A LASER RAMAN SPECTROSCOPIC STUDY
OF
IODINE CATIONS

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By

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
November 1975

DOCTOR OF PHILOSOPHY (1975) McMASTER UNIVERSITY
(Chemistry) Hamilton, Ontario

TITLE: A Laser Raman Spectroscopic Study of Iodine Cations

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NUMBER OF PAGES: ix, 107

ABSTRACT

$I_2^+Sb_2F_{11}^-$, a dark blue crystalline solid, was prepared by reaction of I_2 with SbF_5 using dried liquid SO_2 as solvent. The compound melts at 122°C and is moisture-sensitive. The presence of the I_2^+ cation was established by laser Raman spectroscopy and by X-ray crystallography. The structure determination showed that the I_2^+ cation has an I - I bond length of 2.557(4) Å.

The triatomic cations I_3^+, IBr_2^+ and ICl_2^+ were produced in acidic solutions and their Raman spectra were obtained using specially designed spinning Raman cells. IBr_2^+ and ICl_2^+ were also prepared as the solid compounds $IBr_2^+SO_3F^-$ and $ICl_2^+SbCl_6^-$ and their Raman spectra were recorded. A simple valence force field treatment was applied to the Raman data for these three symmetric IX_2^+ cations. Force constants were calculated and the bond angles of the bent structures were estimated.

The triatomic interhalogen cation I_2Cl^+ was prepared by direct reaction of ICl and $SbCl_5$ to yield solid $I_2Cl^+SbCl_6^-$. By a similar halogen transfer process $I_2Br^+SbCl_5Br^-$ was prepared from IBr and $SbCl_5$. The Raman spectra of both of these dark-colored, low-melting solids were obtained using spinning cell techniques. Observation of Raman bands which could be assigned to a bending mode and to I - I and I - X stretching modes established that these two iodine-containing cations have an unsymmetric angular structure.

The existence of a new polyatomic cation I_n^{n+} containing iodine in a +1 oxidation state is proposed. This species has a strong Raman

band at 195 cm^{-1}. The Raman evidence indicates that I_n^{n+} exists in H_2SO_4 and HSO_3F solutions and also in solid or molten ISO_3F.

ACKNOWLEDGEMENTS

The author would like to express her gratitude for the advice and encouragement given by Professor R.J. Gillespie throughout this work.

The author would also like to thank Drs. C.G. Davies and P.R. Ireland who determined the single crystal X-ray structure of $I_2^+Sb_2F_{11}^-$ which is discussed in this thesis.

Thanks are also due to Mrs. B. Spiers and Mr. J.I.A. Thompson for assistance with the Raman spectrometer, to Mr. R. Palme who constructed the glass apparatus, and to Mr. M. Roberts who fabricated the metal frames for the Raman spinning cell equipment.

The financial assistance which made this work possible is gratefully acknowledged. The Department of Colleges and Universities, Province of Ontario, provided an Ontario Graduate Fellowship and the Department of Chemistry, McMaster University, provided an Assistantship.

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CHAPTER I

Introduction

1. Iodine Cations

(a) Introduction

The halogens are among the most electronegative of the elements and they occur most frequently as fluoride, chloride, bromide or iodide ions in the -1 oxidation state. The heavier atoms in the group also display an increasingly electropositive character and may exist in any one of several positive oxidation states such as in the hypohalite (+1), halite (+3), halate (+5) and perhalate (+7) series of compounds. Furthermore, there is evidence establishing the existence of a series of positive ions containing only halogen atoms with no other element present in the ion. Specifically, there are halogen cations, which contain atoms of only one of the halogens, and interhalogen cations, which contain at least two halogens.

Of the common halogens, iodine is the most electropositive and thus is expected to show the strongest tendency to form positive ions. There was early speculation (1) that the so-called 'positive halogen' involved in the iodination of organic compounds was the iodine cation I^+ or a complex of I^+ with molecular iodine. In 1938, while studying the iodination of chlorobenzene, Masson (2) suggested that the brown solutions formed by iodine and iodosyl sulfate in concentrated sulfuric acid contained I^+, I_3^+ and I_5^+. Subsequent investigations have

(1) shown that I^+ does not exist in solution as a monatomic cation,

(2) confirmed the existence of the I_3^+ and I_5^+ cations, and (3) led to the discovery of an extensive series of halogen and interhalogen cations.

(b) The I_2^+ cation

Considerable interest was also aroused by observations that iodine forms blue solutions in certain solvent systems. Symons and co-workers (3) obtained blue colored solutions by dissolving iodine or iodine monochloride in 65% oleum. In a review (3) published in 1962 which summarized their investigations they proposed that these solutions contained the I^+ iodine cation. Aynsley <u>et al</u>. (4) also attributed the blue color of IF_5 solutions containing iodine and a trace of water to the I^+ cation. Gillespie and Milne (5) subsequently established that the blue iodine species is the diatomic I_2^+ cation and not I^+. In their conductimetric, spectrophotometric, and magnetic susceptibility experiments, solutions of iodine in fluorosulfuric acid were oxidized with peroxodisulfuryl difluoride. It was found that the concentration of the blue cation reached a maximum at the 2:1 mole ratio of halogen to oxidizing agent as in the equation

$$2\ I_2 + S_2O_6F_2 \rightarrow 2\ I_2^+ + 2\ SO_3F^-$$

and not at the 1:1 mole ratio as would be expected for the formation of I^+ according to the equation

$$I_2 + S_2O_6F_2 \rightarrow 2\ I^+ + 2\ SO_3F^-.$$

They observed that I_2^+ is a paramagnetic species with a magnetic moment of 2.0 ±0.1 BM, in agreement with the theoretical value. The peaks of its visible absorption spectrum occur at 640, 490, and 410 nm.

Solutions of iodine in oleum were reinvestigated by Gillespie and Malhotra (6) who confirmed that the blue cation formed in this solvent and also in disulfuric acid is I_2^+. Kemmitt et al. (7) studied the blue solutions formed by iodine with SbF_5, TaF_5, NbF_5, AsF_5 and PF_5 in iodine pentafluoride and by iodine in SbF_5. They interpreted their results on the basis that the I_2^+ cation is present in these solutions. They also isolated some solids which were believed to contain iodine cations. One of these solids was similar to the blue solid prepared more than sixty years earlier in 1906 by Ruff et al. (8) from the reaction of iodine and SbF_5. It was thought to be $(SbF_5)_2I$ but it was probably a mixture of SbF_3 and a fluoroantimonate salt of I_2^+.

Vibrational data for I_2^+ were reported by Gillespie and Morton (9) in 1969. They studied very dilute solutions of I_2^+ in fluorosulfuric acid by laser Raman spectroscopy using 632.8 nm excitation and observed the resonance Raman spectrum of I_2^+. It consists of a fundamental vibrational stretching frequency at 238 cm^{-1} and a series of overtones. Gillespie, Milne, and Morton (10) observed that the blue solutions of I_2^+ in fluorosulfuric acid change to a red-brown color when cooled to temperatures near -89°C, the freezing point of the solvent. With evidence from spectroscopic, cryoscopic, conductimetric and magnetic susceptibility measurements, they suggested that the I_2^+ cation dimerizes to form the I_4^{2+} cation at low temperatures:

$$\underset{\text{blue}}{2\ I_2^+} \rightleftarrows \underset{\text{red}}{I_4^{2+}}$$

The corresponding bromine cation, Br_2^+, was produced by Gillespie and Morton (11, 12) who oxidized bromine with $S_2O_6F_2$ in the superacid HSO_3F - SbF_5 - 3 SO_3. The cherry red solutions have a maximum absorption at 510 nm and the resonance Raman spectrum observed using 514.5 nm excitation showed a fundamental stretching frequency at 360 cm^{-1}. The red paramagnetic salt, $Br_2^+Sb_3F_{16}^-$, was prepared from bromine, bromine pentafluoride and antimony pentafluoride by Edwards, Jones, and Sills (13) who determined its structure by X-ray crystallography.

The Cl_2^+ cation would be expected to be more unstable than Br_2^+ or I_2^+. There is no firm evidence for its existence in solution or in a solid but Cl_2^+ has been observed in the gas phase at very low pressures and a value of 645.3 cm^{-1} for the vibrational frequency was obtained from the electronic absorption spectrum (14).

(c) The I_3^+ and I_5^+ cations

Masson's (2) early speculations concerning the existence of I_3^+ and I_5^+ in sulfuric acid solutions of iodine and iodosyl sulfate seemed to be a possible explanation for the behavior of similar brown solutions (1) formed by iodine with other oxidizing agents such as iodate, periodate and permanganate in strong acids. More recently, Arotsky, Mishra and Symons (15) obtained conductimetric evidence that I_3^+ is produced from iodine and iodic acid in 100% sulfuric acid and they suggested, on the basis of changes in the UV and visible spectra, that I_5^+ may be formed when iodine is added to I_3^+ solutions. Garrett, Gillespie and Senior (16) later confirmed by conductimetric and cryoscopic studies that the I_3^+ cation is produced in sulfuric acid solutions having the mole ratio I_2/HIO_3 = 7.0 according to the equation

$$7\ I_2 + HIO_3 + 8\ H_2SO_4 \rightarrow 5\ I_3^+ + 3\ H_3O^+ + 8\ HSO_4^-.$$

Their observation that the addition of more iodine caused no change in the conductivity or the freezing point of the solutions is consistent with the theory that I_5^+ is formed by the reaction

$$I_3^+ + I_2 \rightarrow I_5^+ .$$

The I_3^+ and I_5^+ cations have also been characterized in fluorosulfuric acid solutions. Gillespie and Milne (5) used $I_2/S_2O_6F_2$ mole ratios of 3.0 and 5.0 to produce I_3^+ and I_5^+ in HSO_3F solutions. Attempts by Morton (17) to observe the Raman spectra of the cations were unsuccessful due to the absorption of the exciting radiation by the brown solutions. Dilution of the samples resulted in the observation, not of an I_3^+ spectrum, but of the intense resonance Raman spectrum of traces of I_2^+ in the solution.

The investigations by Garrett, Gillespie and Senior (16) of iodine cations in the sulfuric acid solvent system also included the study of brown solutions having the mole ratio I_2/HIO_3 = 2.0 which corresponds to a +1 oxidation state for iodine. The I^+ cation with only six valence electrons had been considered to be unstable and, in fact, no evidence was found for its existence. They interpreted their results, as had Masson (2) before them, in terms of a disproportionation of I^+ into I_3^+ and IO^+.

In 1965 Aubke and Cady (18) reported the preparation of two black solids which they made by reaction of I_2 and $S_2O_6F_2$ in the absence of solvent. With equimolar amounts of the reactants a black diamagnetic compound having the empirical formula ISO_3F was produced. With the mole ratio $I_2/S_2O_6F_2 = 3.0$ or by the reaction of ISO_3F with iodine, the product was I_3SO_3F, a compound which presumably contains the I_3^+ cation.

Evidence that the corresponding bromine cation, Br_3^+, is formed in the Br_2-SbF_5 system was presented by McRae (19) in 1966. Gillespie and Morton (11,12) showed that Br_3^+ is formed by the reaction of Br_2 and $S_2O_6F_2$ in HSO_3F-SbF_5-$3\ SO_3$ and they observed one of the Raman frequencies, a single band at 290 cm^{-1}. Preparation of the compound $Br_3^+AsF_6^-$ was recently reported by Glemser and Smalc (20). They prepared the brown solid by oxidation of bromine with $O_2^+AsF_6^-$ or by reaction of bromine and AsF_5 with BrF_3 or BrF_5.

The chlorine cation, Cl_3^+, has not been detected in strong acid solutions but it was characterized by Raman spectroscopy in the yellow compound $Cl_3^+AsF_6^-$ which Gillespie and Morton (21) prepared from Cl_2, ClF, and AsF_5 at -76°C.

2. Triatomic Interhalogen Cations

In 1959 Vonk and Wiebenga (22) prepared the adducts of iodine trichloride with aluminum trichloride and antimony pentachloride. X-ray crystallographic study of the red-orange solids showed that they may be regarded as the ionic compounds $ICl_2^+AlCl_4^-$ and $ICl_2^+SbCl_6^-$ containing the triatomic cation ICl_2^+. Aubke and Cady (18) reported that the reaction of excess Cl_2 with iodine fluorosulfate ISO_3F produced the orange solid ICl_2SO_3F which also presumably contains the ICl_2^+ cation. The electrical conductivity of molten ICl_3 (specific conductance = 9.85 x 10^{-3} $ohm^{-1}cm^{-1}$)(23) has been attributed to the self-ionization:

$$2\ ICl \rightarrow ICl_2^+ + ICl_4^-.$$

From their studies of the system I_2-$SbCl_5$ both Ruff (24) in 1915 and more recently Fialkov and his co-workers (25) have reported evidence for the compound $SbCl_5.2ICl$ which may reasonably be formulated as $I_2Cl^+SbCl_6^-$. The I_2Cl^+ cation may also be present in molten ICl. The electrical conductivity of liquid ICl (specific conductance = 4.52 x 10^{-3} $ohm^{-1}cm^{-1}$ at 31°C) has been attributed to the self-ionization

$$2\ ICl \rightleftarrows I^+ + ICl_2^-$$

or more recently to the self-ionization

$$3\ ICl \rightleftarrows I_2Cl^+ + ICl_2^-$$

It has also been suggested (26) that if I_2Cl^+ is formed in a self-ionization it might possibly be extensively disproportionated to give the I_3^+ and ICl_2^+ cations

$$2\ I_2Cl^+ \rightleftarrows I_3^+ \text{ and } ICl_2^+.$$

There are also reports in the literature that I_2Cl^+ and ICl_2^+ as well as the corresponding bromine-containing cations I_2Br^+ and IBr_2^+ may exist in sulfuric acid solutions. Based on cryoscopic and conductimetric measurements Garrett et.al. (16) proposed that the addition of ICl or IBr to formally +1 iodine solutions (i.e. I_2/HIO_3= 2.0 in H_2SO_4) resulted in the formation of I_2Cl^+ and I_2Br^+, respectively. This theory on the formation of triatomic cations in solution was extended by Senior and Grover (27) who proposed that the addition of Cl_2 or Br_2 to similar sulfuric acid solutions produced the ICl_2^+ and IBr_2^+ cations, respectively. Gillespie and Malhotra (6) gave conductimetric and cryoscopic evidence that the ICl_2^+ cation also exists in solutions of ICl_3 in disulfuric acid.

Several triatomic cations containing fluorine have been prepared as the salts of very weakly basic anions. In 1965 Schmeisser and Ludovici (28) reported the formation of two adducts of iodine trifluoride - $IF_3.AsF_5$ which is stable to -20°C and $IF_3.SbF_5$ which is stable to 45°C. An ^{19}F nmr study (29) of the latter compound established the presence of the IF_2^+ cation. The BrF_2^+ cation has been identified in the 1:1 adducts that bromine trifluoride forms with SbF_5, AsF_5, and BF_3. Edwards and Jones (30) determined the crystal structure of $BrF_2^+SbF_6^-$; infrared and Raman spectra of BrF_2^+ have been reported by Christe and Schack (31) and by Surles, Hyman, Quarterman, and Popov (32). The ClF_2^+ cation has been shown to exist in the adducts of ClF_3 with SbF_5, AsF_5, and BF_3. Vibrational frequencies for ClF_2^+ which were first reported by Christe and Sawodny (33) were later reassigned by Gillespie and Morton (34). The crystal structure of $ClF_2^+SbF_6^-$ was determined by Edwards and Sills (35) and a structural determination of $ClF_2^+AsF_6^-$ was reported by Lynton and Passmore (36).

It has been established that the adducts $AsF_5.2ClF$ and $BF_3.2ClF$ contain the Cl_2F^+ cation. Gillespie and Morton (21) published Raman spectra of these two salts and reinterpreted the infrared spectra reported previously by Christe and Sawodny (37). The literature contains no reports of the formation of I_2F^+ or Br_2F^+.

3. Laser Raman Spectroscopy

Briefly, Raman spectroscopy is the study of light scattering caused by molecules in solids, liquids, or gases. Those molecular vibrations which cause a change in the polarizability of the molecule are Raman active vibrations whereas those which cause a change in the molecular dipole moment are infrared active. During elastic collisions of the incident light with the molecules in the sample there is no change in the energy of the light; therefore, the scattered light has the same frequency as the light source and is observed as a strong band ν_o called the Rayleigh line. Some collisions, however, are inelastic and hence the scattered light displays changes in its energy; this is the basis of the Raman effect. If energy from the incident light is transferred to the sample then the scattered light has less energy and a series of bands, known as Stokes lines, having frequencies less than ν_o will be observed in the Raman spectrum. On the other hand, if energy is gained from the sample there is an equal but opposite shift in frequency resulting in a series of anti-Stokes lines.* The positions of the bands are measured by the frequency shift $\Delta\nu$, usually expressed in wavenumbers (cm^{-1}). The bands form a spectrum corresponding to the frequencies of the Raman active vibrations of the molecule. The observed Raman spectrum, therefore, is characteristic of the molecule under study and is independent of the frequency of the light source.

Considerable information regarding the geometry and bonding of the molecule can be derived from the Raman spectrum. The number

* These are less intense than the Stokes lines and in many cases they are not observed; the intensity of the anti-Stokes lines is related to that of the Stokes lines by the Boltzman factor.

of Raman bands observed is related to the number of atoms in the molecule and to their structural arrangement. The magnitude of a Raman shift, i.e. $\Delta\nu$, the vibrational frequency, is related to the mass of the atoms involved in the vibration and to the strength of the chemical bonds holding the atoms together. Diatomic molecules, both homonuclear and heteronuclear, have a Raman active stretching vibration. Its frequency ν is related to the mass of the vibrating atoms and to the strength of the bond between them by the equation (38)

$$\nu = \sqrt{\frac{k}{4\pi^2 \mu}}$$

$$\text{or} \quad \frac{4\pi^2 c^2}{N} \nu^2 = k \, \frac{M_1 + M_2}{M_1 M_2}$$

c = velocity of light N = Avogadro's Number
μ = reduced mass M_1, M_2 = masses of the atoms
f = stretching force constant (mdyn Å^{-1} if ν is in cm^{-1})

For a bent triatomic molecule all three vibrations are Raman and infrared active. Typically, the unsymmetric structure $X\overset{X}{\diagup\,\diagdown}Y$ (point group C_s) has two stretching modes ν_1 and ν_2 having widely separated frequencies, attributed to X-X and X-Y stretching vibrations, and a low frequency bending mode ν_3. In this structure the vibrational motion can take place only in the plane of symmetry and therefore all three of the vibrations are symmetric with respect to the element of symmetry. Thus ν_1, ν_2 and ν_3 of $X\overset{X}{\diagup\,\diagdown}Y$ are of type (a').

The symmetric structures $X\overset{X}{\diagup\,\diagdown}X$ and $Y\overset{X}{\diagup\,\diagdown}Y$ (point group C_{2v}) have a low frequency bending vibration ν_2 (a_1) and two stretching vibrations whose frequencies are very close together or coincident. The Raman band for the symmetric stretch ν_1 (a_1) is generally much more intense than the band for the asymmetric stretch ν_3 (b_1).* This occurs because there is a much greater change in the polarizability of the molecule during the symmetric stretching vibration than there is during the asymmetric stretching vibration.

For the symmetric structures a simple valence force field treatment of the Raman data may be used to calculate the stretching force constant f and the bending force constant d and to estimate the bond angle α. These quantities are related to the observed frequencies ν_1, ν_2 and ν_3 by the three equations (38) given in the Appendix. This valence force approximation considers those forces which resist extension or compression of valence bonds in the molecule and those which oppose the bending or torsion of bonds. Forces between nonbonded atoms are not directly considered; in the present case this refers to the forces between the terminal atoms of the triatomic structure. This simplified treatment also assumes that there are no interactions between the vibrational modes. However, if interaction force constants are included in the expressions their calculated value is shown to be very small. Therefore, it is valid to consider them to be negligible. Two of the observed frequencies (ν_2 and ν_3) and assumed values of the bond angle α are used to calculate the force constants f and d. Then these values together with the estimated values of α are used to calculate ν_1 in order to find which arbitrarily chosen value of α gives a calculated value of ν_1 which is closest to the observed value.

The recent application of laser beams as the excitation radiation has greatly improved the effectiveness of Raman spectroscopy. A laser

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* For these spectroscopic notations, the plane of the C_{2v} molecule is defined as the zy plane.

is the source of a beam of coherent monochromatic polarized light which may easily be focussed on the sample to provide light of high intensity. It is important that the light source be very strong because the Raman scattered light is very weak, with only one out of 10^6 incident photons producing a Raman signal. The laser makes possible the study of very small samples, such as a drop of liquid or a single crystal, for which a mercury arc light source is not suitable. The use of monochromatic light produces a spectrum having a single band for each Raman active vibration. The fact that the laser beam is highly polarized permits polarization studies to be performed more readily than with a mercury arc lamp. The intensities of the bands are measured, first with a polarization analyser placed between the sample and the spectrometer in a perpendicular position and then in a parallel position with respect to the polarization of the incident laser beam. A great reduction in intensity for a band, i.e. a polarization ratio ρ where $0 < \rho \leqslant 3/4$, shows that the scattered light has retained its polarization and indicates that the molecular vibration giving rise to the Raman band is a symmetric vibration.

Another innovation in Raman spectroscopy is the practice of spinning the sample. This minimizes excessive energy absorption from the beam which is often a problem in the study of colored samples. The tendency of colored solids to melt or decompose and of colored solutions to boil makes their study impossible if the sample is stationary. Kiefer and Bernstein (39) devised a spinning cell which was useful for some colored solutions; they also designed a spinning disc arrangement (40) which was suitable for certain colored solids. Modified versions of these arrangements which were developed during this work are described in greater detail in Chapter II.

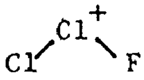
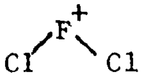
4. Structure of Halogen Cations

The diatomic cations are linear with a halogen-halogen bond length which is expected to be less than that in the neutral halogen molecule, in view of the removal of an antibonding π^* electron during cation formation

$$X_2 \rightarrow X_2^+ + e^-$$

This shortening of the bond length was confirmed, in the case of the Br_2^+ cation by Edwards et al. (13) in their X-ray crystallographic study of $Br_2^+Sb_3F_{16}^-$. They found a Br-Br distance of 2.13 Å in Br_2^+ compared to 2.27 Å in the Br_2 molecule. The shortening and strengthening of the bond is also reflected in the increased Raman frequencies which were observed:-

360 cm^{-1} for Br_2^+ in solution (11)(368 cm^{-1} in the solid)(13) compared to 318 cm^{-1} for the Br_2 molecule (41).

