spectra indicate, bidentate, presumably bridging groups are found for the $SO_3F$ and $SO_3CF_3$ groups with $SO_4$ in $(IO)_2SO_4$ acting as a tetradentate bridging group.[7]

Even though Raman spectroscopy was found to afford well-resolved spectra, the complexity observed and the reported molecular structures[7-9] indicate a complicated bonding situation. Not only simple ionic models such as $IO_2^+IO_3^-$ for $I_2O_5$ or $(IO^+)_n(IO_3^-)_n$[12] for $I_2O_4$ but also conventional views on molecular geometry, coordination number, covalent bonding, and van der Waals interaction are insufficient to describe the complex solid structures encountered in this group of compounds. It is hoped that more definitive x-ray data will become available on the iodine–oxygen derivatives of oxyacids.

**Acknowledgment.** The financial support of the National Research Council of Canada is gratefully acknowledged. Mrs. B. I. Kriszan and Miss M. Rosenberg are thanked for the technical drawings.

**Registry No.** $IOSO_3F$, 58735-49-2; $IO_2SO_3F$, 13537-35-4; $IOSO_3CF_3$, 58735-51-6; $IO_2SO_3CF_3$, 58735-54-9; $(IO)_2SO_4$, 25041-70-7; $I_2O_4$, 12399-08-5; $HI_3O_8$, 12134-99-5; $HSO_3CF_3$, 1493-13-6.

### References and Notes

(1) For part 1 see ref 10.
(2) (a) G. Daehle and A. Kjekshuis, *Acta Chem. Scand.*, **18**, 144 (1964), and references quoted therein; (b) K. Selte and A. Kjekshuis, *ibid.*, **25**, 751 (1971).
(3) M. E. Millon, *Ann. Chim. Phys.*, **12**, 345, 353 (1844); *J. Prakt. Chem.*, **34**, 321, 337 (1845).
(4) F. Aubke, G. H. Cady, and C. H. L. Kennard, *Inorg. Chem.*, **3**, 1799 (1964).
(5) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1236 (1966).
(6) J. R. Dalziel and F. Aubke, *Inorg. Chem.*, **12**, 2707 (1973).
(7) S. Furuseth, K. Selte, H. Hope, A. Kjekshuis, and B. Klewe, *Acta Chem. Scand., Ser. A*, **28**, 71 (1974).
(8) K. Selte and A. Kjekshuis, *Acta Chem. Scand.*, **24**, 1912 (1970).
(9) E. M. Archer, *Acta Crystallogr.*, **1**, 64 (1948).
(10) H. A. Carter and F. Aubke, *Inorg. Chem.*, **10**, 2296 (1971).
(11) P. M. A. Sherwood and J. J. Turner, *Spectrochim. Acta, Part A*, **26**, 1975 (1970), and ref 1–4 therein.
(12) W. E. Dasent and T. C. Waddington, *J. Chem. Soc.*, 3350 (1960); *J. Inorg. Nucl. Chem.*, **25**, 132 (1963).
(13) C. Furlani and G. Sartori, *Ann. Chim. (Rome)*, **47**, 124 (1957).
(14) Yu. S. Grushko, B. G. Lur'e, A. V. Motornyi, and A. N. Murin, *Fiz. Tverd. Tela (Leningrad)*, **10**, 3704 (1968) [*Sov. Phys.—Solid State (Engl. Transl.)*, **10**, 2944 (1969)]; Yu, S. Grushko, B. G. Lure, and A. N. Murin, *Fiz. Tverd. Tela (Leningrad)*, **11**, 2144 (1969) [*Sov. Phys.—Solid State (Engl. Transl.)*, **11**, 1733 (1970)].
(15) (a) "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 482; (b) G. H. Cady and J. M. Shreeve, *Inorg. Synth.*, **7**, 116 (1963).
(16) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(17) I. Masson and C. Argument, *J. Chem. Soc.*, 1702 (1938).
(18) R. G. Gillespie and M. J. Morton, *Q. Rev., Chem. Soc.*, **25**, 553 (1971).
(19) (a) J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2574 (1957); (b) T. Gramstad and R. N. Hazeldine, *J. Chem. Soc.*, 4069 (1947).
(20) A. M. Qureshi and F. Aubke, *Can. J. Chem.*, **49**, 35 (1971).
(21) R. L. Kirchmeier and J. M. Shreeve, *Inorg. Chem.*, **12**, 2886 (1973).
(22) D. F. Smith and G. M. Begun, *J. Chem. Phys.*, **43**, 2001 (1965).
(23) A. Engelbrecht, O. Mayr, G. Ziller, and E. Schandara, *Monatsh. Chem.*, **105**, 796 (1974); H. A. Carter, J. N. Ruddick, J. R Sams, and F. Aubke, *Inorg. Nucl. Chem. Lett.*, **11**, 29 (1975).
(24) J. R. Durig, O. D. Bonner, and W. H. Breazeale, *J. Phys. Chem.*, **69**, 3886 (1965).
(25) P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **11**, 2634 (1972).
(26) P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **12**, 328 (1973).
(27) J. L. K. F. DeVries and R. H. Herber, *Inorg. Chem.*, **11**, 2461 (1972).
(28) J. R. Dalziel, R. D. Klett, P. A. Yeats, and F. Aubke, *Can. J. Chem.*, **52**, 231 (1974).
(29) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2d ed, Wiley-Interscience, New York, N.Y., 1970, p 112.

