**536.** *The Infrared and Raman Spectra of Trifluoroacetaldehyde.*

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The infrared absorption spectrum of gaseous trifluoroacetaldehyde is measured in the range from 400 to 5000 cm.$^{-1}$. The Raman spectrum of the liquid at $-40°$ is photographed and the states of polarization of the lines determined qualitatively. A probable assignment of the fundamental frequencies is suggested. The torsional frequency appears in the Raman spectrum at 184 cm.$^{-1}$: this corresponds to a potential barrier to internal rotation of 9·8 kcal./mole.

THE infrared spectrum of trifluoroacetaldehyde has been studied by Husted and Albrecht.[1] Since their results are restricted to the rock-salt region it seemed worth while, when a sample of the material was prepared and purified for another purpose,[2] to repeat and

Infrared spectrum of trifluoroacetaldehyde.
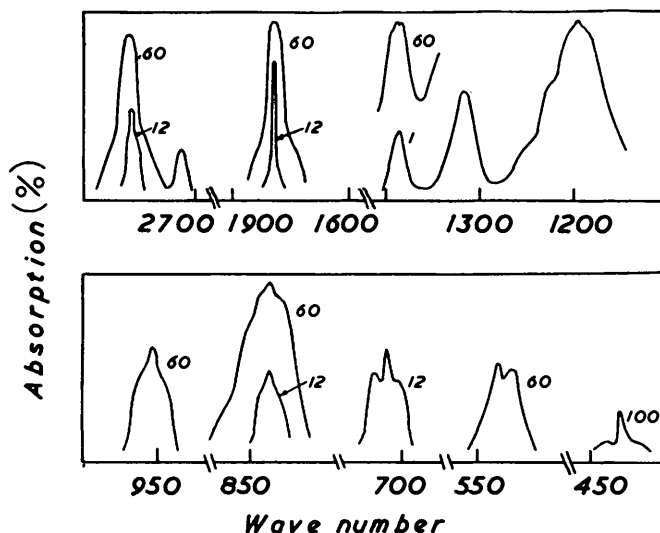
The figures beside the curves indicate pressures (mm. Hg) in a 10 cm. cell.

extend the infrared measurements and also to study the Raman spectrum. Of particular interest in the latter was the observation of the torsional frequency.

The only possible symmetry element of the CF$_3$·CHO molecule is a plane containing the C·CHO grouping and one fluorine atom. The selection rules for this symmetry (point group C$_s$) allow all 15 fundamental modes in both the infrared and Raman spectra. There are 10 modes of class A' which will give polarized Raman lines; five of these are composed mainly of symmetrical stretching and bending, and will be strongly polarized. The five modes of class A'', which include the torsional vibration, will be depolarized.

[1] Husted and Albrecht, *J. Amer. Chem. Soc.*, 1952, **74**, 5422.
[2] Dodd and Smith, *J.*, 1957, 1465.

The major bands in the observed infrared spectrum are illustrated in the Figure. The observed Raman frequencies and the infrared frequencies assigned to fundamentals are given in the Table, which also includes data on intensities and the states of polarization of all but the weakest Raman lines. In the rock-salt region the infrared spectrum closely resembles that reported by Husted and Albrecht : [1] asterisks in the Table indicate the frequencies which were also observed by them. The new infrared bands at 1136 and 1212 cm.$^{-1}$ can only be discerned at favourable pressures, since they tend to be obscured by the very strong band at 1197 cm.$^{-1}$. For two of the infrared bands included in the Table no corresponding Raman lines were observed. Both these bands are stronger than those assigned to overtones and combinations : furthermore their frequencies occur in combinations.

Of the infrared bands not assigned to fundamentals, all but two very weak ones are satisfactorily accounted for as overtones or combinations. The observed frequencies (in cm.$^{-1}$) and assignments are as follow : 589 w ($\nu_{10} + \nu_{14}$, $\nu_2 - \nu_{12}$); 860 vw ($2\nu_9$); ~873 vw ($\nu_{15} - \nu_{10}$, $\nu_{12} - \nu_{14}$, $\nu_4 - \nu_9$); ~890 w ($\nu_{15} + \nu_8$, $\nu_{11} - \nu_{14}$); 1012 w ($\nu_{12} - \nu_{15}$, $\nu_{15} + \nu_7$, $\nu_{14} + \nu_8$); 1089 w ($\nu_1 - \nu_2$); ~1436 vw (?); ~1483 vw ($\nu_{10} + \nu_{11}$, $\nu_{13} + \nu_6$); 1544 w ($\nu_{14} + \nu_{11}$, $\nu_8 + \nu_7$); 1681 w ($2\nu_7$); 1735 m ($\nu_{13} + \nu_{12}$, $\nu_9 + \nu_4$); ~1826 m ($\nu_9 + \nu_3$, $\nu_8 + \nu_{15}$, $\nu_{13} + \nu_4$); 1891 w ($\nu_8 + \nu_{12}$); 2036 w ($\nu_7 + \nu_{12}$); 2132 w ($\nu_7 + \nu_4$); 2283 vw

