I_c	388.8740	388.098	387.289	398.432	397.889
$I_a + I_b - I_c$	3.1174	4.095	5.057	3.115	3.115
τ_{aaaa}	−72.9 ± 0.2				
τ_{bbbb}	−0.629 ± 0.003				
τ_{cccc}	−0.365 ± 0.002	[b]	[b]	[b]	[b]
τ_{abab}	−2.51 ± 0.03				
s[a]	0.10	0.15	0.23	0.21	0.12

[a] s denotes the root mean square deviation in MHz.
[b] Kept fixed at values for the ground state of $CH_2{}^{35}ClCO^{35}Cl$; see text.

TABLE 4

Quadrupole coupling constants (MHz) of chloroacetyl chloride and comparison with related molecules

	$CH_2{}^{35}ClCO^{35}Cl$ (this work)		$CH_2{}^{35}ClCOOH$ [6]	$CH_2FCO^{35}Cl$ [8]	$CH_3CO^{35}Cl$ [7]
	CH_2Cl-group	COCl-group			
χ_{aa}	−64.1 ± 1.3	−46.5 ± 1.4	−47.5 ± 1.4	−47.7	−58.0
χ_{bb}	+25.3 ± 0.7	+23.5 ± 0.8	+10.4 ± 0.7	+23.7	+36.4
χ_{cc}	+38.8 ± 0.6	+23.0 ± 0.7	+37.1 ± 1.2	+24.1	+21.6
θ [a]	20 ° 4 ′	23 ° 16 ′	29 °	22 ° 2 ′	6 ° 28 ′
χ_α	−77.9 ± 1.7	−62.4 ± 1.9	−73.3 ± 2.3	−61.7	−59.2
χ_β	+39.1 ± 1.0	+39.4 ± 1.3	+36.2 ± 1.6	+37.7	+37.6
η [b]	−0.004 ± 0.006	−0.263 ± 0.010	+0.012 ± 0.013	−0.22	−0.27

[a] θ = angle between a-axis and α-axis. [b] $\eta = (\chi_\beta - \chi_{cc})/\chi_\alpha$.

The substitution coordinates of the Cl atoms are: $a = 2.2028 \pm 0.0005$ Å, $b = 0.1354 \pm 0.0012$ Å (CH_2Cl group), and $a = -2.1147 \pm 0.0003$ Å, $b = 0.3487 \pm 0.0003$ Å (COCl group). The error limits given refer to measurement errors only and the small b-coordinates are especially subject to vibrational effects. Nevertheless, the Cl—Cl distance of 4.323 Å is quite reliable and shows that these two atoms occupy the *trans* position.

Table 4 shows that the quadrupole coupling constants for several related molecules are quite similar. The charge distribution in the CH_2Cl group is essentially cylindrically symmetric around the C—Cl bond, whereas considerable asymmetry exists in the COCl group. Sinnott [7] has discussed the origin of this effect for acetyl chloride.

A search for absorption lines due to a second molecular conformation is planned.

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