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# THE PREPARATION AND CHARACTERIZATION

# OF SOME

# BROMOSELENATES(IV)

by

Pierre J. B. Lahaie

A thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of M. Sc. in Chemistry

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## ABSTRACT

The Raman spectra of five bromoselenate(IV) anions, $SeO_2Br^-$, $SeOBr_3^-$, $SeOBr_4^{2-}$, $SeBr_5^-$ and $SeBr_6^{2-}$ as solids and in solution are discussed. Except for $SeBr_6^{2-}$, none of these anions have been characterized before. Raman spectra of these compounds are consistent with models predicted by the valence shell electron pair repulsion theory (VSEPR), except in the case of the $SeBr_6^{2-}$ anion. Compounds of the pentabromoselenate(IV) ion, $SeBr_5^-$, are shown to be polymeric as solids and in concentrated solutions. The isolated $SeBr_5^-$ anion is seen only in dilute solutions in acetonitrile. Evidence is given for the decomposition of the $SeBr_5^-$ ion to $SeBr_2$ and $Br_3^-$ in acetonitrile solution.

The Raman spectra of solutions of selenium dioxide in hydrobromic acid indicate the presence of $H_2SeO_3$, $SeOBr_2$, $SeBr_5^-$ and $SeBr_6^{2-}$. The equilibrium constant for the equilibrium:

$$H_2SeO_3 + 2HBr = SeOBr_2 + 2H_2O$$

has been evaluated.

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## LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| MeCN | Acetonitrile |
| $Me_4NBr$ | Tetramethylammonium Bromide |
| $Et_4NBr$ | Tetraethylammonium Bromide |
| $n\text{-}Bu_4NBr$ | Tetra-n-butylammonium Bromide |
| $Ph_4SbBr$ | Tetraphenylstibonium Bromide |
| $C_x$ | Initial concentration of species (mole $L^{-1}$) |
| $a_{HBr}$ | Molar activity of hydrobromic acid |
| $a_w$ | Activity of water in mole fraction scale |

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# INTRODUCTION

Since the early days when selenium was reacted with elemental halogen[1], the reactivity and stereochemistry of the halo-complexes formed has become an area of much interest. In most of these complexes, selenium is found to be in its penultimate valence state, having a non-bonding lone pair of electrons. Their structures can be predicted by use of the Valence Shell Electron Pair Repulsion (VSEPR) theory of Gillespie[2] with a good degree of certainty, although vibrational and crystallographic techniques have produced a somewhat clearer picture as to the positions of the ligands, including the $4s^2$ lone pair, around selenium.

This introductory chapter reviews the halo and oxyhalo species of selenium in its penultimate valence state. These complexes will be discussed in the order of the extent of halogenation. Therefore, halo complexes of selenium dioxide will be dealt with first and hexahaloselenates(IV) will be seen near the end. The complexes formed when $SeO_2$ is dissolved in various hydrohalic acids will also be discussed at the conclusion of this short review. The complexes studied in the present work will appear in the same order.

Monohalo- and Dihaloselenate(IV) complexes:

Paetzold and Aurich[3] reported the synthesis of $K^+SeO_2F^-$ and recorded its infra-red and Raman spectra. Later studies of the monofluoroselenate(IV) anion[4,5], $SeO_2F^-$, with different counter cations ranging from potassium through to quaternary ammonium cations, show that the ion is isolated and has $C_s$ symmetry; conforming with a pyramidal structure. The further fluorination of $SeO_2F^-$ to $SeO_2F_2^{2-}$ was also studied[4] and although a mixture of $KSeO_2F$ and $K_2SeO_2F_2$ was identified rather than the pure salt, the Raman spectrum of the mixture was consistent with $SeO_2F_2^{2-}$ having a $C_{2v}$ structure similar to the isoelectronic species $ClO_2F_2^-$ [6], $IO_2F_2^-$ [7] and $TeO_2F_2^{2-}$ [8], with the lone pair and the oxygen atoms occupying equatorial positions of a trigonal bipyramid.

Complex formation between selenium dioxide and halide in dimethylsulfoxide (DMSO) has been studied by UV and visible spectroscopy[9] and indicates that in the equilibrium,

$$SeO_2 + X^- = SeO_2.X^- \quad (X = Cl, Br, I)$$

$SeO_2$ acts as a hard Lewis acid. For $SeO_2.X^-$ the chloride species is reported to be the most stable and the iodide the least. The $SeO_2Cl^-$ ion has been studied in detail[10] and

found, via Raman spectroscopy, to be monomeric and have $C_s$ symmetry. Further addition of $Cl^-$ to a solution of $SeO_2Cl^-$ ion in acetonitrile (MeCN) up to 2:1 $Cl^-/SeO_2$ gives no change in the Raman spectrum and shows that no complex ion other than $SeO_2Cl^-$ is formed in MeCN solution.