Fundamental frequencies of trifluoroacetaldyde.

Observed frequencies (cm.$^{-1}$)		Assignment		
Infrared	Raman		Class A' (in-plane)	Class A'' (out-of-plane)
	184 w	ν_{15}		Torsion
	266 w	ν_{10}	CF$_3$ rocking	
	320 m, dp	ν_{14}		CF$_3$ rocking
430 (2)	432 s, p	ν_9	C–C=O bending	
533 (11)	528 m, dp	ν_{13}		CF$_3$ deformation
706* (72)	708 s, p	ν_8	CF$_3$ deformation	
839* (43)	837 vs, p	ν_7	CF$_3$ deformation	
957* (11)		ν_6	C–C stretching	
1136 (15)	1145 w	ν_5	C–F stretching	
1197* (915)	1200 w	ν_{12}		C–F stretching
1212 (80)		ν_{11}		C–H bending
1309* (203)	1305 vw	ν_4	C–F stretching	
1385* (79)	1383 w, p	ν_3	C–H bending	
1784* (81)	1770 s, p	ν_2	C=O stretching	
2870* (40)	2901 s, p	ν_1	C–H stretching	

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, p = polarized, dp = depolarized. Figures in parentheses after infrared fundamentals are approximate molar extinction coefficients. For Raman lines marked neither p nor dp the state of polarization is uncertain.

($2\nu_5$); 2305 vw ($\nu_{11} + \nu_2$); ~2350 w ($\nu_5 + \nu_{11}$, $\nu_6 + \nu_3$); 2372 m ($2\nu_{12}$); 2603 w ($\nu_{11} + \nu_4$, $\nu_1 - \nu_{10}$); 2692 w ($\nu_4 + \nu_3$); 2742 m ($\nu_6 + \nu_2$); ~2820 m ($2\nu_7 + \nu_5$); 2907 m ($\nu_5 + \nu_2$); 2986 vw ($\nu_{12} + \nu_2$); 3100 vw ($\nu_4 + \nu_2$); 3165 vw ($\nu_3 + \nu_2$); 3488 vw ($2\nu_5 + \nu_{12}$); 3565 m ($2\nu_2$); 3606 vw ($3\nu_{12}$); 3693 vw ($\nu_7 + \nu_1$); 4065 vw ($\nu_{12} + \nu_1$); 4216 vw (?); 4509 vw ($2\nu_2 + \nu_6$); 4647 w ($\nu_2 + \nu_1$).

The Table gives the suggested assignment which can be made by comparison with the spectra of CF$_3$·CHCl$_2$; [3] CF$_3$·CF$_2$Cl, CF$_3$·CFCl$_2$; [4] CF$_3$·CHF$_2$; [5] CF$_3$·CN; [6] CF$_3$Br, CF$_3$I; [7] CCl$_3$·CHO, CBr$_3$·CHO; [8] CH$_3$·CHO.[9] It is emphasized that the descriptions of the modes given in the last two columns of the Table are only approximate. In some of the modes considerable mixing must occur.

[3] Nielsen, Liang, and Smith, *J. Chem. Phys.*, 1953, **21**, 1060.
[4] Nielsen, Liang, Smith, and Smith, *ibid.*, p. 383.
[5] Nielsen, Claassen, and Moran, *ibid.*, 1955, **23**, 329.
[6] Edgell and Potter, *ibid.*, 1956, **24**, 80.
[7] Edgell and May, *ibid.*, 1954, **22**, 1808.
[8] Seewann-Albert, *Acta Phys. Austriaca*, 1947—8, **1**, 346.
[9] Pitzer and Weltner, *J. Amer. Chem. Soc.*, 1949, **71**, 2842.