---

Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada L8S 4M1

# A Fluorine-19 Nuclear Magnetic Resonance and Raman Spectroscopic Investigation of the Structure of Iodine Dioxide Trifluoride

R. J. GILLESPIE* and J. P. KRASZNAI

*Received May 21, 1975* AIC50355L

$IO_2F_3$ has been studied by $^{19}F$ NMR and Raman spectroscopy in the liquid state and at low temperature in perfluoro(methyl)cyclohexane and bromine pentafluoride solutions. It is concluded that $IO_2F_3$ exists as a cyclic trimer with cis-oxygen bridges, in the boat conformation, the I═O bonds being perpendicular to the plane containing the bridging bonds.

## Introduction

The synthesis of iodine dioxide trifluoride was first reported by Engelbrecht and Peterfy,[1,2] who concluded from the $^{19}F$ NMR spectrum of the melt that it consisted of a mixture of $C_{2v}$ and $C_s$ isomers of a trigonal-bipyramidal $IO_2F_3$ molecule. Beattie and Van Schalkwyk,[3] however, obtained a simpler $AX_2$ NMR spectrum for the melt and they also found that vapor density measurements indicated polymerization in the vapor phase. On the basis of this evidence Beattie and Van Schalkwyk proposed that $IO_2F_3$ is a cis-oxygen-bridged polymer based on the two possible structural units A and B

A

B

and that there is an equilibrium between monomers and polymers in the gas, liquid, and solution phases. They observed a splitting of the $X_2$ doublet of the $^{19}F$ NMR spectrum of $IO_2F_3$ in perfluoro(methyl)cyclohexane solution at low temperature which they considered to be supporting evidence for a monomer–polymer equilibrium. More recently Engelbrecht and co-workers[4] have reported that their original sample of $IO_2F_3$ was contaminated with $HOIOF_4$ and that a pure sample gave a spectrum similar to that reported by Beattie and Van Schalkwyk.[3] Engelbrecht and his co-workers[4] also reported the mass spectrum of $IO_2F_3$ which shows the presence of dimeric and trimeric species in the gas phase and suggested that $IO_2F_3$ is polymeric with a low degree of polymerization ($n \leq 4$).

We have also studied the structure and properties of $IO_2F_3$ and in this paper we report the Raman spectrum of solid $IO_2F_3$ and the Raman and $^{19}F$ NMR spectra of molten $IO_2F_3$ and its solution in $BrF_5$ and perfluoro(methyl)cyclohexane. Where our work overlaps with that of Beattie and Van Schalkwyk,[3] it agrees reasonably well with theirs but the results of our more extensive investigation lead us to somewhat different conclusions.

## Results and Discussion

**$^{19}F$ NMR Spectra.** A freshly prepared solution of $IO_2F_3$ in perfluoro(methyl)cyclohexane at −36 °C gave a simple $AX_2$ $^{19}F$ NMR spectrum (Table I). The peaks of the $X_2$ doublet

**Table I.** $^{19}$F NMR Parameters for Molten $IO_2F_3$$^a$ and Solutions$^b$ of $IO_2F_3$ in $CF_3C_6F_{11}$ and $BrF_5$

| Solvent | Temp, °C | δ,$^c$ ppm from ext. $CFCl_3$ | | *J*, Hz |
|---|---|---|---|---|
| Melt | 51 | A | −66.2 | 173 |
| | | $X_2$ | −105.2 | |
| $CF_3C_6F_{11}$ | −36 | A | −69.7 | 172 |
| | | $X_2$ | −109.0 | |
| $BrF_5$ | −45 | A′ | −69.6 | 181 |
| | | $X_2$′ | −108.4 | |
| | | A″ | −67.7 | 180 |
| | | $X_2$″ | −108.4 | |
| | | A | −58.5 | 88 ($IF_5$$^d$) |
| | | $X_4$ | −8.8 | |

$^a$ 58.3-MHz spectrum. $^b$ 94.1-MHz spectrum. $^c$ Chemical shifts; from external $CFCl_3$. $^d$ Decomposition product (see text).

showed an asymmetry and in most spectra definite shoulders were observed on the low-field side, but no asymmetry or additional splitting was observed for the A triplet. The separation of the main doublet and the shoulders was estimated to be about 20 Hz. We were unable to resolve the peaks into two sets of doublets as well as in the spectrum reported by Beattie and Van Schalkwyk[3] in which the separation of the doublets was also of the order of 20 Hz. However, we found perfluoro(methyl)cyclohexane to be somewhat unsatisfactory as a solvent for two reasons. First, although $IO_2F_3$ is very soluble at room temperature, we were unable to cool the solution below −30 °C since $IO_2F_3$ separated out of solution at this temperature. Secondly, the room-temperature solution on standing deposited a pale yellow solid, probably another phase of $IO_2F_3$ which decomposed slowly over a period of several hours to $IOF_3$ and oxygen. The $IOF_3$ then reacted with $IO_2F_3$ to give an adduct of composition $IO_2F_3 \cdot IOF_3$, which has been well characterized by $^{19}$F NMR and Raman spectroscopy.[5] The production of this adduct can be easily followed by NMR since it exhibits characteristic $A_2X_2$ and $A_4$ spectra in the F-on-I(VII) region. If the solution is pumped to dryness, a mixture of $IOF_3$ and $IO_2F$ is obtained. Decomposition probably occurs as follows

$$IO_2F_3 \cdot IOF_3 \rightarrow IOF_3 + IO_2F_3\uparrow$$

$$2IOF_3 \rightleftarrows IO_2F + IF_5\uparrow$$

The volatile $IO_2F_3$ and $IF_5$ are pumped away leaving a mixture of $IOF_3$ and $IO_2F$ which have characteristic Raman spectra[6] and can be readily identified.

