The Microwave Spectrum of Dichlorodifluoromethane

Harutoshi TAKEO and Chi MATSUMURA
National Chemical Laboratory for Industry, Honmachi, Shibuya-ku, Tokyo 151

(Received October 12, 1976)

The microwave spectra of three isotopic species of dichlorodifluoromethane have been observed, and the following rotational constants have been obtained:

$A = 4118.90$ MHz, $B = 2638.70$ MHz, $C = 2233.72$ MHz for $^{12}C^{35}Cl_2F_2$
$A = 4092.07$ MHz, $B = 2582.30$ MHz, $C = 2185.54$ MHz for $^{12}C^{35}Cl^{37}ClF_2$
$A = 4115.73$ MHz, $B = 2638.95$ MHz, $C = 2232.86$ MHz for $^{13}C^{35}Cl_2F_2$.

The bond lengths and angles determined from them are r(C–Cl)=1.744 Å, r(C–F)=1.345 Å, ∠Cl-C-Cl=112°33′, and ∠F-C-F=106°14′. The nuclear quadrupole coupling constants in the C–Cl bond axis system are $\chi_{zz}=-82.7$ MHz and $\eta_{\text{bond}}=0.06$.

The chloro and fluoro derivatives of methane have been examined by many investigators,[1] and the molecular structures have been determined by microwave spectroscopy. Lide[2] pointed out that a clear bond shortening occurs upon the substitution of hydrogen atoms by halogen atoms in the series of CH_mCl_n and CH_mF_n, and that the shortening effect is larger in the fluoromethanes than in the chloromethanes. A similar effect can be expected in the series of chlorofluoromethanes, whereas only dichlorodifluoromethane has not been studied of the molecules with the general formula of $CH_lCl_mF_n$. The purposes of this research are to determine the structure of dichlorodifluoromethane precisely and to check the shortening effect in the series of methane derivatives with both fluorine and chlorine atoms.

Experimental

The sample of dichlorodifluoromethane was prepared by the fluorination of tetrachloromethane.[3] Since this reaction also produced trichlorofluoromethane, the sample was purified by gas chromatgraphy. The ^{13}C species was prepared by the same reaction from $^{13}CCl_4$.

The spectrometer used was a conventional Stark modulated type with a 100 kHz square-wave modulation. The X-13 and X-12 klystrons dipped in oil baths were used as 8—18 GHz microwave sources, while 18—36 GHz sources were obtained by the use of harmonic generators. A stability of the microwave frequency of within 0.005 MHz per minute was obtained, and the resolution was about 0.2 MHz with the sample pressure of 5 mTorr. The spectra were all observed with a sample cell cooled with Dry Ice.

Analysis of the Spectra

Hyperfine Structure. The hyperfine structure of the spectrum was predicted and analyzed by using the first-order perturbation theory for the rotational levels of an asymmetric-top molecule containing two nuclei of isotopic spin 3/2 presented by Robinson and Cornwell.[4] The calculated patterns of the hyperfine structures showed that the low-J transitions consist of many weak components with the selection rule of $\Delta F=0, \pm 1$ and $\Delta\varepsilon=0, \pm 2$, while in the high-$J$ transitions only $\Delta F=\Delta J$ transitions have strong intensities. This makes the hyperfine structures of high-J transitions simple and easy to be observed. Some typical patterns of the hyperfine structure in the high-J Q-branch series are shown in Fig. 1. It should be noted that the asterisked components in Fig. 1 shift greatly with the change in the J number, while the ratio of A to B depends only on J, not on the other quantum numbers nor on the quantities of the $\langle eqQ \rangle_J$ values of the upper and lower levels of the transition. The J number in the Q-branch transition can easily be assigned by the measurement of these values, even in the transition with the J number of 15 or more; in fact, $15_{6,10}$—$15_{5,11}$ was assigned without any other information.

