RotationVibration Spectra of Diatomic and Simple Polyatomic Molecules with Long Absorbing Paths IV. The Spectrum of Methyl Fluoroform (CH3CF3) from 19μ to 0.7μ

R. D. Cowan, G. Herzberg, and S. P. Sinha

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

IV. The Spectrum of Methyl Fluoroform (CH₃CF₃) from 19µ to 0.7µ

R. D. Cowan,* G. Herzberg, and S. P. Sinha†

*University of Chicago, Chicago, Illinois*** and National Research Council, Ottawa, Canada*

(Received July 11, 1950)

The absorption spectrum of methyl fluoroform has been investigated with path lengths up to 30 meters in the region 19 to 0.7µ. Three of the fundamentals have been assigned differently from Thompson and Temple. Since the molecule is nearly a spherical top, the ⊥ bands show the same typical PQR structure as do the ∥ bands except when the Coriolis interaction constant ζ is large. This seems to be the case for the degenerate C−F stretching vibration $\nu_9(e)$ and for most binary combinations involving it. The CH₃ rocking vibration $\nu_{10}(e)$ is split into two close components (separation 6 cm⁻¹) a splitting that is here ascribed to the presence of three potential minima separated by low potential maxima. A large number of infra-red bands can be readily interpreted as binary combinations. The relative intensities of fundamentals and of overtone and combination bands are briefly discussed.

A. INTRODUCTION

THE spectrum of fluoroform was investigated in paper I of this series.[1] From the fine structure of the photographic infra-red bands the moment of inertia of the molecule was determined. The resulting value of the C−F distance in CHF₃ was found to be appreciably smaller than in CH₃F. The more recent study of the microwave spectrum by Gilliam, Edwards, and Gordy[2] has confirmed the low value for r(C−F). It appeared of interest to ascertain whether a similar anomaly exists in other molecules containing the CF₃ group. It was with this consideration in mind that an investigation of the spectrum of methyl fluoroform (1:1:1 trifluoroethane) was undertaken. Up to now it has not been possible to resolve the fine structure of the bands of CH₃CF₃ and thus to determine the C−F distance but the results obtained concerning the vibrational structure of the spectrum appear of sufficient interest to warrant publication at this time.

After the results here to be described were obtained, a paper on the infra-red spectrum of methyl fluoroform by Thompson and Temple[3] appeared. Our results confirm in the main those of Thompson and Temple but go beyond theirs in the observation and discussion of overtone and combination bands. In addition, Thompson and Temple's assignment of fundamentals has been somewhat revised. Quite recently a spectrum of CH₃CF₃ in the region 2µ–15µ appeared in the API Catalog of Infra-Red Spectral Data (Serial No. 979, supplied by the Naval Research Laboratory).

B. EXPERIMENTAL

In the region 19µ to 2.5µ the infra-red spectrum of methyl fluoroform was recorded on the Perkin-Elmer infra-red spectrometer in the Spectroscopic Laboratory of the Physics Department at the University of Chicago using prisms of KBr, NaCl, and LiF. The absorbing path was 10 cm at various pressures. In the region 2.5µ to 0.7µ the PbS infra-red spectrometer of Dr. Kuiper[4] at Yerkes Observatory was used with an absorbing path of 30 meters, obtained in the way described in paper I of this series. This spectrometer has glass prisms. In addition the spectrum in the region 1.2µ to 0.7µ was photographed with the 21-foot grating spectrograph of Yerkes Observatory using the same long absorption tube.

In the region 19µ to 2.5µ (Perkin-Elmer spectrometer) individual fine structure lines of the bands of CO₂, CO, CH₄ and H₂O were used for calibration. In the region 2.5 to 0.7µ (Kuiper spectrometer) emission lines of He and Hg and absorption lines of H₂O as well as the zero gaps of several CO₂ bands were used as wave number standards. For the grating spectrograph iron lines of second, third, and fourth order were used.

With the prism instruments the wave number accuracy of sharp peaks in the region of maximum dispersion is estimated to be ±1 cm⁻¹. In the remaining spectral regions the accuracy may be less by a factor 2 or 3. In the region 2.2µ to 2.5µ on account of lack of standards the accuracy is probably only ±5 cm⁻¹. The accuracy in the photographic infra-red would be considerably greater than ±1 cm⁻¹ if it were not for the fact that all bands in this region are quite broad and diffuse.

The methyl fluoroform was obtained through the kindness of Dr. A. F. Benning from the Jackson Laboratory of E. I. du Pont de Nemours and Company. The sample was specified as "substantially pure"

[1] H. J. Bernstein and G. Herzberg, J. Chem. Phys. **16**, 30 (1948).

[2] Gilliam, Edwards, and Gordy, Phys. Rev. **75**, 1014 (1949).

[3] H. W. Thompson and R. B. Temple, J. Chem. Soc. p. 1428 (1948), in future referred to as TT.

[4] Kuiper, Wilson, and Cashman, Astrophys. J. **106**, 243 (1947).

(b.p. −47.5°C) possibly with traces of CH_3CF_2Cl. It was used without further purification.