The triatomic halogen and interhalogen cations X_3^+, XY_2^+ and X_2Y^+ are expected to have a bent structure resulting from a tetrahedral arrangement of four pairs of electrons in the valence shell of the central atom of the cation. This is in contrast to the linear shape of the trihalogen anions X_3^- and XY_2^- which arises from a trigonal bipyramidal arrangement of five electron pairs in the valence shell of the central halogen. Raman spectroscopy has been an effective technique for characterization of halogen and interhalogen cations and in establishing that the least electronegative halogen always occupies the central position. For example, Gillespie and Morton (21) established by laser Raman methods that the Cl_2F^+ cation has the unsymmetric bent structure  and not the symmetric form  which had first been reported (37).

The ClF_2^+ cation was first characterized as a symmetric angular structure by infrared and Raman studies (33, 34) and subsequently this was confirmed by X-ray crystallography (35, 36). In $ClF_2^+SbF_6^-$ the ClF_2^+ cation was found to have a bond angle of 95.9° and a bond length of 1.58 Å while in $ClF_2^+AsF_6^-$ the bond angle is 103° and the bond length is 1.54 Å. The BrF_2^+ cation has also been studied by X-ray crystallography (30) and by infrared and Raman spectroscopy (31, 32) to establish that it, too, has a symmetric bent structure. In $BrF_2^+SbF_6^-$ the BrF_2^+ ion has a bond angle of 93.5° and a bond length of 1.69 Å.

The only iodine-containing cation which has had its structure determined (22) by crystallographic methods is ICl_2^+. The bond angle and bond length were reported as 92.5° and 2.31 Å in $ICl_2^+SbCl_6^-$ and 96.7° and 2.28 Å in $ICl_2^+AlCl_4^-$. Although these may be regarded as ionic compounds it appears that in both cases there is a relatively strong interaction between the cation and the anion by means of chlorine bridges. Recently Evans and Lo (42) reported ^{35}Cl nuclear quadrupole resonance (nqr) data for $ICl_2^+AlCl_4^-$ which showed that two types of chlorine atoms are present in the compound.

The application of the simple valence force field treatment of Raman data to the study of halogen cation structure is demonstrated by the work of Gillespie and Morton (21, 34) on Cl_3^+ and ClF_2^+. The Raman spectrum of $Cl_3^+AsF_6^-$ showed frequencies characteristic of the

AsF_6^- anion and also three bands at 490 (split to 485 and 493), 225, and 508 cm^{-1} which were assigned to ν_1, ν_2, and ν_3, respectively, of the bent Cl_3^+ cation. The observed frequencies for ν_2 and ν_3' and assumed values of the bond angle were used to calculate the stretching force constant f and the bending force constant d which were then used to calculate ν_1. Good agreement with the observed value of ν_1 was obtained for a bond angle of 100° with force constants f = 2.5 mdyn Å^{-1} and d = 0.36 mdyn Å^{-1}. Similar treatment of the observed frequencies for the ClF_2^+ cation in the compounds $ClF_2^+SbF_6^-$, $ClF_2^+AsF_6^-$, and $ClF_2^+BF_4^-$ gave f values of 4.8, 4.7, and 4.6 mdyn Å^{-1} and d values of 0.63, 0.62, and 0.61 mdyn Å^{-1}, respectively, for values of the bond angle in the range 95-100° for all three compounds.

5. Purpose of this work

The purpose of this work was to prepare iodine cations in solution or in solid form and to characterize them by the application of laser Raman spectroscopy. Some of the specific objectives of this investigation were as follows:

(a) To prepare a pure crystalline salt of I_2^+ and to obtain Raman evidence for the hypothesis that I_2^+ in solution dimerizes to form the I_4^{2+} cation.

(b) To obtain by laser Raman methods the vibrational frequencies of the known I_3^+ cation.

(c) To extend the investigation of the series of triatomic interhalogen cations of iodine by preparing the cations which iodine forms with bromine and chlorine and establishing their structure using laser Raman spectroscopy. Although this technique has proved useful for characterization of cations containing fluorine and chlorine, very few vibrational frequencies have been published for iodine-containing cations.

CHAPTER II

Experimental Methods

1. Materials: Source, Preparation, and Purification

Antimony Pentachloride

Reagent grade antimony pentachloride (Allied Chemical Co.) was used without further purification.

Antimony Pentafluoride

Antimony pentafluoride (Ozark-Mahoning Co.), doubly distilled in an atmosphere of dry nitrogen, was transferred on a dry vacuum line or in a dry box using dried syringes.

Arsenic Pentafluoride

Arsenic pentafluoride (Ozark-Mahoning Co.) was used without further purification. It was transferred on a dried Pyrex vacuum line fitted with Nupro valves (supplied by Niagara Valve and Fittings Ltd., Hamilton).

Bromine

Reagent grade bromine (British Drug Houses) was dried over phosphorus pentoxide and distilled on a dried Pyrex vacuum line fitted with Nupro valves.

Chlorine

Chlorine (Matheson Co. Inc.) was dried by passing it through traps containing concentrated sulfuric acid.

Fluorosulfuric Acid

Technical fluorosulfuric acid (Baker and Adamson) which had been purified by double distillation as described by Barr (43) was handled in a dry box using dried syringes.

Iodic Acid

Reagent grade iodic acid (British Drug Houses) was used directly.

Iodine

Reagent grade iodine (Shawinigan Chemicals) was used directly.

Iodine Monobromide

Reagent grade iodine monobromide (British Drug Houses) was used directly.

Iodine Monochloride

Reagent grade iodine monochloride (Eastman Organic Chemicals) was used directly.

Iodine Pentafluoride

Iodine pentafluoride (Matheson Co. Inc.) was purified by contacting it first with sodium fluoride to remove hydrogen fluoride and then with mercury to remove iodine using trap to trap distillation on a vacuum line fitted with Pyrex stopcocks.

Iodine Trichloride

Reagent grade iodine trichloride (British Drug Houses) was used directly.

Peroxodisulfuryl Difluoride

Peroxodisulfuryl difluoride, which had been prepared by literature methods (44, 45), was transferred on a dried Pyrex vacuum line fitted with Nupro valves.

Sulfur Dioxide

Sulfur dioxide (Matheson Co. Inc.) was dried over phosphorus pentoxide and handled on a dried Pyrex vacuum line fitted with Nupro valves.

Sulfuric Acid

100% sulfuric acid was prepared by the addition of fuming sulfuric acid to 95.5% sulfuric acid.

Sulfuryl Fluoride

Sulfuryl fluoride (Matheson Co. Inc.) was transferred on a dried Pyrex vacuum line fitted with Nupro valves.

2. Synthesis of Compounds

Some of the salts of iodine cations were prepared by oxidation of iodine with SbF_5 or AsF_5. Dried liquid SO_2 was used as solvent and the synthesis was carried out in a Dean apparatus (46), shown in Figure 1. This Pyrex vessel consists of two parallel reaction tubes connected by a tube containing a sintered glass filter of medium porosity. The apparatus was constructed with a small Teflon-coated stirring magnet in one of the tubes. The neck of each tube was joined to 1/4" Pyrex tubing to which a Nupro valve was attached. The valve permitted the closing of each tube or attachment of the apparatus to a vacuum line. The reaction vessel was thoroughly dried by warming under a dynamic vacuum. After several hours of pumping at room temperature, dry air was admitted to the vessel which was then weighed.

In a typical synthesis SbF_5 was transferred in a dry box to the reaction vessel using a dried Pyrex syringe and the apparatus was

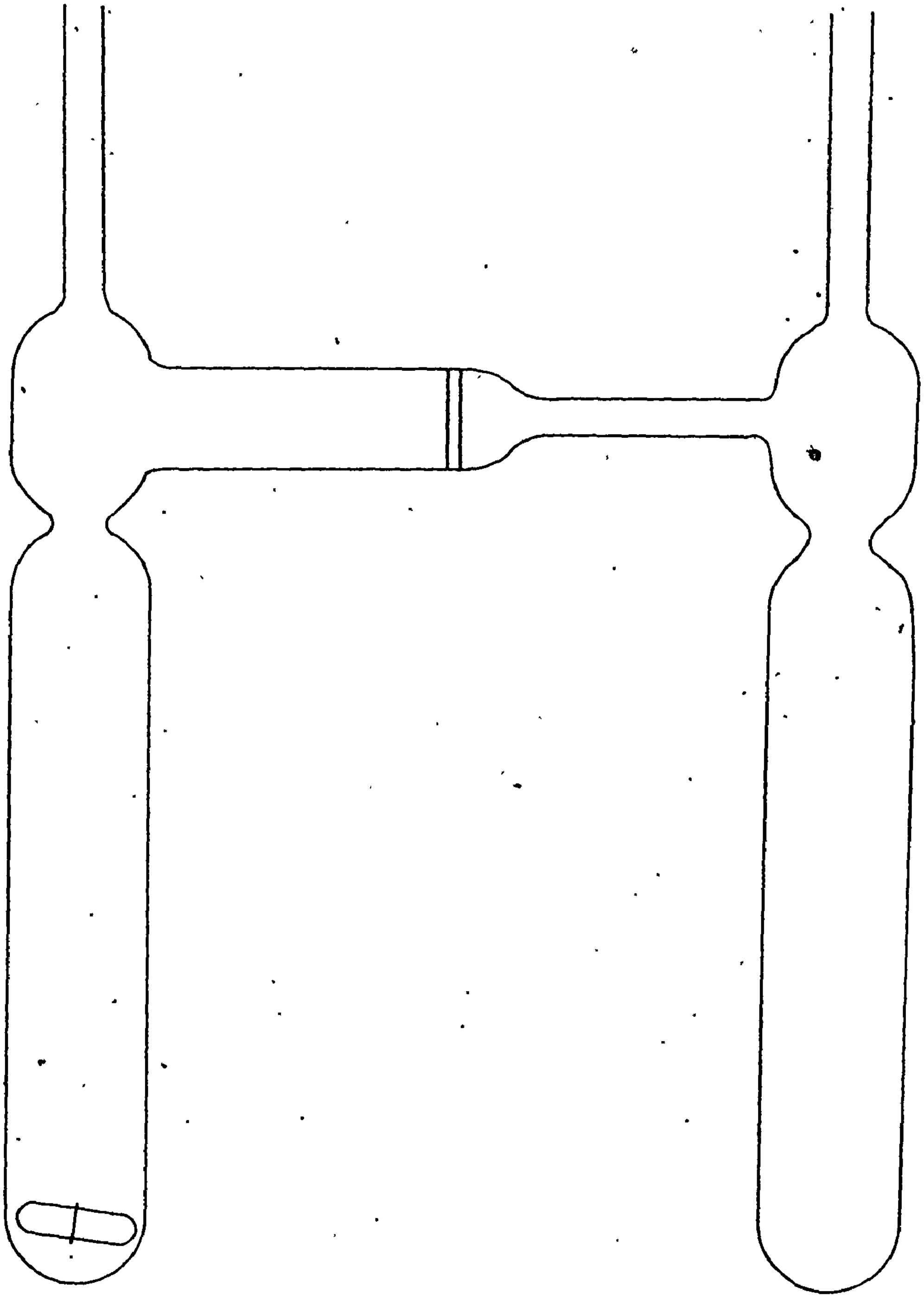


Figure 1. Dean apparatus for synthesis of compounds

weighed. The required stoichiometric amount of I_2 was transferred in the dry box to the magnet side of the vessel and the apparatus was re-weighed to determine the exact amount of I_2 present. The reaction vessel was attached to the vacuum line and the magnet side was placed in a cold bath in the range 0° to −20°C to prevent sublimation of I_2. A bath of dry ice in trichlorethylene (−88°C) surrounded the other tube during evacuation of air from the vessel and during distillation of dried liquid SO_2 (approximately 15 ml) onto the SbF_5. Then both tubes of the apparatus were placed in liquid N_2 and the neck of each tube was heat-sealed using a small hot flame.

When the reaction vessel and its contents had come to room temperature, the apparatus was tilted so that the solution of SbF_5 in SO_2 flowed through the filter to the tube containing I_2 and the magnet. The empty tube was placed in ice-water and a little SO_2 was condensed into it to dissolve any trace of SbF_5 that had not been transferred. Again, the apparatus was tilted to bring the solution of SbF_5 in SO_2 into contact with the iodine. The tube containing the magnet and the I_2 and SbF_5 in SO_2 was placed over a stirring motor. The mixture was allowed to react for several days at room temperature to ensure that the oxidation reaction was complete. One visible product of the reaction was SbF_3. It is a white solid, insoluble in SO_2, which was removed from the solution by filtration, achieved by tipping the apparatus so that the solution flowed through the sintered glass filter. To remove SO_2 from the solution the magnet side was placed in ice-water, then in colder baths, and finally in liquid N_2. When the transfer of SO_2 was complete the tube containing the solid reaction product was separated from the apparatus by heat-sealing the connecting arm. The tube was scored with a file and then opened in a dry box to remove the solid product.

When AsF_5 was used as the oxidant the general procedure was similar except that the I_2 was added first and then the required amount of AsF_5 was distilled into the reaction vessel using a calibrated Pyrex vacuum line. After the reaction was complete the solution was transferred as before through the sintered glass filter. In this case the product was accompanied by AsF_3 which is soluble in SO_2. However, since AsF_3 is volatile it was removed along with the SO_2 by distillation.

3. Raman Spectra

Raman spectra were recorded using a Spex Industries Model 1400 spectrometer employing a double monochromator and a phototube detector with a dc amplifier and a recorder. This instrument is a 3/4 meter Czerny-Turner scanning spectrometer with 1200 gratings per mm blazed at 7500 Å giving a dispersion of 5.5 Å per mm.

The 632.8 nm exciting radiation was from a Spectra Physics Model 125 He/Ne laser giving approximately 80 mW at the sample. The laser beam was reflected through 90° by a dielectric mirror and passed vertically up the sample illuminator which consisted of a 20 Å half-width spike filter, a half-wave plate, an iris diaphragm and an adjustable condensing lens for focussing the beam on the sample.

Peak height was used for all intensity measurements.

A Spectra Physics Model 140 argon-ion laser provided 514.5 nm or 488.0 nm excitation with a power output up to 1,000 mW. This laser was mounted parallel to the He/Ne laser and the beam was first reflected through 90° in a horizontal plane by an adjustable dielectric mirror and was then reflected upwards through 90° by another dielectric mirror to attain a vertical direction before entering the the sample illuminator. With this arrangement the plane of polarization of the beam was at right angles to the direction of observed Raman scattering, as required, without the use of half-wave plates.

The Raman scattered light from the sample was observed at right angles to the incident laser beam. After passing through a polarization scrambler the scattered light was focussed on the entrance slit of the monochromator to give a sharp image. Polarization measurements were taken with an analyser parallel or perpendicular to the incident beam.

Spinning Raman cells (described in the following section) were clamped in the shaft of a small electrical stirring motor. The motor was held in an aluminum frame as shown in Figure 2. It consisted of three horizontal plates and two vertical plates which could be clamped to the sample area of the spectrometer. The rim of the stirring motor rested in the uppermost horizontal plate and slits in these plates allowed east-west and north-south adjustment of the plates and motor. Then four thumb-screws were tightened to keep the plates and motor in position. Three Teflon caps on the underside of this horizontal platform rested on three turn-screws, set in the vertical plates, which allowed vertical adjustments and levelling of the apparatus. Also

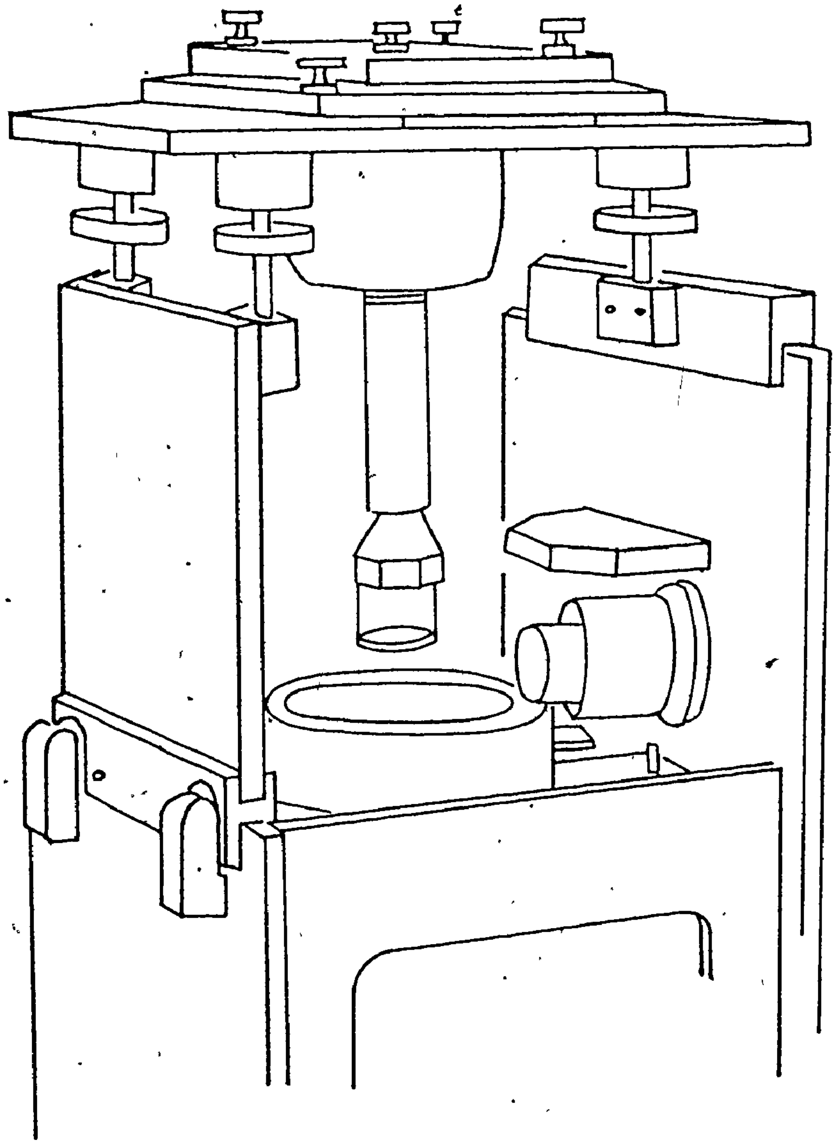


Figure 2. Frame and motor for Raman spinning cells

shown in Figure 2 is a mounting base for a Dewar vessel which was used for low temperature operation. The base of the vessel consisted of two optical flats through which the exciting light passed. The Raman scattered light passed through the curved sides of the vessel.

4. Cells for Raman spectroscopy

(a) Sealed melting-point tubes

Melting-point tubes were filled with a small amount of the sample and temporarily sealed with a plug of Kel-F grease. This operation was performed inside a dry box or dry bag. Then the tubes were brought into the room and heat-sealed using a very small flame. The sealed tube was mounted horizontally during Raman study. If low temperature was required it was placed in a quartz tube having an evacuated jacket, silvered except for a band at the center. Nitrogen was boiled off from a Dewar and passed through the quartz tube to maintain a low temperature which could be measured with a thermocouple.

A similar double-walled quartz tube was also available which could accommodate 5 mm diameter tubes in a similar horizontal arrangement for low temperature Raman studies.

(b) Vycor spinning cell for liquid samples

Colored solutions were studied in a 20 mm diameter cylindrical Vycor cell with an optical flat forming the base. It was constructed from one end of a Beckman UV cell. The cell tapered to a narrow neck which could be stoppered with a Teflon plug. Alternatively, if 1/4" Pyrex tubing was attached using a graded joint then it was possible to flame-seal the neck while the cell was at low temperature on a vacuum line. This modification of the Kiefer and Bernstein (39) rotating cell concept permitted Raman study of solutions containing moisture-sensitive or low-boiling solvents such as HSO_3F, H_2SO_4 and liquid SO_2. A metal collar was attached with rubber cement to the neck of the cell allowing it to be positioned in a rotating shaft which was driven by a small electrical motor at approximately 1000 rpm.

A further modification was the provision for low temperature Raman study which was achieved by surrounding the cell with a Dewar having optical flats at the base. The Dewar was loosely plugged with glass wool to allow free spinning of the motor shaft. Nitrogen was passed through the vessel and a thermocouple inserted into the chilled cavity was used to measure the temperature. This arrangement allowed the study of colored solutions at low temperatures.

(c) Pierced mirror arrangement for solid samples

Crystalline samples prepared in, or transferred to, the Vycor cell described above were positioned higher than the normal position for solutions. A mirror was placed between the bottom of the spinning cell and the focussing lens of the laser beam so that Raman scattering from the spinning sample would be reflected towards the slits of the spectrometer. This 9/16" diameter mirror of 1/8" thickness (manufactured by Applied Physics Specialties Ltd., Toronto) had a 1/16" diameter hole, drilled at a 45° angle through the mirror disc, which allowed the laser beam to pass through the mirror to the spinning sample, as shown in Figure 3. This arrangement effectively placed the sample approximately one inch from its normal position and consequently the focussing lens and the collecting lens required adjustments in order to maximize the intensity of the Raman scattered light reaching the slits.

The use of a pierced mirror which reflects the Raman scattering towards the slits of the spectrometer was first described by Damsgard and Bottger (47) in their study of opaque black solids held in a stationary mount. Kiefer and Bernstein (40) had described a spinning sample technique for solids in which the sample was pressed into the circular groove of a rotating metal plate but this was not suitable for moisture-sensitive compounds. Combining some aspects of these two experimental arrangements has proven to be very useful for the study of highly colored moisture-sensitive solids.