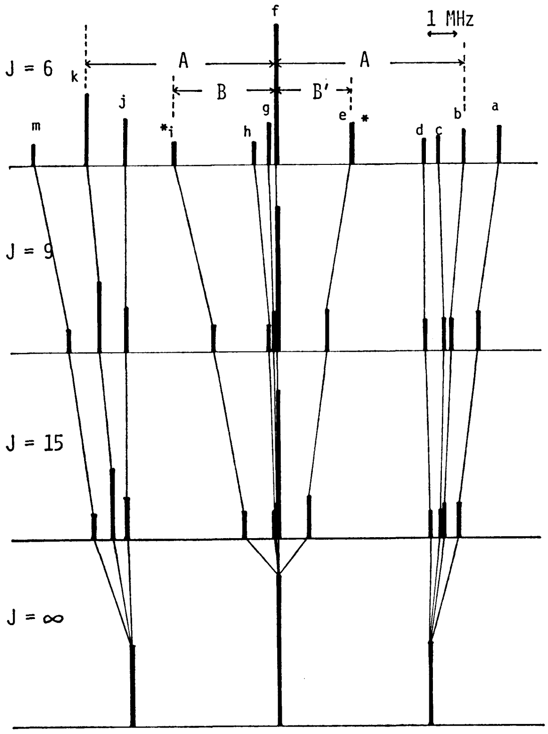

Fig. 1. The J dependance of hyperfine structures with identical nuclei of spin 3/2. The same values of $\langle eqQ \rangle_J$ are used for the calculation. For the notation of the alphabet attached to each component, see Table 1.

The intensity alternation occurs in each hyperfine component depending on the spin weight due to fluorine nuclei. The intensity ratio by spin weight between ε=even and ε=odd components in the $(ee)\leftrightarrow(oo)$ transitions should be 1 to 3, and this ratio should change

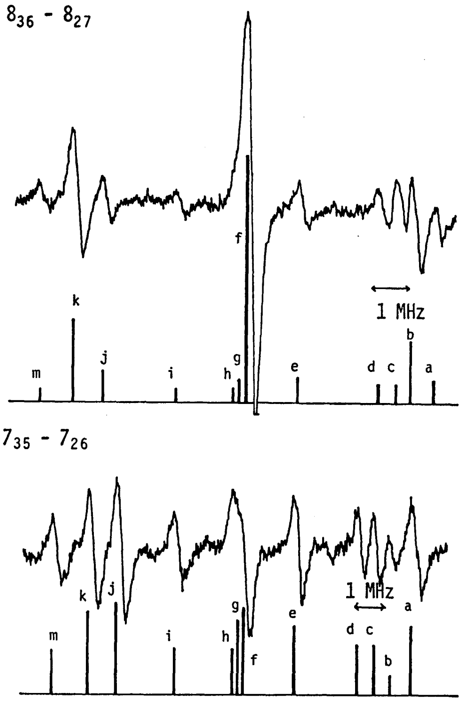

Fig. 2. The recorded and calculated hyperfine structures of $C^{35}Cl_2F_2$.

to 3 to 1 in the $(eo)\leftrightarrow(oe)$ transitions. This phenomenon was also helpful in the assignment of the transitions. The recorded hyperfine structures of the two transitions, which have different spin weights, are shown in Fig. 2. The figures also show that the strong component always exists at the unsplit position, and that it is the strongest in the transition of $(eo)\leftrightarrow(oe)$. Therefore, the measurements of only these components lead to the rotational constants, without any analysis of the hyperfine structures being necessary, if the second-order approximation is correct enough. In the hyperfine structures of the $C^{35}Cl^{37}ClF_2$ species, on the other hand, there are no such components at the exact unsplit positions because the two quadrupole moments are not identical. However, the shifts of the four components which degenerate in the spectrum of the $C^{35}Cl_2F_2$ species are quite small in this case; in fact, the strong sharp lines were always obtained in the hyperfine structure of $C^{35}Cl^{37}ClF_2$ species. It is believed that the difference between the observed peak position of this component and the hypothetical unsplit value is within 0.1 MHz. Therefore, these values were used for the determination of the rotational constants.

Assignment of the Spectrum. The Q-branch series were searched for first in the region predicted by the rotational constants of the assumed structure based on other halogenomethanes, and were assigned by using the method described above. The spectrum of the $C^{35}Cl^{37}ClF_2$ species was assigned first, since the degenerate K-type doubling transitions of this molecule have fairly large Stark effects compared with those of symmetric $C^{35}Cl_2F_2$ species because of the existance of a small μ_a component. The same transitions of the $C^{35}Cl_2F_2$ species were observed with Stark voltages about 1000 V/cm. This suggests that the dipole moment of the molecule is fairly small because of the cancellation of the C–Cl and C–F bond moments. The R-branch transitions were assigned by means of the values calculated from the structure refined by Q-branch transitions. The observed transitions used for the determination of the quadrupole coupling constants are listed in Table 1. The obtained values for the diagonal components of the quadrupole coupling constant tensor along the principal inertial axes are listed in Table 2, along with the diagonalized χ tensor, which was calculated using the molecular structure determined in this study with the assumption that the z axis coincides with the C–Cl internuclear line.

