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Microwave Spectra and Molecular Structures of Fluoroform, Chloroform, and Methyl Chloroform*

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Sufficient isotopic combinations have been studied to make complete structural determinations of fluoroform and chloroform from microwave rotational spectra. The dimensions of CHF_3 are $d_{\text{CH}}=1.098\text{A}$, $d_{\text{CF}}=1.332\text{A}$, and $\angle\text{FCF}=108^\circ 48'$; those of CHCl_3 are $d_{\text{CH}}=1.073\text{A}$, $d_{\text{CCl}}=1.767\text{A}$, and $\angle\text{ClCCl}=110^\circ 24'$. Measurements were made on only the most abundant isotopic species of CH_2CCl_3 . If the CCl_3 configuration as in chloroform and the CH_3 configuration as in methane are assumed, the CC distance in CH_2CCl_3 is found to be 1.55A.

INTRODUCTION

ALTHOUGH fluoroform and chloroform have been the subject of several previous structural investigations both with electron diffraction and with spectroscopy, no complete determination of either structure has before been made. Because of the low electron scattering power of H, no estimate of the CH distance could be made with electron diffraction. The earlier microwave investigations of chloroform^{1,2} and fluoroform³ did not employ sufficient isotopic combinations to make possible unambiguous assignments of the parameters. In the present study the structural determinations of both these molecules have been completed, and a partial evaluation of the structure of methyl chloroform has been made, from measurements on their microwave rotational spectra.

EXPERIMENTAL METHOD

Observations were made with a Stark-modulation spectrograph employing 100-kc square-wave modulation. Frequency measurements were made in the usual way with a secondary frequency standard monitored by comparison with station WWV.

Deuterated fluoroform was prepared by heating ordinary fluoroform with a tenfold molar excess of

heavy water at 120°C in the presence of potassium carbonate for eight days. A portion of the fluoroform was removed from the reaction mixture after one day, and a very weak absorption line corresponding to the species CDF_3 was found. At the end of eight days the CDF_3 absorption line was much stronger indicating that an exchange between D and H had taken place. This research suggests the possibility of using microwave spectroscopy to study exchange reactions. Spectra of other isotopic species of both chloroform and fluoroform were observed for the naturally occurring concentrations.

SPECTRAL CONSTANTS

Frequencies of the rotational lines measured in this research are listed in Table I. Spectral constants derived from these frequencies as well as the previously reported values for other isotopic combinations are listed in Table II. Gilliam, Edwards, and Gordy³ made observations of the most abundant isotopic species, C^{12}HF_3 . The I_B value of this species has also been determined from optical spectra with very good accuracy by Bernstein and Herzberg.⁴ Isotopic combination $\text{C}^{12}\text{HCl}_3$ ³⁵ has been measured by Smith and Unterberger¹ and $\text{C}^{12}\text{DCl}_3$ ³⁵ by Unterberger, Trambarulo, and

TABLE I. Observed rotational absorption frequencies of some isotopic combinations of CHF_3 , CHCl_3 , and CH_2CCl_3 .

Isotopic species	Transition	Frequency (Mc)
C^{12}HF_3	$J=1\rightarrow 2$	$41,287.98\pm 0.40$
C^{12}DF_3	$J=0\rightarrow 1$	$19,842.69\pm 0.40$
$\text{C}^{12}\text{HCl}_3$ ³⁷	$J=5\rightarrow 6$	$37,554.11\pm 0.40$
$\text{C}^{12}\text{H}_2\text{C}^{12}\text{Cl}_3$ ³⁵	$J=7\rightarrow 8$	$37,955.88\pm 0.40$

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† On leave from the Department of Physics, The University of Calcutta, India.

¹ W. V. Smith and R. R. Unterberger, *J. Chem. Phys.* **17**, 1348 (1949).

² Unterberger, Trambarulo, and Smith, *J. Chem. Phys.* **18**, 565 (1950).

