example, in samples with heavy radiation damage.

It should be emphasized that investigation of only the fate of those tritons which are finally incorporated in otherwise unchanged hexose molecules, a selected sample of the recoil atoms is being considered which may not be representative of the behavior or mechanism of reaction of the other recoil tritons. Nevertheless, this does not affect the rather general and incomplete reaction mechanism thus far formulated. Studies are now in progress, on this and other systems, to determine the yields of a wider range of products under several experimental conditions. These results may serve to extend the ideas set forth in this paper.

PRINCETON, NEW JERSEY
UPTON, NEW YORK

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

# The Vibration–Rotational Spectrum of Methyl-$d_3$ Fluoride[1]

BY WALTER F. EDGELL AND L. PARTS

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The Raman and infrared spectra of methyl-$d_3$ fluoride have been obtained. The $Q$ sub-band structure of the perpendicular bands was resolved and lead to the values 2258.0, 1073.3 and 911.0 for the "apparent" band centers and 0.179, −0.286 and 0.241 for the Coriolis coupling constants of $\nu_4$, $\nu_5$ and $\nu_6$, respectively.

## Introduction

The spectra of a number of fluorinated hydrocarbons have been studied in this Laboratory[2] to aid in obtaining an understanding of their interesting chemical and physical behavior.

The observed fundamental frequencies have been the primary experimental source of information for the force field of a molecule. However, additional information is available from Coriolis coupling constants.[3-6] In order to utilizet he information obtainable from such constants, methods have been developed for obtaining their values from band envelopes when the bands corresponding to degenerate vibrations are unresolved.[7,8] These methods have been applied recently to some simple molecules including $CF_4$, $CF_3H$ and $CF_3D$.[7-9] The infrared spectrum of methyl fluoride, $CH_3F$, has been studied previously in some detail.[10-12] A study of the vibration–rotational spectrum of $CD_3F$ was undertaken to provide the remaining data required for a systematic study of the force fields in the fluorine derivatives of methane. This paper deals with the Raman and infrared spectra of $CD_3F$.

## Experimental

The starting point in the preparation of methyl-$d_3$ fluoride was the conversion of 1–2 propylene carbonate by lithium aluminum deuteride to methyl-$d_3$ alcohol.[13] It, in turn, was converted to methyl-$d_3$ $p$-toluenesulfonate, which gave the desired product upon reaction with potassium fluoride.[13] The sample was analyzed mass spectrographically and consisted of 94.4% $CD_3F$ and 5.6% $CD_2HF$.[14]

The infrared spectrum was obtained with a Perkin–Elmer Model 21 spectrophotometer and under higher resolution with an instrument built about a Perkin–Elmer Model 99 double pass monochromator. The frequency range 880–3420 cm.$^{-1}$ was studied with NaCl and LiF prisms. Ammonia,[15] water vapor,[16] carbon monoxide,[16] hydrogen iodide,[16] hydrogen bromide,[15] and methane[15] were used as calibration substances. The calibration curves were based on the average of three runs. The spectrum of $CD_3F$ was scanned from five to nine times, depending on the region being studied, and the results were averaged. The somewhat large number of runs appeared to be essential for obtaining a higher precision for the $Q$ sub-band spacings of the perpendicular bands. A 10-cm. gas cell, equipped with KBr windows, was used. The spectra were taken at pressures ranging from 25 to 760 mm. Each band of $CD_3F$ was scanned with a constant slit. The corresponding calibration spectra were under the same slit conditions.

The Raman spectrum of $CD_3F$ was taken with an Applied Research Laboratories spectrograph which has a dispersion of 15.4 Å./mm. at 4358 Å. The spectra were obtained for the substance in the gas phase, using a multiple reflection cell[17] whose mirrors had a focal length of 50 cm. The pressure was one atmosphere. The spectrum of argon[18] was used for the calibration of the Raman films.

**$A_1$ Fundamentals.**—$CD_3F$ has six normal modes of vibration, *i.e.*, three non-degenerate type $A_1$ vibrations and three doubly degenerate type E vibrations. The assignment of the fundamental frequencies is easily accomplished on the basis of band contours, band intensities and the reported results for the spectra of $CH_3F$,[10-12] $CD_3Cl$,[19-23] $CD_3Br$[19,22-25] and $CD_3I$.[22-24,26]

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[1] Presented before the 128th Meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955.