C. OBSERVED SPECTRUM

The infra-red absorption spectrum of methyl fluoroform from 500 to 6200 cm⁻¹ is plotted in Fig. 1 as determined from the recordings obtained with the Perkin-Elmer and Kuiper spectrometers. Figure 2 shows a recording of the region 6000 to 11700 cm⁻¹ obtained with the Kuiper spectrometer. Table I gives the wave numbers, intensities, band types and assignments of the bands below 6200 cm⁻¹. The bands above 6200 cm⁻¹ are given without assignments in Table II.

In the regions 500–1550 cm⁻¹ and 2850–3200 cm⁻¹ which were also studied by Thompson and Temple the agreement with their absorption curve is very good except that the bands at 684 and 1135 cm⁻¹ which are "weak" and "strong" respectively in their recordings, are absent in our spectra, even in those taken at a higher pressure × path than used by them. Similarly TT's "strong" band at 900 cm⁻¹ is very much weaker on our records. These three bands must therefore be ascribed to impurities.

The spectral range 2850–3200 cm⁻¹ is much better resolved on our records since we were able to use an LiF prism. For this reason it is believed that our value for the wave number of the band at 3034 cm⁻¹ is the correct one even though it deviates by 8 cm⁻¹ from the value given by TT.

Many of the infra-red absorption bands of methyl fluoroform particularly below 6000 cm⁻¹ have a typical *PQR* structure, that is, a sharp central peak (*Q* branch) and two broader and less intense peaks at either side (*P* and *R* branches). These are separated from the central branch by about ±11 cm⁻¹. There are however some bands consisting of a simple broad maximum, e.g. the strong band at 1234 cm⁻¹ in Fig. 1, and others having two equally strong peaks with shoulders on the shortward and longward sides, e.g. the band at 972 cm⁻¹. At wave numbers above 6000 cm⁻¹, presumably due to overlapping of various combination bands, more and more irregular structures appear and in the photographic region very few bands show the simple *PQR* structure. Most of the photographic infra-red bands are very broad and many of these show several somewhat irregularly spaced diffuse peaks on the long- and shortward sides. Even for the bands with *PQR* structure of the photographic region it proved to be impossible to resolve the fine structure.

The intensities given in Tables I and II are based on peak heights assuming the intensity of the strongest band at 1234 cm⁻¹ to be 100,000 and assuming Beer-Lambert's law to hold [that is, the intensity is taken to be proportional to $(1/pl) \log(I_0/I)$ where p and l are pressure and path length and where I_0 and I are incident and transmitted intensity respectively]. Since the dependence of peak height on slit width used and the effect of pressure broadening on peak heights has been neglected, the (relative) intensities given are necessarily quite rough. Nevertheless they are con-
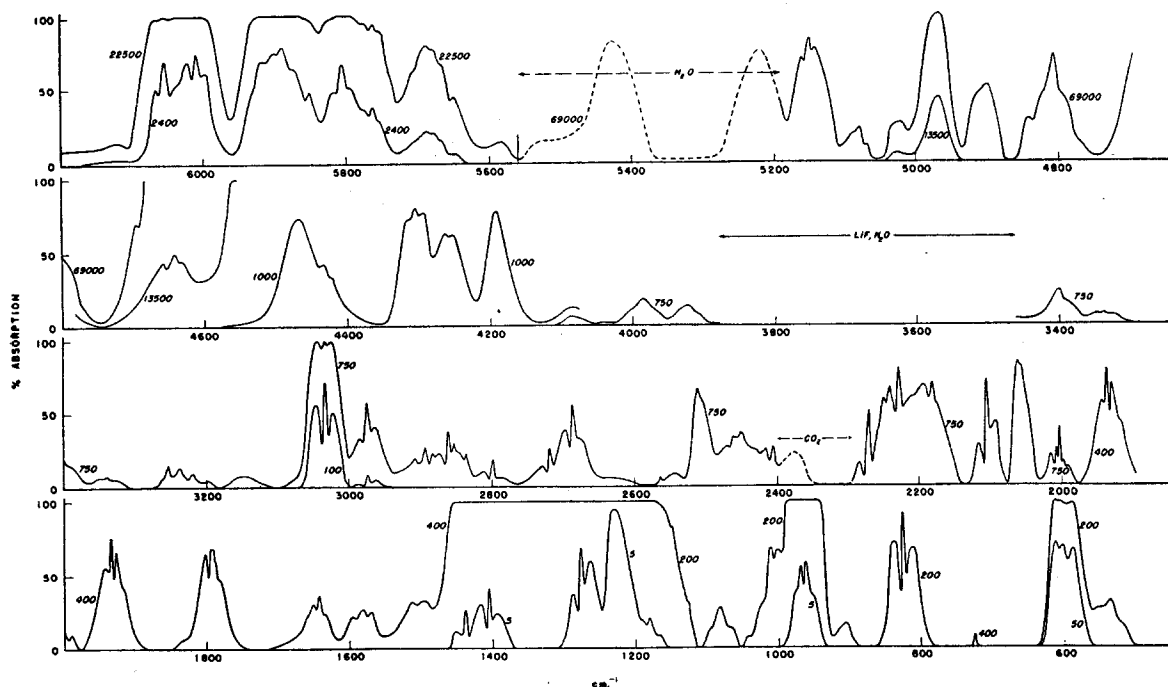

FIG. 1. Infra-red absorption spectrum of CH_3CF_3 from 500 to 6200 cm⁻¹.

