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The Microwave Spectrum and Structure of Chlorofluoromethane[1]

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The microwave spectra of $CH_2Cl^{35}F$ and $CH_2Cl^{37}F$ between 16,100 and 39,000 Mc. have been measured and analyzed. The rotational parameters are $a = 41{,}810.1$ Mc., $b = 5{,}715.7$ Mc., $c = 5{,}194.6$ Mc., and $a = 41{,}738.2$ Mc., $b = 5{,}580.5$ Mc., $c = 5{,}081.6$ Mc., respectively. The structural parameters, calculated with an assumed value of 111°56′ for the H–C–H angle, are $r_{CH} = 1.078 \pm 0.005$ Å., $r_{CCl} = 1.759 \pm 0.003$ Å., $r_{CF} = 1.378 \pm 0.006$ Å. Cl–C–F = 110°1′ ± 2′, $\theta = 125°41' \pm 5'$, where θ is the angle between the C–Cl bond and the projection of the C–H bonds on the symmetry plane. From the hyperfine structure of the $1_{0,1}$–$1_{1,0}$ transition, the quadrupole coupling constants were evaluated as $\chi_a = -52.18 \pm 1$ Mc., $\chi_b = 38.83 \pm 1$ Mc. With certain assumptions, this leads to a value of 6.6% for the per cent. double-bond character of the C–Cl bond.

The structures of the various chlorine- and fluorine-substituted methanes were investigated by Brockway[3] using electron diffraction. Recently, more precise structures of many of these derivatives have been obtained from their microwave spectra,[4] providing a better basis for discussion of the bonding involved. The present study adds CH_2ClF to this list; in addition to the structure, the spectrum yields information about the distribution of charge in the molecule, through the quadrupole hyperfine structure, and a limited amount of information concerning the direction of the dipole moment.

The sample of CH_2ClF studied was the gift of Dr. D. E. Kvalnes of the Jackson Laboratory of E. I. du Pont de Nemours and Company, and is gratefully acknowledged. An infrared spectrum was obtained with the Baird recording spectrometer; comparison with the spectrum published by Plyler and Lamb[5] indicated that no further purification was necessary. The microwave spectrum was observed with a Stark modulation spectrograph[6] using 100 kilocycle square wave modulation. Frequencies were measured by means of harmonics of a 5 Mc. standard frequency monitored by beating with station WWV; they should be accurate to 0.1 Mc. except where otherwise stated.

Analysis of the Spectrum.—Calculations based on approximate structural parameters showed that the molecule is a nearly prolate-symmetric top ($\kappa \sim -0.97$) with the dipole largely along the axis of the intermediate moment of inertia, or b-axis, although the possibility of an appreciable component along the axis of the least moment (a-axis) could not be excluded. Using the methods of King, Hainer and Cross,[7] whose notation is also adopted, it was possible to predict that the only strong lines between 16,000 and 30,000 Mc. would form transitions with $\Delta J = \pm 1$ and $\Delta K = \mp 1 (K = K_{-1})$ and $J = 4$ or greater. In addition there should be a series of lines with $\Delta J = 0$ and $\Delta K = 1$, extending upwards in frequency from about 35,000 Mc.

As a result of the interaction of the chlorine nuclear quadrupole moment with the molecular rotation, all lines involving J's less than about twenty should resolve into hyperfine components. This hyperfine structure proved to be the means of identifying the observed transitions, a task which would otherwise have been nearly impossible in view of the great density of lines in the spectrum.