[2] For the latest publications the reader is referred to W. F. Edgell and C. E. May, *J. Chem. Phys.*, **22**, 1808 (1954); W. F. Edgell and C. J. Ultee, *ibid.*, **22**, 1983 (1954).

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[25] H. B. Weissman, R. B. Bernstein, S. E. Rosser, A. G. Meister and F. F. Cleveland, *J. Chem. Phys.*, **23**, 544 (1955).

[26] M. de Hemptinne and T. Doehard, *Bull. Classe Sci., Acad. roy. Belg.*, **30**, 497 (1946).

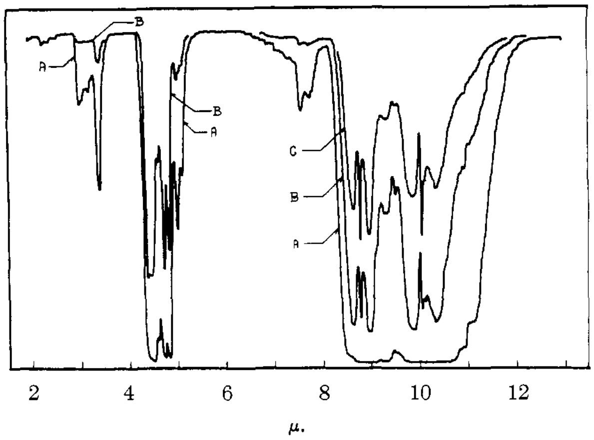

Fig. 1.—The infrared spectrum of gaseous $CD_3F$ from 2–13 $\mu$; cell length 10 cm.; pressure for A, 600 mm., B, 120 mm., C, 40 mm.; NaCl prism; speed 1 $\mu$/195 sec.

A survey infrared spectrum of $CD_3F$ for the 2–13 $\mu$ wave length region is given in Fig. 1. All the fundamental frequencies appear in two groups over relatively narrow frequency ranges, leading to a high degree of overlapping of the bands. There are three strong parallel bands plus one of medium intensity. The frequencies and their assignment are given in Table I. The contours of $\nu_2$ and the resonance pair $\nu_1$, $2\nu_5$ and $2\nu_5$, $\nu_1$ are found in Fig. 2 while that of $\nu_3$ is given in Fig. 3. Three bands of $CD_2HF$ are expected in the region of $\nu_3$ and these presumably give rise to the peak at 1050.0, the pair at 985.2 and 987.8 and the peak at 966.0 cm.$^{-1}$.

Considering the overlapping of the bands the observed P-R separations for the parallel bands are in satisfactory agreement with the calculated value of 41.1 cm.$^{-1}$.

TABLE I

PARALLEL FUNDAMENTALS

| $\nu_{vac}$ (cm.$^{-1}$) | Intensity | Assignment | P-R separation (cm.$^{-1}$) |
|---|---|---|---|
| 970.6 | | $P$ | |
| 991.8 | s | $Q$ $\nu_3$ | 41.3 |
| 1011.9 | | $R$ | |
| 1115.5 | | $P$ | |
| 1136.9 | s | $Q$ $\nu_2$ | 42.1 |
| 1157.6 | | $R$ | |
| 2068.9 | | $P$ | |
| 2089.7 | s | $Q$ $\nu_1, 2\nu_5$ | 42.6 |
| 2111.5 | | $R$ | |
| 2149.8 | m | $Q$ $2\nu_5, \nu_1$ | |
| 2167.0 | | $R$ | |

The observed Raman displacements of the Q-branches of type A bands for $\nu_3$; $\nu_2$; $\nu_1$, $2\nu_5$; and $2\nu_5$, $\nu_1$ are 991, 1137, 2089 and 2149 cm.$^{-1}$. These values, which have been corrected to vacuum, agree within one cm.$^{-1}$ with the corresponding infrared frequencies.