The italic numbers on the curves give the product pressure×path in cm×cm. The regions marked by ◄——► are overlapped by CO_2, LiF, and H_2O bands. The broken-line curves in these regions give only an approximate representation of the absorption spectrum.

sidered to be better than the usual estimates ("strong," "medium," "weak," etc.). It may be noted that the range of intensities covered is very large, extending over seven powers of 10.

D. ASSIGNMENT OF FUNDAMENTALS

The methyl fluoroform molecule belongs to point group C_{3v} irrespective of whether the CH_3 and CF_3 groups are in the eclipsed or the staggered configuration. The point group C_{3v} has the three species A_1 (totally symmetric), A_2 (antisymmetric with respect to the planes of symmetry), and E (degenerate). It is easily seen[5] that methyl fluoroform has five normal vibrations of species A_1, one of species A_2, and six of species E. The first column of Table III describes these twelve vibrations, the second column gives the numbering chosen here, which is in conformity with general practice.[5]

All vibrations except $\nu_6(a_2)$ are infra-red active. For the a_1 vibration the dipole moment oscillates along the axis of symmetry, for the e vibrations perpendicular to it. Therefore, and since the molecule is a symmetric top the a_1 vibrations give rise to ∥ bands, the e vibrations to ⊥ bands.

On the basis of the molecular dimensions obtained from electron diffraction data by Shand and Spurr,[6] Russell, Golding, and Yost[6] calculated the moments of inertia[6a] to be $I_A=159\times10^{-40}$ $I_B=I_C=167\times10^{-40}$ g cm². The molecule is therefore very nearly a spherical top and consequently very little difference may be expected in the appearance of ∥ and ⊥ bands under medium dispersion. This is in agreement with the observation that a large number of the observed bands have PQR structure. Whether a given band with such a structure is a ∥ or a ⊥ band cannot be decided from the band envelope alone.

The separation of successive sub-bands of a ⊥ band is $2[A(1-\zeta_i)-B]$ where A and B are the rotational constants corresponding to I_A and I_B and where $\zeta_i(h/2\pi)$ is the vibrational angular momentum in the degenerate upper state of the band ($|\zeta_i|\leq1$). The separation of the sub-bands of a ⊥ band of methyl fluoroform will be very small and the band will have the same appearance as a ∥ band only if ζ_i is small. If ζ_i is not small the Q branches of the sub-bands will no longer coincide and a broad rather than a sharp central maximum will arise. Similarly the P and R branches of the sub-bands will form much broader features not separated by minima from the central branch which will be the most prominent feature. An example of such a band is the strongest infra-red band of methyl fluoroform, at 1234 cm⁻¹, (see Fig. 1). This band can therefore be classified as a ⊥ band. The same applies to other bands of this shape.

Another band type observed for CH_3CF_3 is one with two rather than three peaks. The strong band at 970 cm⁻¹ (Fig. 1) is a striking example. It is suggested here that the doubling is due to a splitting of the degeneracy associated with the three potential minima of the torsional motion. As is well known[5] a splitting into two levels arises which increases with decreasing potential barrier or increasing amplitude of the torsional mode. It is to be expected that whole-molecule-vibrations such as the rocking modes can also produce such a splitting. The most natural assignment of the band at 970 cm⁻¹ is indeed that of CH_3 rocking $[\nu_{10}(e)]$. It is assumed here that in the state in which this vibration is singly excited the doubling is 6 cm⁻¹ while for the lowest vibrational level it is negligible. As has been shown by Koehler and Dennison,[7] with increasing K (rotation about the symmetry axis) one of the component levels splits further into two components and all
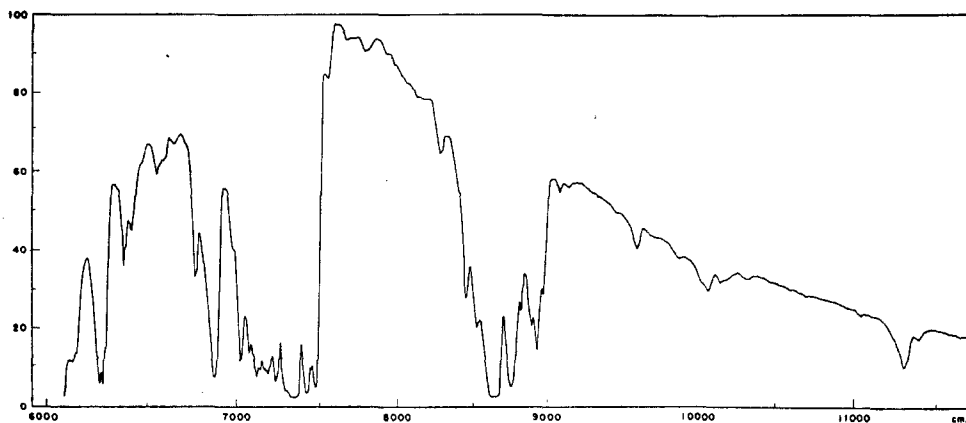
FIG. 2. Recording of the CH_3CF_3 absorption spectrum from 6000 to 11700 cm⁻¹ as obtained with Dr. Kuiper's spectrometer at 70 cm pressure and 3000 cm path. In this recording unlike Fig. 1 absorption bands appear as minima of the curve.

