# Molecular Beam Measurement of Hyperfine Structure in Fluoroform

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The  $J = 1 \rightarrow 0$  transition in CF<sub>3</sub>H and CF<sub>3</sub>D was observed using a molecular beam maser spectrometer. Typical resonance linewidths were 6 kHz (F.W.H.M.). Hyperfine structure due to deuterium quadrupole coupling, spin-rotation and spin-spin interactions was resolved. The strength of the deuterium quadrupole coupling along the bond axis is  $eqQ = 170.8 \pm 2.0$  kHz. Fluorine and hydrogen spin-rotation interaction strengths were obtained.

## I. INTRODUCTION

Microwave absorption lines of fluoroform were first reported by Gilliam, Edwards, and Gordy (1). These were  $J = 1 \rightarrow 2$  lines at approximately 40 GHz. Further measurements of lines of C<sup>12</sup>HF<sub>3</sub>, C<sup>12</sup>DF<sub>3</sub>, and C<sup>13</sup>HF<sub>3</sub> by Ghosh, Trambarulo, and Gordy (2) enabled them to determine the structure of fluoroform. They give the values  $d_{CH} = 1.098 \text{ Å}$ ,  $d_{CF} = 1.332 \text{ Å}$ , and  $\angle FCF = 108^{\circ}48'$ . Transitions with frequencies greater than 80 GHz were measured by Burrus and Gordy (3), who determined the centrifugal stretching constants  $D_J$  and  $D_{JK}$ . The dipole moment was determined to be 1.645 D by Shoolery and Sharbaugh (4), who measured the Stark effect on the  $J = 0 \rightarrow 1$  transition. An extensive study of the microwave spectra of CF<sub>3</sub>H and CF<sub>3</sub>D was done by Costain (5), who used a hot cell to aid in measuring transitions of fluoroform in excited vibrational states. He noted anomalies in the Stark effect of  $CF_3H$ . He measured the absorption intensity  $\alpha$  of the  $J = 0 \rightarrow 1$  transition of CF<sub>3</sub>H at 300°K to be 4.65  $\times 10^{-7}$  $\mathrm{cm}^{-1}$ . Cox and Gordy have reported the Zeeman effect on the rotational spectrum (6). The Zeeman effect has recently been measured under high resolution by Flygare (7).

# **II. EXPERIMENTAL METHODS**

The experimental apparatus has been described previously (8). Basically it is a single cavity molecular beam maser. State selection (leading to population inversion) is accomplished by directing the beam through a quadrupole lens, which uses the Stark effect on the molecule to focus the J = 1 state molecules and defocus the J = 0 state. The molecular beam then passes through a TM<sub>010</sub> mode

cylindrical cavity, which has been thermally tuned to approximately the resonant frequency. A small amount of microwave power is applied to the cavity in order to stimulate the transition of the excited molecules to the ground state. Spectra are measured by slowly sweeping the stimulating signal frequency. The observed resonance line width is determined essentially by the transit time of the molecules through the cavity. The line width is about 6 kHz full width at half height for fluoroform. The beam source is a piece of glass tubing, drawn out to form a nozzle of about 0.15 mm i.d. The beam is collimated by baffles, the last of which has a  $\frac{1}{4}$  inch i.d. round hole.

 $CF_{3}H$  was purchased from the Matheson Corp., sold under the brand name Genetron-23.  $CF_{3}D$  was made by the haloform reaction. Trifluoroacetophenone (obtained from the Pierce Chemical Co.) was combined with a solution of NaOD in D<sub>2</sub>O, and heated gently under reflux until the onset of the reaction (9). The evolved fluoroform was collected in a dry-ice trap.

## III. ANALYSIS OF DATA

The Hamiltonian for the hyperfine splittings of a rotational energy level is as follows (10-13).

$$H = C_o Q + C_R R + C_s S + C_T T + C_U U$$

The coefficients  $C_{\alpha}$  are given in terms of Wigner 3-*j*, 6-*j*, and 9-*j* symbols in Ref. (12) and (13).

Q is the nuclear electric quadrupole coupling strength. It is zero for all atoms in CF<sub>3</sub>H. For D in CF<sub>3</sub>D, it is given by

$$Q = -eQq_J$$
.

R is the strength of the coupling of the hydrogen (or deuterium) nuclear magnetic spin to the molecular rotation  $(I_{\rm H} \cdot J)$ .

S is the strength of the coupling of the sum of the fluorine spins  $I_{\rm F}$  to the molecular rotation. For reasons of symmetry discussed in Ref. (12). the vector sum of the fluorine spins can be regarded as a single spin in this interaction.