**Perpendicular Vibrations.**—The application of the selection rules to the vibrational and rotational term values[27] leads to the following expression for the frequency of the $J^{th}$ line in the $K^{th}$ $Q$ sub-band of a perpendicular band

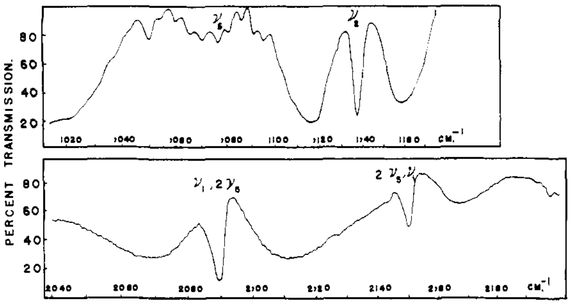

Fig. 2.—The details of the bands associated with $\nu_5$, $\nu_2$, $\nu_1$, $2\nu_5$ and $2\nu_5$, $\nu_1$.

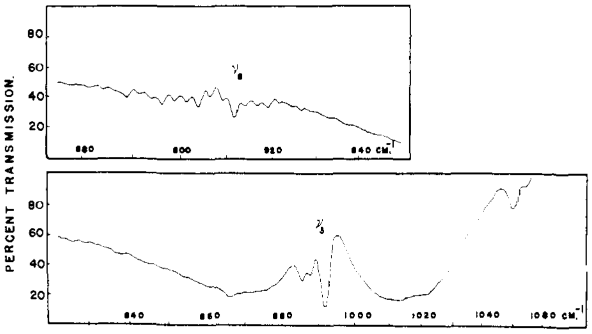

Fig. 3.—The details of the bands associated with $\nu_6$ and $\nu_3$.

$$\nu_{JK} = \nu_0 + [A'(1 - 2\zeta) - B'] + (B' - B'')J(J + 1) \pm 2[A'(1 - \zeta) - B']K + [(A' - A'') - (B' - B'')]K^2 \quad (1)$$

Centrifugal distortion terms have been neglected; $A'$ and $B'$ refer to the excited state while $A''$, $B''$, $J$ and $K$ refer to the ground state. The upper sign applies to the Q sub-bands in the R branch ($\Delta K = +1$) and the lower sign to those in the P branch ($\Delta K = -1$). The third term in this expression extends the $Q$ sub-band over a (usually) small frequency range shading it off toward the high or low frequency side depending upon the sign of $(B' - B'')$. In particular it should be noted that the maximum does not occur at $J = 0$.[25] The actual appearance of such a sub-band depends upon the relative values of the slit width and the sub-band "half width" as well as the spectrometer conditions usually lumped together under the term slit function. When the value of $J$ corresponding to the maximum of the sub-band does not change radically over the sub-bands observed and the resolution of the spectrometer is not sufficient to show the shading off of the sub-bands, as is the case here, one may write for the positions of the observed maxima

$${}^{R,P}Q_K = \nu_0' + [A'(1 - 2\zeta) - B'] \pm 2[A'(1 - \zeta) - B']K + [(A' - B') - (A'' - B'')]K^2 \quad (2)$$

The difference between the apparent band center $\nu_0'$ and the actual center $\nu_0$ is approximately $(B' - B'')J^2_{max}$ for the ${}^RQ_0$ sub-band[25] and, of course, is always less than the observed "half width" of the ${}^RQ_0$ sub-band.

The spacing between adjacent sub-bands is obtained from equation 2. By averaging an equal

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[27] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1951.

number of spacings on both sides of $R_{Q_0}$, the dependence upon the change in moments of inertia is removed

$$\overline{\Delta\nu}^{\text{sub}} = 2[A'(1 - \zeta) - B'] \quad (3)$$

Adding the average sub-band spacings for the three perpendicular fundamentals and dropping the difference between vibrational states yields[5,27]

$$\overline{\Sigma\Delta\nu}^{\text{sub}} = 6A - 7B \quad (4)$$

Use will be made also of the combination sum

$$R_{Q_K} + P_{Q_K} = 2\{\nu_0' + A'(1 - 2\zeta) - B'\} + 2[(A' - B') - (A'' - B'')]K^2 \quad (5)$$

Taking the value of $B = 0.68217$ cm.$^{-1}$ from the reported microwave data for $CD_3F$[28] and the experimental value of the average $Q$ sub-band spacing sum, 10.501 ± 0.314 cm.$^{-1}$ (see below), the rotational constant $A$ has been obtained from equation 4 as 2.546 ± 0.052 cm.$^{-1}$. The Coriolis coupling constant for each band has been obtained by means of equation 3, using the above values of the rotational constants and the average $Q$ sub-band spacing. The apparent band origins have been obtained from equation 2.