(d) Pyrex spinning cells

A simple Pyrex cell arrangement with no mirror also permitted Raman spectra of moisture-sensitive colored solids or solutions to be obtained at room temperature without volatilization or decomposition of the sample in the laser beam. Figure 4 shows a round bottom Pyrex reaction tube of approximately 2 cm diameter which was tapered to a 1/4" diameter neck that could be conveniently stoppered with a Teflon plug or heat-sealed. A collar of electrical tape allowed the cell to be held firmly in the shaft of the electric motor described earlier. The spinning cell was positioned so that the laser beam struck the curved bottom of the cell at a tangential angle of less than 45° and the Raman scattering was analyzed at 90° to the incident beam. This arrangement permitted both preparation and Raman study of a sample to be carried out in the same tube.

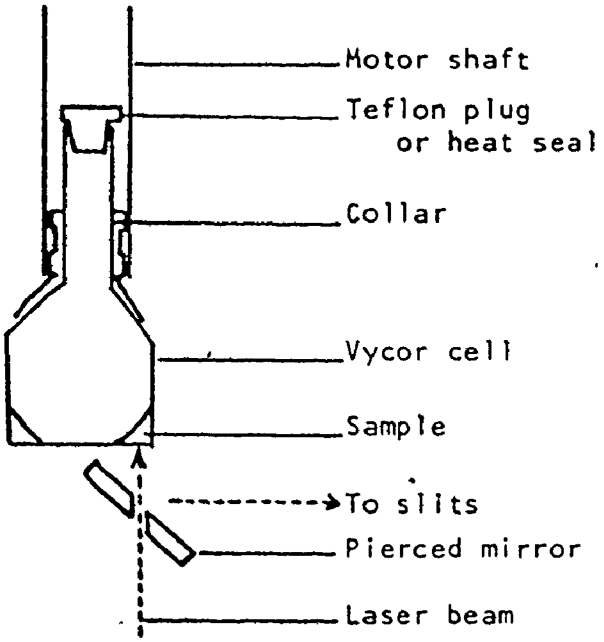


Figure 3. Spinning Vycor cell with 45° pierced mirror

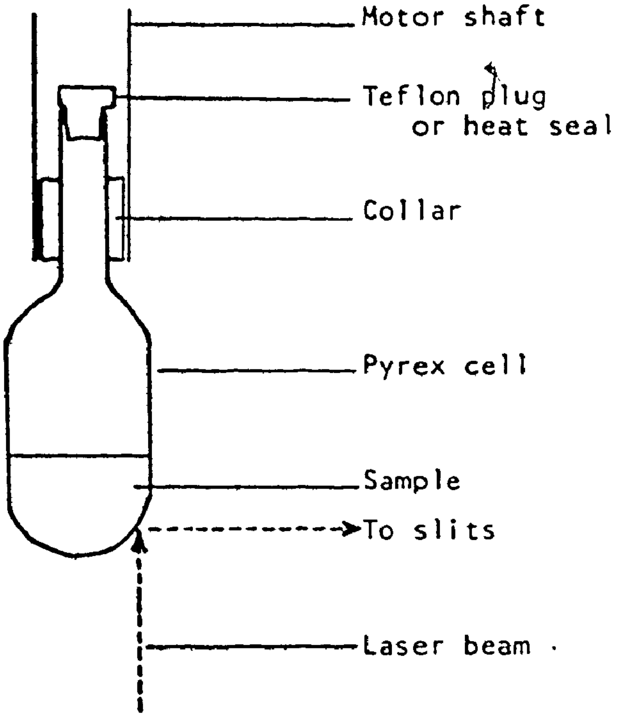


Figure 4. Reaction tube used as a spinning Raman cell

CHAPTER III

Preparation of $I_2^+Sb_2F_{11}^-$

1. Introduction

The blue I_2^+ cation has been characterized in solution in fluorosulfuric and disulfuric acids by conductimetric, spectrophotometric and magnetic measurements (5). A study of the Raman spectra (9) of dilute solutions of I_2^+ in HSO_3F showed that the stretching frequency of the cation is 238 cm^{-1}. This suggested that I_2^+ has a stronger and shorter bond than the I_2 molecule which has a stretching frequency of 213 cm^{-1} and a bond length of 2.66 Å.

No pure crystalline salt of I_2^+ suitable for X-ray crystallographic structure determination had been prepared. In 1906 Ruff (8) and his co-workers had isolated a blue solid from a solution of I_2 in SbF_5. It had the apparent composition $(SbF_5)_2I$ and probably contained the I_2^+ cation, a fluoroantimonate anion, and some SbF_3. In 1968 Kemmitt et al. (7) reported the preparation of some colored solids that contained iodine.. The product which they isolated from a solution of I_2 and IF_5 in SbF_5 contained traces of a white crystalline solid which sublimed at 100°C leaving a blue-black solid whose composition was close to that required for $ISbF_5$ or $I_2Sb_2F_{11}$. The white impurity was probably $IF_4^+SbF_6^-$, an adduct of IF_5 and SbF_5, which is reported (48) to melt at 103°C. They prepared another blue solid by the reaction of I_2 with excess SbF_5 according to Ruff's method described above.

In this case the product must have contained SbF_3 as an impurity which would account for the reported wide melting range of 110-130°C.

A recently developed preparative method (46) has proven to be very effective in a number of syntheses involving SbF_5. It employs dried liquid sulfur dioxide as solvent, in which SbF_3 is insoluble, and a specially designed reaction vessel containing a filter. Use of this method seemed likely to produce a pure crystalline salt of the I_2^+ cation.

2. Synthesis

A description of the Pyrex reaction vessel (Dean apparatus)* used in the preparation of $I_2^+Sb_2F_{11}^-$ and the general preparative method followed are given in Chapter II. A weight of 2.152 g SbF_5 (9.93 mmoles) in dried liquid SO_2 was added to 0.88 g finely ground I_2 (3.47 mmoles) and the solution was stirred for one week at room temperature. White SbF_3 precipitated from the blue solution and was removed by filtering through the sintered glass divider of the reaction vessel. Removal of the solvent by distillation yielded a dark blue crystalline solid which melts sharply at 122-123°C. This preparation is described by the equation

$$2\ I_2 + 5\ SbF_5 \xrightarrow[20°C]{SO_2} 2\ I_2^+Sb_2F_{11}^- + SbF_3\ .$$

The compound is moisture-sensitive and was handled in a dry atmosphere. The elemental analysis* was in satisfactory agreement with that calculated

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* Analysed by A. Bernhardt Microanalytical Laboratory, Elbach, West Germany

for $I_2Sb_2F_{11}$:

Found	I, 36.73;	Sb, 35.27;	F, 27.63
Calculated	I, 35.93;	Sb, 34.48;	F, 29.59

3. Vibrational Frequencies

Crystals of $I_2^+Sb_2F_{11}^-$ sealed in a melting point tube were studied at room temperature using Raman spectroscopy with 632.8 nm He/Ne excitation as described in Chapter II. An intense I_2^+ resonance Raman spectrum with a fundamental at 238 cm^{-1} and two overtones at 476 and 712 cm^{-1} was observed in agreement with spectra reported (9) earlier for I_2^+ in fluorosulfuric acid solution. No anion peaks were observed.

A sample of $I_2^+Sb_2F_{11}^-$ was ground to a fine powder and placed between AgCl windows which were clamped firmly together. These operations were performed in a dry box. Absorption at 660 cm^{-1}, attributed (49) to $Sb_2F_{11}^-$, was observed in the infrared spectrum. The reported (50) weak peak at 485 cm^{-1} which indicates fluorine bridging in the $Sb_2F_{11}^-$ anion was not observed.

A pale blue sample of iodine pentafluoride was placed in a 5 mm tube for Raman study using 632.8 nm excitation. Normally this liquid is colorless but if traces of I_2 and moisture are present a blue color forms which Aynsley et al. (4) had attributed to I^+. When it was shown (5) that the blue species formed by oxidation of I_2 in oleum or HSO_3F is I_2^+ it was assumed, on the basis of UV and visible absorption spectra, that the blue IF_5 solutions must also contain I_2^+. Raman evidence obtained here confirms this assumption. In addition to the reported (51) Raman peaks for IF_5, the characteristic resonance Raman spectrum of I_2^+ consisting of a band at 238 cm^{-1} and an overtone at 476 cm^{-1} was observed.

4. Behavior of I_2^+ at Low Temperature

One reason for synthesizing an I_2^+ salt was to prepare solutions of I_2^+ which would be suitable for low temperature study. Gillespie, Milne and Morton (10) had reported that I_2^+ solutions prepared by oxidation of I_2 with $S_2O_6F_2$ in HSO_3F showed changes in their properties when cooled from room temperature to temperatures in the range -70°C to -90°C. They observed that the color changed from blue to red-brown and the 640 nm absorption peak characteristic of I_2^+ decreased while new peaks at 470, 357, and 290 nm appeared. Magnetic, cryoscopic and electrical conductivity evidence also suggested that a new species was being formed. They proposed that I_2^+ dimerizes at low temperature to form the diamagnetic I_4^{2+} cation:

$$2I_2^+ \rightleftarrows I_4^{2+}$$

The structure of this cation was not known and one purpose of the present work was to investigate this species by Raman spectroscopy.

In addition to the study of the formation of I_4^{2+} in solution, an attempt was made to prepare a solid compound containing the I_4^{2+} dimer. Cooling solid $I_2^+Sb_2F_{11}^-$ to liquid N_2 temperature (-196°C) produced no change in the blue color of the compound. However, a blue solution of $I_2^+Sb_2F_{11}^-$ in SO_2F_2- SO_2 changed color around -85°C and then a red-brown solid precipitated from solution during further cooling to -110°C. The reaction tube (a 5 mm diameter Raman tube with 1/4" diameter Pyrex neck) was attached with a Nupro valve to a vacuum line for removal of the solvent. The tube was surrounded with progressively warmer baths and pumping continued until the solvent mixture was completely removed, leaving a brick-red powdery solid. For Raman study the reaction tube was placed horizontally in a Dewar, as described in Chapter II, but no spectra could be obtained. Even at low temperature the 632.8 nm laser beam decomposed the sample causing a blue spot to form where the beam had illuminated the red sample. Although temperatures around -75 to -85°C had been required for formation of the red colored species, once the solvent was removed the red solid was stable up to approximately -50°C. Then the solid changed irreversibly to a dark blue-black solid.

The color change displayed by solutions of I_2^+, however, is reversible and temperature dependent. Solutions of I_2^+ were prepared by oxidizing I_2 with $S_2O_6F_2$ in HSO_3F or by dissolving $I_2^+Sb_2F_{11}^-$ in HSO_3F. The low temperature Raman study employed melting-point tubes or Vycor spinning cells arranged as described in Chapter II. As the temperature decreased, the intensity of the I_2^+ peak at 238 cm^{-1} diminished but no new peaks were observed with either 632.8 nm or 514.5 nm laser excitation. Possibly the concentrations studied, while correct for detection of the I_2^+ bands at room temperature, were too dilute for obtaining a Raman spectrum of the low temperature species which probably would not display a resonance Raman effect. Even if the experimental difficulties could be overcome it is unlikely that Raman data could be used to characterize the low temperature species. Iodine may be present, not as I_4^{2+} formed by dimerization, but as a mixture of two or more iodine species formed by disproportionation. A mixture of polyatomic iodine cations probably could not be differentiated by Raman spectroscopy. The alternate hypothesis of a disproportionation reaction involving formation of cations having oxidation states other than + 1/2 is discussed below. This hypothesis is consistent with the earlier cryoscopic, magnetic, conductimetric and absorption data.

Gillespie, Milne, and Morton had considered that the disproportionation represented by the equilibrium

$$2\ I_2^{+} \rightleftarrows I_2^{2+} + I_2$$

might exist at low temperature but then they had rejected this possibility because (a) a cation such as I_2^{2+} was not known to exist, (b) existence of molecular I_2 in HSO_3F seemed unlikely, and (c) there would be no decrease in the number of particles present in solution, which would be inconsistent with the observed cryoscopic and conductimetric data. However, data presented in Chapter VI suggest that there is a new polyatomic cation I_n^{n+} in which iodine has a +1 oxidation state. The value of n is not known but it is probably 2, 3 or 4. The cation has a strong Raman band and so it must contain two or more iodine atoms. Then, instead of molecular I_2, the species having an oxidation state less than +1/2 could be I_3^{+} or I_5^{+}. The following disproportionations, therefore, are possible:

$$8\ I_2^+ \rightleftarrows \frac{4}{n}\ I_n^{n+} + 4\ I_3^+$$

$$16\ I_2^+ \rightleftarrows \frac{12}{n}\ I_n^{n+} + 4\ I_5^+$$

In fact, complex equilibria involving three species could exist in this system, as described by the following equations

$$6\ I_2^+ \rightleftarrows 2\ I_2^{2+} + I_3^+ + I_5^+$$

$$10\ I_2^+ \rightleftarrows 2\ I_3^{3+} + 3\ I_3^+ + I_5^+$$

$$6\ I_2^+ \rightleftarrows I_4^{4+} + I_3^+ + I_5^+$$

There was no Raman evidence for any of these species and therefore these proposed disproportionations are speculative. Formation of these species would, however, be consistent with the observed absorption spectra. A summation of the observed absorption bands for I_n^{n+} (290 and 460 nm), I_3^+ (305 and 470 nm) and I_5^+ (270, 345 and 450 nm) results in the reported absorption spectrum (290, 357 and 470 nm) of the low temperature species formed by I_2^+. Thus the earlier experimental results may be re-interpreted on the basis of a disproportionation of I_2^+ to form two or more iodine species with oxidation states other than +1/2.

5. X-ray Crystallography

The structure determination (51a) of $I_2Sb_2F_{11}$ was done by Dr. C.G. Davies and Dr. P.R. Ireland. It showed that $I_2Sb_2F_{11}$ (formula weight 706.30) is monoclinic, C2, with $\underline{a}$ = 13.283(5), $\underline{b}$ = 8.314(3), $\underline{c}$ = 5.571(2) Å and β = 103.75(2)°. A projection of part of the structure down the b axis is shown in Figure 5. Table 1 lists selected bond distances and angles and the atomic positional parameters from which these are derived. The shortest I --- F contact is 2.89 Å indicating that the structure is essentially ionic. The distance between the two symmetry related iodine atoms, i.e. the I - I bond length in the I_2^+ cation, is 2.557(4) Å.

6. Conclusions

Preparation of the blue crystalline compound $I_2Sb_2F_{11}$ followed by Raman and X-ray studies of the solid have shown that it contains the I_2^+ cation. The fundamental stretching vibration of this diatomic species is 238 cm^{-1}, unchanged from the frequency observed for I_2^+ in fluorosulfuric acid solution (9). The iodine-iodine distance of the cation is 2.557 Å which is, as predicted, shorter than the bond distance of 2.66 Å in the I_2 molecule. For the analogous bromine molecule and cation a similar reduction in bond length from 2.27 Å to 2.15 Å is accompanied by an increase in Raman frequency from 318 cm^{-1} (41) to 368 cm^{-1} (360 cm^{-1} for Br_2^+ in solution) (11, 13). Although the Cl_2^+ ion is not known as a stable species either in solution or in the solid state, the stretching frequency and bond length have been obtained from its electronic spectrum in the gaseous state at low pressure (14). Table 2 summarizes the stretching frequencies, absorption maxima, bond lengths and calculated force constants of the halogen molecules and the diatomic halogen cations. The stronger and shorter bond in the X_2^+ cation compared with the X_2 neutral molecule is consistent with the

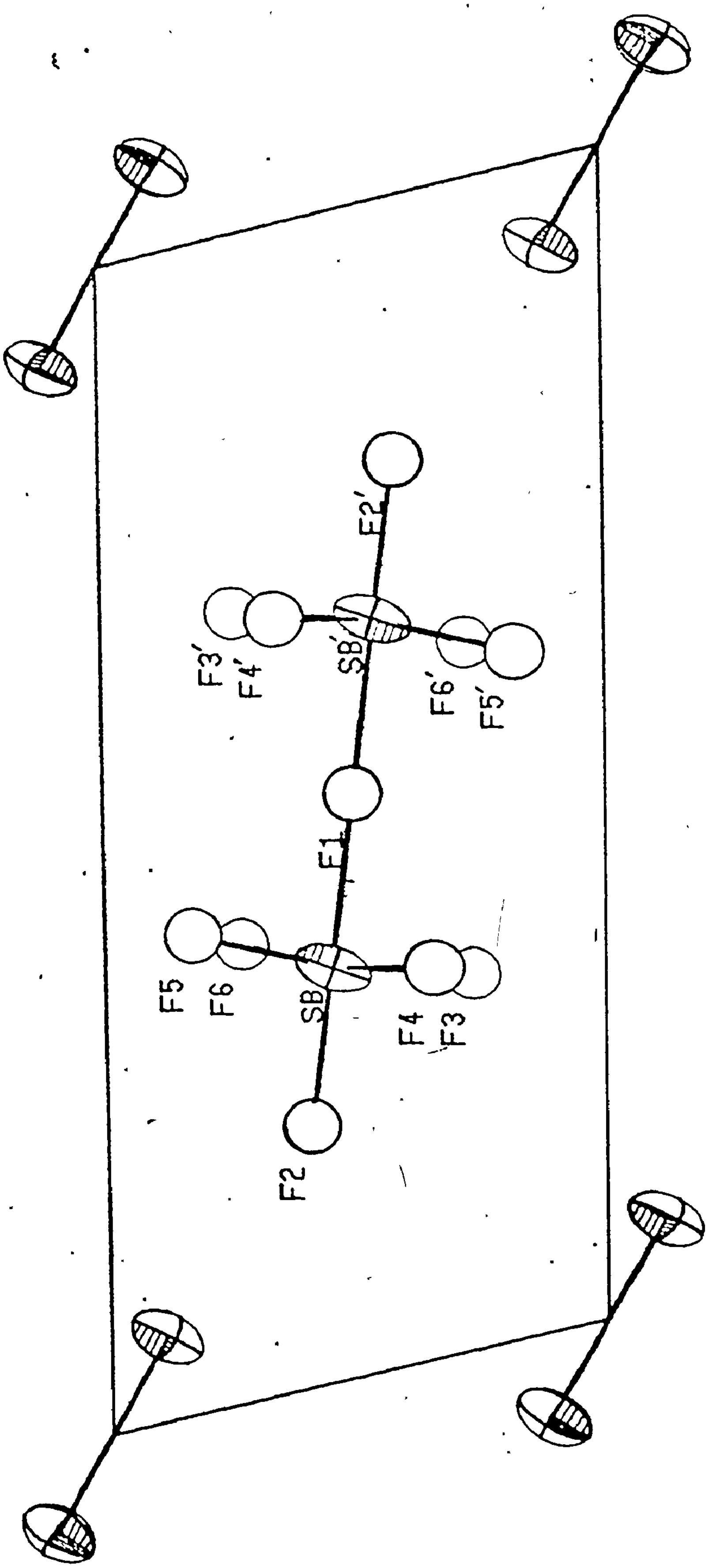


Figure 5. Projection of part of the $I_2^+Sb_2F_{11}^-$ Structure down the _b_ Axis

removal of an electron from an antibonding π^* orbital in the formation of the cation. Photoelectron spectra obtained (52, 53) from the I_2 and Br_2 molecules were reported recently and have been used to assign the electronic spectra of the I_2^+ and Br_2^+ cations.

The color change from blue to red exhibited by solutions of I_2^+ at low temperature has been attributed to a disproportionation of I_2^+. This hypothesis was discussed in relation to the previously proposed theory of dimerization of I_2^+ to form I_4^{2+}. Disproportionation of I_2^+ is thought to produce two or more iodine species, one of which may be a new polyatomic iodine (+1) cation I_n^{n+} which is discussed further in Chapter VI.

Halogen cations are highly electrophilic species that can exist only in the presence of molecules and anions of very low basicity. Fluorosulfuric acid, disulfuric acid, sulfur dioxide, antimony pentafluoride and iodine pentafluoride are suitable solvents for the formation of I_2^+. Although I_2^+ is formed in HSO_3F by oxidation of 2 moles of I_2 with one mole of $S_2O_6F_2$, there is no evidence for the formation of a solid fluorosulfate of I_2^+ when this ratio of reactants is combined in the absence of a solvent. In their study of the $I_2 - S_2O_6F_2$ system Chung and Cady (54) have confirmed the existence of ISO_3F and I_3SO_3F but found no solid with a composition corresponding to I_2SO_3F. Similarly, Merryman, Corbett and Edwards (55, 56) have found no evidence for a tetrachloroaluminate of I_2^+ in the $I_2- ICl - AlCl_3$ system. Apparently solvation of the I_2^+ cation is important in its formation.

In the present work a stable crystalline salt of I_2^+ was obtained with the very weakly basic anion $Sb_2F_{11}^-$ using the very weakly basic solvent SO_2. Several other compounds containing the $Sb_2F_{11}^-$ anion have recently been prepared and their structures determined. The $Sb_2F_{11}^-$ ions in the compounds $XeF_3^+Sb_2F_{11}^-$ (57), $XeF^+Sb_2F_{11}^-$ (58) and $BrF_4^+Sb_2F_{11}^-$ (59) have asymmetric fluorine bridges and the extent of this asymmetry increases with increasing interaction between the cation and the $Sb_2F_{11}^-$ anion as shown by the length of the shortest cation-anion contact. This is accompanied by a lengthening of the Sb-F bond. The data are consistent with an increasing interaction between the cation and the anion in the series XeF_3^+, XeF^+, BrF_4^+ indicating that these cations become increasingly acidic, <u>i.e</u>. increasingly good electron pair acceptors in this order. In $I_2^+Sb_2F_{11}^-$, however, the structure of the $Sb_2F_{11}^-$ ion differs from that found previously. In the present case the anion has a symmetric fluorine bridge with a twofold crystallographic rotation axis passing through the bridging fluorine. The long cation-anion contact distance, although shorter than the sum of the van der Waals radii, indicates that any interaction between these two ions is very small and accordingly one may consider that in this case there is an essentially "free" symmetric $Sb_2F_{11}^-$ ion. One may also conclude that the I_2^+ cation is less acidic than the cations listed above and although it is strongly electrophilic it is not such a strong electron pair acceptor as XeF_3^+, XeF^+ and BrF_4^+.