T is the strength of the direct nuclear magnetic spin-spin interaction between the sum of the fluorine spins  $I_{\rm F}$  and the hydrogen (or deuterium) spin  $I_{\rm H}$ . This can be calculated accurately from the known geometry of the molecule. The explicit expression is

$$T = D_1 \left[ 1 - \frac{3K^2}{J(J+1)} \right],$$

where

$$D_{1} = g_{H}g_{F}\mu_{0}^{2}\langle r_{FH}^{-3}(1 - \frac{3}{2}\sin^{2}\beta)\rangle,$$
  
$$\beta = \not A FHC.$$

U is a similar term for the mutual fluorine spin-spin interaction. It can also be calculated accurately from the known molecular geometry. Its expression is

$$U = -\frac{1}{4} D_3 \left[ 1 - \frac{3K^2}{J(J+1)} \right],$$

where

$$D_3 = (g_{\rm F}\mu_0)^2 \langle r_{\rm FF}^{-3} \rangle.$$

There is also a scalar indirect (electron coupled) spin-spin interaction. Its value for the fluorine-hydrogen interaction in fluoroform has been measured by nuclear magnetic resonance and is 79.1 Hz (14). This interaction is too small to be considered further.

The coupling scheme for each molecule is the usual one, detailed, for example, by Thaddeus, Krischer, and Loubser (11). One of the nuclear spins is coupled to the molecular rotation vector to form an intermediate angular momentum vector

$$\mathbf{F}_1 = \mathbf{I}_1 + \mathbf{J}.$$

The other nuclear spin is added to  $F_1$  to give a resultant total angular momentum vector

$$\mathbf{F} = \mathbf{F}_1 + \mathbf{I}_2.$$

This coupling scheme is convenient if computation of the interactions is to be systematized and done on a computer. The intermediate coupling vector  $\mathbf{F}_1$ merely provides a framework for calculation. However, if one atom, designated as  $I_1$ , has a quadrupole coupling interaction which is much larger than interactions due to other atoms, the energy terms will indeed be nearly diagonal in  $\mathbf{F}_1$ .

Theoretical calculation of the hyperfine energy levels were made by a computer program. This program calculates all matrix elements for all possible combinations of  $\mathbf{F}_1$  and  $\mathbf{F}$ . This need be done only for the upper rotational state, since all levels of the J = 0 state are degenerate. After all the matrix elements were calculated, the matrix was diagonalized, and the subsequent eigenvalues were printed out. The lines were identified from the calculations produced when reasonable values of Q, R, S, T, and U, were used in the program. Relative line intensities were calculated according to the method of Thaddeus, Krischer, and Loubser (11), and these aided in the identification of the transitions. These intensities cannot be relied on absolutely in this experiment, however, since the state selection technique used influences the individual line intensities.

When the hyperfine transitions had been identified, the program was used in conjunction with a fit program to provide a least-squares fit to the spectrum. In this program, interactions T and U were held fixed at the calculated values, and interactions R and S were used as adjustable parameters. Interaction Q was fixed at 0 for CF<sub>3</sub>H, and used as an adjustable parameter in CF<sub>3</sub>D.

$F_1'$	F'	Calculated frequency	Observed frequency	<b>Relative</b> intensity
0	1.5	0	0	1.3
<b>2</b>	0.5	70.4	<b>N</b> .O.	0.7
<b>2</b>	1.5	78.9	79.2	1.3
<b>2</b>	2.5	90.5	92.1	2.0
<b>2</b>	3.5	93.8	92.1	2.7
1	1.5	129.9	127.2	1.3
1	0.5	132.5	N.O.	0.7
1	2.5	135.3	137.8	2.0

	$\mathbf{T}$	łΒ	$\mathbf{L}$	$\mathbf{E}$	I
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EXPERIMENTAL AND CALCULATED TRANSITION FREQUENCIES FOR CF3Dª

<sup>a</sup> Values are in kHz relative to 19 842 125.1 kHz. The calculated center frequency of the transition if no hyperfine structure were present is 19 842 217.8 kHz. Calculated uncertainty for fit =  $\pm 1.5$  kHz.

# IV. RESULTS AND DISCUSSION CF3D

The spectral lines recorded for the transition  $J = 1 \rightarrow 0$  of CF<sub>3</sub>D, together with their assignments, are given in Table I. Also listed is the theoretically predicted spectrum calculated according to the procedure outlined above.  $F_1'$ , F' are the quantum numbers for the J = 1 state. A recorder trace of the spectrum is shown in Fig. 1. The molecular parameters used to calculate his spectrum are listed in Table II. The strengths Q, R, and S were the best fit obtained using a leastsquares fit to the observed hyperfine spectrum. Constants T and U were calculated from the molecular geometry (2) and are included for completeness.

