RotationVibration Spectra of Diatomic and Simple Polyatomic Molecules with Long Absorbing Paths. I. The Spectrum of Fluoroform (CHF3) from 2.4 to 0.7

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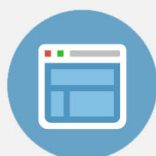
temperature when

$$W = -2kT$$

or

$$q = \frac{4}{N_S},$$

then

$$N_{n-1} = N_S.$$

In other words, the sorption in the next layer below the outer layer is complete when the top layer is half-covered, as would be expected when the hydration of a crystal proceeds in steps. It would appear, then, that the physical fact which distinguishes between sorption of the types represented by the Langmuir, BET, or other equations and hydrate formation is the interaction energy between the sorbed molecules.

When the sorbed molecules are so far apart that no or insufficient interaction energy exists, no region of increase of water sorbed at constant vapor pressure can exist, no separation of the solid into two phases will occur; on the other hand, a gradual increase of the amount sorbed with increase of vapor pressure will be observed.

Application of the equations contained in this paper to new data on the sorption of water by certain high polymers will be carried out at a later date. The work given here is part of a general program of study of the thermodynamics of high polymers for which grants have been gratefully received from the du Pont Corporation, the Research Corporation,[11] the Richardson Company, and the Visking Corporation.

Rotation-Vibration Spectra of Diatomic and Simple Polyatomic Molecules with Long Absorbing Paths.

I. The Spectrum of Fluoroform (CHF₃) from 2.4μ to 0.7μ

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The spectrum of fluoroform has been investigated under high resolution (21-ft. grating) in the photographic infra-red with an absorbing path of up to 60 meters, obtained by multiple reflection according to the method of J. U. White. In addition, with the same path length the spectrum from 1.2 to 2.4μ was obtained under low resolution with a photoelectric infra-red spectrometer. A large number of overtone and combination bands, 47 in all, were found. Two parallel bands in the photographic region were well resolved and analyzed, yielding, for the moment of inertia about an axis perpendicular to the symmetry axis,

$$I_B^{[0]} = 81.08 \times 10^{-40} \text{ g cm}^2$$

From this value, assuming tetrahedral angles and a C−H distance as in methane, the C−F distance in fluoroform is found to be 1.329A, a value that is appreciably lower than that found in methyl fluoride, 1.380A. A provisional vibrational assignment of all the bands is given.

A. INTRODUCTION

THE investigation of the rotation-vibration spectra of diatomic and polyatomic molecules in the photographic infra-red by means of large diffraction gratings makes possible a determination of molecular constants (moments of inertia, internuclear distances, etc.) of very high

precision. Indeed it was only during the last year that this precision has been surpassed by the data obtained from microwave-absorption spectra. The microwave technique is applicable only to a certain group of molecules and to certain molecular constants. Therefore, it remains imperative to continue the study of photographic infra-red spectra. It appears that there are still a number of diatomic and simple poly-

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atomic molecules which ought to be studied in the photographic region, and others for which the information available at present could be greatly extended with improved technique. The present series of investigations is directed at this aim.

The study of molecular absorption spectra in the photographic infra-red entails the use of long absorbing paths. Particularly long paths are required for molecules not containing hydrogen, since their vibrational frequencies are small and therefore only rather high overtones fall into the photographic region. Indeed up to now only for one molecule of this type (CO_2) have photographic infra-red spectra been obtained.[1]

In most infra-red work interest is centered on the fundamentals, and only comparatively short path lengths are used. If long paths are used many overtone and combination bands may be expected in the near infra-red as well as in the photographic region. It seems important to locate as many of these overtone and combination bands as possible in order to obtain a reliable representation of all the vibrational levels of the molecule under consideration and in order to study its potential function. Toward this end, in the present series low dispersion spectra up to 2.4μ have been taken with the same long path as for the photographic high resolution spectra. It

is hoped that later on it will be possible to study also this spectral region with much higher resolution.

A precise knowledge of the higher vibrational levels, as well as of the rotational constants, is not only of interest in the study of molecular structure, but also for the purpose of calculating thermodynamic functions particularly at higher temperatures. This need gives added stimulus to the investigations of infra-red spectra with long absorbing paths.

The present first paper in this series gives the results of the investigation of the spectrum of fluoroform. Spectra of ketene and carbon dioxide have already been taken and are being evaluated. The study of other molecules is being prepared.

B. EXPERIMENTAL

A long absorbing path was obtained by multiple reflection in a comparatively short tube according to the ingenious method suggested by White,[2] with slight modifications. Figure 1 shows the optical arrangement. Three concave mirrors of equal radius of curvature are used. Two of these, A and B, which were cut from one circular mirror as shown in Fig. 1b, are mounted at one end of the tube while the third, C, of a shape indicated in Fig. 1c, is mounted at the other end at a distance equal to the radius of curvature.
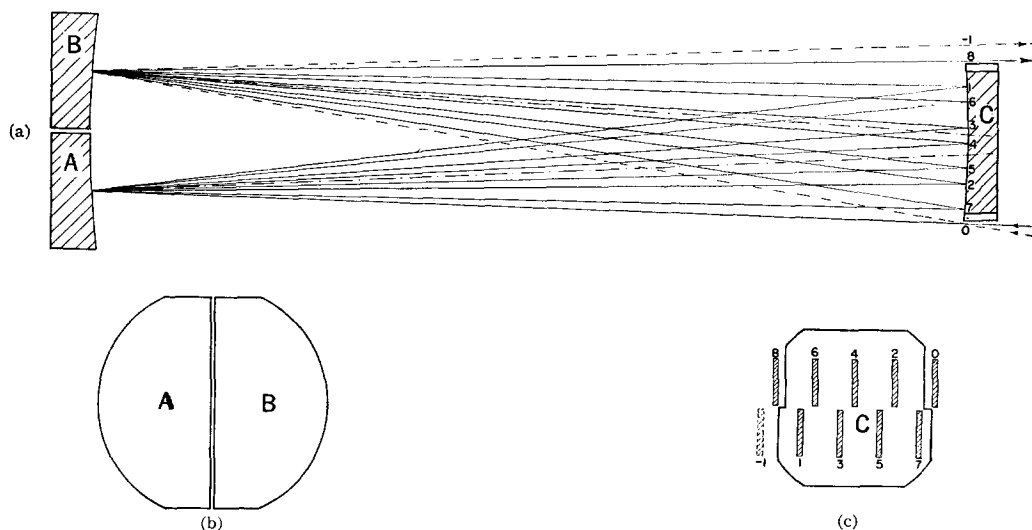