TABLE I

Selected Bond Distances, Angles and Structural Parameters for $I_2^+Sb_2F_{11}^-$

Bond Distances (Å)

Intramolecular	
I-I'	2.557(4)
Sb-F(1)	2.001(7)
-F(2)	1.83(2)
-F(3)	1.96(4)
-F(4)	1.78(4)
-F(5)	1.80(4)
-F(6)	1.87(4)

Intermolecular	
I-F(2)	2.89(2)

Angles (Degrees)

Sb-F(1)-Sb'	166(3)
F(1)-Sb-F(2)	169(2)
-F(3)	85(2)
-F(4)	89(2)
-F(5)	86(2)
-F(6)	82(2)
F(2)-Sb-F(3)	90(2)
-F(4)	99(2)
-F(5)	99(2)
-F(6)	89(2)
F(3)-Sb-F(4)	91(2)
-F(5)	170(2)
-F(6)	87(2)
F(4)-Sb-F(5)	93(2)
-F(6)	171(2)
F(5)-Sb-F(6)	88(2)

Structural Parameters

Atom	X	Y	Z
I	0.0733(1)	0.0	0.8871(5)
Sb	0.3558(1)	-0.006(1)	0.5437(5)
F(1)	0.5	0.022(7)	0.5
F(2)	0.224(1)	0.009(7)	0.588(4)
F(3)	0.316(2)	0.136(4)	0.256(6)
F(4)	0.342(3)	-0.179(5)	0.350(7)
F(5)	0.415(3)	-0.119(6)	0.815(8)
F(6)	0.390(2)	0.180(4)	0.733(6)

TABLE II

Stretching Frequencies, Absorption Maxima, Bond Lengths and Force Constants of Halogen Molecules and Diatomic Halogen Cations

	Stretching Frequency cm^{-1}	Principal Absorption nm	Bond Length Å	Force Constant mdyn $Å^{-1}$
I_2	213	500	2.66	1.70
I_2^+	238	646	2.56	2.12
Br_2	318	410	2.27	2.38
Br_2^+	360	510	2.13	3.05
Cl_2	554	330	1.98	3.16
Cl_2^+	645.3	-	-	4.29

CHAPTER IV

Study of the I_3^+ cation

1. Introduction

The I_3^+ cation had first been postulated in 1938 (2). Since 1960 several groups have confirmed the existence of the ion in solution by conductimetric and cryoscopic methods as described in greater detail in Chapter I (5, 15, 16). Brown I_3^+ solutions were prepared by the oxidation of iodine by iodic acid in sulfuric acid (equation 1) or by reacting iodine with peroxodisulfuryl difluoride in fluorosulfuric acid (equation 2).

$$7\ I_2 + HIO_3 + 8\ H_2SO_4 \rightarrow 5\ I_3^+ + 3\ H_3O^+ + 8\ HSO_4^- \qquad (1)$$

$$3\ I_2 + S_2O_6F_2 \rightarrow 2\ I_3^+ + 2\ SO_3F^- \qquad (2)$$

In the absence of a solvent the latter reaction of I_2 with $S_2O_6F_2$ produced a dark brown solid formulated as I_3SO_3F (18). This compound presumably contains the I_3^+ cation but no structural determinations have been reported.

Vibrational frequencies of I_3^+ also remained unknown due to the experimental difficulties caused by absorption of the laser excitation by the highly colored solutions. Gillespie and Morton (9) attempted to overcome this problem by studying a very dilute solution of I_3^+ in HSO_3F (equation 2) sealed in a melting-point tube. Instead of observing the I_3^+ Raman spectrum they obtained the interesting resonance Raman spectrum produced by traces of I_2^+. They used laser excitation of 632.8 nm which is close to the 640 nm visible absorption maximum of I_2^+. Consequently, an intensely strong I_2^+ resonance Raman signal was produced and the much weaker Raman scattering of the solvent and of the I_3^+ cation were not observed. It seemed likely that the difficulties encountered in observing the I_3^+ vibrational spectrum could be overcome by adjusting the following conditions of the experiment:

1) Raman cell. The solutions of I_3^+ studied previously had been diluted until they were almost colorless to avoid the problem of boiling which occurs when colored solutions sealed in capillary tubes absorb laser beam energy. Use of a spinning Raman cell would be expected to minimize this problem and allow much high concentrations of the brown-colored I_3^+ solutions to be studied.

2) Solvent. In fluorosulfuric acid the diatomic I_2^+ cation shows some disproportionation to I_3^+ and to an iodine (III) species but in sulfuric acid this disproportionation occurs to a greater extent particularly if the solvent is slightly aqueous, <u>i.e.</u> <100% H_2SO_4. Since the triatomic I_3^+ cation is stable in either of these acid solvents it appears that interference from I_2^+ would be minimized if slightly aqueous sulfuric acid rather than fluorosulfuric acid were used as the solvent for Raman studies of I_3^+.

3) Wavelength. The resonance Raman effect (RRE) of I_2^+ is particularly strong when 632.8 nm excitation is used, but by choosing an exciting wavelength which does not coincide with an I_2^+ absorption maximum the RRE would be decreased. Therefore, changing to the 514.5 nm argon laser line would minimize the resonance Raman signal of I_2^+ which

previously had obscured the I_3^+ spectrum.

2. Preparation and Raman Spectra of Solutions of I_3^+

Solutions containing the I_3^+ cation were prepared by reacting iodine and iodic acid in the mole ratio $I_2/HIO_3 = 7.0$ in H_2SO_4 as solvent according to the equation

$$7\ I_2 + HIO_3 + 8\ H_2SO_4 \rightarrow 5\ I_3^+ + 3\ H_3O^+ + 8\ HSO_4^-$$

The mixture of 2.9286 g I_2 (11.5 mmoles) and 0.2954 g HIO_3 (1.68 mmoles) in 86 ml H_2SO_4 was stirred at room temperature in a Pyrex stoppered flask producing 0.1 M I_3^+ solution which was very dark brown in color. The 2% excess of oxidizing agent ensured that there would not be any unreacted iodine or any iodine in an oxidation state less than +1/3. Portions of this solution were diluted to approximately 0.025 M and were studied in the Vycor rotating Raman cell using 514.5 nm laser excitation. In addition to the expected solvent peaks the Raman spectra obtained had bands at 114, 207 and 233 cm^{-1}. The low frequency section of a typical spectrum is presented in Figure 6 and shows the three Raman bands which may be attributed to the I_3^+ cation.

The earlier cryoscopic studies (15, 16) had suggested that the I_5^+ cation is formed in dilute solutions of H_2SO_4 having the mole ratio $I_2/HIO_3 = 12.0$ as described by the equation

$$12\ I_2 + HIO_3 + 8\ H_2SO_4 \rightarrow 5\ I_5^+ + 3\ H_3O^+ + 8\ HSO_4^-$$

Accordingly, 2.3227 g I_2 (9.15 mmole) and 0.1327 g HIO_3 (0.754 mmole) were dissolved in 60 ml of 100% H_2SO_4. Portions of the brown solution were diluted for Raman study in a rotating cell as described above and

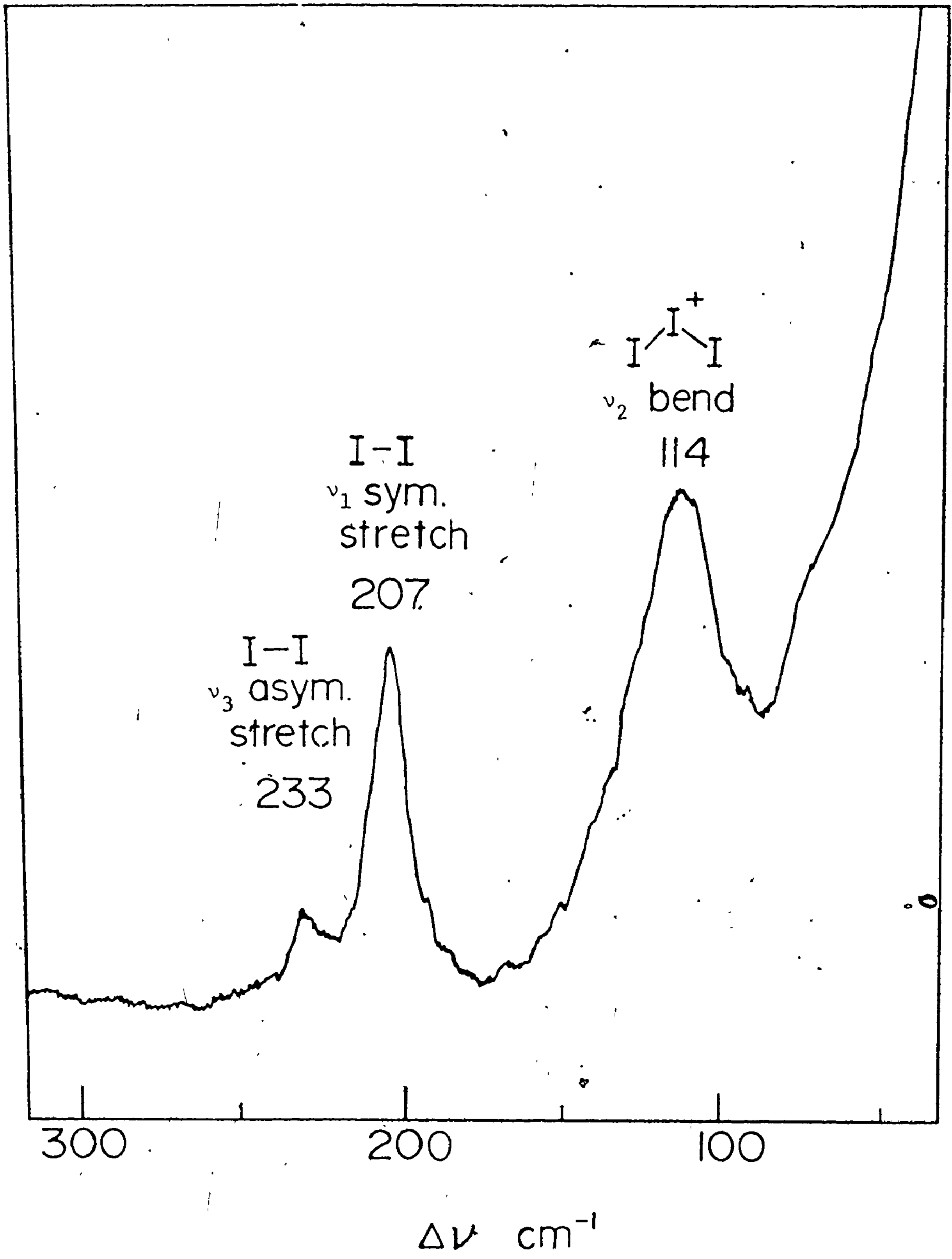


Figure 6. Raman spectrum of I_3^+ in sulfuric acid

spectra were recorded using 632.8 nm and 514.5 nm laser excitation. Peaks were observed at 70, 115 and 207 cm^{-1}, of which 115 and 207 cm^{-1} correspond to observed frequencies for I_3^+. While it is likely that I_5^+ is formed as outlined in the above equation (which describes, in effect, the reaction $I_3^+ + I_2 \rightarrow I_5^+$), it appears that Raman spectroscopy is not a suitable technique for characterization of this cation - the solution probably contains both I_3^+ and I_5^+ in equilibrium and, also, the Raman spectrum of I_5^+ would be expected to be very similar to that of I_3^+ but with additional low frequency bands. Therefore, although the observed frequencies of 70, 115, and 207 cm^{-1} appear to be reasonable for I_5^+, they may not be assigned with certainty to the I_5^+ cation.

3. Preparation of solid salts of I_3^+

The black compound I_3SO_3F had previously been prepared from iodine and $S_2O_6F_2$ by Aubke and Cady (18) and a sample of this material was prepared following their procedure. In the absence of a solvent, 0.2990 g $S_2O_6F_2$ (1.52 mmole) and 1.2633 g I_2 (4.97 mmole) were heated in a Pyrex reaction tube to 90°C and then cooled in liquid N_2 to break up the product. After pumping on the solid to remove any unreacted I_2 the black compound was transferred within a dry box to a Vycor cell (described in Chapter II). Unfortunately even with the use of spinning cell techniques it was not possible to observe a Raman spectrum for I_3SO_3F probably because of its intense absorption in the visible spectrum. Where the laser beam had illuminated the sample there appeared to be a "track" on the cell indicating decomposition of I_3SO_3F.

Iodine was also oxidized with AsF_5 in an effort to obtain an AsF_6^- salt of the I_3^+ cation. The general preparative method used employing liquid SO_2 as solvent is described in Chapter II. Reaction of 0.2711 g I_2 (1.070 mmoles) with 1.07 mmoles AsF_5 yielded a brown solid, which very likely was the compound $I_3^+AsF_6^-$ produced according to the equation

$$3\ I_2 + 3\ AsF_5 \rightarrow 2\ I_3^+AsF_6^- + AsF_3$$

but no elemental analysis was done to confirm this and the sample decomposed before any Raman studies could be done. Probably no Raman peaks would have been observed in view of the problem of absorption consistently encountered for solids containing the dark colored I_3^+ cation.

Some attempts were made to produce a solid I_3^+ salt with $Sb_2F_{11}^-$ as the anion according to the equation

$$3I_2 + 5\ SbF_5 \rightarrow 2\ I_3^+Sb_2F_{11}^- + SbF_3.$$

The general preparative method which employs liquid SO_2 as solvent was followed. The products obtained appeared to be mixtures of dark-colored solids, indicating that SbF_5, instead of forming $SbF_5.SbF_6^-$ (i.e. the $Sb_2F_{11}^-$ anion), had reacted with iodine to produce oxidation states higher than +1/3. It was necessary, therefore, to adjust the I_2:SbF_5 ratio so that the simple SbF_6^- anion would be formed and the iodine oxidation would stop at the + 1/3 state yielding a salt of the I_3^+ cation.

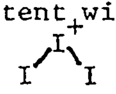
A mixture of 0.7423 g I_2 (2.94 mmole) and 0.6455 g SbF_5 (2.96 mmole) in dried liquid SO_2 was stirred for one week in a Pyrex reaction vessel. White SbF_3 precipitated from the brown solution and was removed by filtering through the sintered glass divider of the reaction vessel. Removal of the solvent by distillation yielded a black crystalline solid which is believed to be the new compound $I_3^+SbF_6^-$ produced according to the equation

$$3\ I_2 + 3\ SbF_5 \rightarrow 2\ I_3^+SbF_6^- + SbF_3.$$

Again, it was not possible to characterize the I_3^+ cation by Raman spectroscopy even with the use of a spinning cell because of absorption in the visible spectrum. However, the solution obtained by dissolving the solid in 100% H_2SO_4 was studied in a spinning Vycor cell (described in Chapter II) using 514.5 nm excitation. The Raman spectrum obtained was identical to that observed for I_3^+ solutions which had been prepared by oxidizing I_2 with HIO_3 in H_2SO_4. Polarization ratios ρ of 0.4, 0.3 and 0.8 were obtained for the 207, 114 and 233 cm^{-1} bands, respectively.

4. Calculations and Conclusions

The observation of three frequencies that may be attributed to the I_3^+ cation leaves no doubt that it has the expected angular structure. The strongly polarized bands observed at 207 and 114 cm^{-1} for this ion in sulfuric acid solution are clearly the symmetric stretching vibration ν_1 (a_1) and the bending vibration ν_2 (a_1), respectively. The observation that the band at 233 cm^{-1} is depolarized confirms its assignment to the asymmetric stretching vibration ν_3 (b_1) of the I_3^+ cation.

For this symmetric structure the simple valence force field treatment described in Chapter I may be used to calculate the stretching and bending force constants and to estimate the bond angle. The results of these calculations are in Table 3. They give good agreement for an approximate bond angle of 114° with stretching force constant $\underline{f}$ = 1.7 mdyn $\mathring{A}^{-1}$ and bending force constant $\underline{d}$ = 0.31 mdyn $\mathring{A}^{-1}$. It may be noted that the average stretching frequency of I_3^+ at 220 cm^{-1} is appreciably lower than that of the I_2^+ ion at 238 cm^{-1} but it is close to the frequency of 213 cm^{-1} reported (41) for the neutral I_2 molecule. In fact, the calculated stretching force constants of I_2 and I_3^+ have the identical value of 1.7 mdyn $\mathring{A}^{-1}$ compared to the higher value of 2.12 mdyn $\mathring{A}^{-1}$ for I_2^+. This is consistent with the fact that in terms of the simple valence bond structure  $I-\overset{+}{I}-I$ both bonds have a formal bond order of 1.0 compared to 1.5 for I_2^+.

The bond angle of 114° calculated for I_3^+ in solution is larger than the values obtained for ICl_2^+ and IBr_2^+. These two interhalogen cations, studied in solution and as solid salts, are discussed in Chapter V. Their spectra have the ν_1 and ν_3 bands very close together or coincident and hence the calculated bond angles are in the range 90 - 95°. For I_3^+, however, ν_1 and ν_3 differ by 26 cm^{-1} and the structure of the cation appears to be similar to that of H_2O, SO_2 or NO_2. These three molecules show considerable differences in their ν_1 and ν_3 frequencies and the calculated and observed bond angles are larger than 105° (14). Recently Merryman, Corbett and Edwards (55,56) reported a value of 97° for the bond angle of I_3^+ in the black solid $I_3^+AlCl_4^-$. Based on ^{127}I nuclear quadrupole resonance studies they predicted a charge distribution of + 0.21 and + 0.24 for the terminal

TABLE III

Force Constants for I_3^+ in H_2SO_4 Solution

$\nu_1 = 207 \quad \nu_2 = 114 \quad \nu_3 = 233\ \text{cm}^{-1}$

Angle deg	f mdyn Å^{-1}	d mdyn Å^{-1}	Calculated ν_1 cm^{-1}
95	1.94	0.351	237
100	1.87	0.339	229
105	1.80	0.328	221
110	1.73	0.316	213
115	1.68	0.304	205

iodine atoms and + 0.76 for the central iodine atom with a bond angle of 97° between the bonding orbitals. Both the nqr treatment and the force field treatment of Raman data give bond angle estimates which are approximate; also, the bond angle of I_3^+ in solution may possibly be greater than the angle in a solid salt such as $I_3^+AlCl_4^-$. In the study of the I_2 - ICl - $AlCl_3$ system the phase I_5AlCl_4 was also obtained. It is described as a greenish-black metallic-looking compound which melts at 50.0 - 50.5°C. Chung and Cady (54), on the other hand, found no evidence for I_5SO_3F in the I_2- $S_2O_6F_2$ system but reported obtaining a new compound I_7SO_3F. In both of these phase studies there was no evidence of the formation of a compound containing I_2^+. However, I_3^+ appears to form readily and to be stabilized by either SO_3F^- or $AlCl_4^-$.

CHAPTER V

Triatomic Interhalogen Cations of Iodine

1. Introduction

The six possible triatomic interhalogen cations which contain iodine and one other halogen have the general formulae IX_2^+ and I_2X^+, where X = F, Cl, or Br. The first cation of the series to be identified was ICl_2^+. In 1959 Vonk and Wiebenga (22) prepared two adducts of the interhalogen compound ICl_3 by reacting it with the Lewis acids $SbCl_5$ and $AlCl_3$. X-ray crystallography established that the two orange solids are essentially ionic compounds although there is apparently some cation-anion interaction _via_ chlorine bridges. The bond angle and bond length of ICl_2^+ were reported as 92.5° and 2.31 Å in $ICl_2^+SbCl_6^-$ and 96.7° and 2.28 Å in $ICl_2^+AlCl_4^-$. The ^{35}Cl nqr studies of Evans and Lo (42) have also confirmed that there are two chemically different types of chlorine present in $ICl_2^+AlCl_4^-$.

Senior and Grover (27) gave conductimetric and cryoscopic evidence that ICl_2^+ is formed in 100% sulfuric acid by the addition of Cl_2 to solutions of H_2SO_4 containing iodine and iodic acid in the mole ratio $I_2/HIO_3 = 2.0$ which corresponds to a nominal +1 oxidation state for iodine. Similarly, IBr_2^+ was reported to form when Br_2 was added to identical H_2SO_4 solutions. The overall equation,

$$2\ I_2 + HIO_3 + 5X_2 \rightarrow 5\,IX_2^+ + 3\ H_3O^+ + 8\ HSO_4^- \\ + 8\ H_2SO_4$$

was presented to describe the formation of these two cations.

Gillespie and Malhotra (6) showed that ICl_2^+ is formed in disulfuric acid solution by the ionization of ICl_3. In contrast to its behavior in disulfuric acid, ICl_3 is only sparingly soluble in 100% sulfuric acid. Senior and Grover, however, found ICl_3 to be soluble in a solution of I_2 and HIO_3 in 100% H_2SO_4. On the basis of a single set of conductivity measurements they suggested that ICl_2^+ may also be formed by the addition of ICl_3 to sulfuric acid solutions containing iodine and iodic acid in the mole ratio $I_2/HIO_3 = 0.33$ which corresponds to a +3 oxidation state for iodine. This reaction was described by the following equation:

$$I_2 + 3\ HIO_3 + 10\ ICl_3 + 24\ H_2SO_4 \rightarrow 15\ ICl_2^+ + 9\ H_3O^+ + 24\ HSO_4^- .$$

Ultraviolet-visible absorption spectra were reported for ICl_2^+ and IBr_2^+; ICl_2^+ shows absorption maxima at 360 nm and 452 nm, while IBr_2^+ has a maximum at 358 nm and a broad shoulder at 540 nm.

In 1965 Aubke and Cady (18) prepared an impure sample of orange ICl_2SO_3F by reaction of iodine fluorosulfate with excess Cl_2. Quite recently Yeats, Wilson and Aubke (60) prepared pure samples of ICl_2SO_3F and IBr_2SO_3F by a similar method. The compounds were characterized by elemental analysis and by infrared study. Incomplete Raman spectra were also reported - three bands at 380, 360 and 161 cm^{-1} were reported for ICl_2^+ but were not assigned and only one frequency at 256 cm^{-1} was reported for IBr_2^+.

