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We thus obtain

$$F = \int \left\{ \frac{\mathbf{E}_{c}^{2}}{8\pi} + \frac{\mathbf{P}_{u}^{2}}{2\alpha_{u}} + \frac{\mathbf{P}_{o}^{2}}{2\alpha_{e}} - \mathbf{P}_{o} \cdot \left(\mathbf{E}_{c} + \frac{\mathbf{E}_{u}}{2} + \frac{\mathbf{E}_{o}}{2} \right) - \mathbf{P}_{u} \cdot \left(\mathbf{E}_{c} + \frac{\mathbf{E}_{u}}{2} + \frac{\mathbf{E}_{o}}{2} \right) \right\} dV. \quad (80)$$

The electric field strength \mathbf{E} is simply the sum $(\mathbf{E}_{e} + \mathbf{E}_{u} + \mathbf{E}_{e})$. Introducing this and the relations, $\mathbf{P}_e = \alpha_e \mathbf{E}, \ \mathbf{P} = \mathbf{P}_e + \mathbf{P}_u$, into Eq. (80) we obtain

$$F = \int \left\{ \frac{\mathbf{E}_c^2}{8\pi} + \frac{\mathbf{P}_u^2}{2\alpha_u} - \frac{\mathbf{P} \cdot \mathbf{E}_c}{2} - \frac{\mathbf{P}_u \cdot \mathbf{E}}{2} \right\} dV$$

which is identical with Eq. (25).

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Normal Vibration Frequencies of CD_3F . Structure of CH_3F and CD_3F from Infrared and Microwave Spectra

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The infrared absorption spectrum of CD₃F has been studied. Simultaneously, the infrared spectrum of CH₃F was reinvestigated. Fundamental vibration frequencies for CD₃F were found together with Coriolis coupling factors for the three degenerate vibrations in CH₃F and CD₃F. The fine-structure analysis gave reliable values for the large rotational constants of CD₃F and CH₃F. The structure of the methyl fluoride molecule is discussed.

I. INTRODUCTION

T present, fundamental vibration frequencies for A the three pairs, CH_3X , CD_3X where X = Cl, Br, and I have been reported in the literature¹ together with data for CH3F.2-4 Fundamental vibration frequencies for CD₃F represent, therefore, a very desirable supplement. In an attempt to produce these data, CD₃F was prepared and its infrared absorption was measured. Also, the spectrum of CH₃F was reinvestigated. Values of the frequencies of the parallel vibrations followed by direct inspection while the localization of the centers of the perpendicular bands necessitated a thorough analysis of the fine structure. Simultaneously, these analyses resulted in values for the small moment of inertia of CH₃F and CD₃F and the Coriolis coupling factors for both molecular species.

II. EXPERIMENTAL PART

A. Preparations

CH₃F and CD₃F were prepared from CH₃Cl and CD₃Cl (synthesized by the method of Noether⁵) and high-grade AgF.⁶ The state of purity of the two methyl chlorides was checked by control of their infrared absorption. In addition, a mass spectrometer run on CD₃Cl showed the purity of the sample to be well over

90%. -0.0057 mole CH₃Cl (or CD₃Cl) was kept heated with 0.032 mole AgF (4.0 g) for 4 hours in a 250-ml sealed-off glass container at 225°C. After cooling, an infrared spectrum of the gaseous reaction mixture was taken which showed that about 20% of the methyl chloride (I) had not reacted. Furthermore, a small amount of a nonidentified compound (II) was detected together with a surprisingly large amount of carbon dioxide (probably originating from a reaction between the glass, the silver fluoride, and the organic compounds). The reaction mixture was analyzed on a 50-cm dry silica-gel column (internal diameter: 4 mm) and Pt-wire detector at room temperature. Peaks corresponding to CO_2 , methyl fluoride, and (I) were clearly visible. At a subsequent separation run (I) and (II) were removed quantitatively as demonstrated by the infrared spectrum. In a second separation run through the column all the CO_2 and part of the methyl fluoride was removed, which produced a final ("light" or "heavy") methyl fluoride completely free of CO₂. In spite of the somewhat wasteful separation procedure the final yield of highly purified product was 35%.