Seleninyl halides

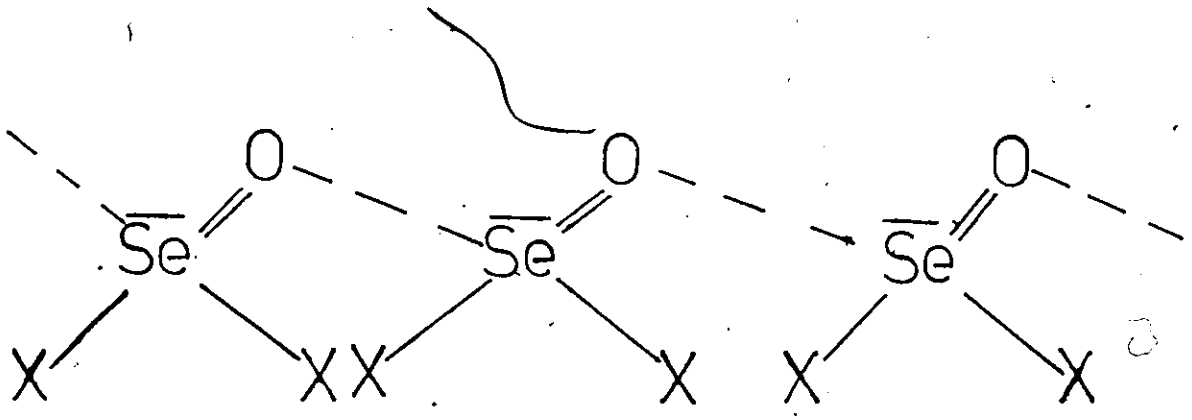
Seleninyl fluoride, $SeOF_2$, is known to be monomeric in the gas phase[11], however Raman spectra of $SeOF_2$[12-14] show that there are frequency shifts and some major relative intensity effects between the spectra of the gas and the liquid. These are not sufficiently great to assume the presence of discrete polymeric species ~~in~~ the liquid. The spectra of both the liquid and the gas suggest a pyramidal structure, as would be predicted from VSEPR theory, since these agree with a species of $C_s$ symmetry. The solid spectrum is somewhat more complex due to a large degree of intermolecular interaction. The crystal structure of $SeOF_2$ at $-35°C$[15] displays a structure consisting of pyramidal $SeOF_2$ units linked together by oxygen and fluoride bridges.

The Raman spectra of the gaseous, liquid and solid oxychloride of selenium, $SeOCl_2$, as well as of a $CCl_4$ solution have been studied[13,16-18]. The spectra indicate associated molecules in the liquid and strong intermolecular

interactions in the solid. Monomeric molecules have been found in the vapor and in dilute solutions. Again, the molecule can be approximated as having $C_s$ symmetry both in the gas and liquid phase as well as in dilute solutions.

The Raman spectra of solid and molten $SeOBr_2$ as well as of a $CCl_4$ solution have been recorded[19] and indicate associated molecules in the molten state and relatively strong intermolecular interactions in the solid. Monomeric pyramidal molecules are present in a $CCl_4$ solution.

As in the case of gaseous and liquid $SeOF_2$, gaseous and liquid $SeOCl_2$ and molten $SeOBr_2$ the Raman spectra indicate pyramidal molecules having $C_s$ symmetry. In liquid $SeOCl_2$ and molten $SeOBr_2$ the associated molecules can be thought of as $SeOX_2$ (X = Cl, Br) units having the central atom acting as an electron acceptor and the neighbouring $SeOX_2$ unit as being an electron donor, as shown below.



Oxotri- and Oxotetrahaloselenate(IV) complexes:

Paetzold and Aurich[20] have prepared and characterized $KSeOF_3$ and they have shown that the $SeOF_3^-$ ion has a trigonal bipyramidal structure, which is consistent with the vibrational spectrum and the VSEPR model. Two of the fluorines are axial while the remaining three positions are occupied by the oxygen atom, the lone pair and the third fluorine atom..

The chloro anions derived from $SeOCl_2$ show an intriguing range of stereochemistries. The 1:1 complex of KCl and $SeOCl_2$, which was first prepared by Wise[21] and later formulated as $K[SeOCl_3]$ by Jackson and Smith[22] has been studied by Raman spectroscopy[20]. The spectrum was assigned for $KSeOCl_3$ assuming monomeric trigonal bipyramidal $SeOCl_3^-$ units. However, a more recent spectroscopic study of the oxotrichloroselenate(IV) anion[10] indicates that for $KSeOCl_3$, the greater complexity of the Raman spectrum and the large shifts in some of the vibrational modes compared to spectra of the same anion with larger counter cations, anion bridging occurs. This bridging probably occurs over chloride but also over oxygen, as in the case of the adducts $SeOCl_2 . SbCl_5$ [28] and $2SeOCl_2 . SnCl_4$ [29] where the oxygen atoms complete the octahedra around Sb and Sn.