In view of the problems with perfluoro(methyl)cyclohexane, bromine pentafluoride was used as a solvent. The $IO_2F_3$ region of the 94.1-MHz $^{19}$F NMR spectrum of a solution of $IO_2F_3$ in $BrF_5$ at −45 °C is shown in Figure 1. In addition to this spectrum peaks were also observed for the solvent and for $IF_5$ which is produced by photochemical decomposition[2] of $IO_2F_3$ to $IOF_3$ and oxygen followed by fluorination of $IOF_3$ by the solvent. The $IO_2F_3$ region of the spectrum is interesting because it shows two $AX_2$ spectra; the two X doublets are almost coincident, but the two A triplets are very well resolved. The coupling constants are, within experimental error, the same for both $AX_2$ spectra. Integration of the two triplets showed that they had relative areas in the constant ratio of 2:1, independent of both temperature and concentration. This result is not in accord with Beattie and Van Schalkwyk's suggestion of a monomer–polymer equilibrium as one would anticipate a variation in the amounts of the various polymers with temperature and concentration of the solution, and it strongly suggests that the two $AX_2$ spectra arise from a single species. Moreover, the Raman spectra of these solutions, which are discussed in detail in the following section, show only one IO double-bond stretching frequency which again seems inconsistent with the idea of a mixture of various polymeric species. The observations, however, are most consistent with

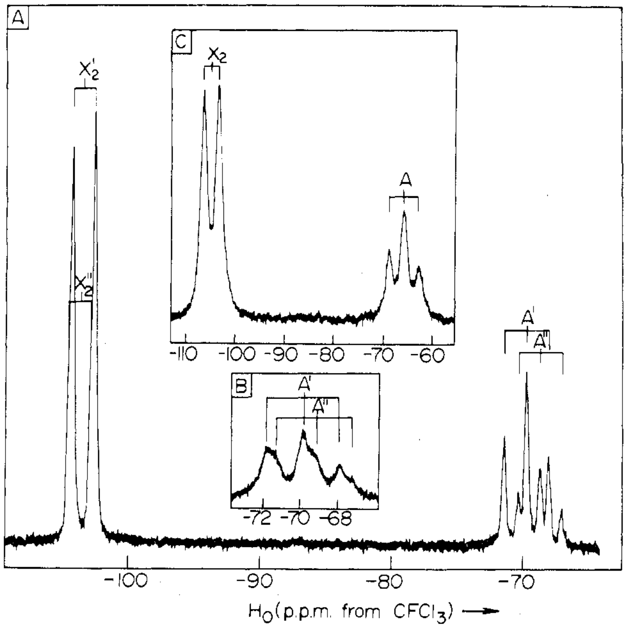
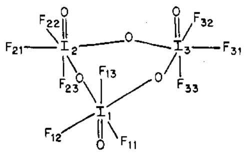
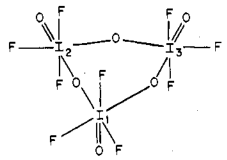
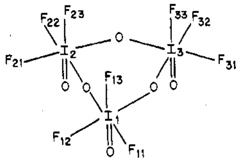
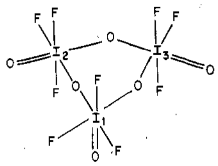
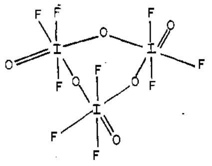
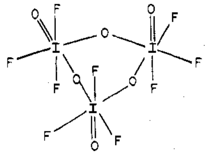
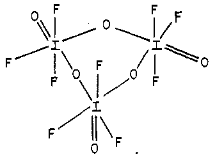
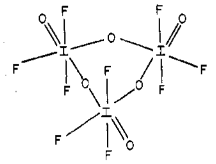
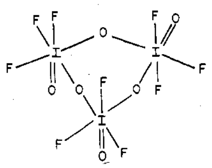


Figure 1. $^{19}$F NMR spectra: (A) $IO_2F_3$ in $BrF_5$ at −45 °C (the $AX_4$ spectra of $IF_5$ and $BrF_5$ are not shown); (B) high-field multiplet at −18 °C; (C) $IO_2F_3$ melt at 51 °C.

