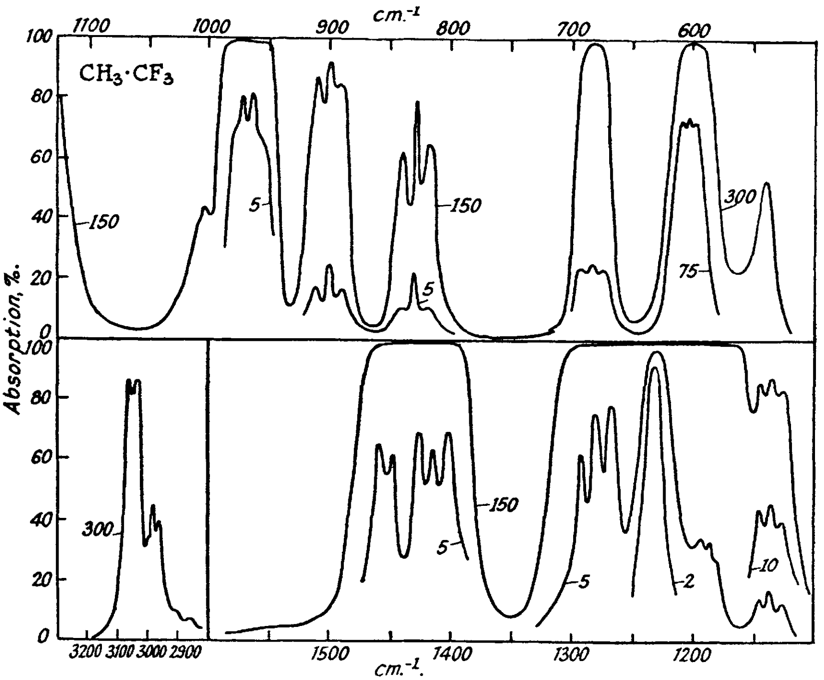
291. *Infra-red Spectra of Fluorinated Hydrocarbons. Part II. "Methyl Fluoroform" (1 : 1 : 1-Trifluoroethane).*

By H. W. Thompson and R. B. Temple.

The infra-red absorption spectrum of methyl fluoroform has been determined between 2 and 20 μ. The results have been correlated with the Raman spectrum and an assignment of vibrational frequencies has been made. The entropy of the molecule has been calculated statistically and compared with the calorimetric value, and it is concluded that there exists a potential barrier of 3250 cals. resisting free rotation of the end groups with respect to each other. Values for other thermodynamic functions have been estimated.

In Part I (Torkington and Thompson, *Trans. Faraday Soc.*, **1945**, **41**, 236), measurements on the infra-red absorption spectra of some fluorinated olefins have been described. The present paper deals with methyl fluoroform, $CH_3{\cdot}CF_3$. The substance was supplied by Imperial Chemical Industries Ltd. (General Chemicals Division), and had been prepared by treatment of the chloro-compound with hydrogen fluoride in presence of antimony fluoride. The spectrum was measured on single- and double-beam recording instruments as described in the preceding paper.

Results and Discussion.—The absorption spectrum is shown in the figure, and the positions of the bands (cm.$^{-1}$) are given in Table I, together wlth the Raman data of Hatcher and Yost (*J. Chem. Physics*, 1937, **5**, 992). It will be noted that many of the bands show a well-defined contour, which is discussed below. The pressures used were 1—300 mm. in a cell 17 cm. in length. At the lowest pressures the band at 1230 cm.$^{-1}$ remained very intense. The characteristics of symmetry of this molecule will depend upon the precise relative orientation of the two end groups CH_3 and CF_3. These groups may be either " eclipsed " or " staggered " (C_{3v}), or in some intermediate position (C_3). There will be twelve normal vibrations, including a torsional mode, six being doubly degenerate. For C_3 symmetry all twelve modes will be



permitted to appear in both Raman and infra-red spectra, and six will be polarised in the Raman effect. For C_{3v} symmetry the torsional vibration will be inactive in both Raman and infra-red spectrum, and of the remaining eleven, five will be polarised in the Raman effect. The approximate form of these vibrations is indicated in Table II.