The early studies of the $I_2 - SbCl_5$ system by Ruff (24) and later by Fialkov et al. (25) provided evidence for the existence of the compound $SbCl_5.2ICl$. In view of the identification of interhalogen cations in other adducts of interhalogens with Lewis acids it has been suggested that $SbCl_5.2ICl$ could reasonably be formulated as $I_2Cl^+SbCl_6^-$, but there was no X-ray structure determination or vibrational study reported in the literature to confirm this. Also, there has been no previous report of the preparation of a crystalline salt of I_2Br^+. Garrett <u>et al</u>.(16)suggested that the cations I_2Cl^+ or I_2Br^+ were produced in solution by the addition of ICl or IBr to solutions of H_2SO_4 containing I_2 and HIO_3 in a 2:1 mole ratio. Their interpretation, however, was not conclusive because their conductimetric and cryoscopic data could also be interpreted in terms of a dissociation to I_3^+ and ICl_2^+ (or IBr_2^+) cations.

Evidence for the existence of I_2F^+ has not been reported. The IF_2^+ cation, however, has been characterized in $IF_2^+SbF_6^-$ by ^{19}F nmr spectroscopy (29). Schmeisser <u>et al</u>. (28) prepared IF_2^+ at low temperature as $IF_2^+SbF_6^-$ and $IF_2^+AsF_6^-$, which were described as unstable yellow solids. The present investigation of iodine cations did not include those containing fluorine; it was concerned only with those interhalogen cations containing iodine bonded to chlorine or bromine. These species were expected to have a darker hue than the yellow color reported for IF_2^+. ICl_2^+ is known to be orange and the $SbCl_5.2ICl$ adduct, which is believed to contain I_2Cl^+, is dark brown. The iodine-bromine cations, IBr_2^+ and I_2Br^+, were expected to be red-brown.

Although vibrational spectroscopy was very useful for the identification and characterization of ClF_2^+ and Cl_2F^+, standard infrared techniques were not applicable in this study because the bending frequencies and the I - I, I - Br, and I - Cl stretching frequencies were expected to occur below 400 cm^{-1}. Also, the application of Raman spectroscopy, while very suitable for the study of low frequency vibrations, would be hampered in this case by the deep color of the samples. Highly colored samples absorb energy from the laser beam and therefore solutions tend to boil and solids tend to decompose during Raman study. Consequently, all of the spinning sample techniques described in Chapter II, which were designed to overcome these problems, were employed. These new methods allowed Raman spectra of highly colored iodine cations to be recorded at room temperature.

2. The ICl_2^+ cation

Crystals of orange $ICl_2^+SbCl_6^-$ were deposited on the flat bottom of a Vycor spinning cell from a hot solution of ICl_3 in excess $SbCl_5$ and then the supernatant solution was decanted. The elemental analysis* of the orange solid was in good agreement with that calculated for $ICl_2^+SbCl_6^-$:

Found	I, 23.94;	Sb, 22.63;	Cl, 53.16.
Calculated	I, 23.84;	Sb, 22.87;	Cl, 53.28

Raman study was performed at room temperature using 632.8 nm and the 45° pierced mirror arrangement described in Chapter II. The observed Raman spectrum is shown in Figure 7 and the frequencies are given in Table 4. An identical, but weaker, spectrum was obtained when a crystal

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* Analysed by A. Bernhardt Microanalytical Laboratory, Elbach, West Germany.

of $ICl_2^+SbCl_6^-$ sealed in a melting-point tube was studied at low temperature using 632.8 nm excitation.

The Raman spectrum for $ICl_2^+SbCl_6^-$ showed bands at 323, 269, 250 and 175 cm^{-1} which may be assigned to ν_1, ν_2 (split into two peaks) and ν_5, respectively, of the octahedral $SbCl_6^-$ anion. These values may be compared with the vibrational frequencies (ν_1 = 335, ν_2 = 291, ν_5 = 174 cm^{-1}) reported by Beattie <u>et al</u>. (61) for the $SbCl_6^-$ anion in $AsCl_4^+SbCl_6^-$. The remaining peaks may be assigned to a lattice vibration (70 cm^{-1}) and to the symmetric bent ICl_2^+ cation. A low frequency band at 148 cm^{-1} is assigned as the ν_2 bending mode of the cation and an intense doublet having peaks at 370 and 362 cm^{-1} is assigned to the symmetric stretching vibration ν_1 of $I^{35}Cl_2^+$ and $I^{35}Cl^{37}Cl^+$, respectively. The observed difference of 8 cm^{-1} between these two bands due to the chlorine isotope effect agrees with the expected difference in frequencies calculated by substituting the masses of ^{35}Cl and ^{37}Cl in equation (3), given in the Appendix. The observed 3:2 ratio of peak intensities for these two bands is also in agreement with the expected 9:6:1 ratio of $I^{35}Cl_2^+$, $I^{35}Cl^{37}Cl^+$, and $I^{37}Cl_2^+$ populations based on a chlorine isotope abundance of 75% ^{35}Cl and 25% ^{37}Cl.

There are no bands outside of the 355 - 370 cm^{-1} region of the spectrum which can reasonably be assigned to the asymmetric vibration ν_3. This band, therefore, must coincide with or be very close to the ν_1 band. The ν_3 band was expected to be less intense than ν_1 and the isotopic splitting was also expected to be less than was observed for ν_1. By substituting the masses of ^{35}Cl and ^{37}Cl in equation (1)

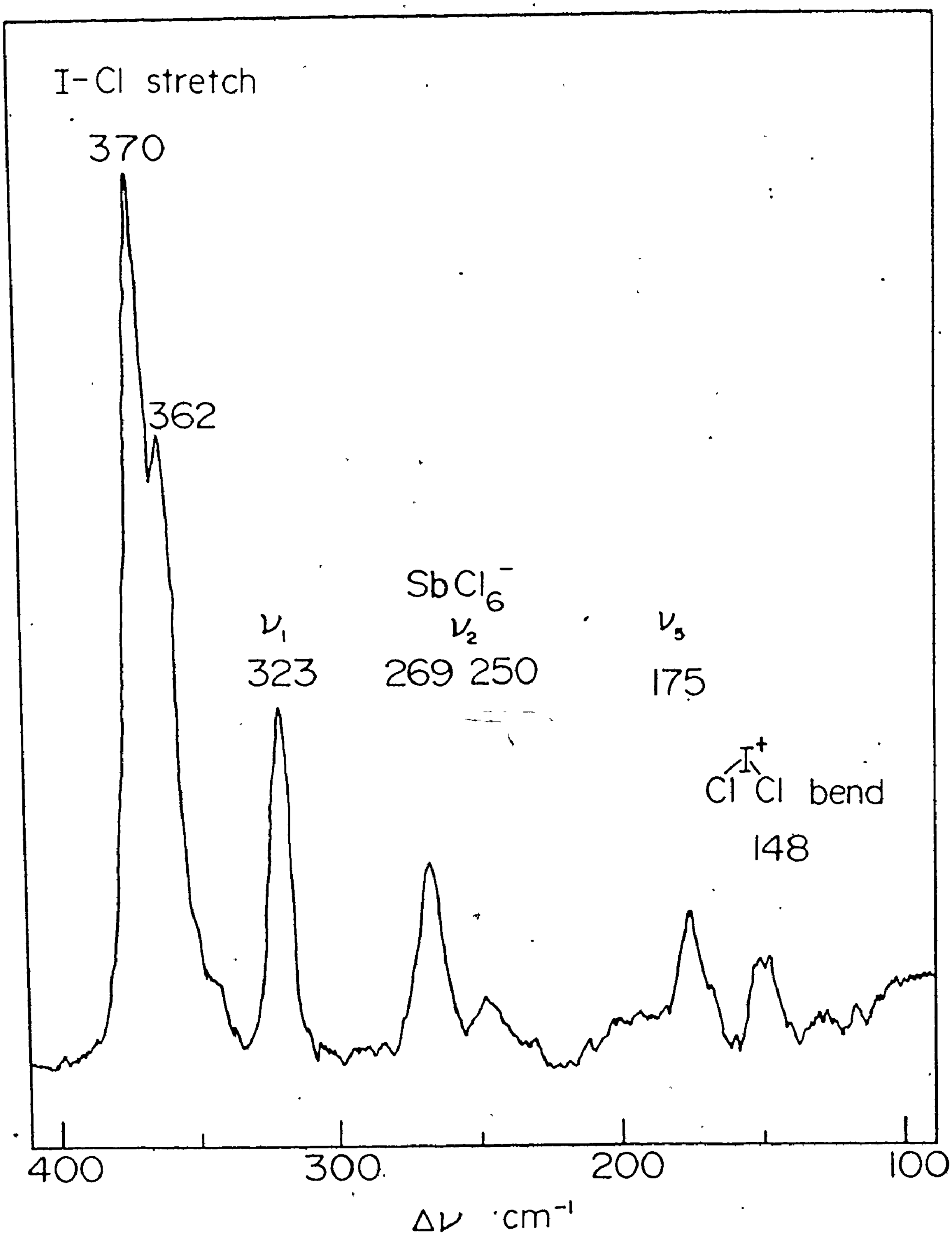

Figure 7. Raman spectrum of $ICl_2^+SbCl_6^-$

Table IV

Raman Spectrum of $ICl_2^+SbCl_6^-$

Relative Intensity	Frequency Shift cm^{-1}	Assignment ICl_2^+ (C_{2v})	Assignment $SbCl_6^-$ (O_h)	Frequencies in Ref. 62 cm^{-1}
	70	lattice		
13	148	ν_2 (a_1)		149
20	175		ν_5 (t_{2g})	176
5	250		ν_2 (e_g)	252
16	269			271
38	323		ν_1 (a_{1g})	324
3	356	ν_1 $I^{37}Cl_2^+$		
70	362	ν_1 ($I^{37}Cl^{35}Cl^+$)		366 (ν_1)
100	370	* ν_1 ($I^{35}Cl_2^+$)		372 (ν_3)

* ν_3 (b_1) lies under the ν_1 (a_1) bands;
for $I^{35}Cl_2^+$ ν_3 is estimated to be 368 cm^{-1}.

of the Appendix, a value of 4 cm^{-1} was calculated for the splittings of ν_3, compared to the observed splitting of 8 cm^{-1} for ν_1. These bands overlap each other so that the total intensity of ν_1 plus ν_3 for each of the two most abundant cationic species is maintained at a 3:2 ratio. Apparently, then, the overlap of ν_1 and ν_3 is symmetric and, therefore, the most reasonable estimates for ν_3 are 368 cm^{-1} for $I^{35}Cl_2^+$ and 364 cm^{-1} for $I^{35}Cl^{37}Cl^+$. Thus ν_1 and ν_3 have very similar frequencies; this is consistent with a bent structure having a bond angle close to 90°. A shoulder which could not be resolved may be assigned to ν_1 (∿356 cm^{-1}) and ν_3 (∿360 cm^{-1}) of $I^{37}Cl_2^+$.

Strictly speaking, the simple valence force field treatment of Raman frequencies using the equations given in the Appendix is applicable to a bent triatomic structure only when both terminal atoms are identical, i.e. are the same isotope. In this case the observed spectrum of $ICl_2^+SbCl_6^-$ consists of bands due to three different isotopic types of ICl_2^+. One may, however, select the bands due to the most abundant isotopic species, $I^{35}Cl_2^+$, from the spectrum and use their frequencies for the calculations providing that a chlorine mass of 35.0 is also used. Although ν_3 is not known exactly, the estimated value of 368 cm^{-1} may reasonably be used for calculation of f and d. The results of the calculations for $I^{35}Cl_2^+$ are summarized in Table 5. Agreement of the calculated ν_1 frequency with the observed ν_1 frequency occurs when 90° is chosen for the bond angle. A stretching force constant f of 2.1 mdyn Å^{-1} and a bending force constant d of 0.19 mdyn Å^{-1} were calculated for the ICl_2^+ cation in solid $ICl_2^+SbCl_6^-$.

TABLE V

Force Constants for ICl_2^+ in $ICl_2^+SbCl_6^-$

$\nu_1 = 370$ $\nu_2 = 148$ Est. $\nu_3 = 368\ cm^{-1}$

Angle deg	f mdyn $Å^{-1}$	d mdyn $Å^{-1}$	Calculated ν_1 cm^{-1}
90	2.16	0.187	370
92.5	2.14	0.186	366
95	2.12	0.184	363

During this investigation the Raman spectrum of $ICl_2^+SbCl_6^-$ was reported by Shamir and Rafaeloff (62). The observed frequencies agree closely as shown in Table 4 but there are some differences in the assignments. The two strong bands which they observed at 366 and 372 cm^{-1} they assign to ν_1 (symmetric stretching) and ν_3 (asymmetric stretching), respectively, on the basis of polarization measurements performed on a single crystal. Polarization measurements on a solid are meaningless unless the orientation of the crystal with respect to the laser beam is known; this information was not reported. It would appear from their data that it is the 372 cm^{-1} peak which is more strongly polarized and thus it should be assigned to ν_1 and not to ν_3. Also, their assignment is contrary to the observation that the intensity of the symmetric stretching vibration is generally greater than the intensity of the asymmetric stretching mode.

Wilson and Aubke have assigned the 161, 360 and 380 cm^{-1} bands of ICl_2SO_3F to ν_2, ν_1 and ν_3, respectively (65). The ν_2 value compares with that reported here but the other two bands are 20 cm^{-1} apart instead of being coincident as observed for $ICl_2^+SbCl_6^-$. (This splitting is too great to be an isotope effect). The assignment of the more intense band (380 cm^{-1}) to ν_3 is contrary to the observation that all of the IX_2^+ ions in this study have a weak ν_3 band. Also, the reported assignments give a calculated angle of 105° which is inconsistent with the results of this study and of the crystallographic study. Possibly the 380 cm^{-1} band is due to ICl (ν = 381 cm^{-1}) in the sample.

Solutions containing the ICl_2^+ cation were produced by two methods. Dried chlorine gas was bubbled through 3.2 ml of a stock iodine +1 solution* that had been placed in a narrow tube. After 10 minutes the color changed from greenish-brown to a light orange. The solution was studied without further dilution in a Vycor spinning cell using 514.5 nm excitation.

Another solution was prepared by placing 0.174 g I_2, 0.0430 g HIO_3 and approximately 20 ml of 100% H_2SO_4 in a stoppered Pyrex flask. While the mixture was stirred slight warming of the solution occurred from the heat of the stirring motor. After the addition of 0.1430 g ICl_3 the green solution became orange. A Raman spectrum was obtained using a Vycor spinning cell and 514.5 nm excitation. Spectra were recorded with the analyser parallel and then perpendicular to the incident laser beam.

The two orange sulfuric acid solutions had identical spectra. A typical spectrum is shown in Figure 8. In addition to solvent peaks two peaks were observed which may be attributed to ICl_2^+. The weak peak at 148 cm^{-1} may be assigned to the bending mode ν_2 and the stronger peak at 387 cm^{-1} may be assigned to I – Cl stretching. In solution the ν_1 and ν_3 modes are coincident and the isotopic splitting is not resolved. Therefore, only one peak was observed. This peak is

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* A stock solution of 100% H_2SO_4 containing I_2/HIO_3 in the mole ratio 2:1 was prepared by dissolving 2.0359 g I_2 (8.02 mmole) and 0.7168 g HIO_3 (4.07 mmole) in 88 ml of 100% H_2SO_4 in a glass-stoppered Pyrex flask. This ratio of reagents produced a brown solution containing iodine in a +1 oxidation state with the concentration of I^+ equal to 0.232 M.

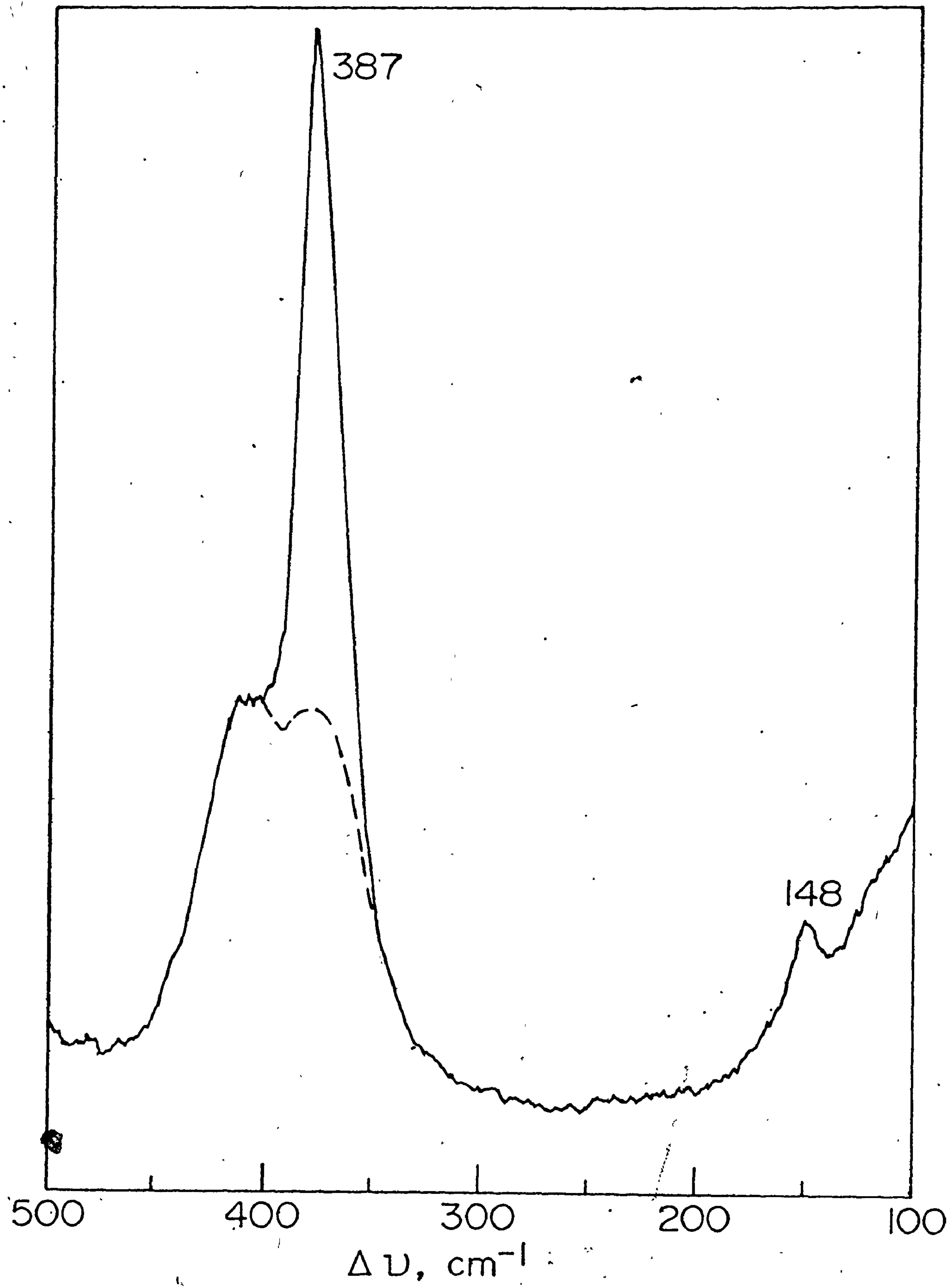

Figure 8. Raman spectrum of ICl_2^+ in Sulfuric Acid

TABLE VI

Force Constants for ICl_2^+ in H_2SO_4 Solution

$\nu_1 = \nu_3 = 387$ $\nu_2 = 148\ cm^{-1}$

Angle deg	f mdyn Å^{-1}	d mdyn Å^{-1}	Calculated ν_1 cm^{-1}
90	2.44	0.190	389
92.5	2.42	0.188	385
95	2.40	0.186	381

in the region where the 392 and 422 cm^{-1} peaks of H_2SO_4 (63) occur. It is superimposed on the 392 cm^{-1} peak whose normal intensity is shown by a dotted line in Figure 8. The I-Cl stretching frequency of 387 cm^{-1} observed for ICl_2^+ in solution is higher than the values (362 and 370 cm^{-1}) for the cation in solid $ICl_2^+SbCl_6^-$. This is probably caused by removal of chlorine bridging between the cation and the anion. In the polarization study the peak at 387 cm^{-1} showed a marked decrease in intensity. This indicates that this Raman band is strongly polarized, with very little contribution from ν_3 which is coincident with and much less intense than ν_1, and confirms the assignment of the band to the symmetric stretching vibration of ICl_2^+.

The results of simple valence force field calculations for the ICl_2^+ cation in H_2SO_4 solution are given in Table 6. Using ν_2 = 148 cm^{-1} and ν_3 = 387 cm^{-1} the calculated ν_1 value equalled the observed value of 387 cm^{-1} when 91° was chosen for the bond angle. A stretching force constant <u>k</u> of 2.4 mdyn $\mathring{A}^{-1}$ and a bending force constant <u>d</u> of 0.19 mdyn $\mathring{A}^{-1}$ were calculated for ICl_2^+ in sulfuric acid solution.

3. The IBr_2^+ cation

Several attempts were made to prepare an IBr_2^+ salt by adding Br_2 to IBr in $SbCl_5$. This method is analogous to an alternate preparation of $ICl_2^+SbCl_6^-$, reported by Vonk and Wiebenga (22), in which a solution of ICl in $SbCl_5$ was treated with Cl_2. However, the observed Raman spectrum of the low-melting dark red-brown solid was similar to that of $I_2Br^+SbCl_5Br^-$, described later in this chapter;

there was no Raman evidence that IBr_2^+ had been formed by this method.

The red-brown solid IBr_2SO_3F was prepared by the method of Yeats, Wilson and Aubke (60). Finely ground I_2 (0.240 g) was reacted with $S_2O_6F_2$(0.19 g) in a Pyrex trap at 60°C for one hour to produce black ISO_3F. An excess of dried Br_2 was distilled onto the ISO_3F and the mixture was heated to 60°C. After cooling the trap and pumping to remove Br_2 the product weighed 0.742 g. The elemental analysis* of the red-brown solid was in very good agreement with that calculated for IBr_2SO_3F:

Found I, 32.72;	Br, 41.45;	F, 5.21
Calculated I, 32.90;	Br, 41.42;	F, 4.93

The compound is moisture-sensitive and the transfer of samples to melting point tubes or to a Vycor cell was performed in a dry box. Crystals sealed in a melting-point tube were studied at low temperature using the 632.8 nm He/Ne laser beam. Raman spectra were also obtained at room temperature with both 632.8 nm and 514.5 nm excitation using a Vycor spinning cell and 45° pierced mirror, as described in Chapter II.

