

THE MICROWAVE SPECTRUM OF MONOCHLOROACETIC ACID

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ABSTRACT

The microwave spectrum, rotational constants and centrifugal distortion parameters for $\text{CH}_2^{35}\text{ClCOOH}$ are reported. The nuclear quadrupole coupling constants are: $\chi_{aa} = -47.5 \pm 1.4$ MHz, $\chi_{bb} = 10.4 \pm 0.7$ MHz, $\chi_{cc} = 37.1 \pm 1.2$ MHz, and the dipole moment components: $\mu_a = 1.658 \pm 0.008$ D, $\mu_b = 2.112 \pm 0.006$ D ($\mu = 2.685 \pm 0.006$ D). From a-substitution coordinates of the Cl atom and the carboxyl H atom the chain of atoms Cl–C–C–O–H is shown to be planar and zig-zag. An estimate of the torsional frequency is given.

INTRODUCTION

In our investigation of the molecular structure of fluoroacetic acid [1] it was found that free molecules of this substance may occur in at least two conformations. A study of chloroacetic acid was undertaken in order to investigate the degree of structural similarity between both compounds. In this paper we describe the microwave spectrum; results of electron diffraction work will be reported by Derissen and Bijen [2].

EXPERIMENTAL

Chloroacetic acid was obtained commercially and purified by low pressure sublimation. Deuterium was introduced into the carboxyl group by reaction of D_2O with chloroacetylchloride. This compound was prepared from chloroacetic acid and PCl_3 , as described by Vogel [3] for acetylchloride.

The microwave spectrometer was a conventional 10 kHz Stark-modulated

instrument. The spectra (20–39 GHz) were recorded at room temperature at a pressure of about 0.03 mm Hg. The accuracy of the frequency measurements was about 0.2 MHz.

ANALYSIS

The spectrum was found to be very rich in lines. The dominating ones are Q-type transitions $J_{2, J-2} - J_{3, J-3}$ with J ranging from 10 to 22 (Table 1). They were identified with aid of a numerical method described earlier [4]. After that, R-type lines were found easily.

TABLE 1

ABSORPTION FREQUENCIES (average values of quadrupole components) FOR THE STRONGEST TRANSITIONS IN THE VIBRATIONAL GROUND STATE

Transition	$CH_2^{35}ClCOOH$		$CH_2^{37}ClCOOH$		$CH_2^{35}ClCOOD$	
	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$
10 _{2,8} –10 _{3,7}	37958.4	–0.14				
11 _{2,9} –11 _{3,8}	36778.0	+0.18	37397.0	–0.02		
12 _{2,10} –12 _{3,9}	35550.1	+0.15	36202.7	–0.01	36435.7	–0.06
13 _{2,11} –13 _{3,10}	34361.0	–0.22			35252.3	+0.00
14 _{2,12} –14 _{3,11}	33303.9	–0.09	33920.8	–0.00	34148.1	+0.15
15 _{2,13} –15 _{3,12}	32473.6	–0.19	33006.3	+0.03	33209.1	–0.14
16 _{2,14} –16 _{3,13}	31957.0	–0.04	32356.2	–0.03	32517.0	+0.07
17 _{2,15} –17 _{3,14}	31830.6	+0.08	32045.7	+0.05	32147.5	–0.01
18 _{2,16} –18 _{3,15}	32157.5	+0.19	32139.2	+0.01	32164.6	–0.06
19 _{2,17} –19 _{3,16}	32988.0	–0.07	32688.7	+0.02	32620.9	+0.15
20 _{2,18} –20 _{3,17}	34358.3	+0.11	33734.9	–0.10	33558.5	+0.01
21 _{2,19} –21 _{3,18}	36292.4	–0.12	35306.2	–0.06	35007.2	–0.02
22 _{2,20} –22 _{3,19}	38796.4	–0.14	37418.0	+0.09	36984.9	–0.03

$$\Delta\nu \equiv \nu_{calc} - \nu_{obs}$$

As for fluoroacetic acid, lines belonging to a number of excited torsional states were observed. For states with torsional quantum number ν greater than 4 the R-type transitions were too weak to be identified, so that no complete set of rotational constants could be obtained. The same applies to the first excited state of a skeletal bending vibration.

The spectrum of the ^{37}Cl species was identified too. Here, as well as in the case of $CH_2^{35}ClCOOD$, only lines belonging to the ground state were analyzed.

