

## RESEARCH NOTES

### Raman spectrum and vibrational assignments for the trifluoroacetate ion

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As part of an investigation of trifluoroacetic acid and its derivatives, the Raman spectrum of the trifluoroacetate ion has been reinvestigated. This ion has received relatively little attention, the one Raman investigation appearing in the literature being that of FONTEYNE [1]; two references to the infrared spectrum were found [2, 3] but neither represents a detailed investigation. FONTEYNE has discussed the complete assignments of this ion but since the frequencies of the  $\text{CF}_3$  group had not been established at the time of his paper, a reconsideration of all assignments appears desirable.

Sodium trifluoroacetate was prepared by careful neutralization of the acid followed by recrystallization. The spectra were obtained from nearly saturated aqueous solutions. The experimental frequencies listed in Table 1 represent averages obtained from several plates and have an estimated uncertainty of 1-2  $\text{cm}^{-1}$  for the sharper bands. The microphotometer tracing shown in Fig. 1 is a representative spectrum although some details are not shown as clearly as on other plates. Qualitative polarization measurements were made by the two exposure method using polaroid cylinders.

A recent electron diffraction investigation of fluoropicrin,  $\text{CF}_3\text{NO}_2$ , has reported that the axes of the  $\text{CF}_3$  and  $\text{NO}_2$  groups do not coincide and that the molecule has an ethane-like structure with one of the trigonal positions around the nitrogen vacant [4]. Since fluoropicrin and the trifluoroacetate ion are isoelectronic, it is likely that the ion also exhibits this structure which belongs to the point group  $C_s$ . This model predicts 9 frequencies in the  $A'$  class and 6 in the  $A''$  class. For the most part, the assignments listed in Table 1 were arrived at by consideration of FONTEYNE's original assignments, together with those made for the normal and deuterated acetate ion [5-7] and the iso-electronic molecule, fluoropicrin [8]. The pattern of frequencies of the latter molecule, particularly, showed a marked resemblance to that of the trifluoroacetate ion and the assignments in this case were of considerable value in deciding on some of the assignments for the trifluoroacetate ion. However, discussion of two assignments for the ion appears desirable in view of the corresponding assignments proposed for fluoropicrin. These involve the two sharp, polarized bands at 601  $\text{cm}^{-1}$  and 729  $\text{cm}^{-1}$  for which the two possible modes are the symmetric  $\text{CF}_3$  and  $\text{CO}_2$  deformation motions. Identification of the latter mode is of some interest to assess the effect of the strong electron attracting power of the  $\text{CF}_3$  group. FONTEYNE originally assigned this motion to a band at 473  $\text{cm}^{-1}$ , a value which appears much too low compared to the value 650  $\text{cm}^{-1}$  which is assigned to this motion in the normal acetate ion. MASON and DUNDERDALE assigned the  $\text{NO}_2$  deformation in fluoropicrin to a band at

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- [5] K. ITO and H. J. BERNSTEIN, *Can. J. Chem.* **34**, 170 (1956).
- [6] L. H. JONES and E. McLAREN, *J. Chem. Phys.* **22**, 1796 (1954).
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- [8] J. MASON and J. DUNDERDALE, *J. Chem. Soc.* 759, (1956).

Table 1. Observed Raman frequencies and assignments for the trifluoroacetate ion in aqueous solution