FIG. 1. Optical arrangement for obtaining a long absorbing path.

[1] In the spectrum of Venus by Adams and Dunham [Astron. Soc. Pac. **44**, 423 (1932)] in the laboratory by Herzberg and Verleger [Phys. Rev. **48**, 706 (1935)].
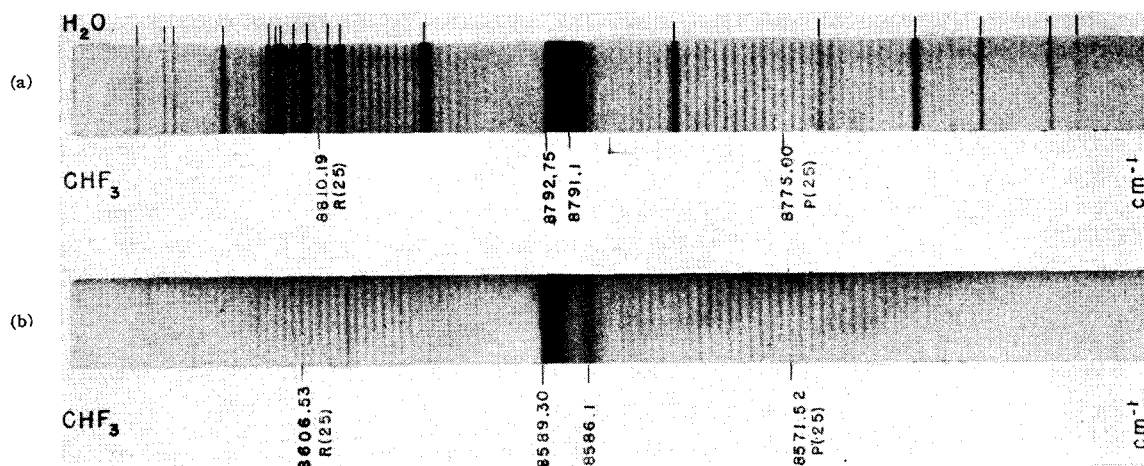[2] J. U. White, J. Opt. Soc. Am. **32**, 285 (1942).

FIG. 2. Spectrogram of the CHF$_3$ bands at (a) 1.1370μ and (b) 1.1639μ.

Light from an automobile headlight bulb is focused on an entrance slit at 0 in Fig. 1a and c. From there the light falls on the two mirrors, A and B, which form images of the slit at 1 and -1, respectively. The image -1 is discarded but is very useful in the adjusting procedure. The mirror C is so adjusted that the light from A received at 1 is reflected to B. With proper adjustment A is imaged on B and no light is lost except by reflection losses. The mirror B then forms an image of 1 at 2, whereupon the light is reflected to A, and so on, until the light emerges at 8 after having traversed the space between the mirrors 16 times. By turning mirror A by small amounts about an axis perpendicular to the plane of the paper of Fig. 1a, the number of images on mirror C, that is, the number of traversals, can be readily changed. In order to accommodate as many images as possible on mirror C and for the purpose of simplifying the adjustment, the even and odd images are separated (by the proper adjustment of mirrors A and B) as shown in Fig. 1c. This diagram also makes it clear why the mirror C has been indented at the top half as shown. The separation of the axes (dot-dash lines) of the two mirrors A and B at C is half the separation of successive odd (or even) images. It is not necessary to have the odd images halfway between the even ones. In fact if the adjustment is made by turning mirror A only, such a symmetrical arrangement of the images will obtain only for a certain number of images depending on the orientation of mirror B.

Thus far two long paths as just described have been set up: a small one in a glass tube of 50 mm diameter, and with 150 cm radius of curvature of the mirrors, and a large one in a galvanized iron pipe of 10 inches diameter and with mirrors of 22 m radius of curvature. With the small tube up to 40 traversals have been obtained, with the large one up to 144 traversals. The resulting path lengths are 60 m and 3168 m, respectively. The limit is set only by the reflection losses and by the number of images that can be accommodated on mirror C. The spectrum of fluoroform has been taken entirely with the small absorption tube, since not enough of the gas was available for the large one.

The photographic infra-red spectra were taken in the first order of a 21-ft. grating ruled by R. W. Wood. This grating has an excellent concentration in the first order of 11,000A and is thus particularly suitable for work with the Eastman I-Z plates. The grating is mounted in a Eagle mounting. A region of 2500A in first order can be covered in one exposure. The dispersion is 2.5 A/mm. While below 9000A the exposure times (on I-N plates) were of the order of a few minutes for 20 traversals, at 11,000A the exposure times were of the order of 24 hours.

Spectra in the region from 1 to 2.4μ were taken with the new infra-red spectrometer built by Dr. G. P. Kuiper for work with the McDonald

telescope.[3] In it a photo-conductive cell is used as the receiving element. The resolving power is 800. The spectrum is recorded on an Esterline-Angus recorder. Depending on the speed of recording, the dispersion on the record varies from 20 to 100 A/mm.