B. Spectroscopic Procedure and the Spectra

The spectra were taken on a Beckman IR 3 instrument with suitable optics (NaCl and LiF). The effective slit width and the pressure applied will be given at the top of the tables containing the experimental results. The cell length was constantly 10 cm. The absolute magnitude of our frequencies may deviate about $\frac{1}{2}$ cm⁻¹ from the true values but apart from this or other kinds of systematic errors (such as those originating from our limited resolving power) it is

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¹G. Herzberg, Infrared and Raman Spectra (D. Van Nostrand Company, Inc., New York, 1945), p. 315. ²W. H. Bennett, and C. F. Meyer, Phys. Rev. 32, 888 (1928). ³K. P. Yates, and H. H. Nielsen, Phys. Rev. 71, 349 (1947). ⁴J. Pickworth, and H. W. Thompson, Proc. Roy. Soc. (London) A222, 443 (1954).

⁵ H. D. Noether, J. Chem. Phys. 10, 664 (1942).

⁶ Andersen, Bak, and Hillebert, Acta Chem. Scand. 7, 236 (1953).

TABLE I. Observed frequencies and interpretation of the perpendicular bands ν_4 , ν_5 , and ν_6 in gaseous CH₃F. $t=30^{\circ}$ C.

か : Seff:	25 mm 1.4 cm ⁻¹	^{ν6} 113 mm 2.5 cm ⁻¹	150 mm 1.8 cm ⁻¹
$PQ_{K}\begin{cases} 9\\8\\7\\6\\5\\4\\3\\2\\1 \end{cases}$	2956.5 2964.4 2971.7 2979.2 2986.8* 2994.4 3001.8	1369.7 1382.1 1393.2 1404.7 ^a 1416.1 1427.3 1437.1 ^a 1449.0 1460.9 ^b	1149.5 1154.9 1160.4 1165.8* 1171.2 1177.0 1182.5* 1188.3 1193.8
${}^{R}Q_{K} \begin{cases} 0 \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \end{cases}$	3009.4ª 3016.9 3024.6 3032.0ª 3038.9 3046.4	1474.7 ^b 1487.4 1498.2 1509.3 ^a 1520.0 1530.7 1541.1 ^a 1552.1	1199.5 ^a 1205.2 1211.0 1216.7 ^a 1222.4 1228.0 1234.0

• Stronger than adjacent lines due to usual strong, weak, weak intensity alternation. For an alternative position of the "band origin" of ν_6 , see text and Table III. • Not the true PQ_1 and RQ_0 lines which are obscured and perturbed by the presence of the parallel band ν_2 .

believed that our "peak" frequencies are good to 0.1 cm^{-1} .

Data for the fine-structure components of the perpendicular bands are given in Tables I and II. Corresponding band-center data are summarized in Table III.

TABLE II. Observed frequencies and interpretation of the perpendicular bands ν_4 , ν_5 , and ν_6 in gaseous CD₃F. $t=30^{\circ}$ C.

p: Sett:	39 mm 1.2 cm ⁻¹	80 mm 1.7 cm ⁻¹	430 mm 1.3 cm ⁻¹
${}^{F}Q_{K} \begin{cases} 13\\12\\11\\10\\9\\8\\7\\6\\5\\4\\3\\2\\1 \end{cases}$	2220.9 2224.0 2227.1 2230.2 2233.2ª 2236.1 2239.0 2242.0ª 2245.2 2248.0 2250.9ª 2253.7 2256.5	1047.9 1053.6 1059.2 1064.3 1069.3	880.9 883.6 888.3 890.9 893.5 895.8* 898.5 900.9
${}^{R}Q_{K} \begin{cases} 0\\1\\2\\3\\4\\5\\6\\7\\8\\9\\10\\11\\12 \end{cases}$	2259.2ª 2262.1 2264.9 2267.6ª 2270.4 2273.1 2275.7ª 2278.4 2281.1 2283.8ª 2286.6 2289.3 2292.0	1075.6ª 1079.9 1085.1 1090.4ª 1095.6 1100.7	903.2 ^a 905.8 908.7 911.0 ^a 913.4 916.0 918.4 ^a 921.2 923.9 926.3