³ Gilliam, Edwards, and Gordy, *Phys. Rev.* **75**, 1014 (1949).

TABLE II. Derived spectroscopic constants of some isotopic combinations of CHF_3 , CHCl_3 , and CH_2CCl_3 .

Isotopic species	B_0 (Mc)	I_B^a ($\times 10^{-40}$ g cm ²)	Reference
C^{12}HF_3	10,348.74	81.0641	b
C^{13}HF_3	10,422.00	81.2741	c
C^{12}DF_3	9,921.35	84.5561	c
$\text{C}^{12}\text{HCl}_3$ ³⁵	3,301.94	254.066	d
$\text{C}^{12}\text{HCl}_3$ ³⁷	3,129.51	268.065	c
$\text{C}^{12}\text{DCl}_3$ ³⁵	3,250.17	258.113	e
$\text{C}^{12}\text{H}_2\text{C}^{12}\text{Cl}_3$ ³⁵	2,372.6	353.58	c

^a Calculated from B_0 using Planck's constant = 6.623773 erg sec.

^b See reference 3.

^c Present work.

^d See reference 1.

^e See reference 2.

⁴ H. J. Bernstein and G. Herzberg, *J. Chem. Phys.* **16**, 30 (1948).

TABLE III. Molecular structures of CHF_3 , CHCl_3 , and CH_2CCl_3 .

	d_{CH}	d_{CF}	$\angle\text{FCF}$
CHF_3	1.098	1.332	$108^\circ 48'$
CHCl_3	$d_{\text{CH}} = 1.073$	$d_{\text{CCl}} = 1.767$	$\angle\text{ClCCl} = 110^\circ 24'$
CH_2CCl_3	$\left. \begin{array}{l} d_{\text{CH}} = 1.093 \\ d_{\text{CCl}} = 1.767 \\ \angle\text{HCH} = 109^\circ 28' \\ \angle\text{ClCCl} = 110^\circ 24' \end{array} \right\}$ assumed parameters		$d_{\text{CC}} = 1.55$

Smith.² These earlier microwave measurements have been combined with ours in our structural evaluations.

Hyperfine structures resulting from the Cl nuclear quadrupole coupling in chloroform and methyl chloroform were not resolved. Nevertheless, because the coupling is small and because the strongest hyperfine components are close to the position of the undisplaced rotational lines, it is possible to obtain an accurate measurement of the position of the rotational lines without resolution and analysis of these structures.

STRUCTURES

Table III lists the structural parameters which were calculated from the rotational constants. The CF distance and FCF angle for fluoroform are in good agreement with the electron diffraction values, $1.34 \pm 0.02\text{A}$ and $109^\circ \pm 2^\circ$, measured by Bauer and Beach.⁵ Similar electron diffraction results have recently been obtained by Brockway.⁶ Our results on chloroform also agree well with the electron diffraction values $d_{\text{CCl}} = 1.77 \pm 0.02\text{A}$ and $\angle\text{ClCCl} = 112^\circ \pm 2^\circ$ for chloroform.⁷

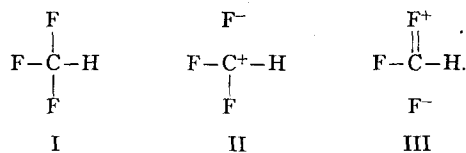
A significant difference in the zero-point vibrational energies of the hydrogen and deuterium containing molecules can cause a rather large possible error in the determination of the CH distance. Since only a minimum number of isotopic combinations for the structural evaluations were measured, no estimate of the limits of error could be made from the internal consistency test. From such tests on other molecules where substitutions or D for H have been made, the limits of error in the CH distance are estimated as 0.02A. Fortunately, because of the small weight of H, such a large possible error in the CH distance does not cause a correspondingly large error in the other parameters.