The fluoroform was obtained through the kindness of Dr. A. F. Benning from the Jackson Laboratory of E. I. du Pont de Nemours and Company. It was specified as "practically pure". Pressures up to 1 atmos. were used for the weaker bands. However, for a satisfactory resolution of the fine structure of the intense bands the use of a lower pressure (about $\frac{1}{5}$ atmos.) proved of great advantage, since the pressure broadening is much reduced at these lower pressures.

C. ROTATIONAL ANALYSIS

A considerable number of photographic infra-red bands were found (see below) but only two of these, at 1.1639μ and 1.1370μ, were sufficiently strong so that their fine structures could be measured. In Fig. 2 spectrograms of these two bands are reproduced as obtained at a pressure of 12 cm and a path length of 18 meters. Both bands consist of a strong central Q branch with a sharp edge at the long wave-length side and a P and R branch on either side of it. In addition, in each band a secondary Q branch occurs which is obviously caused by a difference band forming the $1-1$ band of a sequence starting with the main band (see below). The band 1.1370μ is partially overlapped by the water band at 1.135μ.

The fluoroform molecule is an oblate symmetric top with the figure axis in the direction of the $C-H$ bond. There are parallel and perpendicular bands (with $\Delta K=0$ and ± 1, respectively). There can be no question that the two bands reproduced in Fig. 2 are parallel bands, since the central branch has a sharp edge and since there is only one P and one R branch in each band. To be sure, on account of the comparatively small difference between the moments of inertia I_B and I_C, the Q branches of the sub-bands of a perpendicular band will also form a fairly pronounced central branch; but it will not have a sharp edge, and the P and R branches of different sub-bands will not form apparently

single branches of the whole band as they do for parallel bands. It should be emphasized that, on account of the variation of the rotational constants B and C with the vibrational quantum numbers, parallel bands in the photographic region do not necessarily have this simple structure. Only when the effective moments of inertia differ very slightly in the upper and lower states, can such a simple structure be expected.[4] In the

TABLE I. Wave numbers of the band lines.

	Band at 1.1639μ $\nu_{\mathrm{head}}(Q)=8589.30$		Band at 1.1370μ $\nu_{\mathrm{head}}(Q)=8792.75$	
J	$P(J)$	$R(J)$	$P(J)$	$R(J)$
4		8592.72		8796.12
5		93.33		96.73
6	8585.00	93.97	8788.52	97.42
7	84.37	94.66	87.86	98.18
8	83.64	95.35	87.16	98.84
9	82.94	96.02	86.41	8799.52
10	82.24	96.64	85.72	8800.18
11	81.52	97.31	85.03	00.90
12	80.79	98.08	84.32	01.54
13	80.10	98.76	83.60	02.14*
14	79.45	8599.43	82.91	02.84
15	78.79	8600.07	82.22	03.52
16	78.02	00.73	81.50	04.20
17	77.28	01.38	80.78	04.86
18	76.60	02.06	80.09	05.53
19	75.86	02.68	79.33	06.15
20	75.13	03.30	78.62	06.83
21	74.38	03.98	77.88	07.48
22	73.69	04.64	77.15	08.15
23	72.97	05.29	76.46	08.78
24	72.26	05.94	75.73	09.38*
25	71.52	06.53	75.00	10.09
26	70.79	07.18	74.27	10.74
27	70.02	07.81	73.56	11.43
28	69.31	08.46	72.79	12.00*
29	68.56	09.06	72.18*	— *
30	67.78	09.70	71.40*	13.38*
31	67.06	10.32	70.60	13.95*
32	66.31	10.90	69.86	14.48
33	65.52	11.50	69.12	15.14
34	64.79	12.16	68.34	15.78
35	64.06	12.73	67.63	16.39
36	63.28	13.37	66.86	16.98
37	62.54	13.97	66.08	
38	61.73	14.54	65.37	
39	60.98	15.10	64.59	
40	60.20	15.74	63.89	
41	59.46	16.29	63.13	
42	58.71	16.91	62.23	
43	57.92		61.58	
44	57.11		60.76	
45	56.40		60.10*	
46			59.33	
47			58.55	
48			57.68	
49			56.96	
50			56.20	

* An asterisk indicates overlapping by H_2O lines.

[3] G. P. Kuiper, W. Wilson, and R. J. Cashman, Astrophys. J. **106**, 243 (1947).

[4] See. G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (in future referred to as *I.R.S.*), (D. Van Nostrand Company, Inc., New York, 1945), p. 418.

present case this condition is fulfilled since the vibration of the H atom which is mainly involved (see Section D) changes the moment of inertia but slightly.

In Table I the wave numbers of the lines of the P and R branches, as well as those of the Q heads of the two bands, are given. The numbering of the lines was readily obtained since the head of the Q branch gives very nearly the position of the band origin.

Table II gives the combination differences $\Delta_2 F''(J) = R(J-1) - P(J+1)$ for the two bands. They agree for each J value within the accuracy of the measurements. It should be mentioned however, that an almost equally good agreement is obtained if the numbering in both bands is shifted by one unit. The reason for this insensi-

tivity of the agreement of the combination differences to the numbering is due to the fact that the rotational constants B' in the upper states of the two bands are almost the same. It appears, however, practically certain that the numbering as obtained from the positions of the Q branches is correct. If the effect of centrifugal distortion is included[5] the rotational term values are given by

$$F(J, K) = BJ(J+1) + (C-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4,$$

where

$$B = \frac{h}{8\pi^2 c I_B} \quad \text{and} \quad C = \frac{h}{8\pi^2 c I_C}$$

and D_J, D_{JK}, and D_K are very much smaller than B and C. From this formula it follows immediately that

$$\Delta_2 F(J) = F(J+1, K) - F(J-1, K)$$
$$= (4B - 6D_J - 4D_{JK}K^2)(J+\tfrac{1}{2})$$
$$- 8D_J(J+\tfrac{1}{2})^3.$$