The resolved fine structure of the perpendicular band $\nu_6$ ($R_{Q_0} = 911.6$ cm.$^{-1}$) is shown in Fig. 3. The frequencies and assignments are given in Table II.

TABLE II

$Q$ SUB-BAND FREQUENCIES FOR $\nu_6$

| $\nu_{\text{vac}}$ (cm.$^{-1}$) | Assignment | $\nu_{\text{vac}}$ (cm.$^{-1}$) | Assignment |
|---|---|---|---|
| 881.5 | $P_{Q_{12}}$ | 906.4 | $P_{Q_2}$ |
| 884.5 | $P_{Q_{11}}$ | 909.1 | $P_{Q_1}$ |
| 889.0 | $P_{Q_9}$ | 911.6 | $R_{Q_0}$ |
| 891.5 | $P_{Q_8}$ | 914.0 | $R_{Q_1}$ |
| 894.0 | $P_{Q_7}$ | 916.6 | $R_{Q_2}$ |
| 896.4 | $P_{Q_6}$ | 919.0 | $R_{Q_3}$ |
| 899.0 | $P_{Q_5}$ | 921.5 | $R_{Q_4}$ |
| 901.4 | $P_{Q_4}$ | 924.0 | $R_{Q_5}$ |
| 904.0 | $P_{Q_3}$ | 926.3 | $R_{Q_6}$ |

On the high frequency side the band is strongly overlapped by $\nu_3$, which obscures part of its fine structure. This fact is more clearly seen with records made at higher resolution than Fig. 3. The alternating intensity pattern strong, weak, weak, strong is caused by the statistical weights of the vibration-rotational levels. The $Q$ sub-band of highest intensity has been assigned as $R_{Q_0}$, although there is a possibility that some of its strength may be due to a fundamental of $CD_2HF$ expected in this region. Only the sub-band spacings from $P_{Q_5}$ to $R_{Q_5}$ were used for the analysis of the band. The results are given in Table V. A plot of $R_{Q_K} + P_{Q_K}$ vs. $K^2$ (see Fig. 4) leads to $[(A' - B') - (A'' - B'')] = -0.0035$ cm.$^{-1}$.

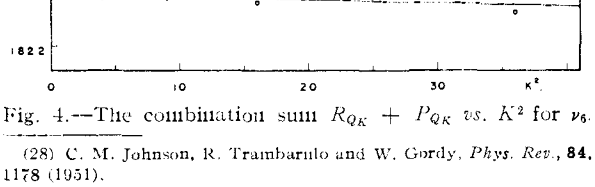

Fig. 4.—The combination sum $R_{Q_K} + P_{Q_K}$ vs. $K^2$ for $\nu_6$.

The details of $\nu_5$($R_{Q_0} = 1076.6$ cm.$^{-1}$) may be seen in Fig. 2 and the sub-band frequencies and assignments are listed in Table III. This band is overlapped on both sides by parallel bands and by a $CD_2HF$ peak whose frequency is 1050 cm.$^{-1}$. Only nine sub-bands could be resolved. Using narrow slit widths the intensity alternation became observable, allowing one to determine the observed band center. The spacings $R_{Q_4}$ to $P_{Q_4}$ were used to obtain the average sub-band spacings. The uncertainty in the value of $\overline{\Delta\nu_5}^{\text{sub}}$ is relatively high if compared with the corresponding values for the other perpendicular bands. The results of the analyses of this band are found in Table V. The scattering of the combination sum $R_{Q_K} + P_{Q_K}$ is too high to allow an estimation of $[(A' - B') - (A'' - B'')]$.