A convenient starting point for the calculation of the hyperfine structure is the formula for the first-order interaction energy[8]

$$E_Q(J,\tau,F) = \frac{2\beta}{2J+1} \sum_{\tau'} \{\chi_a \lambda^a_{J\tau;J\tau'} + \chi_b \lambda^b_{J\tau;J\tau'} + \chi_c \lambda^c_{J\tau;J\tau'}\}$$

Here $\beta = \{{}^3/_4\, C(C + 1) - I(I + 1)J(J + 1)\}/2I(2I - 1)(2J - 1)(2J + 3)$, with $C = F(F + 1) - I(I + 1) - J(J + 1)$, where F is the quantum number of the resultant of $\vec{J}$ and $\vec{I}$. $\chi_s = eQ\delta^2 V/\delta s^2$, where s is, in turn, each of the three principal axes of inertia. The χ's are experimentally determined, with the restriction that their sum be zero. The λ's are the line strengths of the Q-branch transitions $J, \tau \leftrightarrow J, \tau'$ allowed when the dipole moment is along the axis designated by the superscript.

Ordinarily, in applying this formula to an asymmetric top, the λ's must be found by interpolating in the tables.[9] However, Lide[10] has recently derived expressions for the line strengths of slightly asymmetric rotors, which may be substituted in this formula and which readily give explicit equations for the quadrupole energy with corrections in the first order for the asymmetry; second-order asymmetry corrections could also be obtained at the expense of a great deal more effort. This method was used to check the equations derived previously, to the second order, by Knight and Feld[11]; they are repeated here to the first order because the original equations contain a misprint involving the sign of the first-order term. Knight and Feld's work was used to estimate the magnitudes of the second-order asymmetry corrections, which are found to be less than 4% for J's up to twenty; since no second-order quadrupole theory is available, it is hardly justified to include these.

The equations for the various cases and near prolate symmetry are

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[2] Shell Oil Company Predoctoral Fellow.

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[8] See J. K. Bragg, *Phys. Rev.*, **74**, 533 (1948).

[9] P. C. Cross, R. M. Hainer and G. W. King, *J. Chem. Phys.*, **12**, 210 (1944).

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$K = 0$:

$$E_Q = \frac{\beta}{J(J+1)}\{-J(J+1)\chi_a + bf(J,1)[\chi_b - \chi_c]\}$$

$K = 1$, O^+ levels ($K_{+1} = J$):

$$E_Q = \frac{\beta}{J(J+1)}\left\{[3 - J(J+1)]\chi_a + \left[\frac{-J(J+1)}{2} + \frac{bf(J,2)}{4}\right][\chi_b - \chi_c]\right\}$$

$K = 1$, O^- levels ($K_{+1} = J - 1$):

$$E_Q = \frac{\beta}{J(J+1)}\left\{[3 - J(J+1)]\chi_a + \left[\frac{J(J+1)}{2} + \frac{bf(J,2)}{4}\right][\chi_b - \chi_c]\right\}$$

$K = 2$, E^+ levels ($K_{+1} = J - 2$):

$$E_Q = \frac{\beta}{J(J+1)}\left\{[12 - J(J+1)]\chi_a + \left[\frac{bf(J,3)}{6} - bf(J,1)\right][\chi_b - \chi_c]\right\}$$

$K = 2$, E^- levels ($K_{+1} = J - 1$):

$$E_Q = \frac{\beta}{J(J+1)}\left\{[12 - J(J+1)]\chi_a + \frac{bf(J,3)}{6}[\chi_b - \chi_c]\right\}$$

$K \geqq 3$:

$$E_Q = \frac{\beta}{J(J+1)}\left\{[3K^2 - J(J+1)]\chi_a + \left[\frac{bf(J,K+1)}{2(K+1)} - \frac{bf(J,K-1)}{2(K-1)}\right][\chi_b - \chi_c]\right\}$$

with

$$f(J,n) = \frac{1}{4}[J^2 - n^2](J+1)^2 - n^2$$

and the asymmetry parameter

$$b = (\kappa + 1)/(\kappa - 3) = (c - b)/[2a - (b + c)]$$

With a single quadrupolar nucleus of spin $I = 3/2$, the general multiplet obtained whenever J is at least two for both levels of the transition consists of nine components if $\Delta J = 1$, or ten if $\Delta J = 0$. However, the intensities of the four components with $\Delta F = \Delta J$ are far greater than those of the remaining ones if J is four or higher. Further, numerical calculations show that in the present instance, the four strong components will usually coincide in pairs, giving those lines which resolve at all the appearance of doublets. The main exception to this is the case of the very low J Q-branch lines, where the hyperfine multiplets will be quite complex.