A selection of strong ground state transitions, which might be useful for “fingerprinting” the spectrum, is given in Table 1. For these transitions the quadrupole splitting is small, no component being further than 1 MHz away from the centre frequency. A complete list of measured frequencies is available from the

TABLE 2

ROTATIONAL CONSTANTS (MHz), PRINCIPAL MOMENTS OF INERTIA ($\mu\text{\AA}^2$, CONVERSION FACTOR 505376 MHz. u. \AA^2) AND CENTRIFUGAL DISTORTION PARAMETERS (kHz) OF MONOCHLOROACETIC ACID

Values in parentheses denote standard deviations in kHz. Further data: the number of observed R-type (N_R) and Q-type (N_Q) transitions, the maximum value of $J(J_{\text{max}})$ and the root mean square deviation in MHz (s).

ν	$CH_2^{35}ClCOOH$					$CH_2^{37}ClCOOH$					$CH_2^{35}ClCOOD$										
	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	
A	10514.872(17)	10422.687(20)	10329.059(20)	10232.716(16)	10131.443(24)	10514.166(21)	10422.687(20)	10329.059(20)	10232.716(16)	10131.443(24)	10514.166(21)	10422.687(20)	10329.059(20)	10232.716(16)	10131.443(24)	10514.942(45)	10422.687(20)	10329.059(20)	10232.716(16)	10131.443(24)	10514.942(45)
B	2351.358(4)	2351.876(4)	2352.652(5)	2353.772(4)	2355.287(8)	2287.986(6)	2351.876(4)	2352.652(5)	2353.772(4)	2355.287(8)	2287.986(6)	2351.876(4)	2352.652(5)	2353.772(4)	2355.287(8)	2266.218(10)	2351.876(4)	2352.652(5)	2353.772(4)	2355.287(8)	2266.218(10)
C	1946.028(4)	1951.356(5)	1957.094(5)	1963.451(4)	1970.644(8)	1902.400(6)	1951.356(5)	1957.094(5)	1963.451(4)	1970.644(8)	1902.400(6)	1951.356(5)	1957.094(5)	1963.451(4)	1970.644(8)	1887.445(9)	1951.356(5)	1957.094(5)	1963.451(4)	1970.644(8)	1887.445(9)
I_a	48.0630	48.4881	48.9276	49.3883	49.8819	48.0662	48.4881	48.9276	49.3883	49.8819	48.0662	48.4881	48.9276	49.3883	49.8819	48.0627	48.4881	48.9276	49.3883	49.8819	48.0627
I_b	214.9294	214.8821	214.8112	214.7090	214.5709	220.8825	214.8821	214.8112	214.7090	214.5709	220.8825	214.8821	214.8112	214.7090	214.5709	223.0041	214.8821	214.8112	214.7090	214.5709	223.0041
I_c	259.6962	258.9871	258.2278	257.3917	256.4522	265.6518	258.9871	258.2278	257.3917	256.4522	265.6518	258.9871	258.2278	257.3917	256.4522	267.7567	258.9871	258.2278	257.3917	256.4522	267.7567
$I_a + I_b - I_c$	3.2962	4.3831	5.5110	6.7055	8.0006	3.2969	4.3831	5.5110	6.7055	8.0006	3.2969	4.3831	5.5110	6.7055	8.0006	3.3101	4.3831	5.5110	6.7055	8.0006	3.3101
τ_{aaaa}	-38.0(0.1)	-40.4(0.2)				-39.0(ass)	-40.4(0.2)				-39.0(ass)	-40.4(0.2)				-39.4(ass)	-40.4(0.2)				-39.4(ass)
τ_{bbbb}	-2.07(0.03)	-2.18(0.03)				-1.5(0.2)	-2.18(0.03)				-1.5(0.2)	-2.18(0.03)				-1.9(0.3]	-2.18(0.03)				-1.9(0.3]
τ_{ccco}	-0.99(0.02)	-1.14(0.04)				-0.6(0.1)	-1.14(0.04)				-0.6(0.1)	-1.14(0.04)				-1.0(0.2)	-1.14(0.04)				-1.0(0.2)
τ_{abbb}	-6.1(0.1)	-5.4(0.3)				-7.7(0.6)	-5.4(0.3)				-7.7(0.6)	-5.4(0.3)				-4.9(1.1)	-5.4(0.3)				-4.9(1.1)
N_R	67	49	10	8	7	9	49	10	8	7	9	49	10	8	13	9	49	10	8	7	13
N_Q	23	19	13	10	11	17	19	13	10	11	17	19	13	10	13	17	19	13	10	11	13
J_{max}	69	69	20	22	22	22	69	20	22	22	22	69	20	22	22	22	69	20	22	22	22
s	0.27	0.30	0.24	0.19	0.31	0.06	0.30	0.24	0.19	0.31	0.06	0.30	0.24	0.19	0.31	0.12	0.30	0.24	0.19	0.31	0.12

authors on request. The molecular parameters that were calculated from the measured centre frequencies are given in Table 2. In the least squares procedure centrifugal distortion parameters for most vibrational states were kept fixed at values taken from lower states.