Stronger than adjacent lines due to usual strong, weak, weak intensity alternation. For an alternative position of the "band origin" of v6, see text and Table III.

The numbering of the fine-structure components was carried through following Herzberg.⁷ If the procedure was unequivocal, definite band centers would result from its use. As will be seen from Table III, the position of the band origins is somewhat in doubt for the ν_6 band (CH₃F), the ν_5 band (CD₃F), and the ν_6 band (CD₃F). This uncertainty, however, does not influence the conclusions that can be drawn with respect to rotational constants and Coriolis coupling factors.

III. ROTATIONAL CONSTANTS. FUNDAMENTAL VIBRATION FREQUENCIES AND CORIOLIS COUPLING FACTORS

Using the well-known graphical method,⁴ certain quantities can be derived which are functions of the rotational constants A and B (A > B) and the Coriolis coupling factors ζ_4 , ζ_5 , and ζ_6 (where the subscript refers to the normal vibration in question). The material has been summarized in Table IV. Double-prime quantities refer to the vibrational ground state, singleprime constants to vibrationally excited levels.

TABLE III. Fundamental vibration frequencies of CH₃F and CD₃F.

	$CH_{3}F$	$CD_{3}F$
$\nu_1(a_1)$	2964.4	2089.4
$\nu_2(a_1)$	(1464)	1135.0
$v_3(a_1)$	1046.0	987.0
$v_4(e)$	3006.1	2258.3
$v_5(e)$	1466.6	1071.1ь
$\nu_6(e)$	1197.7ª	902.6 or 910.1

* Or 1180.8 if another, almost equally probable numbering of the lines is adopted. ^b Only tentative, but supported by the occurrence of a weak || band at 2149,7 = 2×1074.8 which may have been displaced from its unperturbed position by Fermi resonance with the strong || band at 2089.4.

For CH₃F Thompson⁴ found $A'' - A_4'\zeta_4 - B'' = 3.78_6$ and $A_4' - A_4' \zeta_4 - B_4' = 3.77_6$. For the latter quantity Nielsen³ found 3.81 cm⁻¹. Our results are seen to be in good agreement with Thompson's values although deviations might have occurred since the instrument used by Thompson has much higher resolving power. Nielsen³ also studied the ν_5 band of the CH₃F spectrum. He showed that rather strong perturbing effects are present due to approximate coincidence of the band centers of a parallel band (ν_2) and a perpendicular band (ν_5) . The perturbation may, however, be neglected for high K-values. Following the procedure suggested by Nielsen we have calculated the quantities of Table IV for $\nu_5(CH_3F)$. Our data concerning the ν_6 -band of CH₃F may be compared with Bennett and Meyer's measurements.² Corresponding to our values 2.829 and 2.842 in Table IV, Bennett and Meyer² found 2.813 and 2.829. The deviations are larger than what is believed to be our limit of error. Bennett and Meyer's instrument had higher resolving power than the Beckman IR 3 we are using but it does not seem unfair to

⁷ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 430.