The frequencies of the observed transitions are listed in Table 3. The rotational constants and the centrifugal distortion constants were determined by a least-squares fit of all the transitions listed in Table 3. They are shown in Table 4.

TABLE 1. OBSERVED QUADRUPOLE SPLITTING PATTERNS OF $C^{35}Cl_2F_2$ (MHz)

	ε	F	$5_{3\,3}-5_{2\,4}$		$6_{2\,5}-6_{1\,6}$		$6_{5\,1}-6_{4\,2}$	
			Obsd	Δ[a)]	Obsd	Δ	Obsd	Δ
a	3	$J+1$	8977.85	0.00				
b	0	J	8976.69	0.04	9575.28	0.02		
c	3	J	8975.32	0.01			14913.98	0.01
d	1	$J-1$	8974.87	−0.03			14913.37	−0.01
e	3	$J+2$	8973.07	0.05	9571.00	−0.06	14910.92	0.03
f	2 2 2 2	$J+2$ $J+1$ $J-1$ $J-2$	8969.99	0.01	9568.32	0.02	14908.24	−0.01
g	1	$J+1$	8969.56	0.02			14907.90	−0.01
h	3	$J-1$	8968.76	0.00			14907.45	0.01
i	3	$J-2$	8965.58	0.00			14904.65	0.04
j	3	$J+3$	8964.89	−0.02	9562.79	0.04	14902.93	0.01
k	2 1	J J	8963.30	0.01	9561.34	0.01	14901.55	0.02
m	3	$J-3$						
$\Delta\langle eqQ\rangle_J$[b)]			−10.15	−0.01	−11.03	0.02	−10.61	0.01

TABLE 1. (Continued)

	ε	F	$7_{3\,5}-7_{2\,6}$ Obsd	$\Delta^{a)}$	$8_{1\,7}-8_{0\,8}$ Obsd	Δ	$8_{6\,2}-8_{5\,3}$ Obsd	Δ
a	3	$J+1$	10256.88	0.00	12023.67	0.04	18194.15	−0.01
b	0	J	10256.14	0.00	12022.83	0.04	18193.46	−0.03
c	3	J	10255.62	0.00	12022.31	0.02	18193.08	−0.01
d	1	$J-1$	10255.14	0.00	12021.70	0.01	18192.65	0.03
e	3	$J+2$	10253.00	0.01	12018.69	−0.01		
f	2 2 2 2	$J+2$ $J+1$ $J-1$ $J-2$			12016.80	−0.02	18188.77	−0.01
g	1	$J+1$						
h	3	$J-1$						
i	3	$J-2$	10249.12	0.05	12014.45	0.00	18186.92	0.05
j	3	$J+3$	10247.33	0.00	12011.79	−0.03	18184.77	−0.02
k	2 1	J J	10246.43	−0.01	12010.82	−0.03	18184.02	0.00
m	3	$J-3$	10245.38	0.01			18183.08	−0.02
$\Delta\langle eqQ\rangle_J{}^{b)}$			−7.92	0.01	−10.05	−0.04	−7.93	0.00

a) $\Delta=\nu_{\text{obsd}}-\nu_{\text{calcd}}$. b) The $\langle eqQ\rangle_J$ of upper level minus the $\langle eqQ\rangle_J$ of the lower level.

TABLE 2. QUADRUPOLE COUPLING CONSTANTS OF $C^{35}Cl_2F_2$

$\chi_{aa}=-43.7\pm0.2$ MHz
$\chi_{bb}=\ \ 4.8\pm0.2$ MHz
$\chi_{cc}=\ \ 38.9\pm0.2$ MHz
$\chi_{zz}=-82.7\pm1.3$ MHz
$\eta=\ \ 0.06\pm0.01$

Molecular Structure

The substitution coordinates of the carbon and chlorine atoms were calculated by means of Kraitchman's equation; they led to the C–Cl bond length and the Cl–C–Cl angle. The C–F distance and the F–C–F angle were determined from the coordinates

TABLE 3. OBSERVED AND CALCULATED FREQUENCIES FOR CCl_2F_2 (MHz)