The observed Raman frequencies for $IBr_2^+SO_3F$ are listed in Table 7 and the low frequency region of the Raman spectrum is shown in Figure 9. In addition to peaks which may be assigned to the fluorosulfate anion, three Raman peaks were observed which may be attributed to the IBr_2^+ cation, in contrast to the one peak at 256 cm^{-1} reported

* Analysed by A. Bernhardt Microanalytical Laboratory, Elbach, West Germany

TABLE VII

Raman Spectrum of $IBr_2^+SO_3F^-$

Relative Intensity	Frequency Shift cm^{-1}	Assignment IBr_2^+ (C_{2v})	Assignment SO_3F^- (C_s)	Infrared in Ref. 60 cm^{-1}
8	103	ν_2 (a_1)		
75	252	ν_3 (b_1)		
100	257	ν_1 (a_1)		
1	402		ν_5 (a")	402
3	412		ν_4 (a')	420
1	565		ν_3 (a')	560
			ν_9 (a")	575
1	586		ν_7 (a')	590
2	781		ν_2 (a')	780
25	1060		ν_1 (a')	1062
5	1201		ν_8 (a")	1206
2	1277		ν_6 (a')	1260

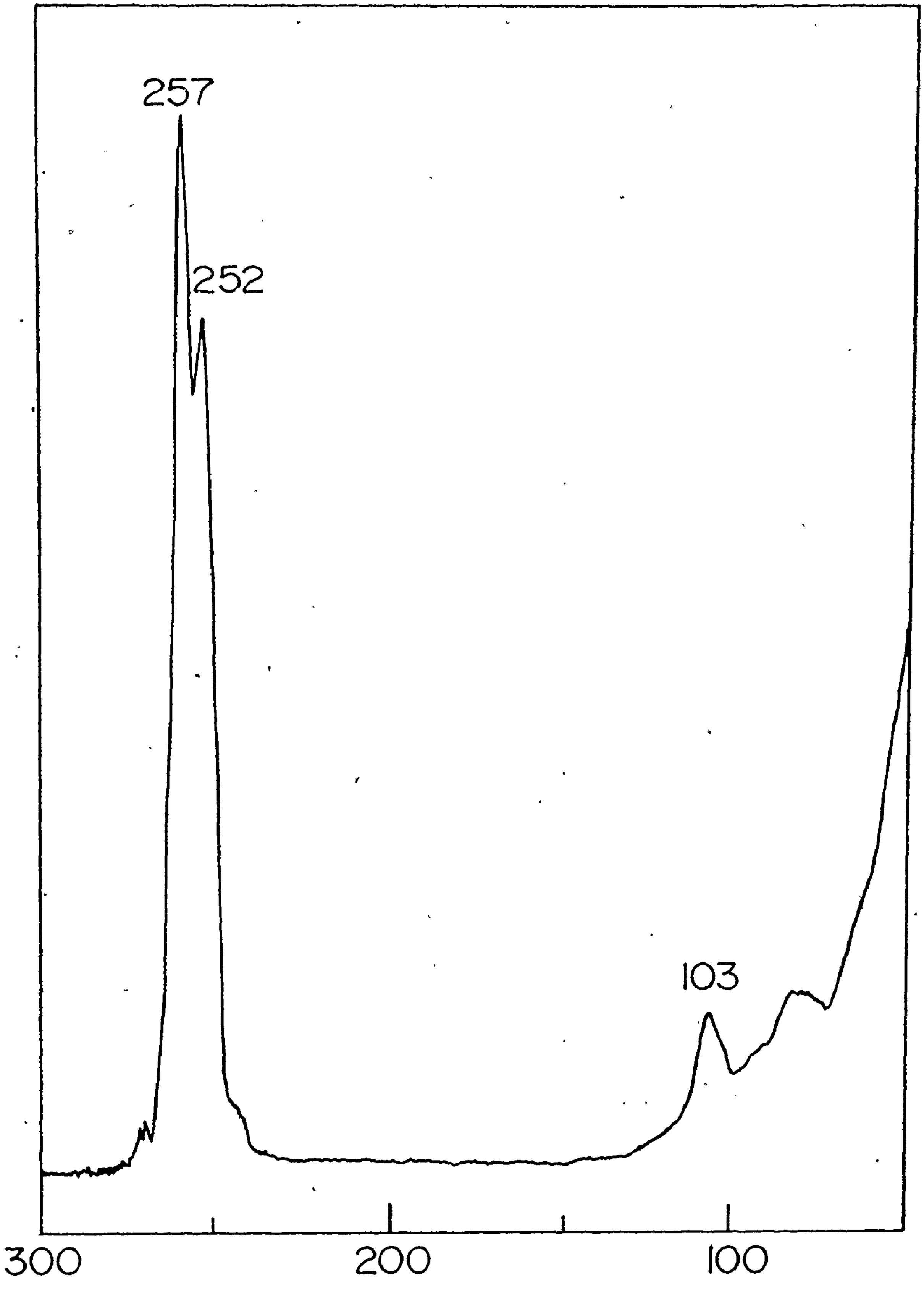

Figure 9. Raman Spectrum of IBr_2^+ in $IBr_2^+SO_3F^-$

TABLE VIII

Force Constants for IBr_2^+ in $IBr_2^+SO_3F^-$

ν_1 = 257 ν_2 = 103 ν_3= 252 cm^{-1}

Angle deg	f mdyn Å^{-1}	d mdyn Å^{-1}	Calculated ν_1 cm^{-1}
90	1.83	0.187	257
92.5	1.80	0.184	252
95	1.77	0.181	248

previously (60). This very strong I - Br vibration was observed to be, in fact, a doublet which could be resolved using narrow slit openings while scanning the Raman spectrum; the peak at 257 cm^{-1} may be assigned to the symmetric stretch ν_1 and the weaker peak at 252 cm^{-1} may be assigned* to the asymmetric stretch ν_3. A very weak peak at 103 cm^{-1} was assigned to the bending mode ν_2 of the bent IBr_2^+ cation. Raman frequencies observed for the fluorosulfate group agree closely with the infrared bands previously reported for this compound which are included in Table 7.

The simple valence force field treatment may also be applied to the symmetric IBr_2^+ cation in solid IBr_2SO_3F. Using ν_2 = 103 cm^{-1} and ν_3 = 252 cm^{-1} and estimated values of the bond angle the stretching force constant f and the bending force constant d were calculated. Then these values were used to calculate ν_1. The results of these calculations are in Table 8. They give good agreement for a bond angle of 90° with force constants f = 1.8 mdyn $\AA^{-1}$ and d = 0.18 mdyn $\AA^{-1}$.

Preparation of the IBr_2^+ cation in solution was carried out by the following three methods:

1) Addition of 0.638 g Br_2 to 15.8 ml of stock iodine + 1 solution. (Br_2 was transferred using a dropper).

2) Dissolution of IBr_2SO_3F in 100% H_2SO_4.

3) Dissolution of IBr_2SO_3F in HSO_3F.

The solutions were studied in spinning Vycor cells, as described in Chapter II, using 632.8 nm and 514.5 nm laser excitation.

* This splitting is too great to be an isotope effect; splitting due to ^{79}Br and ^{81}Br (calculated to be <2 cm^{-1}) is not observed.

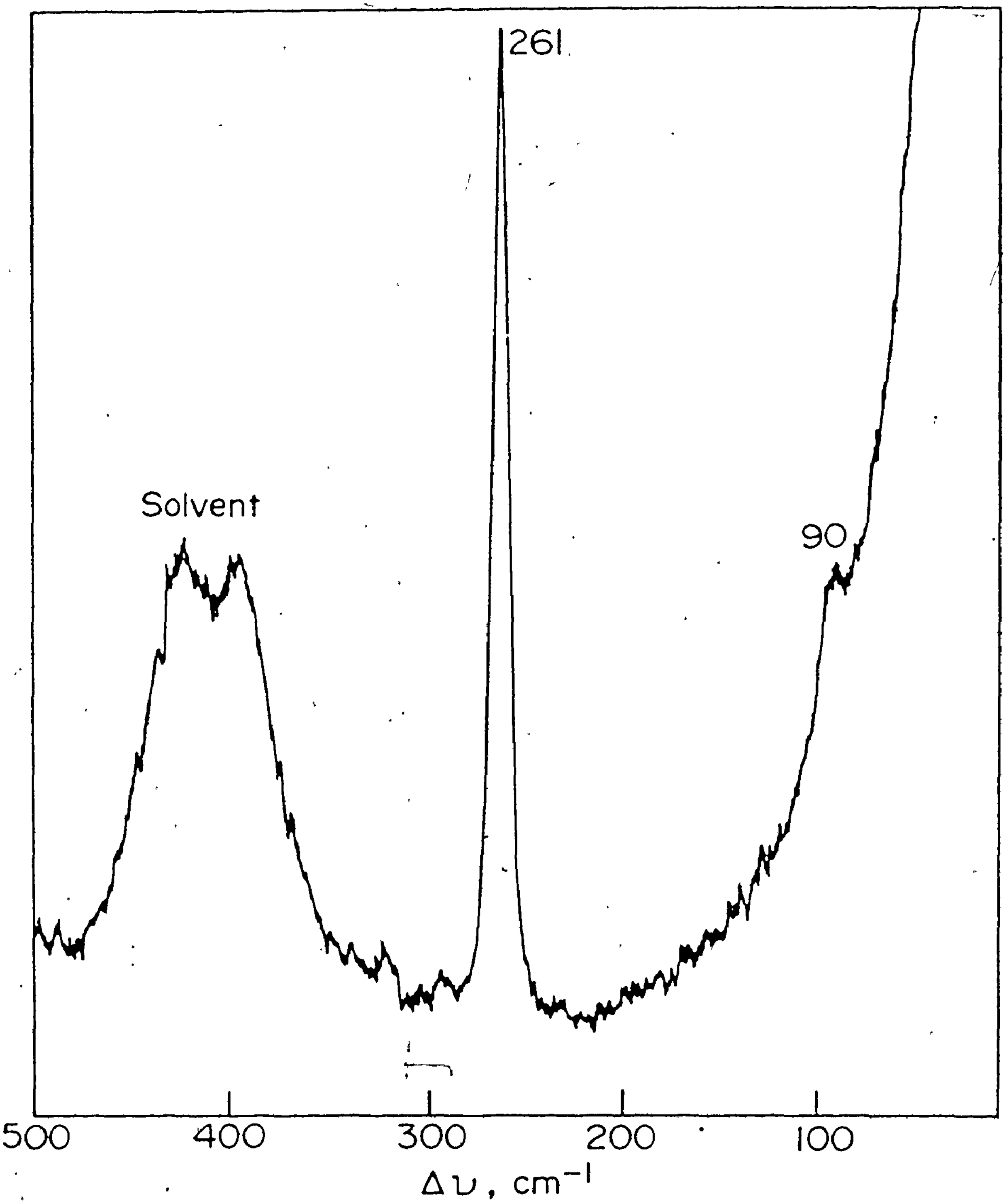

Figure 10. Raman spectrum of IBr_2^+ in Sulfuric Acid

TABLE IX

Force Constants for IBr_2^+ in H_2SO_4 or HSO_3F Solution

$\nu_1 = \nu_3 = 261 \quad \nu_2 = 90\ cm^{-1}$

Angle deg.	f mdyn $Å^{-1}$	d mdyn $Å^{-1}$	Calculated ν_1 cm^{-1}
90	1.968	0.1407	264
92.5	1.935	0.1385	260
95	1.904	0.1362	256

The spectra of all three solutions containing IBr_2^+ resembled the spectrum of the related ICl_2^+ cation which showed a weak low frequency bending mode ν_2 and a single strong peak for the unresolved ν_1 and ν_3 stretching vibrations. For IBr_2^+ in solution the strong peak (ν_1 and ν_3) occurred at 261 cm^{-1} and the weak peak ν_2 was observed at 90 cm^{-1}, as shown in Figure 10. The stretching frequency had shifted upwards (from 252 and 257 cm^{-1}) and the bending frequency had shifted downwards (from 103 cm^{-1}) compared to the values that were observed for the cation in solid $IBr_2^+SO_3F^-$, probably as a result of the loss of cation-anion interaction upon dissolution of the solid. The occurrence of such interaction was previously suggested (60) on the basis of the observation of nine infrared bands for the fluorosulfate group in solid IBr_2SO_3F.

Simple valence force field calculations for IBr_2^+ in solution are summarized in Table 9 . Using ν_2 = 90 cm^{-1} and ν_3 = 261 cm^{-1} . the calculated value of ν_1 equalled the observed value of 261 cm^{-1} when the bond angle was set equal to 92°. Force constant calculations gave force constants $\underline{f}$ = 1.9 mdyn $\mathring{A}^{-1}$ and $\underline{d}$ = 0.14 mdyn $\mathring{A}^{-1}$.

4. The I_2Cl^+ cation

The adduct $SbCl_5.2ICl$ was readily prepared by direct reaction between ICl and excess $SbCl_5$. Transfer of the reactants to a stoppered Pyrex flask was carried out in a dry bag. Then the mixture was warmed in a water bath to 55°C and, on cooling, a dark solid crystallized from solution. Sublimation of the crude product yielded dark brown crystals. The elemental analysis* agreed closely with that calculated for $I_2Cl^+SbCl_6^-$.

Found	I, 40.43:	Sb, 19.22;	Cl, 39.95
Calculated	I, 40.69:	Sb, 19.52	Cl, 39.79

A few crystals were transferred to a Pyrex spinning cell, as described in Chapter II, warmed to form a melt, and then cooled slowly while turning the cell at an angle to deposit a layer of brown crystals on the curved bottom of the cell. The Raman spectrum, recorded at room temperature using 632.8 nm excitation, is shown in Figure 11; the frequencies observed for solid $I_2Cl^+SbCl_6^-$ are reported in Table 10.

Raman bands observed at 335, 296, 260, and 177 cm^{-1} may ~~be~~ assigned to ν_1, ν_2 (split into two peaks), and ν_5 of the $SbCl_6^-$ anion. This agrees with the frequencies ($\nu_1 = 335$, $\nu_2 = 291$, and $\nu_5 = 174$ cm^{-1}) reported for $SbCl_6^-$ in $AsCl_4^+SbCl_6^-$ (61). The remaining frequencies, 124, 187, and 356 cm^{-1}, may be assigned to the bend, the I - I stretch and the I - Cl stretch, respectively, of I_2Cl^+. The observation of frequencies that can clearly be assigned as I - I and I - Cl stretching modes confirms the unsymmetric structure $I\diagup\overset{+}{I}\diagdown Cl$ of this interhalogen cation. Isotopic splitting of the I - Cl peak (I - ^{35}Cl at 356 cm^{-1} and I - ^{37}Cl at 350 cm^{-1}) is shown in the Raman spectrum. The intensities of the peaks are in the expected 3:1 ratio based on chlorine isotope abundance.

Very recently Shamir and Lustig (64) reported Raman frequencies

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* Analysed by A. Bernhardt Microanalytical Laboratory, Elbach, West Germany

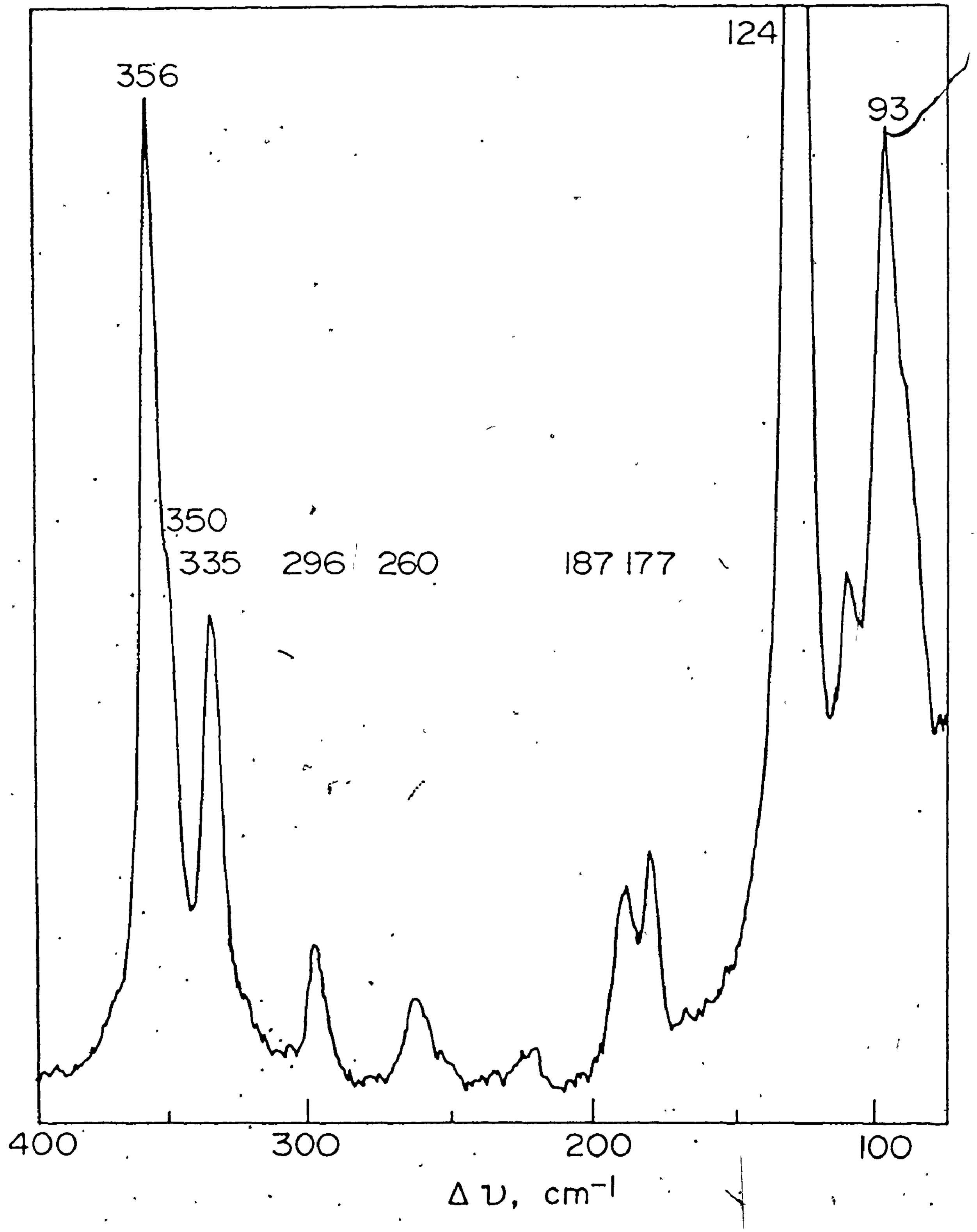


Figure 11. Raman spectrum of $I_2Cl^+SbCl_6^-$

TABLE X

Raman Spectrum of $I_2Cl^+SbCl_6^-$

Relative Intensity	Frequency Shift cm^{-1}	Assignment I_2Cl^+ (C_s)	Assignment $SbCl_6^-$ (O_h)	Frequencies in Ref. 64 cm^{-1}
	93	Lattice		91
90	124	ν_3 (a') (bend)		126
20	177		ν_5 (t_{2g})	177
18	187	ν_2 (a') (I-I)		190
9	260		ν_2 (e_g)	260
14	296			296
48	335		ν_1 (a_{1g})	334
33	350	ν_1 (a') $(I-{}^{37}Cl)$		350
100	356	ν_1 (a') $(I-{}^{35}Cl)$		356

for the same compound which they prepared by the reaction of I_2 with $SbCl_5$ in excess liquid Cl_2. Their reported frequencies which are included in Table 10 are in close agreement with the results of this study. The I_2Cl^+ cation has also been reported to exist in the fluorosulfate, I_2ClSO_3F, recently prepared by Wilson and Aubke (65) by the reaction of ISO_3F with the stoichiometric amount of ICl. The compound was characterized by chemical analysis and infrared study in the barium fluoride region. Raman bands at 126, 197 and 360 cm^{-1} were reported and were assigned to the bend, I - I stretching, and I - Cl stretching modes, respectively. The I - I stretching frequency is higher than the frequency observed for I_2Cl^+ in $I_2Cl^+SbCl_6^-$. This could result from the presence of a different anion in the solid or it could arise from traces of ISO_3F which has a band at 195 cm^{-1} (reported in Chapter VI). The I_2Cl^+ cation has also been characterized recently by ^{35}Cl and ^{127}I nqr spectroscopy. Corbett <u>et al</u>. (56) obtained $I_2Cl^+AlCl_4^-$ in the ICl - $AlCl_3$ system and observed only one of the two expected iodine resonances; it was assigned to the central atom. For $I_2Cl^+SbCl_6^-$ (66), however, both expected iodine transitions were observed and were assigned to the central and terminal iodine atoms of the cation.

Several attempts to detect the I_2Cl^+ cation in solution were unsuccessful. A solution prepared by the addition of 0.40 g ICl to 9.6 ml of stock iodine +1 solution was studied in a Vycor spinning cell using 514.5 nm excitation Solvent peaks were observed but there were no peaks which could reasonably be assigned to I_2Cl^+. Apparently the expected reaction

$$\text{ICl} + \text{"}I^{+}\text{"} \rightarrow I_2Cl^{+}$$

did not occur. There were, however, two unidentified peaks, one at 197 cm^{-1} and a weak peak at approximately 120 cm^{-1}. These may be due to the unreacted "I^{+}" species; they will be discussed further in Chapter VI.

Crystals of $I_2Cl^{+}SbCl_6^{-}$ were dissolved in dried SO_2 but, again, the spectrum of I_2Cl^{+} in solution could not be detected. Using a Vycor spinning cell and 514.5 nm excitation the only peaks observed other than solvent peaks were 211, 423, and 636 cm^{-1}. These are attributed to the fundamental stretching vibration and overtones of the resonance Raman spectrum of I_2 which indicates that the compound decomposed. Vonk and Wiebenga (22) reported that conductivity studies of the related compound $ICl_2^{+}SbCl_6^{-}$ in SO_2 were unsuccessful because this solvent decomposed the iodine-chlorine compound.