These expectations are confirmed by the observed spectrum, which contains a large number of doublets in addition to a number of more complicated patterns at high frequencies. Particularly helpful in identifying the spectrum was the presence of about a dozen doublets with spacings on the order of 6 Mc., since it could be deduced from the equations using estimated χ's that such wide splittings could occur only for transitions with $K = 1 \leftrightarrow K = 2$. The appearance of so many of these transitions in the K-band results from the rather unusual circumstance that, because of the asymmetry, a curve of these frequencies plotted as a function of J passes through a maximum in the middle of the band.

Only one of the widely split doublets resolved further, into a quadruplet, as would be expected for the lowest J's of the series; it could therefore be assigned with some confidence to the transition $8_{2,6}$–$9_{1,9}$ of $CH_2Cl^{35}F$. The Q-branch lines could also be fairly readily identified from the predicted fine structure, furnishing parameters that led to the identification of the remaining lines with J's up to twenty. The importance of the quadrupole effects in arriving at and confirming assignments cannot be overrated, since the spectrum is heavily populated and there are few lines with low enough J's to make the centrifugal distortion so small that unambiguous assignments could be made on the basis of frequency alone.

The presence of the hyperfine structure on all the low J lines had the drawback, however, of making it impracticable to observe any resolved Stark effects, and so obtain quantitative data on the dipole moment. A careful search for lines resulting from the selection rules active if there is a dipole component along the a-axis had completely negative results, so it may be concluded that the dipole moment is within a few degrees of the b-axis. (The b-axis lies within one degree of the bisector of the C–F–Cl angle; the a-axis also lies in the symmetry plane, while the c-axis is perpendicular to it.)

The rotational parameters of the two isotopic species are given in Table I. Table II gives the observed frequencies and the frequencies calculated from these parameters; the latter calculations are made to the nearest megacycle, after which the quadrupole structure, computed to the nearest 0.01 Mc. is superimposed, so that the predicted and observed fine structure may also be compared. The quadrupole calculations are based on parameters evaluated from the $1_{0,1}$–$1_{1,0}$ transition; these are $\chi_a = -52.18$ Mc., $\chi_b = 38.83$ Mc. each ±1 Mc. The limits of error express the fact that the observed frequencies lead to more than enough equations to determine the parameters, and the results of using various groups of equations differ by about a megacycle.

TABLE I

ROTATIONAL PARAMETERS OF CHLOROFLUOROMETHANE

	$CH_2Cl^{35}F$, Mc.	$CH_2Cl^{37}F$, Mc.
a	41,810.1	41,738.2
b	5,715.7	5,580.5
c	5,194.6	5,081.6

Structural Parameters.—The moments of inertia derived from the relations $I_a = 505{,}446.5/a$, *etc.*, are displayed in Table III. The six moments do not suffice to fix the structure of the molecule because of the equality of the combination $I_a + I_b - I_c$ for the two isotopic species, which makes it possible to find only five of the six necessary independent parameters. The H–C–H angle immediately suggests itself as the one to be assumed *a priori*, first because the lightness of the hydrogen atoms makes the moments relatively insensitive to their exact location, and secondly because the measured H–C–H angle varies very little between CH_2Cl_2 and CH_2F_2 (see ref. 4) and would be expected to have an intermediate value here. It must be borne in mind, however, that the limits of error for the CH_2F_2 value are given as ±25′, so that the assumed value of 111°56′ for the present compound cannot be supposed subject to a much smaller uncertainty. The distance between the hydrogen atoms is given by the explicit equation $m_H d^2_{HH} = I_a + I_b - I_c$. The

TABLE II

MICROWAVE LINES OF CH_2ClF

A. Assigned transitions

The frequencies marked with *a*'s were measured under conditions which make them subject to errors up to 1 Mc.

