

Structures of  $\text{CF}_3\text{Cl}$  and  $\text{CH}_3\text{Cl}$ 

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The molecular structures of  $\text{CF}_3\text{Cl}$  and  $\text{CH}_3\text{Cl}$  were determined by refined procedures of electron diffraction. For  $\text{CF}_3\text{Cl}$ , the most probable C-F and C-Cl distances are 1.328 Å and 1.751 Å respectively and  $\angle\text{FCF} = 108.6^\circ$ . Results for  $\text{CH}_3\text{Cl}$  agree with the complete microwave determination. Vibrational amplitudes are in agreement with approximate calculations by Morino.

IT is well known that the introduction of fluorine atoms into organic molecules may have a marked stabilizing influence on the molecules, especially when two or more fluorine atoms are attached to the same carbon atom.<sup>1</sup> Early investigations of the molecular structures of organic fluorides indicated that the C-F bonds and also bonds to other elements attached to the carbon decreased in length as the number of fluorines on the carbon was increased. In particular, a value of  $1.72 \pm 0.03$  Å was reported<sup>2</sup> for the C-Cl bond in  $\text{CF}_3\text{Cl}$  as contrasted with the distance 1.77 Å accepted then for C-Cl in  $\text{CH}_3\text{Cl}$ .

More recent improvements in both the diffraction and spectroscopic techniques for determining molecular structures have made it possible to obtain greater precision in the values for internuclear distances, and more precise values are of special interest among organic fluorides where attempts have been made to obtain a quantitative correlation between changes in internuclear distances and in chemical reactivity due to increasing the number of fluorine atoms. For this reason the examination of  $\text{CF}_3\text{Cl}$  and its comparison with  $\text{CH}_3\text{Cl}$  by the rotating sector method of electron diffraction is

part of a systematic study of the effect of fluorine substitution in molecules of the  $\text{CH}_3\text{X}$  type. In addition, the availability of the results of microwave studies of these two molecules provides an excellent opportunity for comparing the results of the two methods of structure determination.

## PROCEDURE

Diffraction patterns of 40 kv electrons were obtained on Kodak Contrast Lantern Slides using the rotating sector apparatus described in detail elsewhere.<sup>3</sup> Camera distances of 25 cm and 9 cm were used with an  $r^3$  sector to record the patterns from  $s = 3$  to  $s = 34$ . The pressure of the sample at the gas nozzle was 50 mm for  $\text{CF}_3\text{Cl}$  and 75 mm for  $\text{CH}_3\text{Cl}$ . Intensities, obtained by densitometry,<sup>3,4</sup> proved to be sensitive to detail in the pattern to a few parts per ten thousand.

The detailed procedure for the interpretation of the data and the assignment of uncertainties has been described.<sup>5</sup> It includes converting the experimental intensities to the function  $M(s)$  representing the ratio of the "molecular" intensity (i.e., dependent on the interatomic distances) to the atomic or background intensity, correcting  $M(s)$  for non-nuclear scattering, and computing a radial distribution function  $f(r)$  using the expression:

$$f(r) = \int_0^{s(\max)} sM(s) \exp(-bs^2) \sin sr \, ds.$$

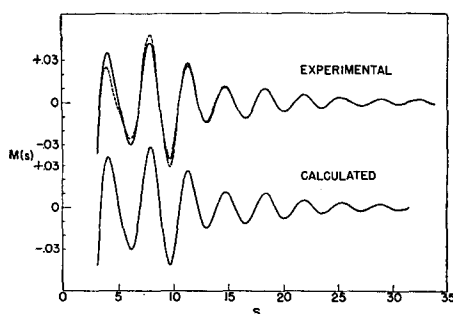


FIG. 1. Electron diffraction intensity curves for  $\text{CH}_3\text{Cl}$ . These are the functions  $M(s)$  representing the ratio of the molecular scattering to the background of atomic scattering. The experimental curves include one corrected for non-nuclear scattering (solid line) and the uncorrected curve (dashed line).