Russell, Golding, and Yost (*J. Amer. Chem. Soc.*, 1944, **66**, 16) quote electron-diffraction measurements of Shand and Spurr as giving the following molecular dimensions : C–F = 1·37 A., C–C = 1·52 A., $\mathrm{C{-}\hat{C}{-}F} = 112°$, $\mathrm{F{-}\hat{C}{-}F} = 107°$. Assuming C–H = 1·09 A. with a tetrahedral methyl group, the calculated moments of inertia were 159, 167, 167 × 10^{-40} g.-cm.^{2}. In this case, the molecule will behave as an almost spherical rotator, and the contour of all bands will show three submaxima with similar spacings and therefore be unhelpful as regards the assignment of frequencies to normal modes.

The absorption bands do, in fact, usually show the three sub-maxima and the spacings between the side maxima are roughly the same, namely, 21—24 cm.$^{-1}$. The band at 968 cm.$^{-1}$, however, differs, in having two central maxima and two outer shoulders, thus appearing like a *B*-type band of Badger and Zumwalt (*J. Chem. Physics*, 1938, **6**, 711). This would imply a vibration with change of electric moment parallel to an intermediate axis of inertia and cannot be reconciled with the above arguments. The contour of the band at 1135 also seems peculiar, and that at 1230 cm.$^{-1}$ was never resolved into sub-maxima.

TABLE I.

Raman.	Infra-red.		Interpretation.
368 (2)			Fundamental
541 (2)	540	(weak)	Fundamental
603 (2)	593 606 616	(strong)	Fundamental
	673 684 695	(weak)	? (1230—540) or torsional combination
	? 733		(2 × 368)
829 (5)	818 828 840	(strong)	Fundamental
	889 900 910	(strong)	(368 + 540)
968 (3)	953 964 971 978	(very strong)	Fundamental, or ?(368 + 606)
	1004 1013	(weak)	? Torsional combination
	1125 1135 1143	(strong)	Fundamental or ?(540 + 606)
	1177 1184 1191	(weak)	(368 + 828)
	1230	(very strong)	Fundamental
1279 (1)	1266 1278 1290	(strong)	Fundamental
	1400 1412 1424	(strong)	Fundamental
1450 (4)	1445 1457	(medium)	Fundamental
2792 (2)			
2825 (1)			(2 × 1412)
2885 (1)	2900		(2 × 1450)
2974 (5)	2960 2974 2984	(weak)	Fundamental
3040 (4)	3031 3042 3052	(strong)	Fundamental
	4200	(weak)	(1230 + 2974)
	4270	(weak)	(1230 + 3042)
	4320	(weak)	(1279 + 3042)
	4480	(weak)	(1445 + 3042)
	5760	(very weak)	(1279 + 1445 + 3042)
	5880	(very weak)	(2 × 2974)
	6000	(very weak)	(2 × 3042)

TABLE II.

	Single.		Doubly degenerate.
ν_1	Symm. CH_3 stretching	ν_2,ν_3	Antisymm. CH_3 stretching
ν_4	Symm. CH_3 deformation	ν_6,ν_7	Antisymm. CF_3 stretching
ν_5	Symm. CF_3 stretching	ν_{10},ν_{11}	CH_3 rocking
ν_8	Symm. CF_3 deformation	ν_{12},ν_{13}	CF_3 rocking
ν_9	C–C stretching	ν_{14},ν_{15}	Skeleton deformation
ν_{18}	Twisting	ν_{16},ν_{17}	Skeleton deformation

Russell, Golding, and Yost attempted to assign the fundamental frequencies on the basis of the Raman spectrum alone. For several reasons it seems desirable now to amend their assignment. We can at once assign the bands at 2974 and 3040 cm.$^{-1}$, the former to ν_1, the symmetrical C–H stretching frequency, and the latter to ν_2, ν_3 the degenerate antisymmetrical C–H stretching mode. The strong infra-red band at 1230 cm.$^{-1}$ has no corresponding Raman interval. It remains intense at the lowest pressures used, and is therefore unlikely to be due to any impurity, and there is little indication of any other spurious bands. On grounds of intensity and approximate magnitude, it seems necessary to asign this frequency to ν_6, ν_7, the degenerate

C–F stretching mode. We should then expect the symmetrical stretching frequency of the CF_3 group, ν_5, to have a value below 1230 cm.$^{-1}$. The only plausible infra-red band for this, for which there exists a corresponding Raman interval, is that at 964 cm.$^{-1}$. This value seems too low, however, for the vibration concerned, since the vibration frequency of the C–F link in compounds of the type $F{-}C(X)_3$ is about 1050—1080 cm.$^{-1}$, and with two fluorine atoms attached to the same carbon atom there is a marked shortening of the C–F linkages. Also, it has been found that fairly intense bands at about 1150 and 1250 cm.$^{-1}$ occur with several fully fluorinated paraffins. This suggests that ν_5 may be connected with the infra-red band at 1135 cm.$^{-1}$. It is perhaps surprising that if this is the symmetrical stretching vibration frequency of the CF_3 group it is not observed in the Raman effect, but reference to the results for several other related compounds suggests that this type of vibration is often weak in the Raman effect. In the case of fluoroform, CHF_3, the Raman line at 1116 cm.$^{-1}$ may be associated with the corresponding mode.