[5] See, for example, G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic molecules* (D. Van Nostrand Company, Inc., New York, 1945).
[6] W. Shand and R. A. Spurr, quoted by Russell, Jr., Golding, and Yost, J. Am. Chem. Soc. **66**, 16 (1944).
[6a] From the microwave spectrum, W. F. Edgell and A. Roberts [J. Chem. Phys. **16**, 1002 (1948)] obtained $I_B=161.8_0\times10^{-40}$ g cm².
[7] J. S. Koehler and D. M. Dennison, Phys. Rev. **57**, 1006 (1940).

TABLE I. Infra-red absorption bands of CH₃CF₃ from 500 to 6200 cm⁻¹.

ν_{vac}(obs.) cm⁻¹	Band type[a]	Intensity[b]	Assignment[c]	ν_{vac}(calc.)[d] cm⁻¹
526	vb P }			
541	b Q }	240	$\nu_5(a_1)$	
558	vb R }			
593	vb P }			
606	b Q }	2740	$\nu_{11}(e)$	
616	vb R }			
732	b	32	$2\nu_{12}(A_1, E)$	736
817	vb P }			
830	s Q }	1490	$\nu_4(a_1)$	
842	vb R }			
911[e]	b	115	$\nu_5+\nu_{12}(E)$	909
967	ph } doublet	21400	$\nu_{10}(e)$	
973	ph }			
1015	bh	750		
1088	bh	200	$2\nu_5(A_1)$, impurity?[f]	1082
1172	b P? }			
1187	s Q? }	5800	$\nu_4+\nu_{12}(E)$	1198
g	R? }			
1234	vb ⊥	100000	$\nu_9(e)$	
1268	b P }			
1281	s Q }	30400	$\nu_3(a_1)$	
1292	b R }			
1397	b P }			
1409	s Q }	12700	$\nu_2(a_1)$	
1421	b R }			
1442[h]	s Q }	7460	$\nu_8(e)$	
1458	b R }			
1520[i]	vb	75	$\nu_5+\nu_{10}(E)$?	1513
1586[i]	vb	66	$\nu_9+\nu_{12}(A_1, E)$, $\nu_6+\nu_8(E)$	1602, ?
1647[i]	s	115	$2\nu_4(A_1)$	1660
1797[i]	b }	380	$\nu_4+\nu_{10}(E)$	{1797
1806	s }			{1803
1883	s	14	$\nu_3+\nu_{11}(E)$	1887
1931	sh }			
1937	s }	440	$2\nu_{10}(A_1, E)$	1940
1945	b }			
1993	b P" }			
2005	s Q }	125	$\nu_2+\nu_{11}(E)$	2015
2008	s Q	55	$\nu_2+\nu_{11}+\nu_6-\nu_6$?	
2016	b R }			
2057	ph }	285	$\nu_4+\nu_9+\nu_6-\nu_6$	
2061	bh }	295	$\nu_4+\nu_9(E)$	2064
2093	b P }			
2107	sh Q }	255	$\nu_3+\nu_4(A_1)$	2111
2116	b R }			
2184	ph }	225	$\nu_9+\nu_{10}(A_1, E)$	2204
2193	vbh }			
2216	vb P }			
2231	s Q }	270	$\nu_2+\nu_4(A_1)$	2239
2243	bh R[k] }			
2252	sh	140	$\nu_3+\nu_{10}(E)$	2254
2261	b P[l] }			
2272	s Q }	135	$\nu_4+\nu_8(E)$	2272
2285	b R }			
(2376)[m]	?	(47)	$\nu_2+\nu_{10}(E)$	2379
2407	s }	28	$\nu_8+\nu_{10}(A_1, E)$	2412
2417	ph }			
2453	bh }			
2463	up }	63	$2\nu_9(A_1, E)$?	2468
2469	bh }			
2512	s	175	$\nu_3+\nu_9(E)$	2515
2545	b P }			
2560	s Q }	12	$2\nu_2(A_1)$	2562
2676	b P }			
2687	s Q }	145	$\nu_2+\nu_3(A_1)$	2690
2698	b {R/P}			
2720	s Q }	51	$\nu_3+\nu_8(E)$	2723
2729	b R }			
2786	b P }			
2799	s Q }	35	$2\nu_2(A_1)$	2818
2812	b R }			
2836	s	40	$\nu_2+\nu_8(E)$	2851
2852	sh Q	52	$2\nu_8+\nu_6-\nu_6$?	
2861	s Q }	80	$2\nu_8(A_1)$ }	
2875	b R }			2884
2883	s P? }			
2894	s Q }	50	$2\nu_8(E)$ }	
2909	p R? }			

TABLE I—Continued.