If the effect of centrifugal distortion is neglected $\Delta_2 F(J)/(J+\tfrac{1}{2})$ would be a constant, $4B$. Actually, as shown by Fig. 3, the observed $\Delta_2 F''(J)/(J+\tfrac{1}{2})$ values show a slight decrease with $(J+\tfrac{1}{2})^2$ indicating the effect of the term $8D_J(J+\tfrac{1}{2})^2$. From the slope of the straight line in Fig. 3 one obtains $D_J'' = 3_8 \times 10^{-7}$ cm^{-1} while the intercept on the ordinate axis gives $4B'' - 6D_J'' - 4D_{JK}''K^2 = 1.3806_4$ cm^{-1}. The term $-6D_J'' - 4D_{JK}''K^2$ may be neglected in view of the magnitude of D_J'' and the consideration that D_{JK}'' would be expected to be of the same order as D_J''. Thus we have

$$B_{[0]}'' = 0.3451_6 \text{ cm}^{-1}.$$

The rotational constants B' for the upper states can be more accurately determined from the $B' - B''$ values obtained by plotting $R(J-1) + P(J)$ against J^2. The same plots also give the band origins ν_0. The resulting B' and ν_0 values are given together with the other rotational constants in Table III. The band origins ν_0 agree very well with the positions of the Q heads given in Table I. The latter contain, of course, the error inherent in measurements of band heads.

It may be mentioned that the $R(J-1) + P(J)$ versus J^2 curves show a slight curvature at high

TABLE II. Combination differences.

J	$\Delta_2 F''(J)$ from 1.1370μ band	$\Delta_2 F''(J)$ from 1.1639μ band	$\Delta_2 F''(J)$ mean
5	7.60	7.72	7.66
6	8.87	8.96	8.92
7	10.26	10.33	10.29
8	11.77	11.72	11.75
9	13.12	13.11	13.12
10	14.49	14.50	14.50
11	15.86	15.85	15.86
12	17.30	17.21	17.26
13	18.63	18.63	18.63
14	(19.92)	19.97	19.97
15	21.34	21.41	21.38
16	22.74	22.79	22.77
17	24.11	24.13	24.12
18	25.53	25.52	25.53
19	26.91	26.93	26.92
20	28.25	28.30	28.28
21	29.68	29.61	29.65
22	31.02	31.01	31.02
23	32.42	32.38	32.40
24	33.78	33.77	33.78
25	(35.11)	35.15	35.15
26	36.53	36.51	36.52
27	37.95	37.87	37.91
28	(39.25)	39.25	39.25
29	(40.60)	40.68	40.68
30	—	42.00	42.00
31	(43.52)	43.39	43.39
32	(44.83)	44.80	44.80
33	46.14	46.11	46.13
34	47.51	47.44	47.48
35	48.92	48.88	48.90
36	50.31	50.19	50.25
37	51.61	51.64	51.63
38		52.99	52.99
39		54.34	54.34
40		55.64	55.64
		57.03	57.03
		58.37	58.37
		59.80	59.80

Values in brackets are from blended lines (* in Table I) and have not been used in forming the mean.

[5] See G. Herzberg, *I.R.S.*, p. 26.
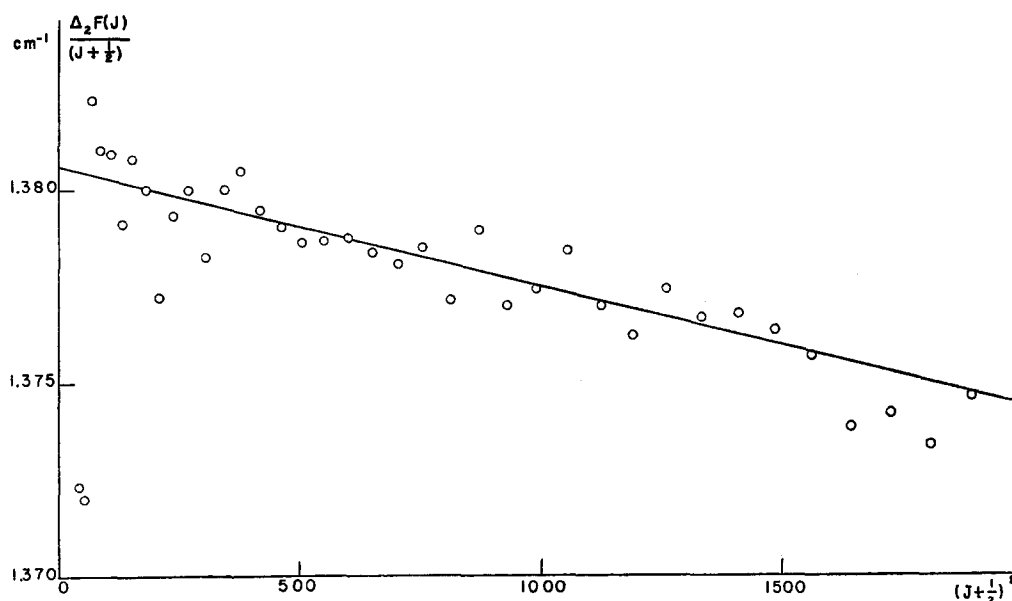
FIG. 3. Combination differences $\Delta_2 F''(J)/(J+\frac{1}{2})$.

J values. This is due to the fact that each "line" is actually a superposition of $J+1$ lines corresponding to $K=0$, 1, 2, $\cdots J$ which spread out more and more to longer wave-lengths as J increases. Therefore in determining $B'-B''$ from the slope of these lines only the first part of these lines up to $J \doteq 30$ was used.