Many lines showed quadrupole splitting due to the chlorine nucleus. For all well-split transitions we could find, the splitting was essentially symmetric with respect to the hypothetical unsplit line. In fact, in the majority of cases there only was a symmetrical doublet with one component due to $F = J \pm \frac{3}{2}$ and the other to $F = J \pm \frac{1}{2}$. From 35 of these doublet splittings in $\text{CH}_2^{35}\text{ClCOOH}$ (Table 3) we

TABLE 3

OBSERVED AND CALCULATED QUADRUPOLE SPLITTINGS (MHz) IN $\text{CH}_2^{35}\text{ClCOOH}$ Root mean square deviation 0.17 MHz. $\Delta\nu \equiv \nu_{F=J\pm\frac{3}{2}} - \nu_{F=J\pm\frac{1}{2}}$.

<i>Transition</i>	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$	<i>Transition</i>	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$
4 _{0,4} -5 _{1,5}	1.6	+1.67	12 _{1,11} -12 _{2,10}	2.1	-2.02
4 _{2,2} -5 _{2,3}	2.1	+2.07	12 _{3,10} -13 _{2,11}	1.2	-1.22
4 _{2,3} -5 _{2,4}	2.5	+2.43	13 _{0,13} -13 _{1,12}	5.5	-5.28
5 _{2,3} -6 _{2,4}	1.0	+1.02	13 _{1,12} -13 _{2,11}	2.3	-2.36
5 _{2,4} -6 _{2,5}	1.3	+1.43	13 _{3,11} -14 _{2,12}	1.5	-1.42
6 _{0,6} -7 _{1,7}	1.1	+1.66	14 _{1,13} -14 _{2,12}	2.6	-2.69
6 _{2,5} -7 _{2,6}	0.9	+0.93	15 _{1,14} -15 _{2,13}	3.2	-2.98
7 _{1,6} -7 _{2,5}	0.8	-0.71	16 _{1,15} -16 _{2,14}	3.4	-3.24
8 _{1,7} -8 _{2,6}	0.9	-0.81	17 _{1,16} -17 _{2,15}	3.4	-3.43
9 _{0,9} -9 _{1,8}	5.6	-5.51	17 _{2,15} -17 _{3,14}	0.6	-0.51
9 _{1,9} -9 _{2,8}	4.6	-4.70	17 _{4,14} -18 _{3,15}	1.0	-1.11
9 _{2,8} -10 _{1,9}	1.3	-1.33	18 _{2,16} -18 _{3,15}	0.8	-0.83
10 _{0,10} -10 _{1,9}	5.9	-5.56	18 _{4,15} -19 _{3,16}	1.4	-1.32
10 _{1,10} -10 _{2,9}	4.2	-4.48	19 _{2,17} -19 _{3,16}	1.0	-1.16
10 _{1,9} -10 _{2,8}	1.4	-1.34	20 _{2,18} -20 _{3,17}	1.5	-1.48
10 _{2,9} -11 _{1,10}	1.5	-1.38	20 _{4,16} -21 _{3,19}	2.4	+2.53
11 _{1,11} -11 _{2,10}	3.9	-4.30	21 _{2,19} -21 _{3,18}	1.7	-1.80
12 _{0,12} -12 _{1,11}	5.5	-5.44			

calculated the quadrupole coupling constants by the least squares method: $\chi_{\text{aa}} = -47.5 \pm 1.4$ MHz, $\chi_{\text{bb}} = 10.4 \pm 0.7$ MHz, $\chi_{\text{cc}} = 37.1 \pm 1.2$ MHz. For the other isotopic species not enough splittings were observed to derive reliable χ -values.

A sign reversal of all three quadrupole coupling constants would produce the same doublet splittings. The signs given above are derived by assuming that the principal quadrupole axis α coincides with the C-Cl bond and that χ_{α} is negative, as usual [5]. Taking the (α, a) angle from a molecular model [2] to be 29° , we calculate $\chi_{\alpha} = -73.3 \pm 2.3$ MHz and $\eta \equiv (\chi_{\beta} - \chi_{\gamma})/\chi_{\alpha} = 0.012 \pm 0.013$. Within our experimental error the charge distribution is, therefore, cylindrically symmetric around the C-Cl bond. A literature value [6] for $|\chi_{\alpha}|$ in the solid state is 73.15 MHz.