a cyclic trimer configuration III (Table II) with the $I_3O_3$ ring in a boat conformation similar to the recently determined structure of the isoelectronic $(SbOF_4^-)_3$ ion.[7] Such a structure has a unique iodine, and the fluorine ligands attached to it will also be unique with respect to the fluorine ligands on the other two iodine atoms of the trimer. However, a cyclic trimer of $IO_2F_3$ has nine geometric isomers and the $I_3O_3$ ring in each has several possible conformations. The various possibilities are listed in Table II which gives the symmetry of the molecule and spin systems for the fluorine ligands in each case. In order to account for the presence of one unique iodine atom in the trimeric structure it is necessary to choose a structure in which one iodine atom lies in a plane of symmetry. This criterion is only met by structures I–IV, but on closer examination of Table II it is clear that structures I–IV are not strictly consistent with the observed NMR data in that none of them is expected to exhibit two $AX_2$ spectra. At this stage, therefore, it is necessary to make a simplifying assumption. The observed NMR spectrum shows that the chemical shifts of the low-field doublets are almost identical, the difference being only of the order of 20 Hz; hence it is reasonable to assume that the fluorine ligands which are responsible for these resonances are very similar in their stereochemical environments and indeed are almost identical. The fluorines responsible for the two triplet resonances are quite different. Considering these observations and taking the $C_s$ conformer of structure III with $I_1$ as the unique iodine as an example, the implications are twofold. First, $F_{21}$ and $F_{22}$ are bonded to the same iodine and with respect to the local $C_s$ symmetry at the iodine they are equivalent to each other. Their environments will be made different by the nonplanarity of the $I_3O_3$ ring, but since these two fluorines are equatorial ligands, the effect of the nonplanarity of the $I_3O_3$ ring on the environments of $F_{21}$ and $F_{22}$ will be very small. Thus, even though $F_{21}$ and $F_{22}$ are not strictly equivalent, the AMX pattern predicted for the three fluorines (Table II) will be a very close approximation to an $AX_2$ pattern. Similar arguments apply to $F_{31}$ and $F_{32}$ and because $I_2$ and $I_3$ are related by a plane of symmetry the fluorines on $I_2$ and $I_3$ give rise to a single $AX_2$ pattern. The equatorial fluorines on $I_1$ also give rise to an $X_2$ pattern and since again the nonplanarity of the ring does not affect these equatorial ligands greatly, the chemical shift of

Table II. The Nine Geometric Isomers of $(IO_2F_3)_3$ with the Symmetries of the Chair and Boat Forms

| Planar structure | No. and type of conformers | Symmetry | Spin systems |
|---|---|---|---|
|  I | 1 planar | $C_s$ | $AX_2 + 2(AMX)$ |
| | 4 boat { | $C_s$ | $AX_2 + 2(AMX)$ |
| | | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
| | 4 chair { | $C_s$ | $AX_2 + 2(AMX)$ |
| | | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
|  II | 1 planar | $C_s$ | $AX_2 + 2(AMX)$ |
| | 4 boat { | $C_s$ | $AX_2 + 2(AMX)$ |
| | | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
| | 4 chair { | $C_s$ | $AX_2 + 2(AMX)$ |
| | | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
|  III | 1 planar | $C_{3v}$ | $3(AX_2)$ |
| | 2 chair | $C_s$ | $AX_2 + 2(AMX)$ |
| | 2 boat | $C_{3v}$ | $3(AX_2)$ |
|  IV | 1 planar | $C_s$ | $AX_2 + 2(AMX)$ |
| | 4 boat { | $C_s$ | $AX_2 + 2(AMX)$ |
| | | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
| | 4 chair { | $C_s$ | $AX_2 + 2(AMX)$ |
| | | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
|  V | 1 planar | $C_{3h}$ | $3(AX_2)$ |
| | 2 boat | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
| | 2 chair | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
|  VI | 1 planar | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
| | 6 boat | $C_1$ | |
| | 6 chair | $C_1$ | |
|  VII | 1 planar | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
| | 6 boat | $C_1$ | |
| | 6 chair | $C_1$ | |
|  VIII | 1 planar | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
| | 6 boat | $C_1$ | |
| | 6 chair | $C_1$ | |
|  IX | 1 planar | $C_1$ | $(AMX)_1 + (AMX)_2 + (AMX)_3$ |
| | 6 boat | $C_1$ | |
| | 6 chair | $C_1$ | |

$F_{11}$ and $F_{12}$ will only be slightly different from that of $F_{21}$, $F_{22}$, $F_{31}$, and $F_{32}$ and this accounts for the small (20 Hz) splitting of the doublet in the NMR spectrum. The environments of the axial fluorines are, however, more greatly affected by the nonplanarity of the $I_3O_3$ ring and this results in a much larger difference between the chemical shifts of $F_{13}$ and $F_{23}$ ($F_{33}$). This accounts for the larger chemical shift difference between the two triplets. This argument applies equally well to the $C_s$ conformers of structure I but does not hold true for structures II and IV since there is no environmental similarity between the equatorial fluorines on $I_1$ and the axial fluorines on $I_2$ and $I_3$. The local stereochemistry about each iodine is identical in structures I and III and this too is consistent with the observation of a unique coupling constant $J_{FF}$ = 180 Hz in the NMR spectrum. Structures II and IV are expected to exhibit at least two coupling constants and on this basis also these structures may be discounted.