	24	CH ₃ F ^{µ5}	V 8
$\begin{array}{c} A_{i'} - A_{i'}\zeta_{i} - B_{i'} \\ A'' - A_{i'}\zeta_{i} - B'' \\ (A_{i'} - A'') - (B_{i'} - B'') \end{array}$	3.773 ± 0.010 3.770 ± 0.010 0.005 ± 0.020	$\begin{array}{c} 5.675 {\pm} 0.020 \\ 5.700 {\pm} 0.020 \\ -0.030 {\pm} 0.005 \end{array}$	$\begin{array}{c} 2.842 \pm 0.005 \\ 2.829 \pm 0.005 \\ 0.009 \pm 0.003 \end{array}$
$\nu_i + A_i'(1-\zeta_i)^2 - B_i'$	3009.4 ±0.5	1474.1 ±0.5	$\begin{cases} 1182.6\\ 1199.5 \\ \pm 0.5 \end{cases}$
	P4	ν5	ν6
$\begin{array}{l} A_{i}' - A_{i}'\zeta_{i} - B_{i}' \\ A'' - A_{i}'\zeta_{i} - B'' \\ (A_{i}' - A'') - (B_{i}' - B'') \end{array}$	${\begin{array}{r} 1.405 {\pm} 0.003 \\ 1.414 {\pm} 0.003 \\ -0.010 {\pm} 0.001 \end{array}}$	$\substack{2.623 \pm 0.010 \\ 2.633 \pm 0.020 \\ -0.010 \pm 0.010}$	$1.263 {\pm} 0.010 \\ 1.265 {\pm} 0.005 \\ 0.008 {\pm} 0.005$
$\nu_i + A_i'(1-\zeta_i)^2 - B_i'$	2259.4 ± 0.5	1074.7 ± 0.5	$\begin{cases} 903.4\\ 910.9 & \pm 0.5 \end{cases}$

 TABLE IV. Functions of rotational constants and Coriolis coupling factors derived from graphical representation of combination differences in cm⁻¹.

assume that the improved recording technique now available may mean a definite improvement, which, in a case like the present, might more than compensate for the somewhat lower resolving power. The rotational constants and the Coriolis coupling factors resulting from the data of Table IV were calculated as follows:

Abbreviating $A_i' - A_i'\zeta_i - B_i' = R_i'$ we get

$$\sum_{4}^{6} R_{i}' = \sum_{4}^{6} (A_{i}' - B_{i}') - \sum_{4}^{6} A_{i}' \zeta_{i}$$

Since the latter sum only constitutes about 5% of the first it is permissible to put $A_4'=A_6'=A_6'=A''$ in this part of the expression which then changes to

$$\sum_{4}^{6} R_{i}' = \sum_{4}^{6} (A_{i}' - B_{i}') - A'' \sum_{4}^{6} \zeta_{i}.$$

Shaffer⁸ has shown that $\sum_{i=1}^{6} \zeta_{i} = (B_{e}/2A_{e})$, where B_{e} and A_{e} are equilibrium rotational constants. Therefore, $A'' \sum_{i=1}^{6} \zeta_{i}$ is close to (1/2)B'', so that

$$\sum_{4}^{6} R_{i}' = \sum_{4}^{6} \left[(A_{i}' - A'') - (B_{i}' - B'') \right] + 3A'' - 3.5B'',$$

or

$$A'' = \frac{1}{3} \sum_{4}^{6} R_i - \frac{1}{3} \sum_{4}^{6} \left[(A_i' - A'') - (B_i' - B'') \right] + \frac{7}{6} B''.$$

TABLE V. Large rotational constant for the ground level (A'')and for the first vibrationally excited degenerate levels (A_i') for CH₃F and CD₃F (in cm⁻¹). Coriolis coupling factors (ζ_i) . Small moment of inertia (I_a) (in 10⁻⁴⁰ gcm²).