5. The I_2Br^{+} cation

In an attempt to produce I_2Br^{+} in solution solid IBr crystals (0.9117 g) were added to 35.0 g (19.0 ml) of stock iodine +1 solution. The mixture was heated and stirred and the resulting brown solution was studied in a Vycor spinning cell using both 632.8 nm and 514.5 nm excitation. When the red beam was used, traces of I_2^{+} in the solution gave peaks at 237 and 476 cm^{-1} due to the resonance Raman effect but when the green beam was used I_2^{+} was not observed. In neither spectrum were peaks observed which could be attributed to I_2Br^{+}. However, in addition to solvent peaks, a weak band at 262 cm^{-1} which may be IBr or a trace of IBr_2^+ and two unidentified bands at 116 and 197 cm^{-1} were observed. These two peaks are probably due to the unreacted iodine +1 species in the stock solution. This species will be discussed in the following chapter.

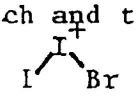
It seemed possible that a crystalline salt of I_2Br^+ might be prepared by transfer of bromide from IBr to a halogen receptor such as $SbCl_5$. This reaction

$$2\ IBr + SbCl_5 \rightarrow I_2Br^+SbCl_5Br^-$$

would be analogous to the chloride transfer which occurs in the preparation of the I_2Cl^+ salt:

$$2\ ICl + SbCl_5 \rightarrow I_2Cl^+SbCl_6^-.$$

Accordingly, IBr and $SbCl_5$ in the mole ratio 2:1 were transferred in a dry bag to a Pyrex spinning cell, as described in Chapter II. The mixture was warmed in a 60°C water bath and then allowed to cool in a refrigerator to yield a dark red-brown solid. Since this solid melts at room temperature the spinning cell was cooled in a stream of nitrogen during Raman study. A Dewar surrounding the cell was not required.

The Raman spectrum obtained using 632.8 nm excitation is given in Figure 12 and the frequencies of the bands are reported in Table 11. The bands at 123, 184 and 247 cm^{-1} may reasonably be assigned to the bend, the I – I stretch and the I – Br stretch, respectively, of the unsymmetric bent  cation. No evidence for the existence of a crystalline salt of I_2Br^+ had been reported previously and there were only two reports of the pentachlorobromoantimonate anion. The $SbCl_5Br^-$ frequencies were assigned by comparison

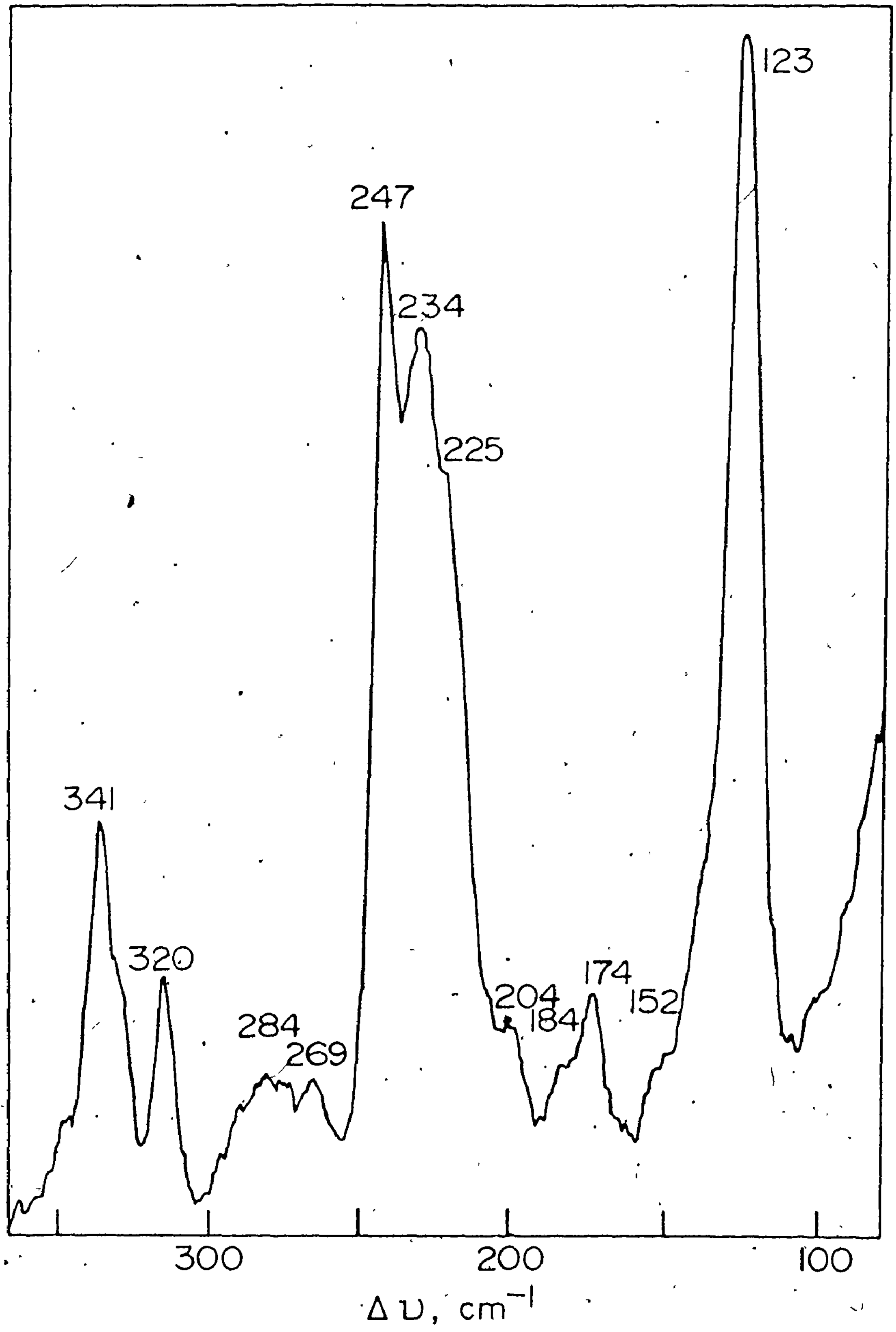


Figure 12. Raman spectrum of $I_2Br^+SbCl_5Br^-$

TABLE XI

Raman Spectrum of $I_2Br^+SbCl_5Br^-$

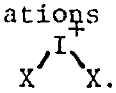
Relative Intensity	Frequency Shift cm^{-1}	Assignments $I_2Br^+(C_s)$	Assignments $SbCl_5Br^-(C_{4v})$	$SbCl_5Br^-$ in $(CH_3CO)SbCl_5Br$* cm^{-1}
100	123	ν_3 (a') (bend)		
6	152		Br-Sb-Cl bend (e)	147
16	174		Cl-Sb-Cl bend (a_1)	170
5	184	ν_2 (a') (I-I)		
4	204			
5	225		Cl-Sb-Cl bend (b_2)	220
75	234		Sb-Br stretch (a_1)	240
90	247	ν_1 (a') (I-Br)		
10	269		Sb-Cl stretch (a_1)	290
10	284			
24	320		Sb-Cl stretch (e)	324
40	341		Sb-Cl stretch (a_1)	340

* Reference 67

with the frequencies recently reported by Goetz, Deneux and Leroy (67) for $CH_3COSbCl_5Br$ which are included in Table 11. The frequencies assigned to $SbCl_5Br^-$ are also in agreement with the bands reported (68) at 158, 173, 223, 289, 308, and 332 cm^{-1} for the anion in $(C_2H_5)_4NSbCl_5Br$.

Very recently Wilson and Aubke(65) reported the preparation of I_2BrSO_3F by the reaction of ISO_3F with IBr. The compound was characterized by chemical analysis and infrared spectroscopy in the barium fluoride region. Raman peaks at 198 and 258 cm^{-1} were reported. Both of these frequencies were also reported by them for IBr_2SO_3F. It seems unlikely that the I - Br stretching frequency would have the same value in both IBr_2^+ and I_2Br^+. Also, the peak at 198 cm^{-1} is probably due to unreacted ISO_3F. The Raman spectrum of ISO_3F will be discussed further in Chapter VI.

6. Conclusions

Laser Raman spectroscopic studies of the solid salts $ICl_2^+SbCl_6^-$ and $IBr_2^+SO_3F^-$ have established that the cations in these solids have, as expected, a symmetric angular structure . The observed frequencies (cm^{-1}) for the cations are:

ICl_2^+: ν_1 = 356, 362 and 370 ν_2 = 148 ν_3 = 368 (est.)

IBr_2^+: ν_1 = 257 ν_2 = 103 ν_3 = 252

For both cations, observed as solid salts, the frequency of the ν_3 band (asymmetric stretching) was slightly less than the ν_1 frequency (symmetric stretching) and the intensity of ν_3 was considerably less than the intensity of ν_1. In the case of ICl_2^+, the stretching vibrations are split due to the effect of chlorine isotopes. There appears to be some cation-anion interaction in these solid salts. This explains the increase in iodine-halogen stretching frequency observed for both cations when they were studied in solution. For ICl_2^+ the frequency is shifted from 362 and 370 cm^{-1} to 387 cm^{-1} while a frequency shift of 257 cm^{-1} to 261 cm^{-1} is observed for IBr_2^+. Judging from the magnitude of the shifts, the effect of chlorine bridging in $ICl_2^+SbCl_6^-$ is greater than the cation-anion interaction in $IBr_2^+SO_3F^-$.

The simple valence force field treatment has been applied to the Raman data obtained for ICl_2^+ and IBr_2^+ in both solid and solution. Stretching and bending force constants were calculated and subsequently they were used to obtain approximate bond angles for the cations. The results of these calculations are summarized in Table 12 .

The ICl_2^+ and IBr_2^+ cations have been characterized in solutions prepared by the addition of Cl_2 or Br_2 to sulfuric acid containing I_2/HIO_3 = 2.0. This confirms the cryoscopic and conductimetric measurements of Senior and Grover (27) who had proposed that the formation of IX_2^+ proceeds according to the overall equation:

$$\begin{aligned} 2\,I_2 + HIO_3 + 5\,X_2 &\rightarrow 5\,IX_2^+ + 3\,H_3O^+ + 8\,HSO_4^- \\ + 8\,H_2SO_4 & \end{aligned}$$

There is, however, no Raman evidence for the existence of I_2Cl^+ and I_2Br^+ in solutions prepared by addition of ICl or IBr to similar iodine-iodic acid solutions, as suggested in the earlier work of Garrett, Gillespie, and Senior (16).

This Raman study has also confirmed that ICl_2^+ is formed in

TABLE XII

Raman Frequencies, Force Constants and Approximate Bond Angles of IX_2^+ Symmetric Cations

	Raman Frequencies, cm^{-1}			Force Constants mdyn $Å^{-1}$		Approximate Bond Angle, deg
	ν_1	ν_2	ν_3	$\underline{f}$	$\underline{d}$	α
ICl_2^+ (soln.)	387	148	387	2.4	0.19	90
ICl_2^+ (solid)	370	148	368*	2.1	0.19	90
IBr_2^+ (soln.)	261	90	261	1.9	0.14	92
IBr_2^+ (solid)	257	103	252	1.8	0.18	90
I_3^+ (soln.)	207	114	233	1.7	0.31	114

* ν_3 is under the ν_1 band; estimated value = 368 cm^{-1}

the reaction described by the equation,

$$I_2 + 3\ HIO_3 + 10\ ICl_3 + 24\ H_2SO_4 \rightarrow 15\ ICl_2^{+} + 9\ H_3O^{+} + 24\ HSO_4^{-}\ .$$

as suggested by Senior and Grover (27).

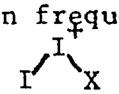
Recently Shamir and Lustig (64b) reported preparation of a trihalogen cation as $BrICl^{+}SbCl_6^{-}$ by combining equal moles of IBr, $SbCl_5$ and Cl_2 at room temperature. Sublimation of the product yielded dark red crystals. Mass spectra results and observed Raman frequencies for the solid were listed but they do not conclusively establish the existence of the $BrICl^{+}$ cation. These results could also be interpreted in terms of a mixture of $ICl_2^{+}SbCl_6^{-}$ and $IBr_2^{+}SbCl_6^{-}$. In fact, the frequencies claimed for $BrICl^{+}SbCl_6^{-}$ (70, 149, 170, 177, 268, 323, 362, 370 cm^{-1}) agree exactly with those reported in this study for $ICl_2^{+}SbCl_6^{-}$. A band at 125 which did not consistently appear in all spectra and a band at 255 cm^{-1} were also reported. The samples apparently had a variable composition and these two bands could be attributed to IBr_2^{+}, or possibly to I_2Br^{+}. In any case, it seems improbable that the I - Cl stretching vibration in the proposed $Br\diagup\overset{I^{+}}{}\diagdown Cl$ cation would be the same as that of the known $Cl\diagup\overset{I^{+}}{}\diagdown Cl$ cation.

In the present study the observation of Raman bands which clearly may be assigned as I - Cl stretching, I - I stretching, and bending establishes that the unsymmetric bent cation I_2Cl^{+} is present in the adduct $SbCl_5 . 2ICl$. This brown solid, then, may be formulated as the salt $I_2Cl^{+}SbCl_6^{-}$. It was easily prepared by direct combination of ICl and $SbCl_5$ rather than by the previously reported method of treating an I_2 - $SbCl_5$ mixture with Cl_2.

The observation of Raman bands which may be attributed to the corresponding unsymmetric bromo-cation I_2Br^+ and to the mixed anion $SbCl_5Br^-$ provides evidence that IBr can form a salt with $SbCl_5$ by bromide transfer, as described by:

$$2\ IBr + SbCl_5 \rightarrow I_2Br^+SbCl_5Br^-$$

This reaction is analogous to the formation of $I_2Cl^+SbCl_6^-$ by chloride transfer from ICl to $SbCl_5$.

The observed Raman frequencies (cm^{-1}) for the unsymmetric bent interhalogen cations  are:

I_2Cl^+: $\nu_{I-Cl} = 356$ $\nu_{I-I} = 187$ $\nu_{bend} = 124$

I_2Br^+: $\nu_{I-Br} = 247$ $\nu_{I-I} = 184$ $\nu_{bend} = 123.$

The observed halogen-halogen stretching frequencies for both the symmetric and unsymmetric triatomic interhalogen cations are listed in Table 13. The I - I stretching frequencies of I_3^+ and the fundamental vibrational frequencies of I_2^+, molecular I_2, IBr, and ICl are also included.

TABLE XIII

Halogen-Halogen Stretching Frequencies in Cations and Molecules Containing Iodine

Cation or Molecule		Raman Stretching Frequencies, cm^{-1}		
		I - I	I - Br	I - Cl
I_2Br^+	in $I_2Br^+SbCl_5Br^-$	184	247	
I_2Cl^+	in $I_2Cl^+SbCl_6^-$	187		356
I_3^+	in solution	ν_1 207 ν_3 233		
I_2	molecular*	213		
I_2^+	in $I_2^+Sb_2F_{11}^-$ and in soln.	238		
IBr_2^+	in $IBr_2^+SO_3F^-$		ν_1 257 ν_3 252	
IBr_2^+	in solution		261	
IBr	molecular*		265	
ICl_2^+	in $ICl_2^+SbCl_6^-$			ν_1 370 ν_3 368 (est.)
ICl_2^+	in solution			387
ICl	molecular*			381

* Reference 41

CHAPTER VI

Evidence for a Polyatomic Iodine +1 Cation

1. Introduction

The first suggestion that iodine exists in the form of positive ions had come in 1938 from the investigations of Masson (2). He observed that the reaction of chlorobenzene with brown solutions of iodine and iodosyl sulfate in sulfuric acid produced chlorotri-iodobenzene and a precipitate of elemental iodine. No iodoso derivatives were produced, suggesting the effective absence of trivalent iodine (IO^+), and it was concluded that "the active iodine in the brown solute is univalent." Masson suggested that the following equilibria are involved

$$IO^+ + 2\,H^+ \rightleftarrows I^{+++} + H_2O \qquad (1)$$

$$I^{+++} + I_2 \rightleftarrows 3\,I^+ \qquad (2)$$

$$I^+ + n\,I_2 \rightleftarrows I^+_{1+2n} \qquad (3)$$

with values of 1 and 2 for n in equation 3 giving rise to the cations I^+, I_3^+ and I_5^+, just as there are the negative iodine ions, I^-, I_3^-, and I_5^-. Successive repetition of the reaction described by equation 4

$$I^+_{1+2n} + RH \rightarrow RI + H^+ + n\,I_2 \qquad (4)$$

accounted for the formation of the observed organic iodination products and for the precipitate of elemental iodine. Masson also suggested that I^+ with only six valence electrons would be very unstable. The equilibrium represented by equation 3 would, then, be far to the right. The equilibrium concentration of I^+ would, therefore, be very small and it should likely be represented as a mixture of IO^+, I^{+++}, I_3^+ and I_5^+ according to an overall equilibrium represented by equations 1, 2 and 3.

Later, Garrett, Gillespie, and Senior (16) studied some of the lower oxidation states of iodine which they produced by reaction of I_2 and HIO_3 in varying proportions using 100% H_2SO_4 as solvent. For the system with the mole ratio $I_2/HIO_3 = 2.0$, in which iodine would be in a formal +1 oxidation state, the following possible reaction schemes were considered:

$$2\ I_2 + HIO_3 + 8\ H_2SO_4 \rightarrow 5\ I^+ + 3\ H_3O^+ + 8\ HSO_4^- \qquad (5)$$

$$2\ I_2 + HIO_3 + 8\ H_2SO_4 \rightarrow 5\ IHSO_4 + 3\ H_3O + 3\ HSO_4^- \qquad (6)$$

$$8\ I_2 + 4\ HIO_3 + 17\ H_2SO_4 \rightarrow 5\ I_3^+ + 7\ H_3O^+ + 5\ IOHSO_4 + 12\ HSO_4^- \qquad (7)$$

Formation of the iodine cation I^+ (equation 5) or of un-ionized iodine (I) hydrogen sulfate (equation 6) was clearly inconsistent with their observed cryoscopic and conductimetric data. Their experimental results were, however, in fairly good agreement with the values required for equation 7 and thus they concluded, as had Masson, that iodine +1 was largely disproportionated to the +1/3 and +3 oxidation states.

Conjecture concerning the existence of I^+ arose again during investigation of the blue solutions formed by iodine in oleum and in other acidic media. Symons et al. (3) proposed that the blue iodine species was I^+. Subsequently,Gillespie and Milne (5) established that the blue iodine cation is the paramagnetic diatomic I_2^+ cation. Evidence for I_2^+ is discussed more fully in Chapters I and III.

Although there is no evidence for the existence, in appreciable amounts, of iodine +1 as a monatomic cation, some evidence has accumulated which suggests that unipositive iodine may exist in some cationic form other than I^+. This evidence arises from some of the Raman spectra obtained during the present investigation of iodine cations and suggests the existence of a new polyatomic cation containing iodine in the +1 oxidation state.

2. Evidence for a new polyatomic iodine +1 cation

(a) Precursor of triatomic cations formed in solution.

The general preparative route used during this study for the formation of triatomic cations of iodine in solution was the addition of halogen to sulfuric acid solutions containing I_2/HIO_3 in the mole ratio 2:1 (referred to in Chapter V as the stock solution). With this proportion of oxidant, iodine would be in a formal +1 oxidation state. Considering the earlier work of Masson (2) and Garrett et al.(16) and in view of the evidence against I^+, it was assumed that iodine +1 disproportionated to +1/3 and +3 oxidation states. Thus the iodine species present in the stock solution were assumed to be I_3^+ and iodosyl hydrogen sulfate $IOHSO_4$ or $I(HSO_4)_3$. On addition of I_2, Cl_2, or Br_2 to portions of the stock solution, production of I_3^+, ICl_2^+, and IBr_2^+ proceeded according to the overall reaction described by

$$2\ I_2 + HIO_3 + 5\ X_2 + 8\ H_2SO_4 \rightarrow 5IX_2^+ + 3\ H_3O^+ + 8\ HSO_4^- \qquad (8)$$

$(X_2 = I_2, Br_2, Cl_2, IBr, ICl)$.

Raman spectra for these three symmetric cations were obtained (cf.Chapters IV and V). In the earlier cryoscopic and conductimetric studies (27) it had been emphasized that the above equation is a net stoichiometric equation and is not intended to represent a mechanism for the formation of triatomic cations. Although the mechanism is not known and regardless of what intermediates are actually involved, the equation does describe the overall behaviour of systems where $X_2 = I_2$, Cl_2, or Br_2. However, when X_2 was ICl or IBr no Raman evidence was obtained to support formation of the unsymmetric cations I_2Cl^+ and I_2Br^+. The latter solution had a band at 262 cm^{-1} which is probably due to IBr. In the spectrum of the solution to which ICl had been added bands due to I - Cl stretching in either ICl or I_2Cl^+ would likely be close to the doublet (392 and 422 cm^{-1}) of H_2SO_4 (63); in this region only solvent bands were observed. Apparently formation of I_2X^+ cations does not occur as described or the reaction was incomplete in these experiments. There was, however, a band at 195 cm^{-1} observed in both spectra. Since the expected triatomic cations were not detected and considering that the same frequency was observed in the spectra of two different reaction mixtures, it appeared that both solutions contained the same species. This suggested the interesting possibility that the species existed in the original iodine +1 stock solution. To investigate this further, a sample of iodine +1 solution (prepared by mixing

0.622 g I_2, 0.2177 g HIO_3 and 40 ml 100% H_2SO_4) was transferred directly to a Vycor Raman Cell. The spectrum which was observed using 514.5 nm excitation is shown in Figure 13. Freshly prepared solutions are a greenish-brown color and their spectra show a band at 238 cm^{-1} due to I_2^+ and a strong band at 195 cm^{-1}. The I_2^+ cation is unstable in 100% H_2SO_4 and with time or by addition of a little water to the solution, the color changes to brown and the I_2^+ peak at 238 cm^{-1} disappears. The frequency of the strong peak at 195 cm^{-1} does not coincide with any of the observed frequencies for I_3^+ (115, 207 and 233 cm^{-1} as reported in Chapter IV). I_3^+ was one of the species assumed to be present in this solution and the other, $I(HSO_4)_3$, would not be expected to have Raman vibrations in this region. The 195 cm^{-1} peak is, however, in the range of observed iodine stretching frequencies - 184 cm^{-1} in solid $I_2Br^+SbCl_5Br^-$, 187 cm^{-1} in solid $I_2Cl^+SbCl_6$, 207 cm^{-1} for I_3^+ in solution and 213 cm^{-1} for molecular I_2 (41), all of which have an I - I bond order of 1.0; I_2^+, with a bond order of 1.5, has a considerably higher stretching frequency at 238 cm^{-1}. Based on the foregoing, the Raman band at 195 cm^{-1}, detected in H_2SO_4 solutions containing I_2/HIO_3 in the mole ratio = 2.0, is assigned to the fundamental stretching vibration of a new iodine +1 cation which may be represented by I_n^{n+}, where n is greater than 1.