The rotational constants B depend on the vibrational quantum numbers v_i according to

$$B_{[v]} = B_e - \sum \alpha_i(v_i + d_i/2),$$

where $d_i = 1$ or 2 depending on whether the vibration v_i is non-degenerate or doubly degenerate. According to the vibrational analysis in Section D, the two photographic bands 1.1370μ and 1.1639μ are $3v_1$ and $2v_1 + 2v_4$, respectively. Therefore the $B'-B''$ value of the former gives $3\alpha_1$ while that of the latter gives $2\alpha_1 + 2\alpha_4$. In this way one obtains $\alpha_1 = 0.00025$ and $\alpha_4 = 0.00021$. Since the other α_i's have not been determined, it is not possible to obtain B_e, the rotational constant for the equilibrium position.

The $B_{[0]}$ value determined above gives the effective moment of inertia in the lowest vibrational level. One obtains, using Birge's[6] conversion factor 27.9865×10^{-40},

$$I_B^{[0]} = 81.08 \times 10^{-40} \text{ g cm}^2.$$

[6] R. T. Birge, Rev. Mod. Phys. 13, 233 (1941).

On account of the effect of Coriolis interaction a determination of the second moment of inertia $I_C^{[0]}$ would require the rotational analysis not only of one but of all three perpendicular fundamentals or of a perpendicular vibration in the Raman effect. Since such analyses have not been carried out, one must be satisfied with the determination of one unknown internuclear distance from $I_B^{[0]}$, assuming plausible values for the others.

It appears very probable that the $C-H$ distance in CHF_3 is closely the same as in methane, that is

$$r(C-H) = 1.0936 \times 10^{-8} \text{ cm}.$$

But even if a value as found in ethylene (1.071) or acetylene (1.0597) would be assumed, the following conclusions would be substantially unaltered. More critical is the assumption made

TABLE III. Rotational constants of CHF_3.

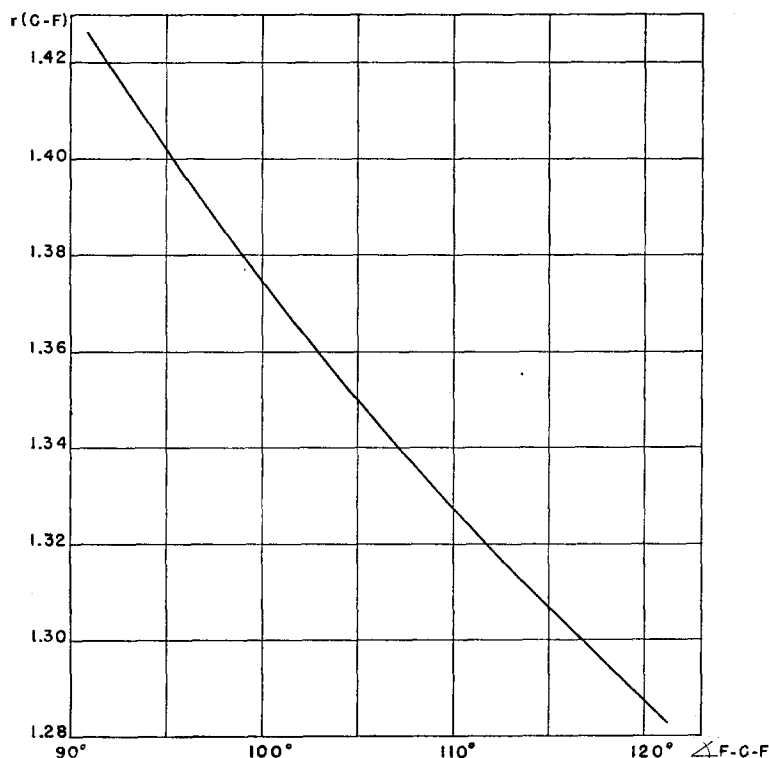|	
$B_{[0]}$	0.3451_6 cm^{-1}
$B_{[v]}$ for $2v_1 + 2v_4$	0.3442_3 cm^{-1}
$B_{[v]}$ for $3v_1$	0.3444_0 cm^{-1}
α_1	0.00025 cm^{-1}
α_4	0.00021 cm^{-1}
D_J	$3_8 \times 10^{-7}$ cm^{-1}
v_0 for $2v_1 + 2v_4$	8589.28 cm^{-1}
v_0 for $3v_1$	8792.70 cm^{-1}
$I_B^{[0]}$	81.08×10^{-40} g cm^2
$I_C^{[0]}$ } calculated assuming tetrahedral	{ 148.67×10^{-40} g cm^2
$C_{[0]}$ } angles	{ 0.1882_5 cm^{-1}

FIG. 4. Variation of the $C-F$, distance for various assumptions about the F-C-F angle, compatible with the observed moment of inertia $I_B^{[0]}$.

for the F-C-F angle. If one assumes a tetrahedral angle the $C-F$ distance remains the only unknown, and one obtains

$$r(C-F) = 1.329 \times 10^{-8} \text{ cm.}$$

For other values of the F-C-F valence angle Fig. 4 gives the corresponding $r(C-F)$ values. It is seen that for F-C-F angles larger than the tetrahedral angle the $r(C-F)$ distance is smaller than the value given above.

It is interesting to compare the $C-F$ distance in fluoroform with that in other related molecules. This is done in Table IV where both spectroscopic and electron-diffraction data are summarized. While the electron-diffraction values are rather larger than the spectroscopic values in all cases where both are available, for either set the $C-F$ distance in CH_3F is appreciably larger than in the molecules containing more than one fluorine atom. Of course by a proper choice of the F-C-F angle in CHF_3 it would be possible to obtain from the above $I_B^{[0]}$ value a $C-F$ distance equal to that in CH_3F. However, the angle would have to be as low as 99°, which seems highly improbable.