	CH₃F	CD₃F
	5.095 ± 0.010	2.563 ± 0.006
A_{4}'	5.099 ± 0.035	2.551 ± 0.020
A	5.075 ± 0.040	2.556 ± 0.030
$A_{\mathfrak{h}}'$	5.116 ± 0.045	2.559 ± 0.030
ζ <u>4</u>	0.093 ± 0.006	0.182 ± 0.006
ζ5	-0.286 ± 0.009	-0.293 ± 0.014
ζB	0.278 ± 0.006	0.240 ± 0.007
I_a (ground level)	5.492 ± 0.010	10.918 ± 0.025
/		

⁸ W. H. Shaffer, J. Chem. Phys. 10, 1 (1942).

This expression is equivalent with Dennison and Johnston's well-known equation,⁹ if the differences between the moments of inertia due to vibrational excitation are ignored. According to this formula for A'', this magnitude may now be computed from the data of Table IV and B'', which may be taken from microwave investigations.^{10,11} From values of A'', B'', and $(A''-A_i'\zeta_i-B'')$ from Table IV, ζ_i 's may now be calculated using $A_i' \sim A''$. Also approximate A_i' -values can be computed since $(A_i'-A_i'\zeta_i-B_i')$ is close to $(A''-A_i'\zeta_i-B'')$. Finally, the band-center frequencies follow (Table III). The results of the numerical calculations are summarized in Table V. We have taken $B''(CH_3F) = 0.85179 \text{ cm}^{-1}$ (reference 10) and $B''(CD_3F) = 0.68214 \text{ cm}^{-1}$ (reference 11).

IV. THE STRUCTURE OF CH3F AND CD3F

Table VI summarizes the data available at present for a calculation of the structure of CH_3F and CD_3F .

If we ignore the changes in distances caused by the "mild" isotopic substitution $C^{12}\rightarrow C^{13}$ sufficient data are available for a complete determination of the structure of CH₃F. In the case of CD₃F some assumption has to be made. We believe that the "mildest" procedure at present is to assume that the C,F distance is unaffected by substitution of H with D. For SiH₃Cl, Bak and collaborators¹² found that the C,Cl distance in SiH₃Cl lay between 2.0472 and 2.0486 A. In SiD₃Cl,

TABLE VI. Experimental moments of inertia (I_a, I_b) for isotopic species of methyl fluoride in amu A². $_aI$ -values are from this research, I_b -values are from microwave investigations.

 		-
$I_{a}(C^{12}H_{3}F) \\ I_{b}(C^{12}H_{3}F) \\ I_{b}(C^{13}H_{3}F) \\ I_{a}(C^{12}D_{3}F) \\ I_{b}(C^{12}D_{3}F) \\ I_{b}(C^{12}D_{3}F) $	$\begin{array}{rrrr} 3.309 & \pm 0.006 \\ 19.79488 \pm 0.00005 \\ 20.33113 \pm 0.00010 \\ 6.579 & \pm 0.012 \\ 24.71806 \pm 0.00005 \end{array}$	

⁹ D. M. Dennison and M. Johnston, Phys. Rev. 48, 868 (1935).
 ¹⁰ Gilliam, Edwards, and Gordy, Phys. Rev. 75, 1014 (1949).
 ¹¹ Johnson, Trambarulo, and Gordy, Phys. Rev. 84, 1178 (1951).

¹¹ Johnson, 1 rambarulo, and Gordy, Phys. Rev. **34**, 1178 (1951). ¹² Bak, Bruhn, and Rastrup-Andersen, Acta Chem. Scand. **8**, 367 (1954).

	${}_{\mathrm{CD}}^{\mathrm{CH}}$ distance	CF distance	$ { HCH \\ DCD } angle $
CH₃F	$1.106_0 \pm 0.001$	$1.3852_7 \pm 0.00005$	109°59′±3′
CD₃F	$1.101_4 \pm 0.001$ $1.100_7 \pm 0.001$	1.38527 (assumed) 1.38627 (assumed)	110°14′±3′ 110°21′±3′

TABLE VII. Structural parameters for CH₃F and CD₃F. Distances in A units

TABLE VIII. Pairs of data (1-6) used in order to get functional relationship between $r_{\rm CH}$ ($r_{\rm CD}$), respectively, $\angle HCH(\angle DCD)$ and $r_{\rm CF}$ in the 1.380–1.400 Å region.