TABLE III

$Q$ SUB-BAND FREQUENCIES FOR $\nu_5$

| $\nu_{\text{vac}}$(cm.$^{-1}$) | Assignment | $\nu_{\text{vac}}$(cm.$^{-1}$) | Assignment |
|---|---|---|---|
| 1054.3 | $P_{Q_4}$ | 1080.7 | $R_{Q_1}$ |
| 1060.0 | $P_{Q_3}$ | 1085.9 | $R_{Q_2}$ |
| 1065.5 | $P_{Q_2}$ | 1091.1 | $R_{Q_3}$ |
| 1070.5 | $P_{Q_1}$ | 1095.1 | $R_{Q_4}$ |
| 1076.6 | $R_{Q_0}$ | | |

TABLE IV

$Q$ SUB-BAND FREQUENCIES FOR $\nu_4$

| $\nu_{\text{vac}}$ (cm.$^{-1}$) | Assignment | $\nu_{\text{vac}}$ (cm.$^{-1}$) | Assignment |
|---|---|---|---|
| 2207.6 | $P_{Q_{17}}$ | 2264.7 | $R_{Q_2}$ |
| 2211.8 | $P_{Q_{16}}$ | 2267.5 | $R_{Q_3}$ |
| 2215.3 | $P_{Q_{15}}$ | 2270.3 | $R_{Q_4}$ |
| 2217.7 | $P_{Q_{14}}$ | 2273.1 | $R_{Q_5}$ |
| 2220.9 | $P_{Q_{13}}$ | 2275.6 | $R_{Q_6}$ |
| 2224.1 | $P_{Q_{12}}$ | 2278.4 | $R_{Q_7}$ |
| 2226.9 | $P_{Q_{11}}$ | 2281.0 | $R_{Q_8}$ |
| 2229.9 | $P_{Q_{10}}$ | 2283.4 | $R_{Q_9}$ |
| 2233.0 | $P_{Q_9}$ | 2286.2 | $R_{Q_{10}}$ |
| 2236.1 | $P_{Q_8}$ | 2288.6 | $R_{Q_{11}}$ |
| 2238.8 | $P_{Q_7}$ | 2291.2 | $R_{Q_{12}}$ |
| 2242.0 | $P_{Q_6}$ | 2294.1 | $R_{Q_{13}}$ |
| 2245.0 | $P_{Q_5}$ | 2296.5 | $R_{Q_{14}}$ |
| 2247.7 | $P_{Q_4}$ | 2298.7 | $R_{Q_{15}}$ |
| 2250.6 | $P_{Q_3}$ | 2301.8 | $R_{Q_{16}}$ |
| 2253.5 | $P_{Q_2}$ | 2305.7 | $R_{Q_{17}}$ |
| 2256.3 | $P_{Q_1}$ | 2307.6 | $R_{Q_{18}}$ |
| 2259.0 | $R_{Q_0}$ | 2309.7 | $R_{Q_{19}}$ |
| 2262.0 | $R_{Q_1}$ | 2312.4 | $R_{Q_{20}}$ |

Figure 5 shows the resolved fine structure of the perpendicular band $\nu_4$ ($R_{Q_0} = 2259.0$ cm.$^{-1}$). The data and assignments are presented in Table IV. The general features of this band are slightly obscured by overlapping with $2\nu_5$, $\nu_1$ of $CD_3F$, and with a type A (2198 cm.$^{-1}$) and a type B (~2266 cm.$^{-1}$) band of $CD_2HF$. However, within the experimental limits of accuracy no irregularities are detectable in the sub-band spacings. The positions of the sub-bands $P_{Q_{17}}$ to $R_{Q_{20}}$ could be determined and the spacings from $P_{Q_{14}}$ to $R_{Q_{14}}$ were used for the analysis of the band. The results are found in Table V. The slope of the line obtained by plotting

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(28) C. M. Johnson, R. Trambarulo and W. Gordy, *Phys. Rev.*, **84**, 1178 (1951).

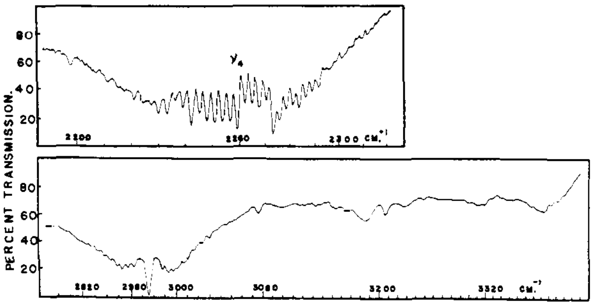

Fig. 5.—The details of $\nu_4$ of $CD_3F$ and the 2976 cm.$^{-1}$ band of $CD_2HF$ plus various overtone and combination bands.