Symmetry class	Vibrational mode	State of polarization	CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup> (aq. soln.)	CF <sub>3</sub> NO <sub>2</sub> * (gas)
<i>a'</i>	$\nu_1$ CO stretch	pol.	1435	1315
	$\nu_2$ C—F stretch (out of phase)	pol.	1202	1277
	$\nu_3$ C—F stretch (in phase)	—	1143	1154
	$\nu_4$ C—C stretch	pol.	844	863
	$\nu_5$ CO <sub>2</sub> deformation	pol.	729	751
	$\nu_6$ CF <sub>3</sub> deformation (in phase)	pol.	601	604
	$\nu_7$ CF <sub>3</sub> deformation (out of phase)	depol.	521	529
	$\nu_8$ CO <sub>2</sub> rock	pol.	410	400†
	$\nu_9$ CF <sub>3</sub> rock	depol.	267	450
<i>a''</i>	$\nu_{10}$ C—O stretch	depol.	1681	1620
	$\nu_{11}$ C—F stretch	pol.	1202	1288
	$\nu_{12}$ CF <sub>3</sub> deformation	depol.	521	529
	$\nu_{13}$ CO <sub>2</sub> rock	—	—	400†
	$\nu_{14}$ CF <sub>3</sub> rock	depol.	437	450
	$\nu_{15}$ Torsion	—	—	220†

\* Frequencies observed in infrared absorption, Ref. [8]; some assignments revised

† Postulated from combination bands and overtones

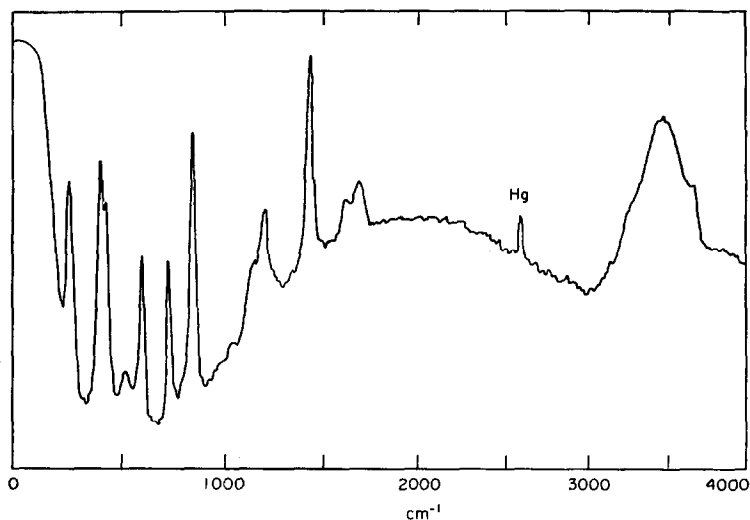


Fig. 1. Raman spectrum of aqueous sodium trifluoroacetate.

604 cm<sup>-1</sup> which suggests that the CO<sub>2</sub> deformation in the trifluoroacetate ion should be identified with the sharp, moderately intense band at 601 cm<sup>-1</sup>. If one accepts this assignment, however, the only assignment which is possible for the symmetric CF<sub>3</sub> deformation motion is at 729 cm<sup>-1</sup>, the corresponding band in the fluoropierin spectrum being at 751 cm<sup>-1</sup>. These latter values seem

unusually high when compared to the  $\text{CF}_3$  deformation assignments in trifluoroacetic acid [2, 9, 10] and other molecules containing the  $\text{CF}_3$  group. Moreover, the band at  $729\text{ cm}^{-1}$  appears sharper than bands associated with the  $\text{CF}_3$  group normally do in the Raman effect. Since the symmetric  $\text{CF}_3$  deformation mode has been assigned a value between  $600$  and  $700\text{ cm}^{-1}$  in most other molecules containing this group, it is likely that the two motions in question are strongly mixed in both the trifluoroacetate ion and in fluoropicrin. The marked similarity in appearance between the bands at  $601$  and  $729\text{ cm}^{-1}$  in the Raman spectrum of the trifluoroacetate ion shown in Fig. 1 supports this hypothesis. Since the assignment of the  $\text{CO}_2$  deformation to a band at  $693\text{ cm}^{-1}$  in the spectrum of trifluoroacetic acid appears well established, there is perhaps some reason for considering the higher of the two bands in the spectrum of the ion to be predominantly the  $\text{CO}_2$  deformation. However, this point cannot be answered conclusively without a normal co-ordinate analysis.

