Short Communication

Vibrational spectrum of iodine trifluoride *

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A vibrational study of iodine trifluoride has not been possible until now owing to its extremely low thermal stability and vapour pressure. However a planar T structure has been deduced for the IF_3 group from the infrared spectra of complexes of iodine trifluoride with organic bases, *i.e.* pyridine and quinoline[1]. Previously it was suggested[1] that solid IF_3 consists of dimers or polymers associated through fluorine bridges, the compound existing in an ionic form as $IF_2^+IF_4^-$.

In this present study we have succeeded in recording the infrared spectrum of solid IF_3 through the use of a new low-temperature technique recently reported by Bayersdorfer, Minkwitz and Jander[2]. In Figure 1 the infrared spectrum of solid IF_3 at $-100°$ is depicted, and the observed frequencies are listed in Table 1 together with those of gaseous ClF_3 and BrF_3[3] as well as matrix-isolated BrF_3[4]. All recorded spectra showed some bands at approximately 205, 320, 375 and 600 cm^{-1}. When the samples were warmed to $-20°$ the intensities of these bands increased, while the characteristic absorptions of IF_3 disappeared. Since IF_3 decomposes to I_2 and IF_5 during preparation, these bands were assigned to the v_9, v_3, v_8 and v_2 vibrational modes of IF_5 respectively[5].

Only five of the six fundamentals expected for a T-shaped IF_3 molecule are unambiguously observed in the spectrum of solid IF_3 (Table 1). The highest frequency band (*ca.* 640 cm^{-1}) may be assigned to the shortest I–F bond, the observed splitting being probably due to site group symmetry. The broad absorption band at about 480 cm^{-1} indicates strong association through fluorine bridges. Since the same band is also the most intense band in the infrared spectrum of solid $IF_3 \cdot py$[6] and almost disappears in the Raman spectrum, this has been assigned to the asymmetric F–I–F stretching mode.

The symmetric mode could not be observed with certainty. In solid $IF_3 \cdot py$[6], v_8(F–I–F) occurs at *ca.* 545 cm^{-1} and is a very strong, distinct band in the Raman spectrum. For this reason, the shoulder at 550 cm^{-1} (see Fig. 1) has been assumed to be the symmetric F–I–F mode in solid IF_3.

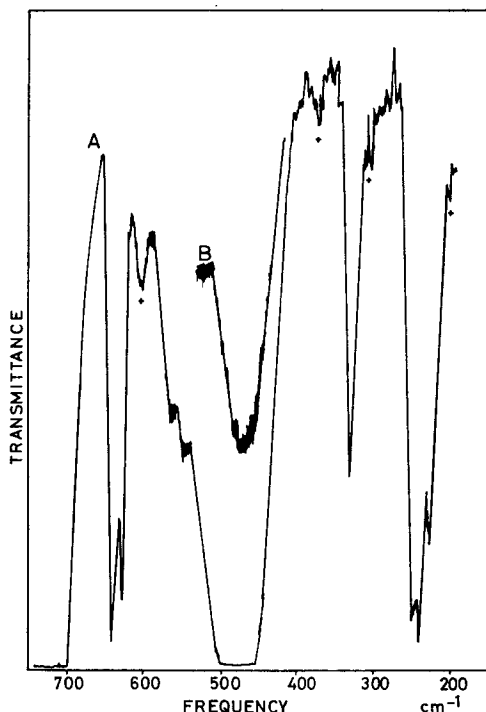* Abstracted from E. LEHMANN, *Dissertation*, Dortmund, 1973.

Fig. 1. The infrared spectrum of IF_3 at $-100°$. Trace A: mole ratio IF_3: Nujol/n-pentane $= 1:3$; Trace B: mole ratio IF_3: Nujol/n-pentane $= 1:6$. $+$ IF_5 absorption bands.

The v_s(F–A–F) stretching frequency increases slightly in the series ClF_3, BrF_3 and IF_3 (Table 1) whereas the v_{as}(F–A–F) frequency decreases considerably with increasing size of the central atom. Hence, the asymmetric F–I–F stretching mode of iodine trifluoride, in contrast to that of ClF_3 and BrF_3, occurs at lower wave numbers than the symmetric mode. The fact that similar smooth trends are observed in the corresponding series of anions ClF_4^-, BrF_4^- and IF_4^{-}[7] lends additional support to the assignment given.

The bands at 331, 240 and 228 cm^{-1} have been assigned to the δ_{as}(in plane), δ(out of plane) and δ_s(in plane) deformation modes, respectively. The assignment has been made in complete analogy with ClF_3 and BrF_3. As already mentioned, no explanation can be given for the splitting of the I–F' stretching mode and of the δ(out of plane) deformation mode (see Fig. 1).

Studies of the Raman spectrum of solid IF_3 are at present in progress and Raman polarization measurements are being made on its solutions in acetonitrile. From these experiments it is hoped to obtain more detailed information on the structure of IF_3.

TABLE 1

THE VIBRATIONAL SPECTRUM* OF IF_3 AND ITS ASSIGNMENT IN COMPARISON TO ISOELECTRONIC ClF_3 AND BrF_3

$ClF_3(g)$[3]		$BrF_3(g)$[3]		BrF_3[4] (matrix isolated)	$IF_3(s)$	Assignment in point group C_{2v}
Raman	IR	Raman	IR	IR	IR	
752.1 744.7 } (p,s)	742 760 } (s)	675 (p,s)	668 682 } (s)	672 (s)	640 628 } (s)	$\nu_1(A_1)$ $\nu(A-B)$
n.o.	702 (vs)	612 (vvw)	604 614 621 } (vs)	592 (vs)	480 (vs)	$\nu_4(B_1)$ $\nu_{as}(B-A-B)$
529,3 (p,s)	538 522 } (m)	552 (p,vs)	547 557 } (w)	545 (mw)	[550 (mw)]	$\nu_2(A_1)$ $\nu_s(B-A-B)$
431 (dp,w)	442 (w)	n.o.	342 350 359 } (vw)	346 (mw)	331 (m)	$\nu_5(B_1)$ δ_{as}(in plane)
337 321 } (p,w)	328 (s)	n.o.	242 (s)	250 (m)	240 245 } (s)	$\nu_6(B_2)$ δ(out of plane)
n.o.	328 (s)	233† (p,w)	242 (s)	235 (mw)	228 (m)	$\nu_3(A_1)$ δ_s(in plane)

* Observed frequencies in cm^{-1}.
† For liquid BrF_3 (see ref. 4).
n.o. = not observed; g = gas; s = solid.

Our infrared study of solid iodine trifluoride confirms the expected trigonal-bipyramidal structure for IF_3 molecules. The formation of fluorine bridges apparently involves the two axial rather than the two equatorial fluorine atoms. Our observations do not support the assumption that IF_2^+ and IF_4^- ions are present and solid IF_3 does not apparently exist in the ionic form $IF_2^+IF_4^-$, but like BrF_3 associates preferentially through covalent fluorine bridges as in the following structure:
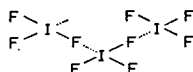
Calculations of the vibrational force constants are at present in progress.

Experimental

Iodine trifluoride was prepared from the elements at $-45°$ in CCl_3F[1] and stored at $-78°$. The apparatus used for the low-temperature studies has been reported elsewhere recently[2]. The samples were prepared as mulls using a Nujol/n-pentane mixture at $-78°$ in an inert gas atmosphere and then cooled down to $-100°$ for IR measurements. The infrared spectra were recorded on a Beckman IR 12 spectrophotometer in the range 4000–200 cm^{-1} using polyethylene sheets of 0.45 mm thickness as windows.

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