An unambiguous determination of the $C-F$ distance as well as the F-C-F angle will be possible once the moment of inertia I_B of "heavy" fluoroform (CDF_3) has been determined from its parallel bands.

The $C-F$ distance given above and the assumption of tetrahedral angles may be used to calculate the moment of inertia $I_C^{[0]}$ about the symmetry axis as well as the rotational constant $C_{[0]}$. The values obtained are included in Table

TABLE IV. C-F distances in different molecules.

| | C-F distance (in 10^{-8} cm) | | F-C-F-angle |
	from spectrum	from electron diffraction	
CH_3F	1.380[a]	1.42[c]	
CH_2F_2	1.320[b]	1.36[c]	106°50'[b]
CHF_3	1.329		109°28' (assumed)
CF_4		1.36[c]	109°28' (assumed)
CF_3CH_3		1.37[d]	107°32'

[a] Derived from the $B_{[0]}$ value given in a recent paper by Yates and Nielsen [Phys. Rev. **71**, 349 (1947)] assuming an H-C-H angle of 111°48' (see G. Herzberg, *I.R.S.*, p. 439). The large deviation from the value given by Herzberg is due to the large change of Yates and Nielsen's $B_{[0]}$ as compared to the earlier one of Bennet and Meyer [Phys. Rev. **32**, 888 (1928)].
[b] From a paper presented by W. H. Shaffer and H. Stewart at the Symposium on Molecular Structure and Spectroscopy at Ohio State University, June 1947.
[c] L. O. Brockway, J. Phys. Chem. **41**, 185 (1937).
[d] W. Shand and R. A. Spurr, quoted in H. Russell, Jr., D. R. V. Golding, and D. M. Yost, J. Am. Chem. Soc. **66**, 16 (1944).

TABLE V. Fundamental frequencies of gaseous CHF_3 after Price.*

Assignment	Infra-red band
$\nu_1^{CH}(a_1)$	3035.6 (s.)
$\nu_2^{CF}(a_1)$	1209 (m.)
$\nu_3(a_1)$	703.2 (m.)
$\nu_4^{CF}(e)$	1351.5 (s.)
$\nu_5^{CH}(e)$	1152.4 (v.s.)
$\nu_6(e)$	509.4
	cm^{-1}

* Note added in proof: New measurements by Price in the long wave-length region seem to indicate that the two low frequency fundamentals ν_3 and ν_6 have to be exchanged since the band at 509.4 cm^{-1} has the appearance of a parallel band while the band at 703.2 cm^{-1} has an indifferent appearance.

III. However, it must be remembered that these values are not a direct consequence of the measured wave numbers as are $I_B^{[0]}$, $B_{[0]}$, and the other constants of Table III.

D. VIBRATIONAL STRUCTURE

The Raman spectrum of fluoroform in the liquid phase has been studied by Glockler and Edgell.[7] The infra-red spectrum of the gas in the region of the fundamentals has been investigated by Price.[8] There is an appreciable shift of the fundamental frequencies in going from the gas to the liquid. Therefore, for the interpretation of the overtone and combination bands found here in the gas, we use the fundamentals determined by Price as given in Table V. The designation is that used by Herzberg.[9] There are three totally symmetric fundamentals (a_1) and three degenerate fundamentals (e).

In addition to the two photographic bands whose fine structure has been analyzed (Section C), a considerable number of fainter photographic bands were previously found by Mackay[10] and have been confirmed in the present work. They extend as far as 7000A. Furthermore, many strong bands were found in the region from 2.4μ to 1.2μ with the photoelectric infra-red spectrometer referred to in Section B. Figure 5 reproduces one of the recordings obtained. The wave numbers of all the observed overtone and combination bands are given in Table VI. The wave numbers measured with the infra-red instrument (marked I. in the second column) are accurate to about ± 5 cm^{-1}; those measured in the photographic region (marked P.I.) are accurate to less than 1 cm^{-1} except in the case of very diffuse bands.

The dispersion of the photoelectric spectrometer is not sufficient to distinguish parallel and perpendicular bands. But even with the high resolution possible in the photographic infra-red it is often difficult to decide whether a given weak band is a parallel or a perpendicular band. If the band has a very broad central branch without a head it is fairly certain that it is a perpendicular band. In one case of such a band, at 10154.6 cm^{-1}, the Q branches of the sub-bands forming this central branch were partially resolved into a series which even showed an indication of the proper intensity alternation (strong, weak, weak, strong) so that its identification as a perpendicular band is beyond doubt. The completely resolved parallel bands, 8589 and 8793 cm^{-1} (Fig. 2), have a sharp edge of their central branches since B' is somewhat smaller than B''. Other bands showing such heads, even
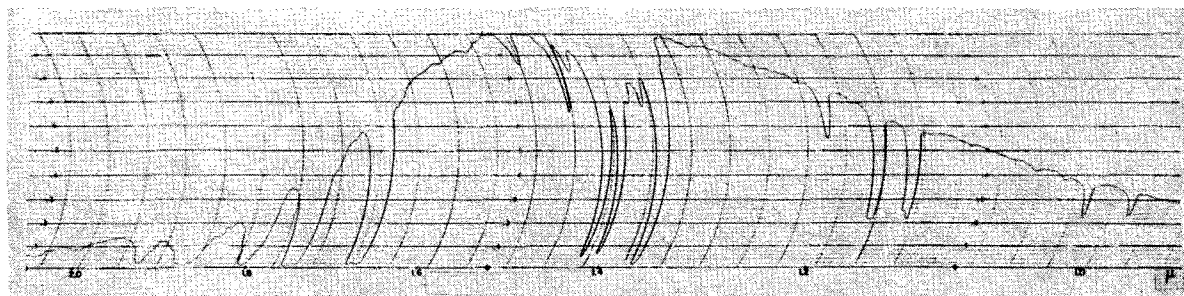
FIG. 5. Infra-red spectrum of CHF_3 obtained with the photoelectric infra-red spectrometer.