No extensive discussion appears necessary for the other assignments given in Table 1. It might be noted that the bands assigned to the remaining motions of the trifluoromethyl group are characteristically rather broad and not too intense (Fig. 1) such that it is not possible to determine whether the degenerate frequencies of the free  $\text{CF}_3$  group have been split. The polarized character of the rocking mode at  $410\text{ cm}^{-1}$  is consistent with the  $C_3$  symmetry which has been assumed for the ion and does not support an "effective"  $C_{2v}$  symmetry based on the  $\text{CF}_3$  and  $\text{CO}_2$  groups being co-axial with a negligible potential barrier hindering free rotation. The latter model was assumed by MASON and DUNDERDALE in their discussion of fluoropicrin and some of their conclusions based on band contours may require revision in the light of the reported structure.

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### Solvent effect and Raman band intensities

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RECENT measurements by several workers on the intensities of Raman vibration bands of molecules dissolved in organic solvents suggest that the refractive index of the medium as a whole effects the observed intensity. In two recent papers [1] from this laboratory similar results were reported for the carbonyl group of alkyl benzoates, and details were given of the experimental method and the corrections applied to obtain the band intensities relative to that of the  $458\text{ cm}^{-1}$  band of pure carbon tetrachloride.

We have made similar measurements on the  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{N}$  group vibration bands in propargyl chloride and vinyl cyanide respectively. The concentration of the solute used in each solvent was close to  $0.1\text{ g/c}^3$ , which gave an intensity sufficiently large for convenient measurement, though still small enough to avoid much solute-solute interaction. The results are summarized in Table 1, and in Figs. 1 and 2 the intensities  $S$  are plotted as a function of the refractive index of the liquid mixture concerned.

It is seen that there is a substantial variation of intensity in the different solvents and a smooth relation with the refractive index. Solvents which might be expected to be anomalous

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- [1] (i) J. P. JESSON and H. W. THOMPSON, (ii) G. H. J. FACER and H. W. THOMPSON; *Proc. Roy. Soc. A* **268**, 68, 79 (1962)