Dipole moment

The Stark shifts of a number of transitions were measured in the usual way, the frequency shift of the $J = 1 \rightarrow 2$ transition in OCS [7] being used to calibrate the absorption cell. Fourth-order terms in the field strength were taken into account:

$$\Delta\nu/E^2 = c^{(2)} + c^{(4)}E^2$$

$$c^{(2)} = k_a\mu_a^2 + k_b\mu_b^2$$

From the observed values of $\Delta\nu/E^2$ the quantity $c^{(4)}E^2$ ($c^{(4)}$ being calculated by the formula given in ref. 1) was subtracted in order to find $c^{(2)}$. This correction ranged from 1% to 9% of $c^{(2)}$. From six values of $c^{(2)}$ (Table 4) the dipole moment components were calculated by the least squares method: $\mu_a = 1.658 \pm 0.008$ D, $\mu_b = 2.112 \pm 0.006$ D; $|\mu| = 2.685 \pm 0.006$ D.

TABLE 4

COMPARISON OF CALCULATED AND OBSERVED STARK COEFFICIENTS $c^{(2)}$ IN $\text{CH}_2^{35}\text{ClCOOH}$
 $\Delta\nu$ in MHz, E in Volt cm^{-1} , μ in Debye; conversion factor $\mu E = 0.50344$ MHz cm D^{-1} Volt $^{-1}$;
 $\Delta \equiv 10^8 |c_{\text{obs}}^{(2)} - c_{\text{calc}}^{(2)}|$.

Transition	M	$10^8 k_a$	$10^8 k_b$	$10^8 c_{\text{obs}}^{(2)}$	$10^8 c_{\text{calc}}^{(2)}$	Δ	$10^{16} c_{\text{calc}}^{(4)}$
5 ₂₄ -6 ₂₅	1	+159.82	+89.29	+853 ± 8	+838	15	-2520
6 ₀₆ -7 ₀₇	1	-8.794	-8.096	-60.32 ± 0.11	-60.29	0.03	-1.90
7 ₀₇ -8 ₀₈	3	-2.422	+30.88	+132.0 ± 0.6	+131.1	0.9	-5.98
	1	-7.156	-5.802	-45.2 ± 0.2	-45.6	0.4	-2.90
8 ₀₈ -9 ₀₉	3	-5.472	+16.910	+59.9 ± 0.4	+60.4	0.5	-7.37
	1	-8.370	-4.409	-43.0 ± 0.3	-42.7	0.3	-16.5

In the six transitions studied no effects of quadrupole splitting were observed. Yet a comparison of calculated quadrupole splittings and Stark shifts showed that the "strong-field case" was by no means reached for all measurements, and that especially for the $M_J = \pm 1$ levels complications should be expected. The fact that no anomalies were observed must be ascribed to a fortuitous cancelling of quadrupole effects when a transition frequency is calculated as the difference between two energy levels disturbed in about the same way.

Torsional motion

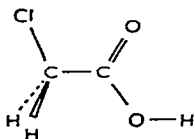
The torsional frequency σ_t might be found from relative intensity measurements on rotational transitions in the various torsional states, but because of the density of the spectrum and the complications due to quadrupole splitting we did not attempt to do this. Instead, an estimate was made from the relation [1, 8] between the $I_a + I_b - I_c$ values and the torsional frequency, giving $\sigma_t = 62$ cm^{-1} .

A much larger value [9] of 243 cm^{-1} used by Johansen [10] must be in error, since we observed lines due to excited torsional states up to $v = 6$. In fact, we believe Johansen's force field to have more defects, since centrifugal distortion parameters calculated from this field were 2 to 10 times greater than our experimental values.

Molecular structure

From the values of $I_a + I_b - I_c$ (Table 2), and the fact that the rotational constants change smoothly with the torsional quantum number v , we deduce that the molecule has a plane of symmetry.

In principle the substitution coordinates of the Cl and H atoms could be obtained from the data available. However, both atoms turn out to have very small b-coordinates; the b_H , in fact, would even be found imaginary. Only the a-coordinates are reliable; they are: $a_{Cl} = 1.7448 \pm 0.0002 \text{ \AA}$ and $a_H = -2.8478 \pm 0.0002 \text{ \AA}$. From the $H \cdots Cl$ distance of 4.5926 \AA the molecular conformation is immediately obvious:



The molecular structure is being investigated by electron diffraction by Derissen and Bijen. The inertial moments and substitution coordinates calculated from their preliminary bond distances and bond angles agree fairly with our results. A full account will be published [2]. The electron diffraction data indicate the presence of at least one more conformation, formed by rotating the carboxyl group 130° about the C-C axis. We have searched carefully for absorption lines belonging to this molecular species, but failed to make an identification. An approximate prediction of the spectrum of this rotamer showed that only for high J -values lines may be expected that compete in intensity with the many weak lines of the first conformation and its vibrationally excited states. Therefore, we doubt that we shall be able to make an assignment for this second conformation.

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