[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Microwave Spectra and Molecular Structure of 1,1,1-Trifluoroethane and its Mono-, Di- and Trideutero Derivatives[1]

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The microwave spectra of CF_3CH_3, CF_3CH_2D, CF_2CD_2H and CF_3CD_3 have been observed in a Stark modulated sweep spectrometer of the Hughes and Wilson type. The frequencies of R-branch transitions in all four molecules are given and an extensive number of Q-branch transition band-heads corresponding to $J \geqq 9$ are reported for the asymmetric molecules. Moments of inertia have been evaluated and a molecular structure consistent with these data has been calculated assuming a rigid rotor model and also that C–H = C–D and ∠CCH = ∠CCD. The following structure was obtained: C–C = 1.530 ± 0.005 Å., C–F = 1.335 ± 0.005 Å., C–H = C–D = 1.085 ± 0.008 Å., ∠CCF = 111°02′ ± 17′ and ∠CCH = CCD = 108°19′ ± 35′.

Introduction

The molecular structure of methylfluoroform has been investigated by use of electron diffraction[3–5] and microwave spectroscopy.[6] The results of the electron diffraction work are summarized in Table I, together with a set of parameters which is compatible with, but not proved by the microwave data of reference 6.

TABLE I

PREVIOUS RESULTS ON CF_3CH_3

	Ref. 3	Ref. 4	Ref. 5	Ref. 6
C–C, Å.	1.45 ± 0.04	1.53 ± 0.04	1.52 ± 0.04	1.54
C–F, Å.	1.35 ± 0.03	1.36 ± 0.02	1.33 ± 0.02	1.33
C–H, Å.	....	.. ..	.. ..	1.093
∠FCF	108.5 ± 2°	107 ± 3°	....	109°
∠HCH	....	....	....	109°28′
∠CCF	112 ± 2°	....	111.5 ± 1.5°	.....

Because of the inconsistencies in the results listed above, it seemed desirable to investigate the microwave spectra of methylfluoroform and its deuterated derivatives in order to establish a definitive set of structural parameters. This effort is part of a larger program dealing with the study of the structure of simple fluorinated molecules and it is hoped that the results herein described will be helpful in extending present day knowledge and understanding of the nature of chemical bonding in such molecular species.

Experimental

The spectrometer used in this investigation has been described elsewhere.[7] Comparison with previous measurements made on the ammonia inversion spectrum[8] indicates that the spectrometer has a precision of ±0.2 mc. or better and is sensitive enough to detect lines having an absorption coefficient of 10^{-7} cm.$^{-1}$. All measurements in this work were made in a K-band wave guide cell. Quantitative intensity measurements were not made.

The samples used by us were prepared in this Laboratory[9] for a study of the Raman and infrared spectra of these molecules. Mass spectral analysis showed that the deuterated samples contained not more than 12% of the other molecular isotopes as impurities. Although the compounds were not further purified, no lines were found to be common to more than one spectrum.

Interpretation of the Spectra

In order to predict the main features of the spectra of these four molecules, the structural parameters of reference 5 were assumed to be correct. It was found that the K-band spectrum (*ca.* 17,000–37,000 mc.) of each symmetric top should consist of only two R-branch transitions, corresponding to J:1 → 2 and J:2 → 3, and, perhaps, some satellites involving the expected low frequency torsional modes.[10,11]

The two asymmetric rotors should deviate only slightly from a prolate symmetric top ($\kappa = -0.90$ for CF_3CH_2D and $\kappa = -0.82$ for CF_3CD_2H). Accordingly, each of the R-branch lines of the symmetric rotors is replaced by a pattern consisting of three closely spaced lines for the J:1 → 2 transition and five for J:2 → 3. These lines should still be accompanied by some torsional satellites. In addition, a rather extensive, although not necessarily complicated, Q-branch structure should occur. These transitions were predicted to form bands having very close line spacing. Bands associated with transitions involving $J \geqq 9$ were expected to appear throughout the K-band.

The only lines from which definite assignments were made were in the R-branches of all four molecules. The extreme simplicity of the R-branch structure made identification very straightforward. Torsional satellites were identified by comparing their relative intensities at room and Dry Ice temperatures. Table II gives the observed frequencies and their assignments. Rotational constants evaluated from these assigned frequencies are presented in Table III. The calculated frequencies listed in Table II are based on these constants.

As indicated in Table III, there is a rather large uncertainty in the constants, A. This is due to the fact that, as mentioned previously, CF_3CH_2D and CF_3CD_2H are only very slightly asymmetric rotors. For such small asymmetries the frequencies of the $^aR_{0,1}$ transitions depend on the rotational constants in such a way that an error of the order of 0.01 mc. in frequency is sufficient to cause an error of the order of 1 mc. in the rotational constant, A.

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[1] From the Ph.D. Thesis of George B. Miller.

[2] Purdue Research Foundation Fellow in Chemistry, 1954–1955, and Procter and Gamble Graduate Fellow in Chemistry, 1955–1956.