ν_{vac}(obs.) cm⁻¹	Band type[a]	Intensity[b]	Assignment[c]	ν_{vac}(calc.)[d] cm⁻¹
2965	b P }			
2975	s Q }	145	$\nu_1(a_1)$	
2986	b R }			
3024	b P }			
3034	s Q }	2300	$\nu_7(e)$	
3046	b R }			
3150	vb	(13)		
3220	s	16 }		
3239	s	23 }	$\nu_6+\nu_7$?	
3256	s	26 }		
3340	sh	97	$\nu_1+\nu_{12}(E)$	3343
3394	h P }	44	$\nu_7+\nu_{12}(A_1, E)$	3402
3403	sh Q }			
3926	vb	18	$\nu_1+\nu_{10}(E)$	3944
3983	b	31	$\nu_7+\nu_{10}(A_1, E)$	4004
4090[n]	b	9.7	?	
4192[n]	b	145	$\nu_1+\nu_9(E)$	4209
4252[n]	b	102	$\nu_1+\nu_3(A_1)$	4255
4264[n]	b	108	$\nu_7+\nu_9(A_1, E)$	4268
4295[n]	b P }			
4306[n]	s Q }	210	$\nu_2+\nu_7(E)$	4315
4317[n]	b R }			
4435[n]	bh	71	$\nu_2+\nu_7(E)$	4443
4470[n]	b	145	$\nu_7+\nu_8(A_1, E)$	4476
4650	vvb	5.1	{$\nu_1+\nu_8+\nu_{12}(E)$ / $\nu_7+\nu_9+\nu_{12}(A_1, E, E, E)$	4623 / 4636
4807	sh	2.1	$\nu_5+\nu_7+\nu_9(A_1, E)$	4809
4901	vb	1.2	$\nu_3+\nu_7+\nu_{11}(A_1, E)$	4921
4971	vb	4.8	$\nu_2+\nu_5+\nu_7(E)$	4983
5022	b	0.52	$\nu_1+\nu_4+\nu_9(E)$	5039
5081	sh	0.47	{$\nu_7+\nu_8+\nu_{11}(A_1, E, E, E)$ / $\nu_4+\nu_7+\nu_9(A_1, E)$	5082 / 5098
5140	s P? }			
5151	s Q }	3.1	$\nu_3+\nu_4+\nu_7(E)$	5145
5161	s R? }			
5220[i]	?	(2.5)	$\nu_7+\nu_9+\nu_{10}(A_1, E, E, E)$	5238
5429[i]	?	(1.9)	{$\nu_7+\nu_8+\nu_{10}(A_1, E, E, E)$ / $\nu_1+2\nu_9(A_1, E)$	5446 / 5442
5583	sh	0.67	$2\nu_3+\nu_7(E)$	5596
5689	vbh	10.8	$\nu_2+\nu_3+\nu_7(E)$	5724
5755	b P }			
5763	s Q }	36	{$\nu_1+2\nu_2(A_1)$ / $\nu_1+\nu_2+\nu_8(E)$	5793 / 5826
5775	b R }			
5797	b P }			
5807	s Q }	56	{$\nu_1+2\nu_8(A_1, E)$ / $2\nu_2+\nu_7(E)$	5859 / 5852
5818	b R }			
5852	s	(32)	{$\nu_2+\nu_7+\nu_8(A_1, E)$ / $\nu_7+2\nu_8(A_1, E, E, E)$	5885 / 5918
5877	b P }			
5890	s Q }	75	$2\nu_1(A_1)$	5950
5903	b R }			
5920	b	(50)	$\nu_1+\nu_7(E)$	6009
5998	s P? }			
6011	s Q }	70 }		
6023	s R }			
6042	h P? }		$2\nu_7(A_1, E)$	6068
6056	s Q }			
6067	b R }	59 }		

[a] Abbreviations: s =sharp, b =broad, vb =very broad, h =hump (i.e., no distinct maximum), ph =peak with side humps, sh =sharp peak with side humps, bh =broad peak with side humps, u =unsymmetrical. P, Q, R refer to peaks that are likely to be due to P, Q, R branches respectively.

[b] These are relative intensities based on the value 100,000 for the strongest band at 1234 cm⁻¹. Intensities in brackets are uncertain because of overlapping.

[c] Only the infra-red active species are given.

[d] Based on the harmonic oscillator approximation.

[e] TT give a strong band with peaks at 889, 900, and 910 which can hardly be identical with the weak band at 911 reported here.

[f] This band is not given by TT but does appear in the API record. It may be due to an impurity. TT find instead a strong band at 1135 cm⁻¹ which is absent here.

[g] Overlapped by the strong band at 1234 cm⁻¹.

[h] The P branch of this band coincides with the R branch of the band at 1409 cm⁻¹ as confirmed by the high intensity of the 1421 cm⁻¹ peak.

[i] Overlapped by H₂O lines, therefore not very accurately measured.

[j] This P branch seems to be overlapped by other features.

[k] This peak is higher and less broad than expected for the R branch of the band 2231. It is very probably overlapped by the second component of $\nu_3+\nu_{10}$.

[l] This was measured as a shoulder on a background of large slope.

[m] Overlapped by CO₂ band.

[n] These wave numbers are less accurate because of lack of good standards in this region.

three component levels, with further increase in K, change periodically their relative order. The intensity distribution in the wings of the band at 970 cm⁻¹ is characteristically different from that in other bands. More detailed calculations will be required to ascertain whether the observed band envelope can actually be accounted for by the torsional splitting.

The other vibrations associated with the CH₃ group are easily assigned if their frequencies in other molecules containing the CH₃ group are remembered. The frequencies 2975 and 1409 cm⁻¹ are due to the symmetric CH stretching and CH₃ deformation vibrations respectively while 3034 and 1442 are due to the corresponding degenerate vibrations (Thompson and Temple).[3] considered 1408 and 1442 as forming $\nu_8(e)$ with the

TABLE II. Infra-red absorption bands of CH_3CF_3 from 6200 to 14000 cm^{-1}.