$R_{Q_K} + P_{Q_K}$ as a function of $K^2$ (see Fig. 6) gives $[(A' - B') - (A'' - B'')] = -0.01_1$ cm.$^{-1}$.

To provide a consistent treatment, the data in the literature[10–12] for $CH_3F$ have been reanalyzed using the above methods. The results are collected in Table V. It is gratifying to note that the values of $\zeta$ and $\nu_0'$ for $\nu_4$ are so close to those obtained by Pickworth and Thompson[12] using more refined methods of treating the data.

TABLE V

SUMMARY OF THE $Q$ SUB-BAND ANALYSIS OF THE PERPENDICULAR BANDS OF $CH_3F$ AND $CD_3F$[a]

| | $CH_3F$ | $CD_3F$ |
|---|---|---|
| $\overline{\Delta\nu_4}^{sub}$ | 7.858 ± 0.034 | 2.814 ± 0.039 |
| $\overline{\Delta\nu_5}^{sub}$ | 11.433 ± .188 | 5.183 ± .244 |
| $\overline{\Delta\nu_6}^{sub}$ | 5.650 ± .045 | 2.503 ± .032 |
| $\Sigma\overline{\Delta\nu_0}^{sub}$ | 24.668 ± .267 | 10.501 ± .314 |
| $B^b$ | 0.85183 | 0.68217 |
| $A$ | 5.105 ± .044 | 2.546 ± .052 |
| $\zeta_4$ | 0.090 ± .005 | 0.179 ± .009 |
| $\zeta_5$ | −0.287 ± .008 | − .286 ± .022 |
| $\zeta_6$ | 0.280 ± .002 | .241 ± .010 |
| $\nu_4$ $R_{Q0}$ | 3009.28 | 2259.0 |
| $\nu_0'$ | 3005.95 | 2258.0 |
| $\nu_5$ $R_{Q0}$ | 1475.3[c] | 1076.6 |
| $\nu_0'$ | 1468.1[c] | 1073.3 |
| $\nu_6$ $R_{Q0}$ | 1199.8[c] | 911.6 |
| $\nu_0'$ | 1198.4[c] | 911.0 |

[a] Data for $\nu_4$ of $CH_3F$ from reference 12, and for $\nu_5$ and $\nu_6$ from reference 10. The units of $\Delta\nu_i$, $B$, $A$, $\nu_i$ are cm.$^{-1}$. Following $Q$ sub-band spacings were used for calculating the average spacings for the bands: $CH_3F$: $\nu_4(P_{Q_4} - R_{Q_4})$, $\nu_5(P_{Q_8} - R_{Q_8})$, $\nu_6(P_{Q_7} - R_{Q_7})$. $CD_3F$: $\nu_4(P_{Q_{14}} - R_{Q_{14}})$, $\nu_5(P_{Q_4} - R_{Q_4})$, $\nu_6(P_{Q_5} - R_{Q_5})$. [b] The values of $B''$ reported in reference 28 have been used here. [c] The values of $R_{Q_0}$ and $\nu_0'$ have been corrected to vacuum wave numbers.

The perpendicular bands of gaseous $CD_3F$ have also been observed in the Raman effect. Because of the diffuse character of these unresolved bands it was not possible to locate their centers with accuracy.

**Overtone and Combination Bands.**—Several strong overtone and combination bands have been observed. The frequencies and assignments, which were made on the basis of analogy with corresponding bands in the spectra of $CH_3Cl$[29] and $CH_3I$,[30] are found in Table VI. Most of them may be seen in Fig. 5.