In order to differentiate between I and III it is necessary to consider the temperature dependence of the NMR spectrum. On warming the $BrF_5$ solution to −18 °C the line widths increase and the two A triplets are no longer well resolved (Figure 1 inset). The NMR spectrum of the melt at 51 °C is that of a simple $AX_2$ system and at 90 °C the spectrum is essentially unchanged[3] with the exception of the observation of impurity lines assignable to small amounts of thermal and photodecomposition products. Thus, there appears to be an exchange process in the melt and in the solutions which makes all three iodine atoms in the trimer equivalent. Since fluorine–fluorine coupling is maintained even at +90 °C, the exchange cannot proceed by iodine–fluorine bond rupture but it presumably involves either the breaking and re-forming of an iodine–bridging-oxygen bond or the interconversion of conformers at a rate which is fast on the NMR time scale. The interconversion of conformers can occur very readily in structure III, since changing from a boat conformation to a chair and then to another boat form exchanges $I_1$ and $I_2$ and ultimately $I_2$ and $I_3$. In fact, changing from the boat conformation to a chair form results in a collapse of the two $AX_2$ multiplets since the chair form has $C_{3v}$ symmetry and by symmetry the iodines are all equivalent. The exchange process is a little more difficult to envisage in structure I since it involves the cleavage of an iodine–oxygen single bond to give a five-coordinate intermediate which then can rearrange and re-form an iodine–oxygen bond. Again taking $I_1$ as the unique iodine initially, the first step in the exchange is the rupture of one of the $I_3$–O bonds giving rise to a chain with a five-coordinate end unit containing $I_3$. Rotation of 180° about the other $I_3$–O single bond and subsequent re-formation of the cleaved $I_3$–O single bond gives rise to a structure where $I_2$ is the unique iodine. However, the five-coordinate intermediate is not the most favored since in a trigonal-bipyramidal system of the type $AX_2Y_3$, the most electronegative ligands Y favor the axial position whereas in the one suggested they remain cis to each other. Furthermore, this exchange relies on cleaving only the $I_2$–O and $I_3$–O bonds. If $I_1$ is the unique iodine and $I_1$–O is cleaved followed by rotation of the five-coordinate intermediate and re-formation of $I_1$–O, a different isomer (e.g., isomer III) is formed. Hence this type of exchange should give rise to a mixture of isomers which is not consistent with our observations.

Structure III in which the $I_3O_3$ ring is in the boat conformation is, therefore, the most probable structure of $IO_2F_3$ in $BrF_5$ at −48 °C. At 50 °C in the melt, there appears to be fast interconversion between the boat and chair forms.

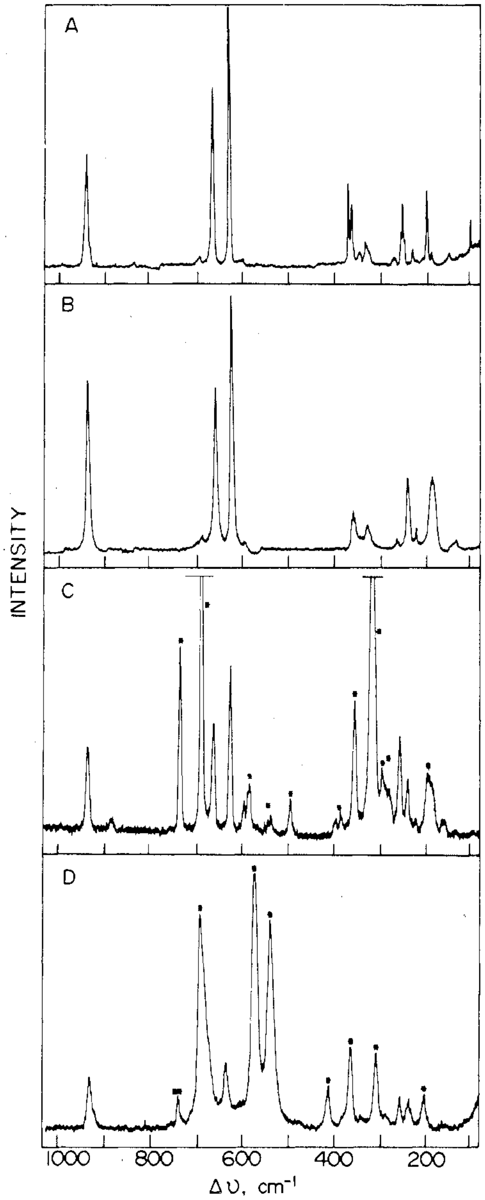


Figure 2. Raman spectra: (A) solid $IO_2F_3$ at −100 °C in glass sample tube; (B) molten $IO_2F_3$ at 50 °C in glass sample tube; (C) solution of $IO_2F_3$ in perfluoro(methyl)cyclohexane at −36.5 °C recorded in FEP sample tube; (D) solution of $IO_2F_3$ in $BrF_5$ at −48 °C recorded in FEP sample tube. Asterisks denote bands arising from solvent or FEP.