(b) Precursor of triatomic cations in solid salts.

Solid IBr_2SO_3F was prepared for this investigation according to the method of Yeats, Wilson and Aubke (60) by reaction of excess Br_2 with iodine fluorosulfate (ISO_3F). Earlier, Aubke and Cady (18)

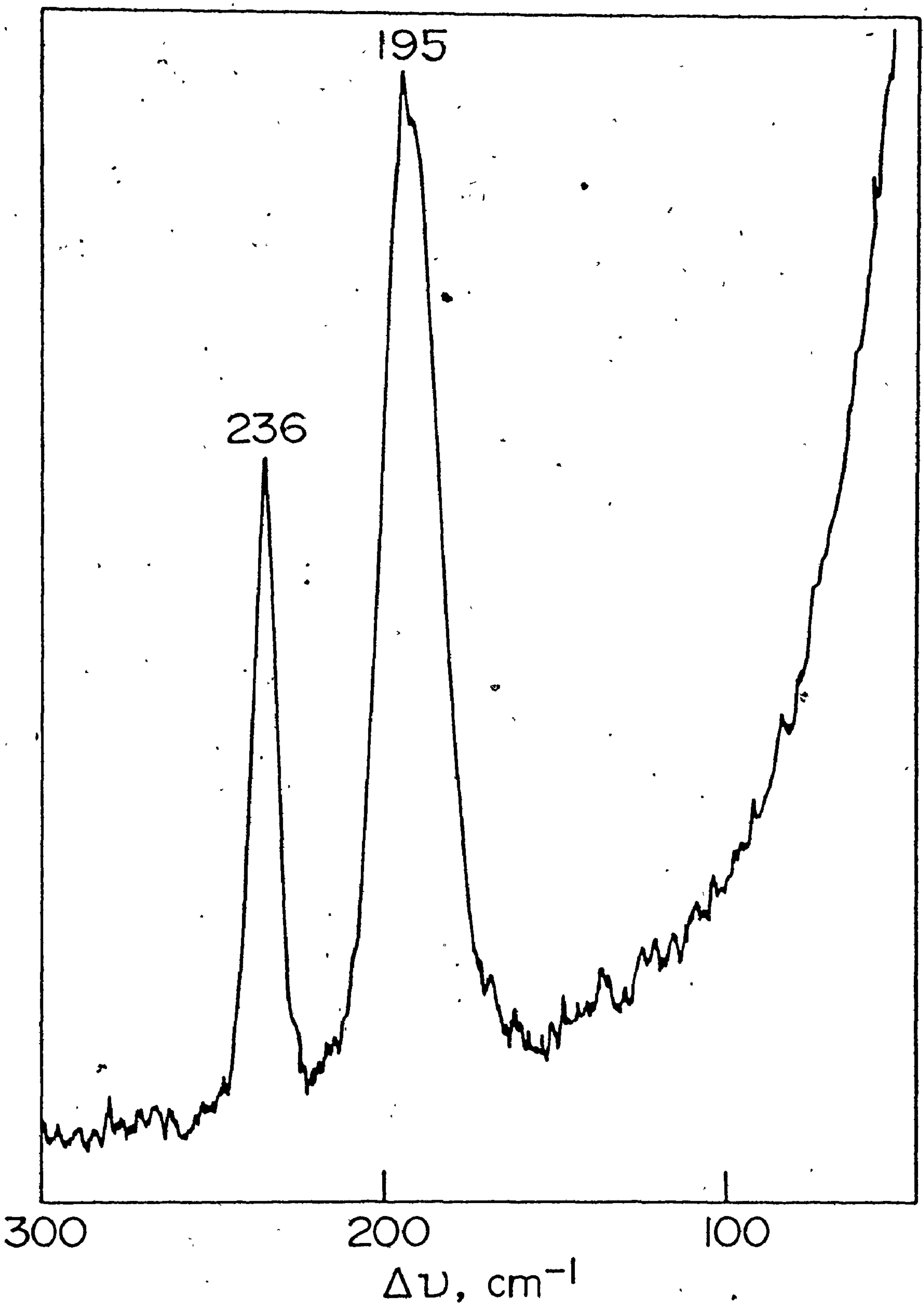


Figure 13. Raman spectrum of sulfuric acid solution containing I_2/HIO_3 = 2.0

had reported that reaction of ISO_3F with I_2 produced I_3SO_3F and reaction of ISO_3F with excess Cl_2 produced ICl_2SO_3F. This general preparative route, described by the equation,

$$ISO_3F + X_2 \xrightarrow{60°C} IX_2SO_3F \tag{9}$$

has recently been extended by Wilson and Aubke (65) to include preparation of I_2ClSO_3F and I_2BrSO_3F. In this method, ISO_3F is an essential reactant in the production of triatomic halogen and interhalogen iodine cations. Its role is similar to that of the iodine +1 solution, described above, and it, too, contains iodine in a formal +1 oxidation state. Solid ISO_3F is described as a black, diamagnetic compound which melts at 51.5°C. It was first prepared by Aubke and Cady (18) by reaction of equal moles of I_2 and peroxodisulfuryl difluoride, according to the equation

$$I_2 + S_2O_6F_2 \rightarrow 2\ ISO_3F.$$

The structure of ISO_3F is not known and X-ray structural determination is probably not feasible due to the tarry consistency and low melting point of the compound. Although infrared study indicates that iodine in ISO_3F is not covalently bonded, the ionic form $I^+SO_3F^-$ seems unlikely. Also, the deep color of the solid suggests that it may contain I - I bonds. To further investigate its structure, ISO_3F was prepared using the literature method (18) and the Raman spectrum of the solid was obtained at room temperature using 514.5 nm excitation. During Raman study the sample was contained in the spinning Pyrex cell (described in Chapter II) in which it had been prepared. A single band at 195 cm^{-1} was observed. Then hot air was directed to the spinning cell to melt the sample. The resulting black viscous syrup does not wet Pyrex and it flowed up the walls of the spinning cell. The position of the cell was adjusted so that a spectrum of the melt could be recorded. Again, a peak at 195 cm^{-1} was observed. This Raman evidence suggests that ISO_3F contains an iodine species having two or more iodine atoms. It has the same fundamental stretching frequency that was observed for the iodine +1 solutions and one may conclude that the same iodine cation I_n^{n+}, is present in both systems. Apparently this cation retains its structure when ISO_3F is in a molten state; this is interesting because the general preparative method (equation 9) requires the reactants to be heated beyond their melting points. Quite probably, then, the iodine cation which reacts with halogen molecules to form triatomic halogen and interhalogen iodine cations is present in both solid ISO_3F and in molten ISO_3F.

The I_n^{n+} structure is also retained when ISO_3F is dissolved in 100% H_2SO_4. A Raman spectrum of this solution, observed using a Vycor spinning cell and 514.5 nm excitation, showed two peaks - a very strong peak at 195 and a weaker band at 238 cm^{-1}. In fact, the spectrum was identical to that observed for a freshly prepared solution containing $I_2/HIO_3 = 2.0$ in 100% H_2SO_4. Although Chung and Cady's (54) study of the I_2 - $S_2O_6F_2$ system showed no evidence for a solid of the composition I_2SO_3F, Gillespie and Milne (5) have established that reaction of $S_2O_6F_2$ and I_2 in the mole ratio 1:1 and 2:1 in fluorosulfuric acid produces I_2^+. The maximum amount of I_2^+ is produced using a 2:1 mole ratio. Apparently when ISO_3F is dissolved in sulfuric acid I_2^+ as well as

I_n^{n+} cations exist in the solution, indicating that some of the iodine +1 must disproportionate to +1/2 and +3 oxidation states. The I_2^+ cation is less stable than I_n^{n+} and, after addition of a little water, the 238 cm^{-1} peak disappears. Thus I_n^{n+} can exist in solutions that are made up from <100% H_2SO_4.

(c) Iodine in oleum

A freshly prepared solution of iodine in 30% fuming sulfuric acid was studied in a Vycor spinning cell using 514.5 nm excitation. In addition to solvent peaks there was the characteristic Raman band observed at 238 cm^{-1} which is due to I_2^+ and another band of approximately equal intensity at 195 cm^{-1} which may be attributed to the proposed I_n^{n+} species.

(d) I_2-AsF_5 compound in fluorosulfuric acid

Solid compounds containing I_2^+ or I_3^+ cations are discussed in Chapters III and IV. In one experiment, 1.4166 g I_2 (5.58 mmole) was reacted with 1.20 g AsF_5 (7.04 mmole) using the general preparative method described in Chapter II. This was a 26% excess of AsF_5 over the 1:1 mole ratio of reactants required to produce $I_3^+AsF_6^-$. After slow distillation of some of the SO_2 from the brown solution dark crystals began to form. The remaining supernatant solution was decanted through the sintered glass filter and the SO_2 side of the apparatus was placed in liquid N_2 for one hour before the product side was sealed off. The elemental analysis* was definitely not in

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* Analysed by A. Bernhardt Microanalytical Laboratory, Elbach, West Germany

agreement with that calculated for $I_3^+AsF_6^-$:

Found	I, 52.50;	As, 20.48:	F, 26.11
Calculated	I, 66.83	As, 13.15	F, 20.01

Although the solid may have contained some I_3^+, most of the iodine was probably in oxidation states greater than +1/3 because of the large excess of oxidant used in the preparation. The dark brown color of the solid hampered detection of Raman bands even with the use of spinning cells. However, a solution of this solid in HSO_3F, studied in a Pyrex spinning cell using 514.5 nm excitation, showed a strong band at 238 cm^{-1} (I_2^+) and a somewhat weaker band at 195 cm^{-1}. The latter band appears to be due to an iodine cation in an oxidation state greater than +1/3 or +1/2. Probably it should be assigned to the new iodine cation I_n^{n+} in which iodine is in a +1 oxidation state.

(e) IBr_2SO_3F in fluorosulfuric acid

The preparation of IBr_2SO_3F is described in Chapter V. This compound, dissolved in HSO_3F, was studied with 632.8 nm excitation using a Vycor spinning Raman cell, as described in Chapter II. Bands which may be attributed to IBr_2^+ were observed at 90 and 261 cm^{-1} and traces of I_2^+ produced an intense peak at 238 cm^{-1}. However, when 514.5 nm excitation was used the spectrum shown in Figure 14 was obtained. In addition to the bands already described there was a peak at 200 cm^{-1} which may be attributed to I_n^{n+} and there was another peak at 290 cm^{-1} which might be due to IBr^+ (previously unreported) or to Br_3^+ [reported

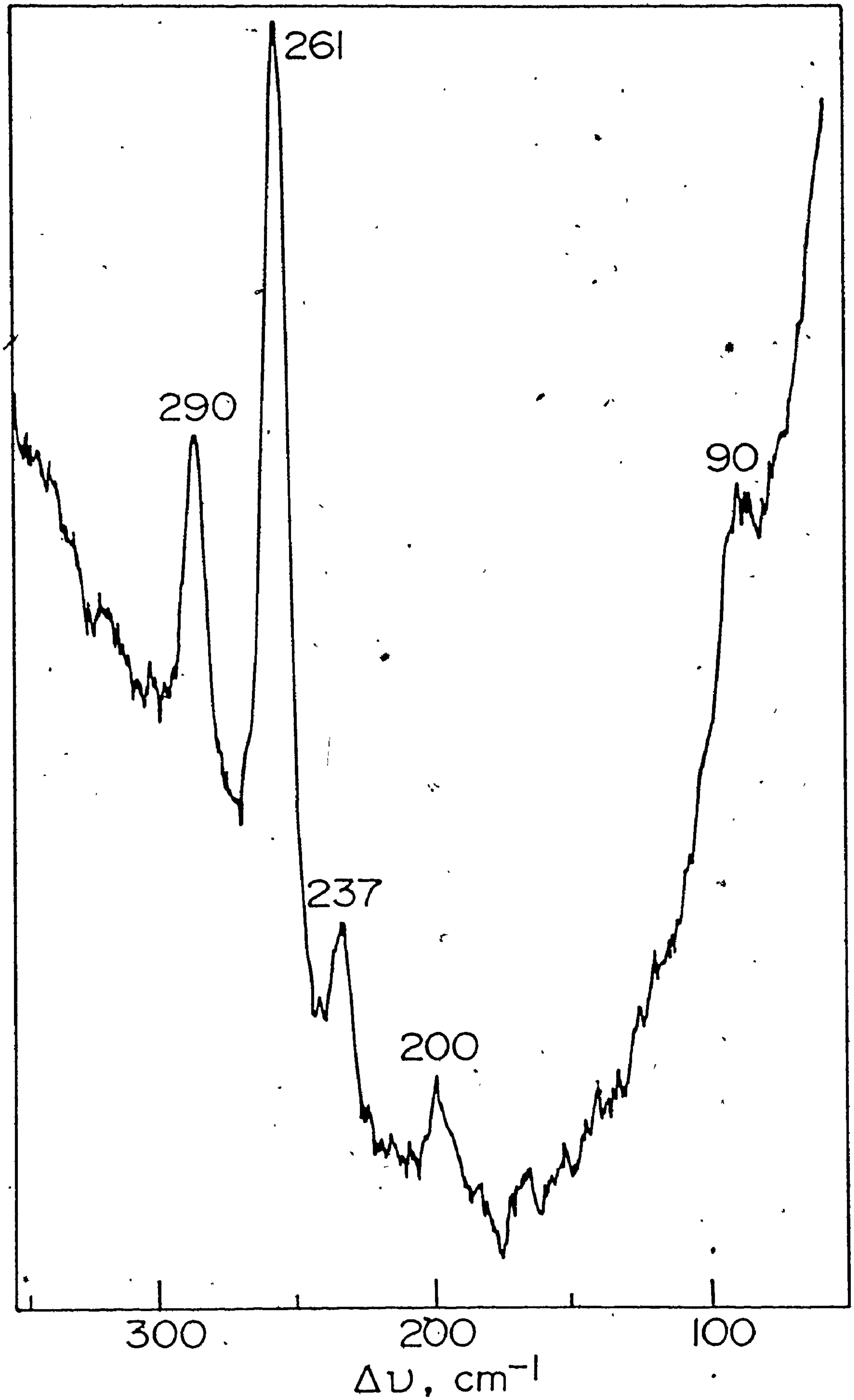


Figure 14. Raman spectrum of $IBr_2^+SO_3F^-$ dissolved in HSO_3F

by Gillespie and Morton (12) to occur at 290 cm^{-1}].

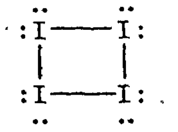
(f) Absorption measurements

Stock solutions containing I_2/HIO_3 = 2.0 and a solution of ISO_3F in 100% H_2SO_4 were studied using a Cary 14 UV and visible spectrophotometer. The same absorption spectra were obtained for both solutions. Initially the solutions appeared pale green and the observed spectra had absorptions at 290, 460 and 640 nm. Upon addition of water the color changed to brown and the 640 nm band (I_2^+) disappeared. The bands at 290 and 460 nm may be attributed to the more stable I_n^{n+} cation. The absorption data, however, are not conclusive evidence for a new species because I_3^+ has a very similar spectrum with bands reported (5) at 305 and 470 nm. Nevertheless the bands reported here may indeed be due to a new species distinct from I_3^+. McRae (19) prepared a red-brown solid by reaction of I_2 with SbF_5. The absorption spectrum of a solution of this solid in 100% H_2SO_4 was identical to the spectrum observed in this study.

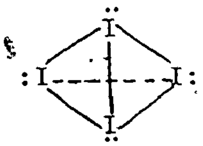
3. Conclusions

The experimental results reported above provide evidence for the existence of a new polyatomic cation containing iodine in a +1 oxidation state. This species may be formulated as I_n^{n+} where $n \geq 2$. The Raman spectrum of this cation consists of a strong band at 195 cm^{-1} which appears to be polarized. In spectra obtained using the 514.5 nm laser there is a very weak overtone at 392 cm^{-1}. In some of the observed spectra there was a very weak band at approximately

115 - 120 cm^{-1}. In other spectra, however, this region could not be scanned because of the wide band of scattered exciting radiation. If this band is real then it would be assigned to a bending mode of I_3^{3+} or I_4^{4+}. The I_n^{n+} cation would have a total of 6n valence electrons. For I_4^{4+} with 24 valence electrons a square planar configuration (a)



(a)



(b)

seems more plausible than a tetrahedral arrangement (b) which requires only 20 valence electrons. For I_3^{3+} with 18 valence electrons the most likely structure would be an equilateral triangle. These structures are proposed on the assumption that all of the atoms in the I_n^{n+} cation are equivalent. The hypothetical I_3^{3+} cation would, however, be isoelectronic with the ozone molecule O_3, a structure in which the atoms are not equivalent. Ozone has a bent structure (C_{2v} symmetry) and the bonds have some double bond character. Although double bond formation seems unlikely for iodine the possibility of I_3^{3+} having a structure similar to that of O_3 can not be entirely ruled out. The existence of the I_2^{2+} cation appears to be the least likely of the proposed structures for I_n^{n+}. Formation of I_2^{2+} would involve removal of two electrons from antibonding orbitals of I_2. The vibrational frequency of I_2^{2+} would, therefore, be expected to be greater than 238 cm^{-1}, the observed vibrational frequency of I_2^+. The frequency observed for I_n^{n+} (195 cm^{-1}) is, in fact, less than that observed for I_2^+ or for molecular I_2 (213 cm^{-1}). Also, the hypothetical I_2^{2+} cation would probably be paramagnetic (due to the presence of two unpaired electrons) as are the known isoelectronic molecules O_2, Se_2 and Te_2. This would not be consistent with the reported diamagnetism of ISO_3F which, presumably, contains the I_n^{n+} cation.

The I_n^{n+} cation appears to exist in solid ISO_3F, in molten ISO_3F, and in H_2SO_4 or HSO_3F solutions containing I_2 and the stoichiometric amount of oxidant to form the +1 oxidation state. In this study the characteristic I-I stretching vibration at 195 cm^{-1} was observed in the spectra of

(1) solutions containing $I_2/HIO_3 = 2.0$ in H_2SO_4.
(2) solutions of ISO_3F in H_2SO_4.
(3) solution of I_2 in 30% oleum.
(4) solution of I_2- AsF_5 compound in HSO_3F.

The existence of the I_n^{n+} cation helps to explain some of the discrepancies in earlier studies of iodine cations. Symons (69) studied blue solutions of I_2 in oleum and found that the value obtained for the magnetic moment of the proposed I^+ cation was less than expected. (The blue species is actually I_2^+ but his value would still be low). To explain this, he suggested that the cation was in equilibrium with $IHSO_4$, IHS_2O_7 or ISO_3^+ in which it would be covalently bonded. In fact, the solutions that he studied may have contained a mixture of I_2^+ and I_n^{n+}. The low temperature behavior of I_2^+ solutions, previously attributed to a dimerization of two I_2^+ ions to form I_4^{2+}, may possibly be explained instead in terms of a disproportionation of I_2^+. Disproportionation would produce two or more iodine species having oxidation states other than + 1/2. One of the possible species with an oxidation state greater than + 1/2 is the I_n^{n+} cation.

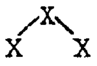
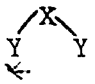
It is interesting to note that Masson considered two hypotheses involving I^+. In the first (described earlier in this chapter) he proposed that I^+ was represented by a mixture of IO^+, I^{+++}, I_3^+ and I_5^+. Alternatively, he proposed a 'micelle' hypothesis, "wherein the triply-charged iodous cation takes up an iodine molecule (or more) but without then dividing into univalent ions: that is

$$I^{+++} + n\,I_2 \rightleftarrows I_{1+2n}^{+++}$$

This hypothesis meets the observed fact that the solubility of iodine per iodous molecule does not much vary with the iodous concentration." (2).

Elucidation of the I_n^{n+} structure will be most interesting. The low melting (m.p. 50.5°C) black ISO_3F is not a suitable solid for X-ray structural determination. However, preparation of iodine (I) trifluoromethanesulfonate ISO_3CF_3 has recently been reported by Dalziel and Aubke (70). It is described as a brown, very hygroscopic solid, melting at 122°C, prepared by reaction of iodine tris(trifluoromethanesulfonate) $I(OSO_2CF_3)_3$ with I_2. The observed infrared frequencies were reported but the authors were unable to obtain a Raman spectrum. The only comment concerning the structure of this compound was the suggestion that it may be a polymeric structure with a polydentate SO_3CF_3 group. Instead, on the basis of evidence presented here, it seems likely that ISO_3F and ISO_3CF_3 both contain iodine in the same structural configuration. That configuration is probably I_n^{n+} with $n \geqslant 3$.

APPENDIX

For the symmetric structures  and  (point group C_{2v}) a simple valence force field treatment of the Raman data was used to calculate approximate values of the stretching force constant f and the bending force constant d; the bond angle α was also estimated. These quantities are related to the observed Raman frequencies ν_1 (sym. stretch), ν_2 (bend) and ν_3 (asym. stretch) by the equations (38):

$$(1) \qquad \frac{4\pi^2c^2}{N}\nu_3^2 = f[\frac{1-\cos\alpha}{M_x} + \frac{1}{M_y}]$$

$$(2) \qquad \frac{4\pi^2c^2}{N}(\nu_1^2 + \nu_2^2) = f[\frac{1+\cos\alpha}{M_x} + \frac{1}{M_y}] + 2d[\frac{1-\cos\alpha}{M_x} + \frac{1}{M_y}]$$

$$(3) \qquad [\frac{4\pi^2c^2}{N}]^2 \cdot \nu_1^2 \cdot \nu_2^2 = \frac{fd2}{M_y}[\frac{2}{M_x} + \frac{1}{M_y}]$$

where M = Atomic Weight and N = Avogadro's Number. If ν is in cm^{-1} and c is in cm sec^{-1}, then the units of the force constants f and d are mdyn $\mathring{A}^{-1}$.

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