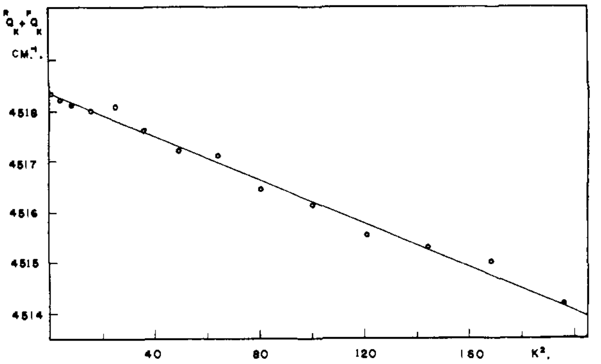

Fig. 6.—The combination sum $R_{Q_K} + P_{Q_K}$ vs. $K^2$ for $\nu_4$

TABLE VI

OVERTONE AND COMBINATION BANDS OF $CD_3F$

| $\nu_{vac}$(cm.$^{-1}$) | Intensity | Assignment | Obsd. band type |
|---|---|---|---|
| 1955.3 | | $P$ | |
| 1976.6 | w | $Q$ $2\nu_3$ | $A_1$ |
| 1998.1 | | $R$ | |
| 3076.6 | vvw | Q $\nu_1 + \nu_3$ | $A_1$ |
| 3100.0 | | $R$ | |
| 3153.8 | vvw | $Q$ $\nu_1 + \nu_2$ | $A_1$ |
| 3165.5 | vvw | $R_{Q_0}$ $\nu_4 + \nu_6$ | E |
| 3185.2 | | $P$ | |
| 3207.0 | vw | $Q$ $2\nu_5 + \nu_2$ | $A_1$ |
| 3228.7 | | $R$ | |
| 3249.7 | vvw | $2\nu_5 + \nu_2$ | E |
| 3280.7 | | $P_{Q_9}$ | |
| 3289.7 | | $P_{Q_6}$ | |
| 3300.6 | | $P_{Q_3}$ | |
| 3311.2 | vvw | $R_{Q_0}$ $\nu_4 + \nu_5$ | E |
| 3319.5 | | $R_{Q_3}$ | |
| 3329.0 | | $R_{Q_6}$ | |
| 3393.8 | vw | $R_{Q_0}$ $\nu_4 + \nu_2$ | E |
| 3404.5 | | $R_{Q_3}$ | |
| 3412.2 | | $R_{Q_6}$ | |
| 3420.0 | | $R_{Q_9}$ | |

An independent check for the assignment of two perpendicular combination bands ($\nu_4 + \nu_5$ and $\nu_4 + \nu_2$) was obtained from the calculated spacing of the $Q$ sub-bands. Apparently only the enhanced $Q$ sub-bands were observed whose respective spacings are 9.7 ± 0.9 cm.$^{-1}$ and 8.7 ± 1.3 cm.$^{-1}$. The calculated values of these spacings, based on the $\zeta$'s for the perpendicular fundamentals, are 9.5 and 8.4 cm.$^{-1}$.

**$CD_2HF$ Bands.**—The partially deuterated methyl fluoride $CD_2HF$ has nine non-degenerate normal modes of vibration. Even though the sample of $CD_3F$ contained only 5.6% $CD_2HF$, evidence for eight bands attributable to this species was observed. The identification of the $CD_2HF$ bands has been based on the known frequencies of $CH_3F$, $CD_3F$, $CD_3X$, $CD_2HX$,[22,24] $CDH_2X$[22,24] and $CH_3X$ (X = Cl, Br, I). The observed frequencies of what are presumed to be the band centers are 966.0, 986.5, 1050.0, 1308.8, 2198.3, 2266 and 2975.6 cm.$^{-1}$. The eighth band may be seen in Fig. 1 but its center could not be located with certainty because of interference from water vapor.

An example of the structure of type C bands in

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(29) A. H. Nielsen and E. F. Barker, *Phys. Rev.*, **46**, 970 (1934). Some of the assignments of Nielsen and Barker have been revised by Herzberg, ref. 27, p. 313.

(30) G. Herzberg and L. Herzberg, *Can. J. Research*, **27B**, 332 (1949).