**Raman Spectra.** The Raman spectra of the solid, melt, and solutions of $IO_2F_3$ in $BrF_5$–perfluoro(methyl)cyclohexane are shown in Figure 2, and Table III lists the frequencies and approximate assignments for the stretching motions of the $IO_2F_3$ cyclic trimer with structure III. In view of its complexity it is not possible to make a complete assignment on the basis of any of the trimeric structures but it can be reasonably assigned on the basis of a monomeric unit of the trimer assuming that the three monomeric units are only rather weakly coupled. Such a unit of the trimer has $C_s$ symmetry, and a total of 15 fundamental vibrations with symmetry designations 9 A' + 6 A'' are expected to be observed in the Raman spectrum. Fifteen bands were observed in the liquid but considerably more were observed in the solid which could be due to either solid-state effects or to the sharpness of the lines allowing observation of small splittings due to coupling between the monomeric units. In solution eight polarized lines with $\rho$ less than 0.5 and two other lines (602 and 256 cm$^{-1}$) whose polarization is uncertain were observed. The strongly polarized band at 918 cm$^{-1}$ in the melt, 913 cm$^{-1}$ in $BrF_5$ solution at −48 °C, and 918 cm$^{-1}$ in $CF_3C_6F_{11}$ solution at −36 °C is assigned to the I═O stretching frequency. This fre-

Table III

| Ir spectrum, $cm^{-1}$ (gas)[a] | Raman data | | | | | Assignment |
|---|---|---|---|---|---|---|
| | Spectra, $cm^{-1}$ | | Depolarizn ratio | Spectra, $cm^{-1}$ | | |
| | Solid[b] | Liquid[c] | | Soln in $BrF_5$[e,f,h] | Soln in $CF_3C_6F_{11}$[f,g,h] | |
| 915 m | 915 (26)<br>911 sh | 918 (68) p | 0.10 | 913 (80) | 918 (52) p | I=O str |
| 890 m | | | | | | |
| | | | | | 877 (8) p | I=O str of $IOF_3$ impurity |
| 730 w | | | | | | |
| 695 vs | 688 (2) | 687 (2) dp[d] | | | | $IF_{eq}$ asym str |
| 676 s | | | | | | |
| 658 vs | 659 (42) | 659 (64) p | 0.10 | 666 sh | 664 (70) | $IF_{ax}$ str |
| | 627 (100) | 624 (100) p | 0.06 | 629 (100) | 629 (100) | $IF_{eq}$ sym str |
| 612 m | | | | | | |
| 605 sh | 599 (2) | 602 (2) p[d] (?) | | | | $I_3O_3$ sym breathing mode |
| 570 w | | | | | | |
| 480 sh | | | | | | |
| 425 sh | | | | | | |
| | 378 (19) | 371 (15) p | 0.31 | 380 (15) | | |
| | 371 (14) | 366 sh dp | | | | |
| | 352 (3) | 356 (5) dp | | | | |
| | 338 (5)<br>333 (3) | 342 (10) dp | | 342 (12) | | |
| | 280 (2) | 278 (4) dp | | 289 (13) | | |
| | 263 (8)<br>260 (14)<br>256 (6) | 256 (27) p (?) | 0.67 | 256 (43) | 257 (36) | Def modes |
| | 238 (14) | 239 (8) p | 0.33 | | 239 (12) | |
| | 206 (18)<br>195 (3) | 202 (20) p | 0.19 | 201 (52) | 206 (30) | |
| | 158 (2) | 149 (4) p | 0.47 | | | |
| | 111 (7)<br>72 (7) | 98 (1) p | 0.20 | | | |

[a] A. Engelbrecht, O. Mayr, G. Ziller, and E. Schandara, *Monatsh. Chem.*, **105**, 796 (1974). [b] Solid at −100 °C. [c] Melt at +50 °C; p = polarized; dp = depolarized; sh = shoulder. [d] Polarization ratios for these two bands were obtained from $HSO_3F$ solution. [e] −48 °C. [f] Solvent peaks and peaks due to the FEP container have been subtracted from the list of frequencies. [g] −36.5 °C. [h] Intensities in parentheses are based on $IO_2F_3$ peaks.

quency compares well with the I=O stretch in $IOF_5$,[8,9] which has a frequency of 927 $cm^{-1}$. The bands at 877 and 546 $cm^{-1}$ in the $CF_3C_6F_{11}$ solution spectrum are probably due to an $IOF_3$ impurity. The 600–700-$cm^{-1}$ region of the spectrum is difficult to assign with confidence since this is the characteristic stretching frequency region for both I–O and I–F single bonds. The most intense band in this region might be expected to be the $I_3O_3$ ring symmetric breathing mode; however, in the isoelectronic species $(SbOF_4^-)_3$ the corresponding $Sb_3O_3$ ring mode is assigned on the basis of force constant calculations to a band at 475 $cm^{-1}$ which is only 40% as intense as the Sb–F stretching mode.[10] Furthermore, the profile of this region of the spectrum is very similar to that of the spectrum of $IOF_5$ and therefore the two strongly polarized bands at 659 and 624 $cm^{-1}$ are assigned to the I–F axial and equatorial stretching frequency, respectively, by analogy with the corresponding bands in $IOF_5$ which occur at 680 and 640 $cm^{-1}$. It is possible that the $I_3O_3$ breathing mode is underneath the two strongly polarized bands at 659 and 624 $cm^{-1}$; however, we tentatively assign this mode to the weak band at 602 $cm^{-1}$. The depolarized band at 687 $cm^{-1}$ is assigned to the I–F equatorial asymmetric stretch and compares well with the doubly degenerate $\nu_8(e)$ mode in $IOF_5$ which is found at 710 $cm^{-1}$ and represents the $IF_4$ asymmetric stretch. No attempt was made to assign the deformation modes as insufficient information is available on which to base such an analysis. The vibrational frequencies in the solid, melt, and solution spectra of $IO_2F_3$ are very similar and we conclude that $IO_2F_3$ has a cyclic oxygen-bridged trimeric structure in all of these phases.