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[10] H. T. Minden and B. P. Dailey, *Phys. Rev.*, **82**, 338A (1951).

[11] B. P. Dailey, H. Minden and R. G. Shulman, *ibid.*, **75**, 1319A (1949).

TABLE II

R-BRANCH SPECTRA

f, mc. Obsd.	*f*, mc. Calcd.	Assignment
	CF_3CH_3	
20,742.3	20,742.3	1 → 2
31,114.1	31,113.5	2 → 3
	CF_3CD_3	
18,423.6	18,423.6	1 → 2
27,510.5	......	^{a}
27,563.0	......	^{a}
27,597.5	......	^{a}
27,635.9	27,635.4	2 → 3
	CF_3CH_2D	
19,818.9	19,818.6	$1_0 \rightarrow 2_{-1}$
19,846.6	19,846.3	$1_{-1} \rightarrow 2_{-2}$
19,876.6	19,876.2	$1_1 \rightarrow 2_0$
29,695.6	......	^{a}
29,727.4	29,727.2	$2_{-1} \rightarrow 3_{-2}$
29,766.6	29,776.8	$2_{-2} \rightarrow 3_{-3}$
29,770.8	29,771.1	$2_1 \rightarrow 3_0$
29,775.5	29,775.4	$2_2 \rightarrow 3_1$
29,814.7	29,813.7	$2_0 \rightarrow 3_{-1}$
	CF_3CD_2H	
19,034.7	19,034.7	$1_0 \rightarrow 2_{-1}$
19,090.0	19,091.8	$1_{-1} \rightarrow 2_{-2}$
19,157.8	19,157.8	$1_1 \rightarrow 2_0$
	CF_3CD_2H	
28,519.5	......	^{a}
28,549.1	28,549.4	$2_{-1} \rightarrow 3_{-2}$
28,607.4	......	^{a}
28,625.8	28,626.7	$2_{-2} \rightarrow 3_{-3}$
28,645.7	28,644.4	$2_1 \rightarrow 3_0$
28,661.7	28,662.1	$2_2 \rightarrow 3_1$
28,705.6	......	^{a}
28,734.7	28,733.8	$2_0 \rightarrow 3_{-1}$

[a] Excited torsional states.

TABLE III

THE ROTATIONAL CONSTANTS, MC.

CF_2CH_3	$B = (5185.58 \pm 0.04)$
CF_3CD_3	$B = (4605.90) \pm 0.04)$
CF_3CH_2D	$A = (5545 \pm 240)$
	$B = (4976.27 \pm 0.04)$
CF_3CD_2H	$C = (4947.43 \pm 0.04)$
	$A = (5409 \pm 240)$
	$B = (4804.83 \pm 0.04)$
	$C = (4743.29 \pm 0.04)$

The use of the Q-branch spectra to eliminate the uncertainty in these constants, *A*, was found to be unsatisfactory due to the difficulty of making proper assignment to each individual line within the various series. In order to make specific assignments of these lines it would be necessary to be sure that the observed band-heads were the true ones. The distribution of intensities within each series, however, is such that it is by no means certain that the true band-head was observed. An alternative method of assignment would involve making precise assumptions as to the effect of centrifugal distortion but, in view of the lack of relevant experimental data, such assumptions did not appear to be justified.

In order to obtain frequencies leading to a precise evaluation of *A*, one would have to observe transitions associated with the component of the dipole moment along the axis perpendicular to the *a*-axis and lying in the molecular plane of symmetry. These would be $^bR_{1,1}$ transitions for CF_3CH_2D and $^cR_{1,0}$ transitions for CF_3CD_2H. Calculations based on the assumed structure and on the measured dipole moment of methylfluoroform[12,13] showed that the dipole components in question could be expected to be about one hundredth the value of the dipole components along the *a*-axes. Hence, one would expect these transitions to be very weak and, indeed, no such transitions were observed in spite of a careful search of the regions in which they would be expected.

Table IV lists the apparent band-heads and the number of transitions observed in each of the Q-branch series of the asymmetric tops.[14]

The structure and location of each Q-branch series is in good agreement with predictions based on a rigid, slightly asymmetric rotor model. In particular, one expects and finds that the lines will be closely spaced, with separations of a few megacycles, for the lower *J*-values in each series, and spacing increasing steadily toward higher *J*'s (lower frequencies). From the apparent beginning of each series, the intensities rapidly approach a maximum with increasing *J* and then drop off gradually as *J* is further increased.

TABLE IV

APPARENT BAND-HEADS OF THE Q-BRANCH SPECTRA

CF_3CH_2D *f*(mc.)	CF_3CH_2D No. of lines obsd.	CF_3CD_2H *f*(mc.)	CF_3CD_2H No. of lines obsd.
22,547.5	28	22,816.8	12
22,832.5	12	24,075.5	27
23,557.6	17	25,312.8	18
24,568.5	27	26,028.0	7
25,575.4	33	26,546.9	31
26,272.5	6	26,739.5	6
26,582.5	25	27,793.7	30
27,589.6	11	29,011.8	20
28,597.8	31		
29,599.2	25		

Determination of the Structure

Methylfluoroform and its deuterated derivatives can be described structurally by the general molecular formula CF_3CX_2Y. Assuming that each molecule is a rigid rotor and that isotopic substitution at any one atom affects only the coördinates of that atom, one finds that seven parameters completely describe the structure above.