It is interesting that the bond angles and the CH distance in fluoroform are so close to those for methane. The CH length suggests that this bond is formed primarily with an sp^3 hybridized orbital of the C. Although the CF distance, 1.332A, is considerably shorter than the added covalent radii of C and F, 1.51A, the three C orbitals which form bonds to fluorine are presumably also sp^3 hybridized. The most likely cause for the marked shortening of the CF bonds is the ionic resonance of

Form II with I, as suggested by Schomaker and Stevenson,⁸ and the resonance of I with Form III, as proposed by Pauling.⁹ The Schomaker-Stevenson rule which predicts a decrease of about

$$0.09|x_A - x_B| = 0.13\text{A}$$

would account for the greater part of the shortening.



Although the bond angles are nearly tetrahedral in CHF_3 , it does not seem probable that the CF distance would be significantly smaller in this molecule than it is in CF_4 . A single, early electron-diffraction measurement gives the CF distance in CF_4 as $1.36 \pm 0.02\text{A}$. A remeasurement of CF_4 with electron diffraction seems worthwhile. The CF distances in CF_3Cl reported by Coles and Hughes¹⁰ and in other CF_3X molecules found by Sheridan and Gordy¹¹ are in good agreement with the fluoroform value.

It is interesting to compare the structures of fluoroform and chloroform. In fluoroform, the CH distance and $\angle\text{HCF}$ are slightly larger than those expected for tetrahedral carbon, whereas in chloroform the corresponding values appear to be slightly smaller than the tetrahedral values. Differences in angles can be explained on the basis of the larger size of the Cl, which causes a repulsion of the Cl atoms and thus increases $\angle\text{ClCCl}$ above the tetrahedral value of $109^\circ 28'$. The surprising feature is that the CH distance in chloroform is shorter than that in fluoroform and even shorter than that in methane, 1.093A. Although the error caused by the difference in zero-point energy mentioned above might barely account for the deviation in the methane value, it is not probable that this accounts for the observed CH distance in chloroform being shorter by 0.03A than that in fluoroform since deuterium substitution was employed in both determinations. Nevertheless, it is difficult to account for the shorter chloroform distance. From the fact that $\angle\text{HCCl}$ is smaller than $109^\circ 28'$, one might predict that the C bonding orbital in CH would have less than 25 percent s character and hence that the CH bond length would be longer than that in methane. For similar reasons, one might expect the CH in fluoroform to be slightly shorter than 1.093A. Actually, the opposite trend is indicated by the present structural determinations.

As the lines of CCl_3CH_3 were rather weak, it was possible to measure only the most abundant isotopic

⁸ V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.* **63**, 37 (1941).

⁹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945), second edition, p. 236.

¹⁰ D. K. Coles and R. H. Hughes, *Phys. Rev.* **76**, 858 (1949).

¹¹ J. Sheridan and W. Gordy (to be published).

⁵ S. H. Bauer and J. Y. Beach, quoted by P. W. Allen and L. E. Sutton, *Acta Cryst.* **3**, 46 (1950).

⁶ L. Brockway (private communication to J. Sheridan).

⁷ L. Brockway, *Revs. Modern Phys.* **8**, 231 (1936).

combination. Nevertheless, it is believed that the CC distance estimated for this molecule is reasonably accurate. There is no obvious reason why the CH₃ and CCl₃ configuration should be significantly different from those of methane and chloroform which are assumed in the determination of d_{CC} . The value obtained for d_{CC} , 1.55Å, is in accord with CC single bond lengths in other

hydrocarbons. No evaluation of the CC distance in this molecule by other methods has been made.