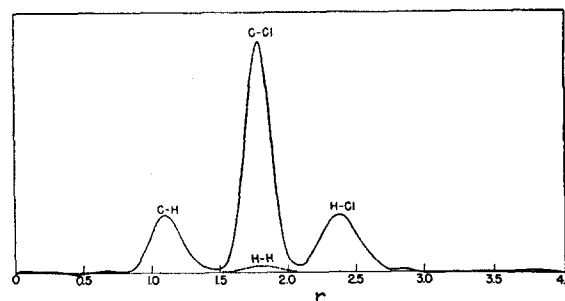


FIG. 2. Radial distribution function for  $\text{CH}_3\text{Cl}$ .

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<sup>1</sup> A. L. Henne and T. Midgley, Jr., *Am. Chem. Soc.* **58**, 882 (1936); A. L. Henne, "Aliphatic Fluorides," in H. Gilman, *Organic Chemistry* (John Wiley and Sons, Inc., New York, 1943), Vol. I, Chap. II.

<sup>2</sup> L. O. Brockway and R. L. Livingston, Report to Naval Research Laboratory, Contract No. N1735-7912, June 30, 1944.

<sup>3</sup> L. O. Brockway and L. S. Bartell, *Rev. Sci. Instr.* **25**, 569 (1954).

<sup>4</sup> L. S. Bartell and L. O. Brockway, *J. Appl. Phys.* **24**, 656 (1953).

<sup>5</sup> Bartell, Brockway, and Schwendeman, *J. Chem. Phys.* **23**, 1854 (1955); L. S. Bartell, *J. Chem. Phys.* **23**, 1219 (1955).

TABLE I. Distances and amplitudes determined from the radial distribution curves for  $\text{CH}_3\text{Cl}$  and  $\text{CF}_3\text{Cl}$ .

$r_{RD}$		$l_{ij}(\text{e.d.})$	$l_{ij}(\text{calc.})^*$
<b><math>\text{CH}_3\text{Cl}</math></b>			
C—H	$1.11 \pm 0.01 \text{ \AA}$	$0.089 \pm 0.010 \text{ \AA}$	$0.078 \text{ \AA}$
C—Cl	$1.784 \pm 0.003$	$0.060 \pm 0.004$	$0.050$
H—Cl	$2.38 \pm 0.01$	$0.119 \pm 0.010$	$0.114$
<b><math>\text{CF}_3\text{Cl}</math></b>			
C—F	$1.328 \pm 0.002$	$0.049 \pm 0.002$	$0.045$
C—Cl	$1.751 \pm 0.004$	$0.054 \pm 0.005$	$0.050$
F—F	$2.158 \pm 0.003$	$0.058 \pm 0.003$	$0.056$
F—Cl	$2.539 \pm 0.003$	$0.066 \pm 0.003$	...

\* Approximate calculations by Morino, reference 7.

For direct comparison with the experimental  $M(s)$  curve a theoretical  $M(s)$  curve based on assumed equilibrium internuclear distances and vibrational amplitudes is computed using the function:

$$M(s) = \sum_i \sum_j' c_{ij} \exp(-l_{ij}^2 s^2 / 2) (\sin sr_{ij}) / sr_{ij}.$$

#### $\text{CH}_3\text{Cl}$

Figure 1 compares the experimental  $M(s)$  functions for  $\text{CH}_3\text{Cl}$ , including the uncorrected curve and the curve corrected for non-nuclear scattering, with the theoretical function for the model determined by the radial distribution curve. The ratios of the  $s$  and  $s_0$  values read from the maxima and minima of the theoretical and experimental curves show an average deviation of 0.0025. The radial distribution function was calculated with the damping function  $\exp(-0.0023 s^2)$  and is shown in Fig. 2. The distinctness with which the weak hydrogen distances appear is an illustration of the effectiveness of the rotating sectormicrophotometer method. The relative areas of the peaks agree with the theoretical areas to within one percent. The experimental amplitudes of vibration,  $l_{ij}$ , obtained from the distribution curve and corrected for the small error due to the failure of the Born approximation,<sup>6</sup> are listed in Table I. The results are in fairly good agreement with the approximate calculations of Morino<sup>7</sup> for amplitudes of atomic pairs in given groups without regard to the molecules in which they occur.