The five lines recorded give rise to four pieces of experimental data, since one of the lines is chosen arbitrarily as zero. Thus three adjustable parameters are fit to four data points, thereby providing an internal check. As further evidence of correct assignments, the observed intensities were found to correspond reasonably well to the predicted relative intensities of the transitions, and the fit of the calculated spectrum to the observed spectrum is good. We note that the F' = 1 lines are stronger than the F' = 2 lines as observed previously (8).

The most interesting parameter to be obtained from this spectrum is the quadrupole coupling strength Q. The constant Q for this molecule is given as

$$Q = -eQq_J$$

where q for a symmetric top molecule has the form (15)

$$q_J = \frac{\partial^2 V}{\partial Z^2} \frac{3K^2}{J(J+1)} - 1,$$

where  $\partial^2 V/\partial Z^2$  is taken along the symmetry axis of the molecule. In this simple case we note  $Q = -eq_{zz}Q$  where  $eq_{zz}Q$  is the quadrupole coupling tensor along the bond axis which coincides with the symmetry axis.



FIG. 1. Recorder trace of the  $J = 1 \rightarrow 0$  transition in CF<sub>3</sub>D. Frequency is in kHz relative to 19 842 217.8 kHz.

Salem (16) relates the electron charge times field gradient to the force constant for hydrogen stretch in diatomic molecules. It is interesting to compare eq and k(stretch force constant) for more complex molecules. The infrared spectral data for CF<sub>3</sub>D was interpreted by Long *et al.* (17) from data by Polo and Wilson (18). They obtained 12 force constants corresponding to vibrational modes of the molecule. They found the C-D stretching constant to be  $5.00 \times 10^5$  dynes/cm. Our value of eq is  $4.06 \times 10^5$  dynes/cm. In CH<sub>4</sub> the force constant k is  $5.92 \times 10^5$ 

TABLE	II
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Interaction	$CF_{3}D$	CF <sub>8</sub> H	
Q	$-170.8 \pm 2.0$	0.	
$\check{R}$	$3.5 \pm 1.0$	$24.5 \pm 3.0$	
$\boldsymbol{S}$	$4.6 \pm 1.0$	$5.4 \pm 1.5$	
$T^{ m b}$	0.897	5.843	
$U^{ ext{b}}$	-2.618	-2.618	

Hyperfine Interaction Strengths for CF<sub>3</sub>D and CF<sub>3</sub>H as Determined by a Least-Squares Fit to Observed Spectra<sup>a</sup>

<sup>a</sup> Values are in kHz.

<sup>b</sup> These parameters were calculated from the known molecular structure and are included here for completeness.

EXPERIMENTAL AND CALCULATED TRANSITION FREQUENCIES FOR CF3HB

$F_1'$	F'	Calculated frequency	Observed frequency	Observed intensity
1.5	3	21.3	21.3	2.5
1.5	<b>2</b>	17.5	21.3	2.5
1.5	1	-1.1	0.2	1.0
0.5	1	-23.5	-24.2	0.6
0.5	<b>2</b>	-27.5	-24.2	0.6

TABLE III

<sup>a</sup> Values are in kHz relative to line center if no hyperfine structure were present at 20 697 690.2 kHz.

dynes/cm and the value of eq is  $4.63 \times 10^5$  dynes/cm (19). We see that eq is about 80% as large as k for two examples including a methyl group. Salem's "covalent" model predicts that eq should be  $\sim 70\%$  of k. This seems to be rather good agreement for such simple models.

It is interesting to compare our value of deuteron quadrupole coupling with other values for the methyl group. Shoemaker and Flygare (20) report a value of  $eq_{zz}Q = 176 \pm 15$  kHz for CD<sub>3</sub>C = C—H. A value of  $eq_{zz}Q = 191.5 \pm 0.8$  has been obtained for CH<sub>3</sub>D in a molecular beam electric resonance experiment (19).

## V. RESULTS AND DISCUSSION: CF<sub>3</sub>H

For CF<sub>3</sub>H, there were only three lines completely resolved. The quadrupole moment is zero so there were two adjustable parameters to fit the data. Naturally, this reduces the confidence level of the derived parameters somewhat. Table III presents the observed spectral lines, the calculated lines, relative intensities, and assignments. Table II lists the interaction strengths determined. For more dependable results, the spectrum might possibly be measured using a two-cavity maser, which can have a linewidth of 350 Hz (12), as opposed to 6 kHz in the pres-

ent experiment. We note that the fluorine spin-rotation constants are in agreement for CF<sub>3</sub>D and CF<sub>3</sub>H. If we multiply R for CF<sub>3</sub>D by  $g_{\rm H}/g_{\rm D}$ , the ratio of the gvalues, we get 22 ± 6 kHz which is in agreement with the listed value of R for CF<sub>3</sub>H.

It would be useful to obtain spin-rotation constants for another rotational state so that the complete spin-rotation tensors could be obtained. This would allow calculation of paramagnetic and diamagnetic shielding tensors for this molecule.

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