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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 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 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, CF_3NO_2, has reported that the axes of the CF_3 and 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 cm^{-1} and 729 cm^{-1} for which the two possible modes are the symmetric CF_3 and 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 CF_3 group. FONTEYNE originally assigned this motion to a band at 473 cm^{-1}, a value which appears much too low compared to the value 650 cm^{-1} which is assigned to this motion in the normal acetate ion. MASON and DUNDERDALE assigned the NO_2 deformation in fluoropicrin to a band at

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

Symmetry class		Vibrational mode	State of polarization	$CF_3CO_2^-$ (aq. soln.)	CF_3NO_2* (gas)
a'	ν_1	CO stretch	pol.	1435	1315
	ν_2	C—F stretch (out of phase)	pol.	1202	1277
	ν_3	C—F stretch (in phase)	—	1143	1154
	ν_4	C—C stretch	pol.	844	863
	ν_5	CO_2 deformation	pol.	729	751
	ν_6	CF_3 deformation (in phase)	pol.	601	604
	ν_7	CF_3 deformation (out of phase)	depol.	521	529
	ν_8	CO_2 rock	pol.	410	400†
	ν_9	CF_3 rock	depol.	267	450
a''	ν_{10}	C—O stretch	depol.	1681	1620
	ν_{11}	C—F stretch	pol.	1202	1288
	ν_{12}	CF_3 deformation	depol.	521	529
	ν_{13}	CO_2 rock	—	—	400†
	ν_{14}	CF_3 rock	depol.	437	450
	ν_{15}	Torsion	—	—	220†

* Frequencies observed in infrared absorption, Ref. [8]; some assignments revised
† Postulated from combination bands and overtones

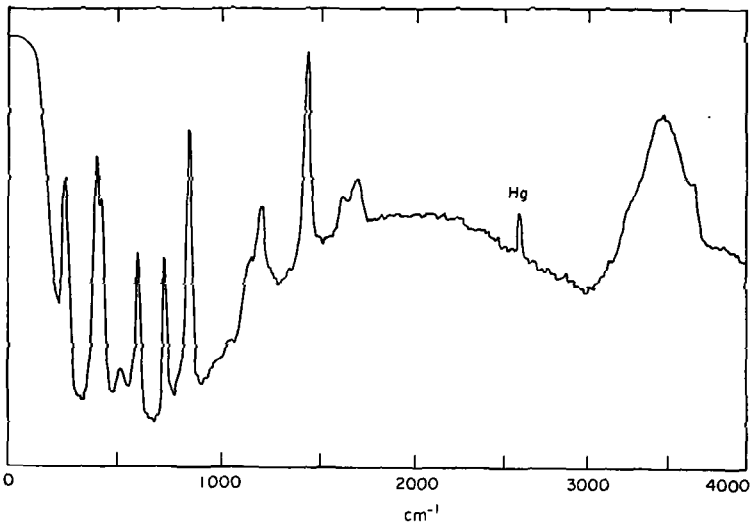

Fig. 1. Raman spectrum of aqueous sodium trifluoroacetate.

604 cm^{-1} which suggests that the CO_2 deformation in the trifluoroacetate ion should be identified with the sharp, moderately intense band at 601 cm^{-1}. If one accepts this assignment, however, the only assignment which is possible for the symmetric CF_3 deformation motion is at 729 cm^{-1}, the corresponding band in the fluoropicrin spectrum being at 751 cm^{-1}. These latter values seem

unusually high when compared to the CF_3 deformation assignments in trifluoroacetic acid [2, 9, 10] and other molecules containing the CF_3 group. Moreover, the band at 729 cm^{-1} appears sharper than bands associated with the CF_3 group normally do in the Raman effect. Since the symmetric CF_3 deformation mode has been assigned a value between 600 and 700 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 cm^{-1} in the Raman spectrum of the trifluoroacetate ion shown in Fig. 1 supports this hypothesis. Since the assignment of the CO_2 deformation to a band at 693 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 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 CF_3 group have been split. The polarized character of the rocking mode at 410 cm^{-1} is consistent with the C_s symmetry which has been assumed for the ion and does not support an "effective" C_{2v} symmetry based on the CF_3 and 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 cm^{-1} band of pure carbon tetrachloride.

We have made similar measurements on the C≡C and C≡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 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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