The positions,  $r_{RD}$ , of the maxima of the radial distribution peaks listed in Table I are averages of the centers of the peaks at different ordinates corrected for the expected asymmetry.<sup>5</sup> In this case where the exceptionally complete microwave determination<sup>8</sup> enjoys a distinct advantage in accuracy over the electron diffraction result it is gratifying to see that the structure deduced by diffraction (Table II) is completely confirmed. Here the diffraction value for the C—Cl bond to

Table II. Comparison of electron diffraction and microwave results for  $\text{CH}_3\text{Cl}$  and  $\text{CF}_3\text{Cl}$ .

	Electron diffraction	Microwave
<b><math>\text{CH}_3\text{Cl}</math></b>		
C—H	$r_v = 1.11 \pm 0.01 \text{ \AA}$	$1.113 \text{ \AA}$
C—Cl	$r_v = 1.783 \pm 0.003 \text{ \AA}$	$1.7810 \text{ \AA}$
<HCH	$110 \pm 2^\circ$	$110^\circ 31'$
<b><math>\text{CF}_3\text{Cl}</math></b>		
C—F	$r_v = 1.328 \pm 0.002 \text{ \AA}$	$1.328 \pm 0.002 \text{ \AA}^*$
C—Cl	$r_v = 1.751 \pm 0.004 \text{ \AA}$	$1.748 \pm 0.009 \text{ \AA}^*$
<FCF	$108.6 \pm 0.4^\circ$	$(108.6 \pm 0.4^\circ)$

\* Values computed from the spectroscopic moments of inertia and the diffraction value of the angle. The uncertainties include only the effect of uncertainty in the bond angle and ignore experimental and interpretational errors.

be compared with the spectroscopic value,  $r_v$ , is very slightly less than  $r_{RD}$ . It should be pointed out that the beautifully precise microwave result is neither the equilibrium internuclear separation nor the most probable separation, due to the asymmetry of  $P(r)$ . The equilibrium separation is about 0.008  $\text{\AA}$  less than  $r_v$  for the C—Cl bond.

#### $\text{CF}_3\text{Cl}$

The experimental and theoretical intensity curves for  $\text{CF}_3\text{Cl}$  are compared in Fig. 3. In the earlier electron diffraction investigation the discrepancy between the uncorrected  $M(s)$  and the nuclear  $M(s)$  in the vicinity of the third maximum contributed to the selection of a somewhat erroneous model. The average deviation of the  $s/s_0$  ratios is 0.0012, and if allowance is made for the effect of anharmonicity,<sup>5</sup> the agreement is even somewhat better.

The radial distribution function shown in Fig. 4 resolves each of the internuclear distances so well that there is no ambiguity in locating the positions of the component peaks. The relative areas of the resolved peaks agree with the theoretical areas to within the uncertainty (near the foot of the peaks) of separating the asymmetric components. Measurements of the amplitudes and distances in the molecule are listed in Tables I and II.

A distribution function,  $P(r)$ , computed on the basis of a Morse type potential function<sup>9</sup> has maximum positions,  $r_m$ , which are very nearly the same as the maxima,  $r_{RD}$ , for both C—F and C—Cl in the experimental distribution function  $f(r)$ , which is related to  $P(r)/r$ . The effect of the damping factor  $\exp(-0.0023 s^2)$  in  $f(r)$  is almost precisely compensated in this case by the effect of dividing  $P(r)$  by  $r$ . Although the centers of gravity of the distributions are approximately 0.003  $\text{\AA}$  greater than the positions of the maxima, the spectroscopically determined  $r_v$  should be nearly identical to  $r_m$  (and  $r_{RD}$ ).