Transition	$C^{35}Cl_2F_2$ Obsd	$\Delta^{a)}$	$C^{35}Cl^{37}ClF_2$ Obsd	Δ	$^{13}C^{35}Cl_2F_2$ Obsd	Δ
$2_{1\,2}-1_{0\,1}$	10820.10	0.09			10814.50	0.24
$2_{2\,0}-1_{1\,1}$			14926.96	−0.18	15058.80	−0.11
$2_{2\,1}-1_{1\,0}$	14590.33	−0.04	14461.43	−0.24	14580.00	0.02
$3_{0\,3}-2_{1\,2}$	13194.22	−0.09	12860.45	−0.22		
$3_{3\,0}-2_{2\,1}$	23080.42	−0.10	22891.20	0.03	23064.72	0.00
$4_{3\,1}-3_{2\,0}$					19320.30	0.20
$4_{1\,4}-3_{0\,3}$	31274.68	0.02				
$5_{4\,2}-4_{3\,1}$			35792.38	0.23		
$7_{5\,3}-7_{4\,4}$			15112.84	−0.17		
$7_{5\,2}-7_{4\,3}$	14757.18	0.01			14727.94	−0.06
$8_{3\,6}-8_{2\,7}$	11229.62	0.05			11230.35	−0.05
$8_{5\,4}-8_{4\,5}$	14804.22	0.08	15044.03	−0.15	14776.82	−0.06
$8_{5\,3}-8_{4\,4}$	14484.36	−0.16				
$8_{6\,3}-8_{5\,4}$	18206.20	0.05	18501.98	−0.09		
$8_{6\,2}-8_{5\,3}$	18188.58	−0.12	18487.00	−0.18		
$10_{5\,6}-10_{4\,7}$	14807.40	−0.05			14783.23	0.00
$10_{7\,4}-10_{6\,5}$			21821.06	0.12	21428.02	0.13
$10_{7\,3}-10_{6\,4}$	21459.46	0.03	21813.86	0.09		
$11_{5\,7}-11_{4\,8}$	14973.63	−0.03			14953.17	0.06
$11_{6\,5}-11_{5\,6}$	17456.24	0.08	17813.23	0.02		
$11_{7\,4}-11_{6\,5}$	21317.08	−0.04	21681.01	0.15	21275.32	−0.08
$11_{7\,5}-11_{6\,6}$			21704.20	−0.05	21304.36	−0.02
$12_{7\,6}-12_{6\,7}$	21194.02	0.05	21559.25	0.06	21152.18	0.06
$12_{7\,5}-12_{6\,6}$			21429.57	−0.09	21070.04	−0.02

a) $\Delta=\nu_{\text{obsd}}-\nu_{\text{calcd}}$.

Table 4. Rotational constants and centrifugal distortion constants of CCl_2F_2 (MHz)

	A	B	C	$I_c-I_a-I_b$ [a]
$^{12}C^{35}Cl_2F_2$	4118.90(04)	2638.70(02)	2223.72(02)	87.972(04)
$^{12}C^{35}Cl^{37}ClF_2$	4092.07(07)	2582.30(05)	2185.54(06)	87.973(10)
$^{13}C^{35}Cl_2F_2$	4115.73(03)	2638.95(02)	2232.86(02)	87.962(04)
$^{12}C^{35}Cl_2F_2$	d_J = −0.00135(95)			
	d_{JK} = −0.00222(63)			
	d_K = 0.00165(41)			
	d_{WJ} = 0.0000011(3)			
	d_{WK} = 0 (fixed)			

a) amuÅ^2.

of fluorine atoms, which were themselves obtained by the use of the first-moment equation for b-coordinates and the value of I_c–I_a–I_b for the c-coordinates. They were also determined by a least-squares fit of all the observed rotational constants, the C–Cl length and the Cl–C–Cl angle being fixed to the previously determined values. The structural parameters obtained by the two methods are in good agreement with each other. They are listed in Table 5.

Table 5. Coordinates of atoms (Å) and the structural parameters determined from them

	Cl	C	F
a	±1.4506(13)	0	0
b	−0.6591(29)	0.3083(20)	1.1158(26)[a]
c	0	0	±1.0759(03)[b]
	r(C–Cl) = 1.744±0.004 Å		
	r(C–F) = 1.345±0.003 Å		
	∠Cl–C–Cl = 112°33′±31′		
	∠F–C–F = 106°14′±23′		

a) Calculated from the first moment equation.
b) Calculated from the value of $I_c-I_a-I_b$.