ν_{vac}(obs.) cm^{-1}	Band type[a]	Intensity[b]
6260	sh } doublet	1.7
6275	sh }	1.8
6379	sh Q	0.34
6421	b	0.21
6552	bh	0.066
6645	vb	0.019
6762	b	0.44
6875	bh	1.5
7028	sh Q	1.1
7073	s[c]	0.72
7115–7250	vb[c]	1.0
7348	bh	5.2
7417	s } doublet	2.5
7427	b }	2.4
7452	s	0.40
7482	s Q?	2.2
7545	b	0.10
8272	vb	0.13
8421	b (P.I.)	(0.2)[d]
8431	b (P.I.)	(0.4)[d]
8443	b (P.I.)	0.63
8483	b (P.I.)	(0.2)[d]
8494	b (P.I.)	(0.3)[d]
8506	b (P.I.)	(0.5)[d]
8522	b (P.I.)	0.85
8536	b (P.I.)	(0.3)[d]
8556	b (P.I.)	(0.3)[d]
8574	b (P.I.)	(0.8)[d]
8593	b (P.I.)	(0.8)[d]
8604	b (P.I.)	(0.8)[d]
8613	b (P.I.)	(0.8)[d]
8624	b (P.I.)	(0.8)[d]
8640	b (P.I.)	(0.8)[d]
8650	vb (P.I.)	7.0
8758	vb (P.I.)	1.9
8814.8	sh Q (P.I.)	0.71
8887	sh	0.79
8924	sh Q (P.I.)	1.0$_7$
8969	h	0.52
9069.9	sh Q (P.I.)	0.052
9134	vb	0.033
9598	vb	0.099
9881	vvb	0.063
10070	vb (P.I.)	0.17
10147	vb (P.I.)	0.10$_8$
10180	vb (P.I.)	0.077
10325	vb	0.036
11309	vb (P.I.)	0.52
11394	vb (P.I.)	0.12
13833	vb (P.I.)[e]	(0.08)

[a] See footnote a of Table I. In addition (P.I.) refers to bands obtained with the 21-ft. grating in the photographic infra-red.
[b] See footnote b of Table I.
[c] Overlapped by H_2O, therefore not accurately measured.
[d] These are faint diffuse peaks which are superimposed on the longward wings of the main broad bands at 8443, 8522 and 8650 cm^{-1}. They have been resolved on the photographic infra-red plates only.
[e] Observed in the photographic infra-red only since it was beyond the range of Kuiper's infra-red spectrometer.

degeneracy removed and adopted $\nu_2(a_1) = 1278$ cm^{-1}. However the doubling appears much too large and 1408 and 1442 are close to the symmetric and degenerate CH_3 deformation vibrations of CH_3CN and CH_3CCH.

The frequency 1281 cm^{-1} is here assigned to the symmetric C$-$F stretching vibration $\nu_3(a_1)$ in spite of the fact that the corresponding degenerate frequency 1234 cm^{-1} (strongest infra-red band, definitely a $\perp$ band, see above) is lower. This assignment appears

necessary since the frequency 1135 used by Thompson and Temple is due to an impurity. In support of this assignment of the C$-$F stretching vibrations are the facts (1) that the only two frequencies of CF_3CCl_3 that can be assigned to C$-$F stretching modes[8] are 1250 and 1214 cm^{-1}, (2) that the means of the two $\parallel$ and the two $\perp$ C$-$F stretching vibrations of C_2F_6 are 1270 and 1243 cm^{-1} respectively.[9]

By comparison with other molecules containing C$-$C bonds the C$-$C stretching vibration is readily assigned to the observed band at 830 cm^{-1}; comparison with C_2F_6 yields the assignment of the CF_3 deformation vibrations $\nu_5(a_1) = 541$, $\nu_{11}(e) = 606$ cm^{-1}. The CF_3 rocking vibration $\nu_{12}(e)$ must very probably be identified with the Raman band 368 cm^{-1} which is beyond the region investigated in the infra-red. Thus far there is no way of assigning the torsion oscillation $\nu_6(a_2)$ unambiguously.

The frequencies thus assigned to the normal vibrations of fluoroform are summarized in the last column of Table III. The second last column gives for comparison the assignments of Thompson and Temple. The third column of Table III gives the Raman frequencies observed for liquid CH_3CF_3 by Hatcher and Yost.[10] In addition to the fundamentals given the Raman shifts 2792, 2825, and 2885 cm^{-1} were observed which presumably correspond to the infra-red bands of the gas at 2799, 2836, and 2894 cm^{-1}. Since at one time it was considered possible that the assignment of $\nu_1(a_1)$ and $\nu_7(e)$ had to be exchanged, Dr. A. E. Douglas, then at the Department of Physics of Pennsylvania State College, determined the polarization of the two Raman lines 2974 and 3040 finding the first strongly polarized, the second depolarized. This confirms the present assignment of these two frequencies. It is surprising that of the two CH_3 deformation vibrations $\nu_2(a_1)$ does not appear in the Raman spectrum while $\nu_8(e)$ does.