Observed frequency	Intensity	Calculated frequency	Transition	Isotopic species
16,487.12	M	16,504.49	$9_{2,7}-10_{1,10}$	35
16,492.71	M	16,510.16		
17,648.07	W	17,639.27	$16_{2,14}-17_{1,17}$	37
17,652.92	W	17,644.73		
18,916.70	M	18,893	$16_{3,14}-17_{2,15}$	35
18,961.29	M	18,954.46	$16_{2,14}-17_{1,17}$	35
18,967.52	M	18,961.54		
19,232.16	W	19,232	$4_{1,4}-5_{0,5}$	37
19,917.48	S	19,995.28	$19_{3,16}-20_{2,19}$	37
19,919.07	S	19,996.72		
20,011.22	W	19,988.13	$17_{2,15}-18_{1,18}$	37
20,016.47	W	19,993.87		
20,619.17	S	20,618.69	$4_{1,4}-5_{0,5}$	35
20,620.26	S	20,619.79		
20,621.30	S	20,620.89		
21,084.05	M	21,065.27	$17_{2,15}-18_{1,18}$	35
21,090.31	M	21,072.73		
21,429.80	W	21,326.37	$21_{2,19}-22_{1,22}$	35
21,437.05	W	21,335.63		
21,596.35	W	21,565.98	$18_{2,16}-19_{1,19}$	37
21,600.0^a	W	21,572.02		
21,603.23	W	21,583.45	$21_{2,19}-22_{1,22}$	37
21,608.55	W	21,590.55		
21,834.20	M	21,803.12	$14_{3,11}-15_{2,14}$	35
21,836.00	M	21,804.88		
22,395.57	M	22,363.07	$18_{2,16}-19_{1,19}$	35
22,402.23	M	22,370.93		
22,413^a	W	22,489.61	$20_{2,18}-21_{1,21}$	35
22,419.25	W	22,498.39		
22,889.15	M	22,840.85	$19_{2,17}-20_{1,20}$	35
22,895.76	M	22,849.15		
23,937.44	M	23,966	$10_{2,9}-11_{1,10}$	37
24,020.97	M	24,028.68	$8_{2,6}-9_{1,9}$	35
24,021.75	M	24,029.42		
24,026.92	M	24,034.53		
24,027.57	M	24,035.27		
24,048.17	M	24,130.06	$19_{3,16}-20_{2,19}$	35
24,050.16	M	24,131.94		
25,494.60	M	25,466	$14_{3,11}-15_{2,14}$	37
25,518.46	S	25,517	$6_{2,5}-7_{1,6}$	35
25,791.65	W	25,800.71	$8_{2,6}-9_{1,9}$	37
25,796.15	W	25,805.29		
25,878.70	M	25,840	$17_{3,15}-18_{2,16}$	37
26,215.43	M	26,178.82	$13_{3,11}-14_{2,12}$	37
26,216.84	M	26,179.18		
27,498.50	M	27,525.06	$10_{2,9}-11_{1,10}$	35
27,500.30	M	27,526.94		
27,711.27	W	27,711	$6_{2,5}-7_{1,6}$	37
30,984.37	M	30,984	$5_{1,5}-6_{0,6}$	37
31,816.40	S	31,836.95	$17_{3,15}-18_{2,16}$	35
31,818.03	S	31,839.05		
32,035.40	M	32,039.92	$7_{2,5}-8_{1,8}$	35
32,041.58	M	32,046.08		
32,659.51^a	M	32,660.60	$5_{1,5}-6_{0,6}$	35
32,660.83	M	32,661.86		
32,662.11	M	32,663.12		
33,703.27	W	33,708.58	$7_{2,5}-8_{1,8}$	37
33,708.06	W	33,713.42		
36,592.71^a	W	36,593.01	$1_{0,1}-1_{1,0}$	35
36,611.22	W	36,611.22		
36,616.50	W	36,616.50		
36,620.92	W	36,621.13		
36,624.40	W	36,624.27		
36,652.77^a	W	36,651.41	$1_{0,1}-1_{1,0}$	37
36,657.47^a	W	36,657.07		
36,660.75^a	W	36,660.56		
36,663.42^a	W	36,663.19		
37,129.14^a	W	37,129.70	$2_{0,2}-2_{1,1}$	35
37,132.67^a	W	37,133.04		
37,136.25^a	W	37,136.67		
37,140.00^a	M	37,140.00		
37,146.66^a	W	37,146.13		
37,149.50	M	37,149.76		
37,153.50^a	W	37,153.09		
37,158.82^a	W	37,158.30	$2_{0,2}-2_{1,1}$	37
37,166.20^a	W	37,165.99		
37,924.77^a	W	37,926*	$3_{0,3}-3_{1,2}$	37
37,930.0^a	W	....	....	
37,938^a	W	....	....	
37,940.52^a	W	37,943*	$3_{0,3}-3_{1,2}$	35
37,950^a	W	....	....	
37,952^a	W	....	....	