Discussion

The obtained C–Cl and C–F bond distances are compared with those of other halogenomethanes in Fig. 3. The values indicated by black circles have been determined by using many isotopic data; they seem to be precise enough. On the other hand, the values indicated by white circles may have fairly large ambiguities because they were obtained from few isotopic data. As Lide[2] pointed out, the carbon-halogen distances in the CH_3Cl, CH_2Cl_2, $CHCl_3$ series and the CH_3F, CH_2F_2, CHF_3 series show a quite regular shortening upon further substitution of the hydrogen by the halogen, and the C–F shortening is more marked than the C–Cl shortening. In the figure we can see that the C–Cl shortening occurs as a fluorine is added to the molecule. The C–F shortening is also seen as a chlorine is added. It is interesting to note that the bond shortening upon the substitution of a fluorine is always more marked than that upon the substitution of a chlorine. The irregularities in $CClF_3$ and CCl_3F may be attributed to the improper analyses of their molecular structures, since the assumption of some structural parameters seem to be invalid for the analyses of these molecules. Therefore, the precise re-determination of the molecules indicated by white circles in the figure is necessary for a further detailed discussion.

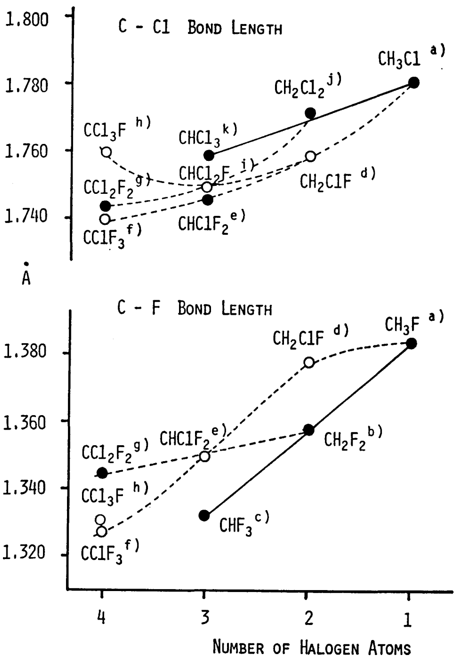

Fig. 3. The plot of carbon-halogen bond lengths versus number of halogen atoms in halogenomethanes.

a) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958). b) E. Hirota, T. Tanaka, A. Sakakibara, Y. Ohashi, and Y. Morino, *J. Mol. Spectrosc.*, **34**, 222 (1970). c) S. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952). d) N. Müller, *J. Am. Chem. Soc.*, **75**, 860 (1953). e) D. B. Mclay and C. R. Mann, *Can. J. Phys.*, **40**, 61 (1962). f) J. Sheridan and W. Gordy, *J. Chem. Phys.*, **20**, 591 (1952). g) This work. h) M. W. Long, Q. Williams, and T. Weatherly, *J. Chem. Phys.*, **33**, 508 (1960). i) D. B. Mclay, *Can. J. Phys.*, **42**, 720 (1964). j) R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **20**, 1420 (1952). k) M. Jen and D. R. Lide, Jr., *J. Chem. Phys.*, **36**, 2525 (1962).

Gordy and Cook[5] have shown that the change in quadrupole coupling constants obtained by the pure nuclear quadrupole resonance is quite regular in the CCl_4, CCl_3F, CCl_2F_2, CCl_3F series and that the change can be interpreted in terms of hyperconjugation. The χ_{zz} obtained in the present study, however, is fairly large compared with the value expected from their figure. As far as we know, this value is the highest in the coupling constants obtained for chlorine nuclei attached to carbon atoms. For a detailed discussion, it is desirable to determine the χ_{zz} by the analysis of the off-diagonal element of the χ tensor in the principal axis system, which can be obtained from the measurement of the second-order quadrupole effect. However, all the transitions measured in this study fit the calculated values within the limits of experimental errors without the second-order terms.

References

1) See the note in Fig. 3.
2) D. R. Lide, Jr., *J. Am. Chem. Soc.*, **74**, 3548 (1952).
3) H. D. Mallory, *J. Am. Chem. Soc.* ,**74**, 839 (1952).
4) G. W. Robinson and C. D. Cornwell, *J. Chem. Phys.*, **21**, 1436 (1953).
5) W. Gordy and R. L. Cook, "Microwave Molecular Spectra," ed by W. West, Interscience Publishers, New York, N. Y. (1970), p. 592.