The relative intensities of the fundamentals in the infra-red are noteworthy: the two strongest infra-red bands are those at 1234 and 1280 cm^{-1} which are due to C$-$F stretching vibrations. The weakest (allowed) fundamental in the infra-red is the symmetrical C$-$H stretching vibration at 2975 cm^{-1} with less than 1/500 of the intensity of the 1234 cm^{-1} band.

E. OVERTONE AND COMBINATION BANDS

In addition to the fundamentals discussed in the preceding section there are a large number of overtone and combination bands (Tables I and II). As indicated in Table I most of the bands below 6200 cm^{-1} can be assigned as binary combinations of the fundamentals of Table III. Indeed, the ease with which this assignment is possible is a further strong indication of the correctness of the fundamentals. Many of the overtone

[8] G. Glockler and C. Sage, J. Chem. Phys. 9, 387 (1941).
[9] J. R. Nielsen, C. M. Richards, and H. L. McMurry, J. Chem. Phys. 16, 67 (1948).
[10] J. B. Hatcher and D. M. Yost, J. Chem. Phys. 5, 992 (1937).

and combination bands whenever they can be properly resolved show the typical *PQR* structure. However it is significant that the binary combinations $\nu_4+\nu_{10}$ at 1802, $\nu_9+\nu_{10}$ at 2189 and $\nu_8+\nu_{10}$ at 2412 cm⁻¹ which involve the rocking vibration $\nu_{10}(e)$ have a doublet structure similar to that of ν_{10} (see Fig. 1). Other combinations of this type are either overlapped or in regions of insufficient resolving power so that the presence of the splitting cannot be ascertained. In the case of the overtone $2\nu_{10}$ a larger splitting is expected which is further complicated by the fact that there would be a splitting into an A_1 and an E component even without the torsional splitting. The observed band at 1937 cm⁻¹ does indeed show a more complicated appearance than the fundamental (see Fig. 1).

Similarly, it is noteworthy that, in all cases in which it can be ascertained, the binary combinations involving $\nu_9(e)$ do not show the *PQR* structure characteristic of most other bands but show a broad maximum in agreement with the behavior of the fundamental. This is in agreement with expectation since the ζ-value of combinations $\nu_i(a_1)+\nu_k(e)$ is the same as for $\nu_k(e)$ while for combinations $\nu_i(e)+\nu_k(e)$ it is $\zeta_i+\zeta_k$ for the E component of the resultant state.

In several cases, for example $2\nu_8$ and $2\nu_7$, the expected splitting into two bands (species A_1 and E of the upper state) is observed. The magnitude of this splitting (33 and 45 cm⁻¹ for $2\nu_8$ and $2\nu_7$ respectively) is of the same order as that observed previously for CH₃I.[11]

In the last column of Table I, for all overtone and combination bands the calculated wave numbers are given, based on the assumed assignment and neglecting anharmonicity. The deviations from the observed values are of the right order of magnitude expected for the effect of anharmonicity.

Several bands in Table I are assigned as combination bands involving the inactive frequency $\nu_6(a_2)$. In case of bands of the type $\nu_i+\nu_6-\nu_6$ the peaks are very close to peaks of the main bands ν_i. While the assignment seems reasonably certain in these cases it does not allow a determination of $\nu_6(a_2)$. The assignment of difference or summation bands of the type $\nu_i\pm\nu_6$ is very doubtful in all cases. A reliable assignment and therefore an unambiguous determination of $\nu_6(a_2)$ would be possible if the effect of temperature on the difference bands $\nu_i-\nu_6$ could be established.

The bands above 6200 cm⁻¹ are of necessity ternary or higher combinations. Since there are twelve fundamentals the number of ternary and higher combinations is so large that unique assignments are hardly possible particularly since it is not possible to distinguish ‖ and ⊥ bands. It is however clear that the bands in the region 7000–7500 cm⁻¹ are due to ternary combinations involving two C−H stretching frequencies and a CH bending or deformation frequency while the bands in

[11] G. Herzberg and L. Herzberg, Can. J. Research **B27**, 332 (1949).

TABLE III. Fundamentals of CH₃CF₃.

Description	Designa-tion	Wave number		
		Raman effect of the liquid	TT	Present work
Symmetric C−H stretching	$\nu_1(a_1)$	2974	2974	2975
Symmetric CH₃ deformation	$\nu_2(a_1)$		1278	1409
Symmetric C−F stretching	$\nu_3(a_1)$	1279	1135	1281
Symmetric C−C stretching	$\nu_4(a_1)$	829	828	830
Symmetric CF₃ deformation	$\nu_5(a_1)$	541	540	541
Torsion	$\nu_6(a_2)$			
Degenerate C−H stretching	$\nu_7(e)$	3040	3042	3034
Degenerate CH₃ deformation	$\nu_8(e)$	1450	{1450, 1412}	1442
Degenerate C−F stretching	$\nu_9(e)$		1230	1234
Degenerate CH₃ rocking	$\nu_{10}(e)$	968	968	970
Degenerate CF₃ deformation	$\nu_{11}(e)$	603	606	606
Degenerate CF₃ rocking	$\nu_{12}(e)$	368	(368)	(368)

the region 8500–9000 are due to ternary combinations of the C−H stretching vibrations. The few peaks at 11350 cm⁻¹ may similarly be classed as $4\nu_{\text{CH}}$ and the weak band at 13833 cm⁻¹ as $5\nu_{\text{CH}}$.