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Spectroscopic Studies in the Near Ultraviolet of the Three Isomeric Dimethylbenzene Vapors.* I. Absorption and Fluorescence Spectra of *Para*-Dimethylbenzene†

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The absorption spectrum of *para*-xylene between 2850 and 2350Å was photographed using a 3-meter grating spectrograph, and the corresponding fluorescence spectrum between 3125 and 2720Å was photographed with a Bausch and Lomb medium quartz spectrograph. The electronic transition involved is interpreted as $^1A_{1g} - ^1B_{3u}$ with the 0, 0 band at 36733 cm⁻¹. Progressions in the fluorescence spectrum involve the totally symmetric vibrations 829 and 1208 cm⁻¹, while progressions of the corresponding frequencies 775 and 1185 cm⁻¹ appear in the absorption spectrum. A weak portion of the spectrum is identified with a so-called forbidden transition involving the β_{1g} -component of the 606 ϵ_g^+ benzene vibration. This β_{1g} -vibration has a frequency of 648 cm⁻¹ in the ground state and of 552 cm⁻¹ in the upper state. The α_{1g} -component of the ϵ_g^+ benzene vibration in *para*-xylene has a lower state frequency of 458 cm⁻¹ and the upper state value of 367 cm⁻¹. The Tesla luminescence spectrum is interpreted in relation to the fluorescence and absorption spectra.

INTRODUCTION

CONSIDERABLE spectroscopic data in the form of absorption, emission, fluorescence, phosphorescence, infrared, and Raman spectra have been recorded for the dimethylbenzenes C₆H₄(CH₃)₂ (more commonly known as the xylenes). Among the earliest investigations, if not the earliest, of the absorption spectra of the xylenes are those by Pauer¹ in 1897 who studied them in solution and in the vapor phase. Recent reliable data for the solution spectra have been published by Conrad-Billroth² and Wolf and Herold.³ Optical density curves may also be found in the *Catalog of Ultraviolet Spectrograms*.⁴ Kronenberger⁵ has studied the near ultraviolet absorption of *meta*-xylene in the vapor and in the solid state. He mentions that he compared his plates of the vapor absorption with corresponding enlargements of

V. Henri. No later publication of these results from Henri's laboratory could be found. M. B. Hall and P. Cole photographed the xylene spectra in 1943,⁶ but because of war research these spectroscopic studies were not pursued further.

Absorption studies in the vacuum ultraviolet of the individual xylenes in a *n*-heptane solution have been carried out by Platt and Klevens.⁷ In this same spectral region Price⁸ and co-workers have obtained the spectra of the xylenes in the vapor phase.

Emission spectra in the near ultraviolet which must be considered as the counterpart of the absorption in this region have been obtained in a Tesla discharge through xylene vapor by McVicker⁹ and co-workers. The near ultraviolet fluorescence spectrum of *ortho*-xylene was reported by Marsh¹⁰ in 1923, but similar data could not be found for the vapors of the other two isomers. Fluorescence of the xylenes in alcoholic solutions, as well as other related facts, have been included in the recent book on fluorescence and phosphorescence by Pringsheim.¹¹ The Raman spectra of

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¹ J. Pauer, *Ann. Physik und Chem.* **61**, 363 (1897).

² H. Conrad-Billroth, *Z. physik. Chem.* **B29**, 170 (1935).

³ K. L. Wolf and W. Herold, *Z. physik. Chem.* **B13**, 201 (1931).

⁴ American Petroleum Institute Research Project 44 at the National Bureau of Standards, *Catalog of Ultraviolet Spectrograms*. Serial No. 55, 56, and 57. *O*-xylene, *M*-xylene and *P*-xylene, contributed by the Texas Company, Beacon, New York.

⁵ A. Kronenberger, *Z. Physik* **63**, 494 (1930).

⁶ Communication to Dr. H. Sponer from Dr. M. B. Hall.

⁷ J. R. Platt and H. B. Klevens, *Chem. Revs.* **41**, 301 (1947).

⁸ Price, Hammond, Teegan, and Walsh, *Disc. Faraday Soc.* **9**, 53 (1950).

⁹ McVicker, Marsh, and Stewart, *J. Chem. Soc.* **125**, 1743 (1924).

¹⁰ J. K. Marsh, *J. Chem. Soc.* **123**, 3315 (1923); *Phil. Mag.* **49**, 971 (1925).

¹¹ P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc. New York, 1949).