## Experimental Section

$IO_2F_3$ was prepared by the method of Engelbrecht and Peterfy[1,2] and was purified by pumping it through a U-tube containing dry potassium sulfate to absorb any fluorosulfuric acid contaminating the product.

Bromine pentafluoride was obtained from the Ozark Mahoning Co. and purified by bubbling fluorine through it until the solution turned colorless. It was then distilled on top of dry sodium fluoride to remove traces of HF.

Perfluoro(methyl)cyclohexane was obtained from I.C.N. Canada Ltd. and was dried by storing it over molecular sieves.

Raman and $^{19}F$ NMR instrumentation and methodology have been described elsewhere.[11,12]

$IO_2F_3$ was handled in a drybox and NMR samples were prepared in FEP NMR tubes fitted with 0.25-in. Kel-F adaptors and Teflon valves.

The $BrF_5$ solution of $IO_2F_3$ was kept below −18 °C at all times to prevent the reaction between $BrF_5$ and $IO_2F_3$ to give $IOF_5$, bromine, oxygen, and fluorine.

**Acknowledgment.** We thank Dr. F. Riddell for helpful discussion of the NMR spectra. We also thank Mr. Paul Spekkens for valuable discussion during the course of this work and the preparation of the manuscript. We thank the National Research Council of Canada for financial support of this work.

**Registry No.** $(IO_2F_3)_3$, 58735-48-1; $IO_2F_3$, 25402-50-0.

## References and Notes

(1) A. Engelbrecht and P. Peterfy, *Angew. Chem., Int. Ed. Engl.*, **8**, 768 (1969).
(2) A. Engelbrecht, P. Peterfy, and E. Schandara, *Z. Anorg. Allg. Chem.*, **384**, 202 (1971).
(3) I. R. Beattie and G. J. Van Schalkwyk, *Inorg. Nucl. Chem. Lett.*, **10**, 343 (1974).
(4) A. Engelbrecht, O. Mayr, G. Ziller, and E. Schandara, *Monatsh. Chem.*, **105**, 796 (1974).
(5) R. J. Gillespie and J. P. Krasznai, submitted for publication.
(6) H. Carter and F. Aubke, *Inorg. Chem.*, **10**, 2297 (1971).
(7) W. Haase, *Acta Crystallogr., Sect. B*, **30**, 2465 (1974).

(8) D. F. Smith and G. M. Begun, *J. Chem. Phys.*, **43**, 2001 (1965).
(9) J. H. Holloway, H. Selig, and H. S. Claassen, *J. Chem. Phys.*, **54**, 5405 (1971).
(10) W. Haase, *Ber. Bunsenges. Phys. Chem.*, **76**, 1000 (1972).
(11) R. J. Gillespie and B. Landa, *Inorg. Chem.*, **12**, 1383 (1973).
(12) P. A. W. Dean and R. J. Gillespie, *J. Am. Chem. Soc.*, **91**, 7260 (1969).

Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada L8S 4M1

# Raman Spectral Studies of α-$XeF_3^+SbF_6^-$, β-$XeF_3^+SbF_6^-$, $XeF_3^+Sb_2F_{11}^-$, $XeF_3^+AsF_6^-$, $XeOF_3^+SbF_6^-$, $XeOF_3^+Sb_2F_{11}^-$, and $XeO_2F^+Sb_2F_{11}^-$

R. J. GILLESPIE,* B. LANDA, and G. J. SCHROBILGEN

*Received March 7, 1975* AIC50173R

We have studied the reactions of $SbF_5$ with $XeF_4$, $XeOF_4$, and $XeO_2F_2$ and also the reaction of $AsF_5$ with $XeF_4$. The Raman spectra of the solid products and their solutions in HF or $SbF_5$ indicate that they may be formulated as the salts α-$XeF_3^+SbF_6^-$, β-$XeF_3^+SbF_6^-$, $XeF_3^+Sb_2F_{11}$, $XeF_3^+AsF_6^-$, $XeOF_3^+SbF_6^-$, $XeOF_3^+Sb_2F_{11}$ and $XeO_2F^+Sb_2F_{11}^-$. Complete assignments of the spectra have been made for the cations. These assignments are consistent with the known T-shaped structure of $XeF_3^+$ and they indicate that $XeOF_3^+$ has a structure based on a trigonal bipyramid with the oxygen and one of the fluorines occupying two of the equatorial positions and that $XeO_2F^+$ has a pyramidal structure. The Raman spectra also provide evidence for the existence of fluorine bridges between the cation and the anion in these compounds. In the $SbF_6^-$ compounds the $O_h$ symmetry of the isolated anion is reduced by the fluorine bridges and in the majority of the compounds bands are observed which may reasonably be assigned to the vibrations of the Xe---F---M bridge. As the crystal structures of $XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$ are known, it was possible to carry out a factor-group analysis in these cases which accounts well for all the bands observed in the Raman spectra of the solids.