$1 { I_{a}(C^{12}H_{3}F) \ I_{b}(C^{12}H_{3}F) }$	3.309 amu A ² 19.79488
$2 iggl\{ I_a({ m C}^{12}{ m H}_3{ m F}) \ I_b({ m C}^{13}{ m H}_3{ m F})$	3.309 20.33113
$3 \begin{cases} I_{a}(C^{12}H_{3}F) \\ I_{b}(C^{12}D_{3}F) \end{cases}$	3.309 24.71806
$4 \begin{cases} I_{a}(\rm C^{12}D_{3}F) \\ I_{b}(\rm C^{12}H_{3}F) \end{cases}$	6.579 19.794.88
$5 \begin{cases} I_{a}(C^{12}D_{3}F) \\ I_{b}(C^{13}H_{3}F) \end{cases}$	6.579 20.33113
$6 \begin{cases} I_a(C^{12}D_3F) \\ I_b(C^{12}D_3F) \end{cases}$	6.579 24.71806

it was found to be between 2.0479 and 2.0493 A. The geometry of CD₃F was therefore first calculated using the same C,F distance as found in CH₃F. In addition, it was calculated using a 0.001 A higher value. The results of our calculations are given in Table VII.

If one takes the position that it is not permissible to mix data from isotopic species (as just done) because of differences in the interaction between vibration and rotation, the following procedure may be applied. With improved electron-diffraction technique, Brockway et al.¹³ found that the C,F distance in CH₃F is 1.386-1.396 A. If this information is combined with I_a (from infrared data) and I_b (from microwave data) for CH₃F we obtain a C,H distance equal to 1.105-1.093 A. The angle HCH becomes 110°6'-111°49'. For these quantities Brockway measured 1.105-1.085 A and 107°30'-111°30'. Obviously the spectroscopic data means a *narrowing* of the uncertainty interval, making it safe to conclude that the C,H distance in CH₃F is longer than in CH₄ and that the angle HCH is larger than the tetrahedral. The estimate (made by Townes and collaborators¹⁴) that the C,H distance in CH₃Cl,

 $CH_{3}Br$, and $CH_{3}I$ is everywhere equal to 1.113 A, seems to be somewhat high.

A third line of attack would be to combine infrared and microwave data from all isotopic species in as many ways as possible. This can be done, for example, by choosing pairs of data (1-6) as shown in Table VIII and calculating the geometrical parameters for a series of assumed C,F distances, here chosen in the 1.380-1.400 A interval. Each pair yields two curves, giving, respectively, $\angle \varphi = 180^{\circ} - \angle$ HCF, and the C,H distance, as functions of the C,F distance (see Fig. 1). In this approximation



one cannot distinguish between C,H and C,D distances, or between HCF and DCF angles. Drawing of these curves reveals an "area of intersection" in the middle of both graphs. The "center of gravity" of the areas of intersection lies in both graphs at a C,F distance equal to 1.390 A. The areas extend to the limits 1.104-1.095 A in the C,H(C,D) distance and $71^{\circ}40'-72^{\circ}10'$ in the φ angle, or $110^{\circ}36'-111^{\circ}4'$ in the HCH angle $\left[\sin\frac{1}{2}(\angle \text{HCH})\right]$ $=(\sqrt{3}/2)\sin\varphi$. As seen, a prolongation of the C,H distance and an enlargement of the HCH angle as compared with methane is again established.

 ¹³ Brockway, Thornton, and Bartell, as cited in Ann. Rev. Phys. Chem. 5 (Annual Reviews, Inc. Stanford, California, 1954), p. 397.
 ¹⁴ Miller, Aamodt, Dousmanis, Townes, and Kraitchman, J. Chem. Phys. 20, 1112 (1952).