* These frequencies do not include quadrupole structures; overlapping of the isotopic multiplets and experimental difficulties in measuring the frequencies made it impossible to assign individual hyperfine components.

B. OTHER LINES, FREQUENCIES IN MC.

Frequency	Intensity	Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
16,117.91		21,966.23	M	25,708.51	M	30,843.59	S
Mc	S	22,234.17	M	26,257.63	W	30,992.18	M
16,166.58	W	22,251.93	W	26,368.30	W	31,023.24	M
16,296.9^a	W	22,253.07	W	26,429.08	M	31,509.67	S
16,419.80	W	22,443.0^a	W	26,551.16	M	31,535.33	M
17,228.62	M	22,446.6^a	W	26,616.38	S	31,887.8^a	W
17,331.76	W	22,564.64	M	26,617.97	S	31,922.92	M
17,416.50	W	22,892.11	W	26,920.64	M	31,924.32	M
17,782.62	S	22,919.28	M	27,138.5^a	W	32,479.50	S
17,783.68	S	23,088.58	M	27,781.00	W	33,051.68	M
17,978.22	S	23,154.47	S	27,869.96	M	33,057.8^a	W
18,229.29	S	23,158.02	M	28,006.22	M	33,162.40	M
18,381.82	S	23,408.54	M	28,007.90	M	33,224.05	M
18,382.50	S	23,450.31	W	28,462.5^a	W	33,404.40	M
18,584.59	W	23,452.00	W	28,526.33	W	33,406.00	M
19,076.34	M	23,602.58	S	28,746.70	M	33,633.04	M
19,273.78	W	23,703^a	W	28,887.99	M	33,677.98	M
19,316.96	M	23,711.04	S	29,252.29	W	33,733.21	S
19,400.74	S	23,727.50^a	W	29,358.15	W	33,769.71	S
19,447.26	S	23,883.90	M	29,463.66	S	33,787.00	S
19,624.74	M	24,105.38	M	29,658.40	W	36,583.05^a	W
19,640.67	S	24,250^a	W	29,925.4^a	M	36,585.2^a	W
19,687.12	W	24,345.15	S	29,926^a	M	36,587.57^a	W
19,868.76	S	24,349.08	S	29,997.2^a	W	36,631^a	W
20,042.38	S	24,349.84	S	30,100^a	W	37,914	M
20,143.55^a	W	24,928.22	W	30,219.4^a	M	37,957^a	W
20,285.53^a	W	25,082.26	W	30,220.7^a	M	37,962.76^a	M
20,469.5^a	W	25,088.20	W	30,290.67	M	38,198^a	M
21,053.4^a	M	25,197.90	W	30,292^a	M	38,199.27^a	M
21,298.60	S	25,214.92	W	30,580.73	W	38,423.18^a	M
21,626.6^a	W	25,619.82	M	30,645^a	W	38,928.22^a	M
21,915.40	M	25,628.67	W	30,659.9^a	W	39,021.44^a	M
21,965.24	M	25,707.52	M	30,837.8^a	M	39,028.46^a	M