$CD_2HF$ is the band whose center appears at 2975.6 cm.$^{-1}$ (see Fig. 5). The general features of this band, *i.e.*, the PQR structure, the P–R spacing, and the resolvable fine structure superimposed on the P and R branches, agree with those expected from an asymmetric top molecule whose calculated moments of inertia are: $I_A = 9.00_3 \times 10^{-40}$, $I_B = 37.4_1 \times 10^{-40}$ and $I_C = 39.40 \times 10^{-40}$ g./cm.$^2$

**The Molecular Dimensions of $CD_3F$ and $CH_3F$.**—Using the value of $I_B''$ determined from microwave spectrum[28] of $CD_3F$, known atomic masses,[31] $1.104 \times 10^{-8}$ cm. as the C–D distance,[32] and the value of $I_A$ obtained from the average sub-band spacing sum of $CD_3F$, the remaining molecular dimensions were calculated. The following values were obtained: $r_{C-F} = 1.385 \times 10^{-8}$ cm., ∢DCD = 110°20′, and ∢DCF = 108°35′. To define the structure of $CH_3F$, the microwave value of $I_B''$ for methyl fluoride,[28] atomic masses,[31] the calculated C–F distance from $CD_3F$, and the value of $I_A$ obtained from the average sub-band spacing as given in Table V were employed. The calculated values of the molecular parameters for $CH_3F$ are: $r_{C-H} = 1.105 \times 10^{-1}$ cm., ∢HCH = 109°54′, and ∢HCF = 109°02′.

**Force Constants.**—A preliminary calculation of the intramolecular forces was made on the basis of the following simple potential function which is often used for methyl halides

$$2V = f_{CH}\,\Sigma(\Delta r_{CH_i})^2 + f_{CF}(\Delta r_{CF})^2 + f_{HCH}\,\Sigma(d_{CH}\,\Delta\alpha_{ik})^2 + f_{HCF}\,\Sigma(d_{CH}\Delta\beta_i)^2 + 2f_{CF,\,HCF}\,(\Delta r_{CF})\Sigma(d_{CH}\Delta\beta_i) \quad (5)$$

The symbol $\Delta r_{CH_i}$ refers to the change in the i'th C–H distance, $\Delta\alpha_{ik}$ refers to the change in ∢$H_iCH_k$, and $\Delta\beta_i$ represents the change in ∢$H_iCF$. It has been assumed here that the angles are tetrahedral and $r_{CH} = 1.105 \times 10^{-8}$ cm. has been used for both $CH_3F$ and $CD_3F$. The *G* and *F* matrices derived previously[33] were used. The force constants for $CH_3F$ and $CD_3F$ in terms of the given potential function were calculated separately. The values of $f_{CH}$, $f_{HCF}$ and $f_{HCH}$ were obtained from the secular equations for perpendicular vibrations. From the secular equations for parallel vibrations, $f_{CF}$ and $f_{CF.HCF}$ were obtained using $\lambda_2$ and $\lambda_3$. Table VII contains the results. The constants calculated in this manner for $CH_3F$ and $CD_3F$ differ and the interaction constant for $CH_3F$ has an imaginary part. It must be concluded that such a simple function does not adequately represent the forces of these molecules. However the values obtained for $CD_3F$ are believed to be a closer representation than those obtained for $CH_3F$.

TABLE VII

THE FORCE CONSTANTS OF $CH_3F$ AND $CD_3F$[a]

| Constant | $CH_3F$ | $CD_3F$ |
|---|---|---|
| $f_{CH}$ | 4.80 | 4.86 |
| $f_{CF}$ | 6.07 | 5.43 |
| $f_{HCF}$ | 0.825 | 0.760 |
| $f_{HCH}$ | 0.426 | 0.465 |
| $f_{CF.HCF}$ | 0.713 ± 0.32i | 0.513 |

[a] Stretching constants: $\times 10^6$ dynes/cm.; bending constants: $\times 10^5$ dynes/cm. rad.; interaction constants: $\times 10^6$ dynes/cm. rad.$^2$.

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ADDED NOTE.—After the preparation of this paper F. H. Anderson, B. Bak and A. Brodersen have presented a paper on the infrared spectrum of $CH_3F$ and $CD_3F$ before the European Molecular Spectroscopy Group at Oxford. The values obtained by them for the band centers of two of the three perpendicular bands are in reasonable agreement with those given here. No values for the Coriolis coupling constants were cited. Major attention was devoted to the problem of molecular dimensions and their results are in reasonable agreement with ours.

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