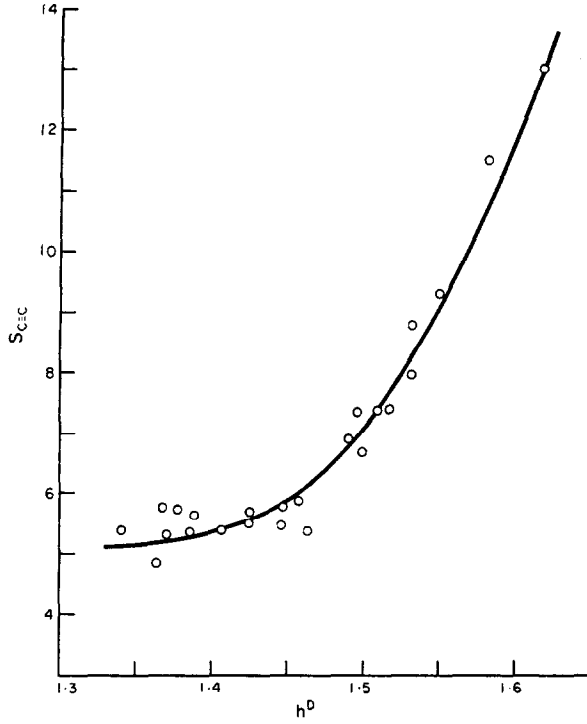


Fig. 1

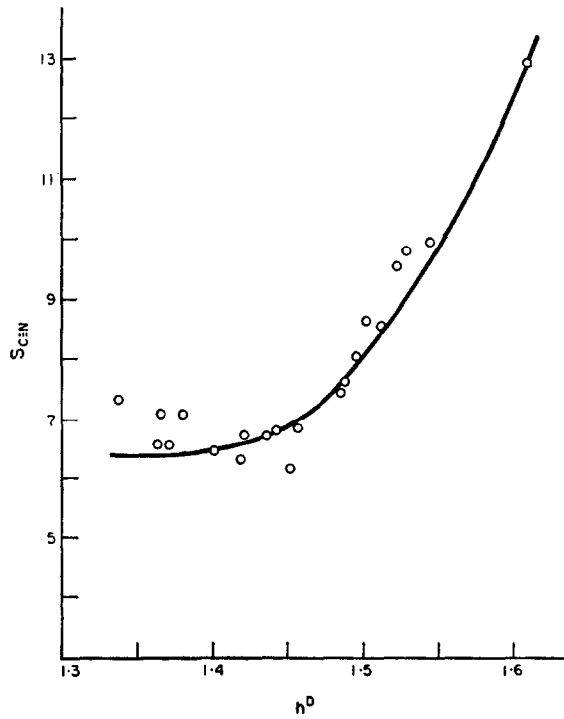


Fig. 2

Table 1.

Solvent	C≡C band			C≡N band		
	<i>S</i>	<i>n<sup>D</sup></i>	<i>S'</i>	<i>S</i>	<i>n<sup>D</sup></i>	<i>S'</i>
Methanol	5.37	1.34	4.28	7.35	1.336	5.82
1: 1: 2 Trifluoro-trichloro ethane	4.86	1.364	4.04	6.49	1.362	5.36
Acetone	5.8	1.367	4.84	6.57	1.363	5.43
Ethanol	5.34	1.369	4.48	7.11	1.365	5.91
Di-isopropyl ether	5.77	1.376	4.89	6.52	1.372	5.48
n-Hexane	5.40	1.382	4.63	7.11	1.379	6.06
n-Butyl chloride	5.39	1.405	4.83	6.48	1.400	5.74
Methylene dichloride	5.70	1.425	5.31	6.71	1.420	6.18
Cyclohexane	5.52	1.424	5.14	6.34	1.419	5.82
Chloroform	5.80	1.443	5.60	6.77	1.440	6.47
1: 2-Dichloro ethane	5.50	1.445	5.32	6.73	1.439	6.43
Carbon tetrachloride	5.90	1.457	5.93	6.14	1.452	6.03
Fluorobenzene	5.39	1.463	5.43	6.87	1.456	6.81
Toluene	6.93	1.490	6.75	7.45	1.484	7.38
Benzene	7.35	1.495	7.08	7.56	1.487	7.41
Tetrachloro ethylene	6.68	1.498	6.38	8.05	1.493	7.77
Methyl benzoate	7.39	1.510	6.84	8.67	1.504	8.14
Chlorobenzene	7.42	1.517	6.75	8.58	1.510	7.92
Benzyl alcohol	7.99	1.532	7.00	9.82	1.528	8.68
Methylene dibromide	8.82	1.531	7.74	9.57	1.522	8.57
Bromobenzene	9.32	1.549	7.84	9.94	1.544	8.43
Bromoform	11.59	1.583	9.03	—	—	—
s-Tetrabromo ethane	13.02	1.621	9.36	12.98	1.610	9.53

because of possible hydrogen bonding interactions appear to conform with the general trend. Whether this correlation of the intensity with refractive index is connected with some internal field effect, or alternatively arises from the application of erroneous corrections in allowing for reflection losses and other experimental factors, is still uncertain. If the band intensities are computed by including the reflection loss factor of WOODWARD and GEORGE [2], but omitting that of BERNSTEIN and ALLEN [3], the values *S'* listed in Table 1 still show a regular trend with refractive index.

We are inclined to believe that in spite of some uncertainties with regard to these corrections, there is a residual and significant refractive index effect, as suggested by recent results of other workers [4], but this matter is being examined further by changes in the experimental method.

If the curves of Fig. 1 and 2 are extrapolated to very low values of the refractive index, they appear to reach an asymptotic value which may correspond to the intensity of the band in the vapour phase.

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[4] See for example D. G. REA, *Anal. Chem.* **32**, 1638 (1960).