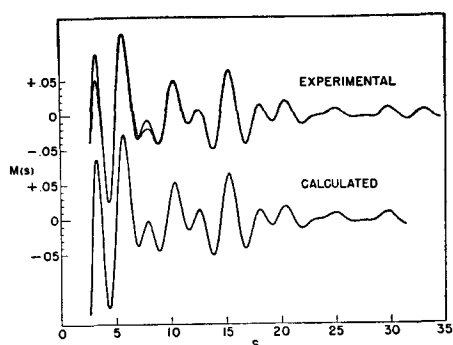
The microwave study<sup>9</sup> of  $\text{CF}_3\text{Cl}$  was not sufficiently complete to permit the determination of the molecular structure but yielded moments of inertia in agreement

<sup>6</sup> L. S. Bartell and L. O. Brockway, *Nature* **171**, 978 (1953).

<sup>7</sup> Morino, Kuchitsu, Takahashi, and Maeda, *J. Chem. Phys.* **21**, 1927 (1953).

<sup>8</sup> Miller, Aamodt, Dousmanis, Townes, and Kraitchman, *J. Chem. Phys.* **20**, 1112 (1952).

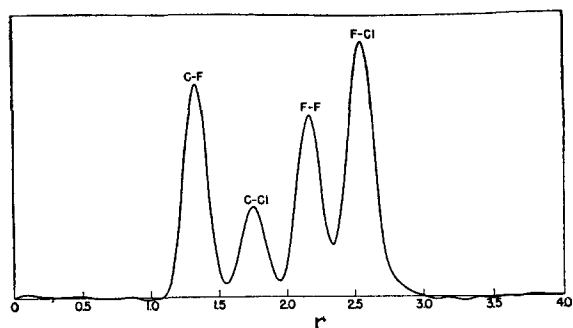
<sup>9</sup> D. K. Coles and R. H. Hughes, *Phys. Rev.* **76**, 858 (1949).

FIG. 3. Electron diffraction intensity curves for  $\text{CF}_3\text{Cl}$ .

with the diffraction results to within interpretational error. In the original estimates of the internuclear distances from the microwave data it was assumed that the FCF angle was tetrahedral. The diffraction data show that the angle is certainly less than the tetrahedral value, in agreement with recent determinations of the FCF angle in other compounds. Accordingly, as already pointed out by Sheridan and Gordy,<sup>10</sup> the original estimates of the distances were in error, particularly in the case of the C—Cl distance. The microwave results listed in Table II were recalculated from the spectroscopic data using the FCF angle determined by diffraction, with the listed uncertainties indicating the sensitivity of the parameters to the  $0.4^\circ$  uncertainty in the FCF angle without regard to the additional appreciable error involved in the conventional reduction of spectroscopic data.

The angle reported for the diffraction determination was calculated from the estimated most probable positions of the nuclei. The uncertainty in the interpretation of the data in terms of the angle which arises from the nonlocalization of the nuclei was judged to be about as great as the uncertainty due to experimental error and both sources are included in the reported uncertainty.

<sup>10</sup> J. Sheridan and W. Gordy, *J. Chem. Phys.* **20**, 591 (1952).

FIG. 4. Radial distribution function for  $\text{CF}_3\text{Cl}$ .

The diffraction and recalculated microwave results agree exactly for the C—F bond and very closely for the C—Cl bond.

The decrease in the length of the C—Cl bond on substitution of three fluorine atoms in methyl chloride is 0.032 Å, with an uncertainty of 0.006 Å. This may be compared with the previous estimate of 0.05 Å with an uncertainty nearly as large. Of special interest is the fact that the C—Cl bond in methyl chloride is shortened by 0.015 Å on substitution of three chlorines for the hydrogens and by an additional 0.017 Å on fluorine substitution. The substitution of three fluorines into either  $\text{CH}_3\text{Cl}$  or  $\text{CCl}_4$  is accompanied by a tremendous decrease in the ease of removing chlorine from the molecule by a hydrolysis or other substitution reactions, but this increase in chemical stability is accompanied by the rather small changes in bond distance amounting to 0.03 Å or less.

#### ACKNOWLEDGMENTS

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