[7] G. Glockler and W. F. Edgell, J. Chem. Phys. 9, 224 (1941).
[8] W. C. Price, unpublished.
[9] G. Herzberg, I.R.S., p. 316.
[10] A. E. Mackay, Master's thesis, University of Saskatchewan, 1942.

TABLE VI. Overtone and combination bands of CHF$_3$.

ν_{vac}, observed (cm^{-1})	Band type[a]	Assignment[b]	ν_{vac}, calculated[g] (cm^{-1})
4340	v.s. I. $\perp$[c]	$\nu_1+\nu_4(E)$	4387
4540	v.w. I.	$3\nu_4+\nu_6(A_1+3E)$	4580
4685	v.w. I.	$\left.\right\}\nu_1+\nu_5+\nu_6(A_1+E)$	4702
4715	v.w. I.		
4770	v.w. I.	$\nu_1+\nu_2+\nu_6(E)$	4759
4872	v.w. I.	$\nu_1+\nu_4+\nu_6(A_1+E)$	4901
5047	v.w. I.	$\nu_1+\nu_3+\nu_4(E)$	5087
5186	m. I.	$\nu_1+2\nu_4-\nu_6[A_1+2E]$	5185
5330	s. I.	$\nu_1+2\nu_5(A_1+E)$	5340
5530	s. I.	$\nu_1+\nu_4+\nu_5(A_1+E)$	5539
5699	v.s. I. (doublet)	$\left.\right\}\nu_1+2\nu_4(A_1+E)$	see text
5728	v.s. I.		
5938	v.s. I.	$\nu_1+\nu_2+\nu_5+\nu_6(A_1+E)?$	5911
5978	v.s. I. (doublet)	$2\nu_1(A_1)$	see text
6290	v.w. I.	$\nu_1+\nu_2+\nu_3+\nu_4(E)$	6296
6435	v.w. I.	$2\nu_1+\nu_6(E)$	6492
6664	w. I.	$2\nu_1+\nu_3(A_1)$	6678
6853	m. I.	$\nu_1+2\nu_4+\nu_5(A_1+2E)$	6851
6906	w. I.	$\nu_1+2\nu_4+\nu_2(A_1+E)$	6908
7023	s. I.	$\nu_1+3\nu_4(A_1+E)$	7050
7100	s. I.	$2\nu_1+\nu_6(E)$	7130
7318	v.s. I.	$2\nu_1+\nu_4(E)$	7329
8135	v.w. I.	$2\nu_1+\nu_3+\nu_4(E)$	8029
8270	m. I.	$2\nu_1+2\nu_5(A_1+E)$	8283
8551.0	v.w. P.I.	$2\nu_1+2\nu_4(E)$	see text
8589.30	m. P.I. ‖ head	$2\nu_1+2\nu_4(A_1)$	
8586.1	w. P.I. ‖ head	$2\nu_1+2\nu_4+\nu_6-\nu_6$	see text
8791.1	w. P.I. ‖ head	$3\nu_1+\nu_6-\nu_6$	
8792.75	m. P.I. ‖ head	$3\nu_1(A_1)$	see text
9540	v.w. I.	$3\nu_1+\nu_3(A_1)$	9493
9730.0	v.w. P.I. $\perp$	$2\nu_1+2\nu_4+\nu_6(A_1+2E)$	9742
9881.6	w. P.I.[d]	$2\nu_1+3\nu_4(A_1+E)$	9941
9938.3	v.w. P.I. $\perp$	$3\nu_1+\nu_6(E)$	9945
10154.6	w. P.I.[e] $\perp$	$3\nu_1+\nu_4(E)$	10144
11109.2	v.w. P.I. line	$3\nu_1+2\nu_5(A_1+E)$	11098
11279.1	v.w. P.I. $\perp$	$\left.\right\}3\nu_1+\nu_4+\nu_5(A_1+E)$	11297
11300.2	v.w. P.I. line		
11346.2	v.w. P.I. line	$3\nu_1+2\nu_4+\nu_6-\nu_6[2A_1+4E]$	
11347.2	w. P.I.[f] line	$\left.\right\}3\nu_1+2\nu_4(A_1+E)$	see text
11497.0	v.w. P.I. $\perp$?		
11555.5	v.w. P.I. ‖ head	$4\nu_1+\nu_3-\nu_3[A_1+E]$	
11559.2	v.w. P.I. ‖ head	$4\nu_1+\nu_6-\nu_6[A_1+E]$	
11563.4	w. P.I. ‖ head	$4\nu_1(A_1)$	see text
12620.1	v.w. P.I. $\perp$	$\left.\right\}3\nu_1+3\nu_4(A_1+E)$	12699
12641.5	v.w. P.I. line		
14002.8	v.w. P.I. line	$\left.\right\}4\nu_1+2\nu_4(A_1+E)$	see text
14037	v.w. P.I. $\perp$?		

[a] The intensities are indicated by v.s., s., m., w., and v.w. meaning very strong, strong, medium, weak, and very weak, respectively. I. and P.I. indicate bands measured with the photoelectric infra-red spectrometer and with the 21-ft. grating in the photographic region, respectively. ‖ and $\perp$ refer to bands that have been identified as parallel or perpendicular bands. Bands marked with "line" have a line-like but diffuse central branch whose center was measured. They may be either parallel or perpendicular bands. Parallel bands marked head show a pronounced head of the central branch to which the wave number of the first column refers.