The frequency 2870 cm.$^{-1}$ (infrared), 2901 (Raman) can at once be assigned to C–H stretching and is close to the values 2863 and 2848 cm.$^{-1}$ for CCl_3·CHO and CBr_3·CHO respectively. The carbonyl stretching frequency occurs at 1784 cm.$^{-1}$ (infrared), 1770 (Raman). The value rises with increasing electronegativity of the attached groups, thus : 1740 (CH_3·CHO), 1742 (CBr_3·CHO), 1762 (CCl_3·CHO). This frequency is even higher in the acid halides, the value being 1866 in acetyl fluoride [10] and about 1890 in fully fluorinated acid fluorides.[11] The C=CH_2 stretching frequency is similarly affected : it occurs at 1649 cm.$^{-1}$ in propene [12] and at 1670 in CF_3·CH=CH_2.[13]

The next group of five fundamentals comprises three C–F stretching modes ($2A' + A''$) and two C–H bending modes ($A' + A''$). In CCl_3·CHO and CBr_3·CHO, where there are no close neighbours, the two C–H bending frequencies occur at 1350 and 1025 cm.$^{-1}$ and at 1352 and 1000 cm.$^{-1}$. In CF_3·CHCl$_2$ the values 1325 and 1192 are assigned to these modes. On the other hand the very great intensity of the 1197 cm.$^{-1}$ band of CF_3·CHO in the infra-red spectrum and the very low intensity in the Raman spectrum indicate that it is a C–F stretching mode; and the same probably applies to the infrared band at 1309 cm.$^{-1}$. The C–H bending modes are accordingly assigned to 1385 and 1212 cm.$^{-1}$, the remaining C–F stretching frequency being at 1136 cm.$^{-1}$. Interchange of ν_5 and ν_{11} is, however, equally reasonable.

The assignment of 957 cm.$^{-1}$ to the C–C stretching mode is consistent with similar assignments in CH_3·CHO (1114 cm.$^{-1}$, strong in infrared; very weak in Raman), CCl_3·CHO (985 cm.$^{-1}$, weak in Raman), and CBr_3·CHO (979 cm.$^{-1}$, weak in Raman). The next four frequencies comprise the C–C=O bending mode (A') and three CF_3 deformation modes ($2A' + A''$). The C–C=O bending frequency is given as 525 cm.$^{-1}$ in CH_3·CHO and 618 cm.$^{-1}$ in CCl_3·CHO. The CF_3 deformation frequencies of the other molecules mentioned all lie in the region 840—550 cm.$^{-1}$, and our assignment is consistent with this. Owing to the closeness of their frequencies, none of these modes will be even approximately pure. The frequencies 320 and 266 cm.$^{-1}$ are assigned to CF_3 rocking.

The envelopes of seven of the infrared bands are fairly well defined. As can be seen from the Figure, the bands at 430, 706, 839, and 957 cm.$^{-1}$, and probably those at 1385 and 2870 cm.$^{-1}$, have PQR contours. The apparent PR separation varies somewhat but is clearly seen as about 16 cm.$^{-1}$ at 430 and 706 cm.$^{-1}$. The band at 533 cm.$^{-1}$ shows no zero branch and a smaller PR separation of 12 cm.$^{-1}$. These facts are not easily reconciled with the assignments suggested in the Table and discussed above. Assuming point-group C_s with the bond lengths C–F = 1·36, C–C = 1·54, C–H = 1·09, C=O = 1·21 Å and the bond angles C–C–F = C–C–H = 109° 28', C–C=O = 119°, we calculate the principal moments of inertia to be $I_x = 101$, $I_y = 172$, and $I_z = 174$ a.m.u. (atomic mass units) Å^2 (x- and y-axes in the plane of symmetry, z-axis perpendicular thereto). No decision can be made as to the orientation of the CHO group with respect to the CF_3, since the moments of inertia are identical for both configurations of point group C_s so long as the CF_3 group retains its 3-fold symmetry about the C–C axis. Increase of the C–C=O angle to 130° gives $I_x = 101$, $I_y = 177$, and $I_z = 179$ a.m.u. Å^2. According to these results, which show the models to be near-symmetric tops, the class A' modes are expected to have mixed type A and type B contours, and the class A'' modes type C. In view of the fairly pronounced Q branches to be expected for both type A and type C, the observation of PQR contours provides no criterion for assignment. It may be significant, however, that the bands for which PQR contours are observed are all (with the exception of that at 957 cm.$^{-1}$) assigned to class A' on the evidence of the polarization of the corresponding Raman lines; whereas the band at 533 cm.$^{-1}$ has the appearance and about the expected PR separation of type B, at variance with its assignment to class A'' if the axis of inter-mediate moment of inertia is in the symmetry plane. Thus the contours would accord

[10] Dodd, unpublished observation.
[11] Haszeldine, *Nature*, 1951, **168**, 1028.
[12] Kilpatrick and Pitzer, *J. Res. Nat. Bur. Stand.*, 1947, **38**, 191.
[13] Haszeldine, personal communication.