From the four isotopic species, microwave data yield a total of eight moments of inertia which are related to the structure of CF_3CX_2Y by eight nonlinear equations containing the seven parameters as unknowns. The exact form of these equations is determined when the parameters are explicitly defined. However, of the eight moments available,

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[12] R. G. Shulman, B. P. Bailey and C. H. Townes, *Phys. Rev.*, **78**, 145 (1950); **76**, 472A (1949).

[13] S. N. Ghosh, R. Trambarulo and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952); *Phys. Rev.*, **87**, 172A (1952).

[14] The frequencies of the more than 360 individual lines are listed in reference 1.

only six are known with sufficient accuracy to permit their use in determining the structure. Taking into account also the fact that the moments of inertia are not very sensitive to the locations of the relatively light hydrogen and deuterium atoms, it seemed best to assume that the geometry of the molecule, CF_3CX_2Y, was completely unaffected by isotopic substitution. The configuration then depends on only five parameters which must be evaluated using a method of successive approximations.

The results of these considerations are presented in Table V in the form of a set of bond distances and angles giving the best agreement with the observed moments of inertia. Table VI compares the results of this set with the observed moments. It can be seen that the calculated values are in good agreement with the observed ones. The structural parameters determined in this work are in excellent agreement with the values obtained by Brandt and Livingston[5] (Table I).

TABLE V

MOLECULAR PARAMETERS

C–C, Å.	1.530 ± 0.005
C–F, Å.	1.335 ± 0.005
C–H, Å.	1.085 ± 0.008
∠CCF	111°02′ ± 17′
∠CCH	108°19′ ± 35′

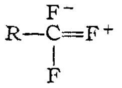
TABLE VI

MOMENTS OF INERTIA IN GCM.^{2} × 10^{40}

	Moment	Obsd.	Calcd.
CF_3CH_3	I_b	161.812	161.861
CF_3CD_3	I_b	182.177	182.177
CH_3CH_2D	I_a	151.3[a]	153.3
	I_b	168.618	168.610
	I_c	169.601	169.638
CF_3CD_2H	I_a	155.1[a]	155.3
	I_b	174.634	174.635
	I_c	176.900	176.918

[a] The uncertainty in these moments is ±6.8 whereas the uncertainty in all other moments is ±0.007.

The C–F bond distance and the CCF angle are consistent with those values found in other molecules containing the CF_3 group.[15] In particular, comparison with the fluoromethane series[16] shows that the C–F bond distance determined for CF_3CH_3 has about the expected value for a singly bonded CF_3 group (C–F = 1.385 Å. in CH_3F, 1.358 Å. in CH_2F_2 and 1.326 Å. in CHF_3). It has been postulated[16] that the slight shortening of the C–F bond and slight closing of the FCF angle in CHF_3 can be associated with the occurrence of resonance structures[17] of the type



$$\mathrm{R{-}\overset{\displaystyle F^-}{\underset{\displaystyle F}{C}}{=}F^+} \qquad \text{(I)}$$

It is certainly conceivable that structures of this type can also contribute to the slight closing of the tetrahedral umbrella of the CF_3 group in CF_3CH_3.

Since the C–H distance in Table V is based upon the assumption that C–H = C–D, it probably represents an average value lying somewhere between the true values of the C–H and C–D bond distances. By analogy with the results obtained by Miller, *et al.*,[18] for the methyl halides, the C–D bond could be expected to be shorter than the C–H bond by perhaps 0.009 Å.

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Heats of Adsorption of Hydrogen and Helium on Prepared Surfaces*

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Measurements have been made of the heats of adsorption of helium on titanium dioxide powder which had varying amounts of argon preadsorbed on it. Some measurements of the heats of adsorption of hydrogen were also made on similar systems. It is assumed that high energy sites for physical adsorption occur at surface roughnesses and faults. The experimental data are discussed in terms of this model, and it is seen that this work provides an excellent confirmation of this hypothesis.

Introduction

In a recent publication by the authors and Tykodi,[1] an analysis was made of the isotherms and heats of adsorption of a number of rare gases on titanium dioxide. The data were fitted to a model in which lateral interaction in the adsorbate was neglected, but in which the surface heterogeneity of the adsorbent was taken into account. A single site distribution function was taken to characterize the titanium dioxide surface in all cases. The physical considerations underlying the choice of distribution function were as follows: the major portion of the adsorption sites (about 60%) were considered to be those formed by the flat surface of the adsorbent, having energies which could be estimated by calculating the energy due to dis-

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