remaining parameters were obtained by a technique of successive approximations; the limits of error are those resulting from the uncertainty of about half a degree in the H–C–H angle. The best values are

r_{CH} = 1.078 ± 0.005 Å. ∠H–C–H = 111°56′ ± 30′ by assumption

r_{CCl} = 1.759 ± 0.003 Å. ∠Cl–C–F = 110°1′ ± 2′

r_{CF} = 1.378 ± 0.006 Å. θ = 125°41′ ± 5′

where θ is the angle between the C–Cl bond and the projection of the C–H bonds on the symmetry plane. For comparison, the parameters derived from electron diffraction[3] are $r_{\mathrm{CCl}} = 1.76 \pm 0.02$ Å., $r_{\mathrm{CF}} = 1.40 \pm 0.03$ Å.; $\angle$Cl–C–F = 110 ± 2°.

TABLE III

MOMENTS OF INERTIA (IN AT. WT. × Å.^{2}) OF CHLOROFLUOROMETHANE

Atomic weights used: C, 12.00382; H, 1.008123; Cl^{35}, 34.97867; Cl^{37}, 36.97750; F, 19.00450

	$CH_2Cl^{35}F$	$CH_2Cl^{37}F$
I_a	12.0891	12.1099
I_b	88.431_2	90.573_7
I_c	97.302_3	99.466_0

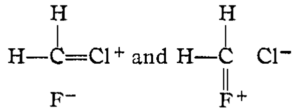
Quadrupole Coupling.—If it is assumed that the C–Cl bond coincides with the z-principal axis of the quadrupole coupling dyadic, a transformation of axes may be used to find the components of the dyadic in its principal system. The other two axes must lie in the plane of symmetry (x-axis), and perpendicular to it (y-axis). The result, using the Cl^{35} data, is $\chi_{xx} = 31.63$ Mc., $\chi_{yy} = 38.83$ Mc., $\chi_{zz} = -70.46$ Mc., all ±1 Mc. Independent data were not obtained for the other isotope, the ratio of 1:1.2688[12] for the coupling constants in Cl^{37} to those in Cl^{35} being used in predicting the fine structure.

Following Dean[13] an estimate of the fractional double-bond character, f, of the C–Cl bond may be made from the relation $3f/(2 - f) = (\chi_{xx} - \chi_{yy})/\chi_{zz}$. The result is 6.6%, in agreement with the observed bond shortening, and with Pauling's estimate[14] from the diffraction data.

The value of χ_{zz} may be compared with that of -75.13 reported for CH_3Cl[15] and of -78.4 for CH_2Cl_2.[16] The lowering of the coupling constant may result partly from increased double-bond character and partly from increased ionic character[17] of the C–Cl bond.

Discussion

The structure is essentially in agreement with the electron diffraction results and is compatible with those of the other halogenated methanes. The most striking feature is the marked shortening of the C–Cl bond as compared to molecules not containing fluorine; the observed value is in line with that of 1.74 Å. calculated for CF_3Cl by Sheridan and Gordy.[18] The quadrupole data indicate that the shortening of both carbon–halogen bonds is probably due largely to contributions of the resonance forms



$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{=}Cl^{+}}\\ \\ \mathrm{F^{-}}\end{array} \quad \text{and} \quad \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C\quad Cl^{-}}\\ \|\\ \mathrm{F^{+}}\end{array}$$

postulated by Pauling.[14] Inductive effects in the carbon–halogen bonds may also contribute to the variation in length (see ref. 4, footnote 15). The relative importance of these and possibly other effects will evidently be debatable until a rigorous quantum-mechanical approach becomes possible.

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