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more satisfactorily with the suggested assignments if the dimensions of the molecule were such that I_z were the intermediate moment. We have not investigated what variations (if any) of the model would lead to this result.

The frequency 184 cm.$^{-1}$ remains and is assigned to the torsional mode, *i.e.*, twisting about the C–C bond. This is of particular interest since it allows an estimate of the height of the potential barrier preventing free rotation. If it is assumed that the potential energy for this type of motion is given by $\frac{1}{2}V_0(1 - \cos 3\theta)$, where V_0 is the potential barrier separating each of the three minima of potential energy and θ is the torsional angle, and if it is further assumed that the vibration is simple harmonic, then it follows [14] that $\nu_{15} = 3(V_0 B_1 B_2/B)^{\frac{1}{2}}$, where B_1, B_2, and B are respectively the rotational constants for the two groups CF_3 and CHO and for the whole molecule about the torsion axis. Reasonable values for the molecular dimensions give moments of inertia about the torsion axis of 165×10^{-40} g. cm.^{2} for CF_3 and $30\cdot2 \times 10^{-40}$ g. cm.^{2} for CHO. These lead to the value 9·8 kcal./mole for the height of the potential barrier, which may be compared with 10·1 kcal./mole for $CF_3\cdot CHCl_2$, 9·1 for $CF_3\cdot CF_2Cl$, and 11·9 for $CF_3\cdot CCl_3$.[15] Pitzer and Weltner [9] give a value near 1 kcal./mole for $CH_3\cdot CHO$, and more recently Wilson [16] has estimated it as 1·13 : for ethane the figure [17] is about 2·9 kcal./mole. The high values for the fluorinated compounds may arise from the large electronegativity of the fluorine and the consequent strong repulsions between non-bonded atoms. The effect is more marked in torsion against a CHO group than against a CH_3. Thus partial fluorination of ethane leads to only small increases in the potential barrier, the values for $CHF_2\cdot CH_3$ and $CH_2F\cdot CH_3$ being respectively 3·18 and 3·31 kcal./mole.[16] Unfortunately no independent thermodynamic data are available for trifluoroacetaldehyde to permit the spectroscopic conclusions to be checked.

EXPERIMENTAL

Trifluoroacetaldehyde was prepared by Rosenmund reduction of the acid chloride as recommended by Brown and Musgrave : [18] further details are given elsewhere.[8] The infrared absorption spectrum of the vapour was measured in the region 400—5000 cm.$^{-1}$ with a Grubb-Parsons double-beam spectrometer, prisms of potassium bromide, sodium chloride, and lithium fluoride being used. The Raman spectra were photographed with the apparatus previously described [19] (Toronto arc excitation, Hilger E 518 spectrograph). The states of polarization of all but the weakest lines were determined qualitatively by the method of incident polarized light, by use of suitable Polaroid cylinders surrounding the Raman vessel. The sample (*ca.* 0·5 ml.) was distilled *in vacuo* into the Raman vessel and maintained liquid at $-40°$. The exciting line was Hg 4358 Å : a sodium nitrite filter was used to reduce the intensity of primary lines of shorter wavelength. Exposures up to 8 hr. were given, and Kodak Special Scientific plates used. The recorded frequencies, determined in the usual manner with a copper arc spectrum as standard, are probably correct to within ± 3 cm.$^{-1}$ for strong, sharp lines. For the weaker lines the errors may be larger.

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[14] Herzberg, " Infra-red and Raman Spectra," Van Nostrand, New York, 1945, p. 226.
[15] Luft, *J. Chem. Phys.*, 1954, **22**, 155.
[16] Wilson, *Spectroscopia Molecular*, 1956, **5**, 44.
[17] Pitzer, *Discuss. Faraday Soc.*, 1951, **10**, 66.
[18] Brown and Musgrave, *J.*, 1952, 5049.
[19] Rolfe and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1030.