## Introduction

A large number of complexes of $XeF_2$ and $XeF_6$ have been prepared with a variety of strong Lewis acids,[1] e.g., pentafluorides such as $SbF_5$ and $RuF_5$, and it has been established by several techniques, including Raman and $^{19}F$ NMR spectroscopy and x-ray crystallography that these complexes have ionic structures in which the cations are $XeF^+$ [2-5] and $XeF_5^+$ [5-14] or the fluorine-bridged cations $Xe_2F_3^+$ [2,3,7,15] and $Xe_2F_{11}^+$.[10,16,17] There has been, however, a marked lack of information on possible similar complexes of $XeF_4$ and the oxyfluorides $XeOF_4$ and $XeO_2F_2$. Indeed, because $XeF_4$ was found not to form stable complexes with $AsF_5$,[18] $IrF_5$,[18] and $RuF_5$,[19] it was concluded by Bartlett and co-workers that $XeF_4$ is a weaker base than either $XeF_2$ or $XeF_6$. Nevertheless, there was some evidence that $XeF_4$ and $XeOF_4$ do form complexes with $SbF_5$. Cohen and Peacock[20a] reported that xenon tetrafluoride or mixtures of xenon tetrafluoride and difluoride dissolve in antimony pentafluoride with gas evolution to give green solutions. On removing the solvent at 25 °C they obtained an easily decomposed white solid in addition to the yellow $XeF_2{\cdot}2SbF_5$ complex, but they were unable to isolate the white compound in a pure state. They assumed that it was the adduct $XeF_4{\cdot}2SbF_5$, but the composition was never determined. Some conductivity evidence[20b] has been given for compound formation between $XeF_4$ and $PF_5$ and between $AsF_5$ and $SbF_5$. However, the conclusions from this work that $SbF_5$ forms the compounds $2XeF_4{\cdot}SbF_5$ and $XeF_4{\cdot}4SbF_5$ are not in agreement with subsequent work. Several years ago, Selig[21] reported the formation of the stable complex $XeOF_4{\cdot}2SbF_5$, but no structural information was obtained for this compound. There has been no previous information on complexes of $XeO_2F_2$.

We have now shown that $XeF_4$, $XeOF_4$, and $XeO_2F_2$ all form complexes with antimony pentafluoride and that these complexes contain the cations $XeF_3^+$, $XeOF_3^+$, and $XeO_2F^+$. $XeF_4$ also forms a rather unstable complex with $AsF_5$.

Preliminary reports of our results have been given in two brief communications.[22,23] Since then we have published[24] the details of the x-ray crystallographic determination of the structure of β-$XeF_3^+SbF_6^-$ and of the preparation and $^{19}F$ NMR spectra of solutions of the cations $XeF_3^+$, $XeOF_3^+$, and $XeO_2F^+$.[25] Subsequent to our preliminary communications, Bartlett and co-workers published their determination of the structure of $XeF_3^+Sb_2F_{11}^-$ [26] and also a paper on the preparation and Raman spectra of $XeF_3^+$ and $XeOF_3^+$ salts.[27] The x-ray crystallographic studies have shown that β-$XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$ both contain the T-shaped $XeF_3^+$ cation, which is strongly fluorine-bridged to the anion. The present paper reports the Raman spectra of α- and β-$XeF_3^+SbF_6^-$, $XeF_3^+Sb_2F_{11}^-$, $XeOF_3^+SbF_6^-$, $XeOF_3^+Sb_2F_{11}^-$, and $XeO_2F^+Sb_2F_{11}^-$. Assignments of the vibrational spectra have been made for the cations $XeF_3^+$, $XeOF_3^+$, and $XeO_2F^+$. In the cases of β-$XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$, factor-group analyses of the spectra based on the known crystal structures have been carried out.

## Results and Discussion

**The Complexes $XeF_4{\cdot}SbF_5$ and $XeF_4{\cdot}2SbF_5$.** These two complexes are readily prepared by direct reaction between $XeF_4$ and $SbF_5$ at room temperature, the latter by using an excess of $SbF_5$ and the former by fusing $XeF_4{\cdot}2SbF_5$ with an excess of $XeF_4$ at 80 °C.[25] The compounds are stable yellow and pale yellow-green solids, respectively.

Another form of $XeF_4{\cdot}SbF_5$ may be prepared from $SbF_5$ and excess $XeF_4$ in anhydrous HF. Crystallization from solution at room temperature followed by removal of excess solvent and $XeF_4$ under vacuum yielded pale yellow-green crystalline $XeF_4{\cdot}SbF_5$. We designate the high-temperature form, prepared at 80 °C, α-$XeF_3^+SbF_6^-$ and the room-temperature form β-$XeF_3^+SbF_6^-$. The Raman spectra of the compounds $XeF_3^+Sb_2F_{11}^-$, $XeF_3^+AsF_6^-$, and α- and β-$XeF_3^+SbF_6^-$ are given in Table I and Figures 1 and 2.

The spectra are consistent with the ionic structures $XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$ which have now been established by x-ray crystallography.[24,26] The $XeF_3^+$ ion is T shaped with $C_{2v}$ symmetry and has a structure which is quite similar to that of the "isoelectronic" molecules $ClF_3$ and $BrF_3$. Six normal modes, all Raman and infrared active, are expected for the $XeF_3^+$ cation with $C_{2v}$ symmetry, namely, three $a_1$ modes, two $b_1$ modes, and and one $b_2$ mode. Assignments for these modes and also for the anion modes are given in Table I. They are made on the basis of published spectra for the anions and the spectra of related molecules including, in