[b] The species of the allowed components of the transition moment are given in brackets. For all but the difference bands they coincide with the species of the upper states (omitting the A_2 substates). *Note added in proof:* There will be a few changes of species if ν_3 and ν_6 are interchanged; see footnote (a) of Table V.

[c] This band was also measured by Price with 10-cm path, at 4310 cm^{-1}. The identification of the band as $\perp$ band is due to him.

[d] This band has a very peculiar structure. There is a strong violet-shaded head to which the wave number given in column 1 refers; in addition there is a diffuse band shaded apparently to longer wave-lengths.

[e] This band shows more clearly than any other photographic band the expected structure of a perpendicular band. The series of Q branches is partially resolved, and the appropriate intensity alternation (strong, weak, weak, strong) is just recognizable.

if the P and R branches are too weak to be observed, must also be identified as parallel bands. However, there is a considerable number of bands whose central branches (frequently the only feature observed) are like diffuse lines. They may either belong to parallel bands for which $B' \approx B''$ or to perpendicular bands for which the spacing of the sub-bands, which is $2[B-C(1-\zeta)]$, is small because the Coriolis interaction constant ζ happens to be close to -0.84.

It was expected that the series of bands ν_1, $2\nu_1$, $3\nu_1$, $4\nu_1$, $\cdots$ (that is the overtones of the C$-$H vibration) would be the most prominent feature of the near infra-red spectrum of fluoroform, as it is for chloroform. Actually there are in each case two neighboring parallel bands of similar intensity rather than one. The two bands analyzed in Section C (see Fig. 2) form one such pair, namely, the one corresponding to $3\nu_1$. It is readily seen that these pairs of bands can be interpreted as $v_1\nu_1$ and $(v_1-1)\nu_1+2\nu_4$, since $2\nu_4$ has a magnitude similar to ν_1, particularly to the latter's higher vibrational quanta, and since one substate of $2\nu_4$ has the same species as ν_1, that is A_1. The separation of the two components of a pair is larger than 200 cm^{-1} and therefore Fermi resonance will affect the positions of the levels only slightly, even though it may affect the intensities to an appreciable extent. The shortward components of each pair which represent ν_1, $2\nu_1$, $3\nu_1$, $4\nu_1$, are 3035.6, 5978, 8792.7, and 11563.4, respectively. The separations of successive vibrational levels of the CH vibration are, therefore, 3035.6, 2942.$_4$, 2824.$_7$, and 2770.7 cm^{-1}. The levels can be represented approximately by

$$3088.0v_1 - 52.4v_1^2,$$

although the deviation for $v_1=4$ is much larger than compatible with the accuracy of the measurements, probably because of a non-negligible cubic term. The anharmonicity $x_{11}=52.4$ is of the right order for a CH vibration (compare for example those of HCN and C$_2$H$_2$).

The separations of $\nu_1+2\nu_4$, $2\nu_1+2\nu_4$, $\cdots$ from ν_1, $2\nu_1$, $\cdots$, respectively, are 2663.$_4$, 2611.$_3$, 2554.5, and 2439.4 cm^{-1}. The accelerated de-

[f] Accompanied by a diffuse fine structure on both long and short wave-length sides.

[g] These were calculated with old values, 700 and 514 cm^{-1}, for ν_3 and ν_6.

crease again points to a cubic term in the energy expression. Neglecting this, the anharmonic term x_{14} comes out to be approximately 28 cm^{-1}. However, this anharmonic coefficient does not represent very well bands of the type $v_1v_1+v_4$ and $v_1v_1+3v_4$. This is probably because the observed bands $v_1v_4+2v_4$ are parallel bands, having the A_1 component level as upper state while the bands $v_1v_1+v_4$ are perpendicular bands, the upper state having the species E only. For $v_1v_1+3v_4$ the situation is more complicated.

The vibrational data here obtained are not sufficient to determine all the anharmonicity coefficients x_{ik}. Since, in addition, the effect of cubic terms and of Fermi resonance is difficult to take into account accurately at the present stage, we give in the last column of Table VI, for all bands other than those just discussed, the wave numbers computed by simply adding to the observed wave numbers of the bands of type v_1v_1 and $v_1v_1+2v_4$ the fundamental or sum of fundamentals involved according to the assignments given.[11] On account of the effect of anharmonicity and the other reasons mentioned above, one should not expect a very close agreement of calculated and observed wave numbers.

[11] See footnote (g) of Table VI.

The only reason for listing the calculated values is as support for the assignments given in the third column.

The central branches of the strong photographic bands are accompanied by weaker companions which must clearly be interpreted as difference bands of the type $v+v_i-v_i$ in which a low frequency fundamental is excited in both upper and lower state of the main band. Their positions relative to the main band are determined by the anharmonicity constants and cannot be predicted.

The Mercury Photosensitized Reactions of Ethylene Oxide*

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The reactions of ethylene oxide with Hg($^3P_1$) atoms have been investigated at 25°C at pressures between 10- and 600-mm Hg, and at 200°C and 300°C at 100-mm Hg. The principal products are H$_2$, CO, CH$_3$CHO and a polymer; smaller amounts of CH$_4$, C$_2$ hydrocarbons and formaldehyde are also formed. The nature of the products and the very small effect of pressure on the reaction are best explained by a mechanism based principally on the formation of the activated ethylene oxide molecule, with a minor portion of the reaction proceeding via a C—H split.

INTRODUCTION

THE reactions between Hg($^3P_1$) atoms and the lower hydrocarbons have been studied

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in some detail.[1] It appears that, in general, the unsaturated hydrocarbons react principally by the transfer of energy from the excited mercury

[1] See E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946).