The band at 1278 cm.$^{-1}$ with corresponding Raman interval is clearly a fundamental, and can be assigned to ν_4, the symmetrical deformation of the methyl group. The infra-red bands at 1412 and 1450 cm.$^{-1}$ are assigned to ν_{10}, ν_{11}, the degenerate bending mode which may be largely controlled by motion of atoms in the methyl group, if it is assumed that the degeneracy has been removed. Both these values are used in the interpretation of bands at higher frequencies. The infra-red band at 828 cm.$^{-1}$ also found in the Raman spectrum can be assigned to ν_9, the mode which is mainly controlled by a stretching of the C–C bond.

Values of other fundamentals are almost certainly 968, 540, 606, and 368 cm.$^{-1}$, all of which appear in the Raman spectrum and three at least in the infra-red spectrum. These are assigned on grounds of magnitude and general considerations to ν_{12}, ν_{13}; ν_8; ν_{14}, ν_{15}; and ν_{16}, ν_{17}. We thus have the following array of fundamentals, to which the torsional frequency must be added : 3040(2), 2974(1), 1430(1), 1412(1), 1278(1), 1230(2), 1135(1), 968(2), 828(1), 606(2), 540(1), 368(2). It is possible that the infra-red bands at 684 and 1008 may be due to some combination involving the torsional frequency. It remains impossible to explain the anomalous contours of the bands referred to above, although this may arise through an accidental overlapping of combinations with the fundamental frequencies concerned.

Russell, Golding, and Yost have measured the entropy of this substance and have compared the calorimetric value at 224·4° K. with that computed from their vibrational assignment. The assignment of fundamentals now proposed differs somewhat from theirs, but since most of the frequencies are fairly high, the calculated vibrational entropy is not very sensitive to these differences. The re-calculation is summarised as follows :

	cals./° K./mol.
Calculated entropy :	
Translation–rotation	60·19
Vibration	2·22
Total	62·41
Calorimetric entropy :	63·95
Contribution of torsion	1·54

If it is assumed that the potential during internal torsion about the C–C bond follows a function of the form $V = \frac{1}{2}V_0(1 - \cos 3\theta)$, the estimated discrepancy leads by the method of Pitzer and

TABLE III.

T, °K.	$-(F^\circ - E^0_0)/T$, transl.–rot.				$(H^\circ - E^0_0)/T$, vib.			$(H^\circ - E^0_0)$, kcals.
	transl.–rot.	vib.	torsion.	total.	vib.	torsion.	total.	
250	52·99	0·80	0·71	54·51	2·16	1·08	11·19	2·80
300	54·42	1·24	0·93	56·59	3·06	1·26	12·27	3·68
400	56·73	2·39	1·30	60·42	5·02	1·49	14·46	5·78
500	58·49	3·72	1·67	63·88	6·93	1·62	16·50	8·25
600	59·94	5·15	2·00	67·09	8·70	1·67	18·32	10·9

T, °K.	S°,				C_p,		
	transl.–rot.	vib.	torsion.	total.	vib.	torsion.	total.
250	60·94	2·96	1·80	65·70	6·78	2·02	16·75
300	62·37	4·30	2·17	68·84	8·81	2·14	18·90
400	64·68	7·41	2·78	74·87	12·87	2·18	23·00
500	66·44	10·65	3·28	80·37	16·17	2·08	26·20
600	67·89	13·85	3·66	85·40	18·81	1·97	28·73

Gwinn (*J. Chem. Physics*, 1942, **10**, 428) to a barrier potential of 3250 cals., not significantly different from that found by Russell, Golding, and Yost.

In Table III some thermodynamic properties have been calculated for several temperatures. Although the values are subject to the usual limitations arising from vibrational anharmonicity, as well as other possible minor errors in the molecular dimensions, they may be useful for general purposes.

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THE PHYSICAL CHEMISTRY LABORATORY, OXFORD.

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