It is well known that the intensities of overtone and combination bands depend on the magnitude of the mechanical and the electrical anharmonicity associated with the motions involved. Since very little is known about the electrical anharmonicity no definite predictions of intensities can be made. However it is significant that the first overtones of the C−F stretching vibrations ν_3 and ν_9 are quite weak, less than 1/1000 of the fundamentals (which are the strongest bands in the spectrum), while the first overtones of the C−H stretching vibrations are much stronger relative to the fundamentals (which are quite weak, see Section D). This behavior is in agreement with the relative magnitudes of the mechanical anharmonicities.

F. CONCLUSION

As mentioned previously in spite of the use of low pressure (to avoid pressure broadening) and of high dispersion (2.5A/mm) the rotational fine structure of the photographic infra-red bands was not resolved. The reason for this must be sought in the fact that the difference between the moments of inertia of the upper and lower states is considerable so that the Q branches of the sub-bands are not line-like and, in the case of ‖ bands, different sub-bands do not coincide. This is unlike the case of CHF₃ where the upper states of the overtones of the CH vibration have the same I_A as the ground state. By investigating less high overtones or fundamentals of species A_1 in the region made excessible for high resolution work by the use of photoconductive cells a determination of the moment of inertia I_B of CH₃CF₃ should be possible. For a better understanding of hindered rotation a high resolution study of bands involving the fundamental $\nu_{10}(e)$ and of difference bands involving $\nu_6(a_2)$ would be very promising.

Thompson and Temple[3] have calculated the thermo-

dynamic functions of CH_3CF_3 on the basis of the approximate moments of inertia mentioned above and of their choice of fundamentals. With the modified assignment of fundamentals given in the present work slight changes of the values of the thermodynamic functions will arise. However it does not seem worth while to carry out a recalculation at the present time before the high resolution studies suggested in the preceding paragraph have been carried out.

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

V. The Spectrum of Isocyanic Acid

C. REID*

National Research Council, Ottawa, Canada

(Received July 24, 1950)

The spectrum of isocyanic acid has been examined in the photographic infra-red using a 21-ft. grating spectrograph and path lengths up to 500 m. The rotational structure of several bands has been analyzed and the energy levels and moments of inertia determined. With their help the coarse rotational structure of two of the fundamentals has also been analyzed. The molecular parameters fitting best our data and published electron diffraction results for the C—N and C—O bond distances are: $r(\text{H}-\text{N})=1.00_0\text{A}$, $\measuredangle\text{H}-\text{N}-\text{C}=125.5°$.

A. INTRODUCTION

IT has been shown in another paper[1] where a summary of previous work and a vibrational analysis is given, that the gas prepared by thermal depolymerization of cyanuric acid and loosely called cyanic acid is, in fact, isocyanic acid $\text{H}-\text{N}=\text{C}=\text{O}$. The basis for this assignment is (a) the marked similarity between three of the fundamentals to those of CO_2 with which $\text{H}-\text{N}=\text{C}=\text{O}$ is isosteric and isoelectronic and (b) a comparison of the hydrogen stretching frequency with that of HNCS.

These arguments suggest also that the $\text{N}=\text{C}=\text{O}$ group is linear as might be expected, and, since the general appearance of the spectrum is not that of a linear molecule, that the H atom is not collinear with the rest of the molecule.

Before the present investigation no analysis of the photographic infra-red spectrum of HNCO had been made. Some observations in the photographic infra-red[1] suggested that the rotational structure was rather complicated. However, if the NCO group is linear one would expect a simpler spectrum similar to that of hydrazoic acid, which has been interpreted without great difficulty.[2,3] This expectation is in fact fulfilled.

B. EXPERIMENTAL

Isocyanic acid was prepared from cyanuric acid as described in reference 1. The photographic infra-red

TABLE I. HNCO fundamentals.*

Assignment	Observed frequency cm⁻¹
$\nu_1(a')$	3531
$\nu_2(a')$	2274
$\nu_3(a')$	1527
$\nu_4(a')$	798
$\nu_5(a')$	572
$\nu_6(a'')$	670

* See reference 1.

TABLE II.

Assignment	Band center cm⁻¹	Type*	Rotational analyses*
ν_4	798	h	c
ν_1	3531	h	c
$2\nu_1+\nu_2$	9162	h	c, f
$3\nu_1$	10145.1	h	c, f
$2\nu_1+\nu_2+\nu_3$	10525	$\parallel$	c, f
$3\nu_1+\nu_4$	10988	h	f
$4\nu_1$	13217	h	f

* h =hybrid band; $\parallel$ =predominantly parallel band; c =coarse rotational structure analyzed; f =fine rotational structure analyzed.

* Now at the University of British Columbia, Vancouver, B. C., Canada.
[1] G. Herzberg and C. Reid. Presented at the Faraday Society Symposium on Spectroscopy and Molecular Spectra, September, 1950.

[2] Herzberg, Patat, and Verleger, Zeits. f. Electrochemie 41, 522 (1935).
[3] E. H. Eyster, J. Chem. Phys. 8, 1935 (1940).