Cordes[23] has shown that there are essentially infinite chains of $SeOCl_2$ molecules linked by $Cl^-$ bridges in 8- hydroxyquinolinium oxotrichloroselenate(IV). In this case, the anion consists of a distorted square pyramid about selenium. Each selenium is surrounded by one oxygen and five chlorine atoms. The selenium oxygen bond distance of 1.59Å is equal to that found in the 1:2 addition compound of seleninyl chloride and pyridine[24] and is comparable to the selenium-oxygen distance in $SeOCl_2$, determined via electron diffraction[25] to be 1.61Å. The five selenium-chlorine distances vary considerably; two of these, 2.23 and 2.27Å, are similar to values found by McCullough[26,27] for a number of selenium-chlorine compounds. Two other chlorine atoms, at 2.96 and 2.99Å, are almost exactly equidistant between two selenium atoms. The fifth chlorine neighbor of each selenium is at a distance of 3.3Å, slightly shorter than the sums of the non-bonding radii, 3.8Å. If the distances of 2.96Å and 2.99Å are considered too long to be covalent bonds, they can be interpreted as some type of ion-dipole association where the compound would be best described by the formula $RH^+ - Cl^-.SeOCl_2$.

The recent study on the $SeOCl_3^-$ ion[10] also shows that in the case of the tetraethylammonium and tetrapheny-larsonium compounds, $Et_4NSeOCl_3$ and $Ph_4AsSeOCl_3$ respectively,

the spectra are very similar to each other and to $SeOCl_3^-$ in acetonitrile. The presence here of an isolated $SeOCl_3^-$ ion is confirmed and this anion has $C_s$ symmetry, as previously suggested by Paetzold and Aurich[20] for $KSeOCl_3$, with the trigonal bipyramidal coordination around selenium. 8-Hydroxyquinolinium oxotrichloroselenate(IV), $C_9H_8NO^+SeOCl_3^-$, exhibits weak chloride bridging and its spectrum is that of $SeOCl_2$ units moderately perturbed by the chloride bridges.

The polymeric nature of some of these compounds suggests that the $SeOCl_3^-$ ion should readily accept a chloride ion to give the $SeOCl_4^{2-}$ ion. Cordes and Bi-Cheng Wang[30] prepared the dipyridinium salt of this ion and studied its crystal structure. $C_{10}H_8N_2H_2^{2+}$ $SeOCl_4^{2-}$, dipyridinium(II) oxotetrachloroselenate(IV) also contains five coordinate selenium. Selenium-chlorine distances vary from 2.244 to 2.99Å. The four Se-Cl bonds in each $SeOCl_4^{2-}$ unit can be grouped into three categories; bonds of 3.0Å which can be characterized as some type of ion dipole association, those of 2.24Å, normal single bonds, and bonds of intermediate distance, 2.5Å. Thus the anion is best approximated as trigonal bipyramidal $SeOCl_3^-$ ions, each with a distant weakly bonded chloride anion.

The oxotetrafluorotellurate(IV) anion, $TeOF_4^{2-}$ [8], which is isoelectronic in valence electrons with the $SeOCl_4^{2-}$ ion, has a discrete square-pyramidal structure with the oxygen occupying the axial position. The Raman spectra of $(Et_4N)_2$ $SeOCl_4$ and $(Ph_4As)_2$ $SeOCl_4$ and $(Et_4N)_2$ $SeOCl_4$ in acetonitrile[31] are very similar to each other and very different from that of the $SeOCl_3^-$ ion. These complexes display discrete $SeOCl_4^{2-}$ ions having $C_{4v}$ symmetry, where the square-pyramid around selenium has the oxygen occupying the axial position trans to the lone electron pair.

There is no report of the analogous $SeOF_4^{2-}$ ion in the literature.

Penta- and hexahaloselenate(IV) complexes:

The reaction of liquid $SeF_4$ with an alkali metal fluoride gives salts of the $SeF_5^-$ ion[11]. Christe[32] has observed the vibrational spectra of $CsSeF_5$, finding the results consistent with the anion having $C_{4v}$ symmetry. Raman spectra of pentachloroselenate(IV) complexes[10] indicate that the $SeCl_5^-$ ion also has $C_{4v}$ symmetry.

Seel and Massat[33] have reported the isolation of the nitrosonium salt of the hexafluoroselenate(IV) ion, $(NO)_2SeF_6$. However, in the reaction of $NO_2F$ with $SeF_4$, Aynsley et al[34] succeeded only in preparing the pentafluoro species $(NO_2)SeF_5$. Salts of the hexachloro and hexabromose-

lenate(IV) ions, $SeCl_6^{2-}$ and $SeBr_6^{2-}$, have been isolated by a number of authors. Hendra and Jovic[35] have studied the vibrational spectra of some of these compounds and have found them to have octahedral symmetry. A later study on the $SeCl_6^{2-}$ ion via Raman spectroscopy[10] supports this conclusion. A crystal structure determination on $K_2SeCl_6$ [36] has also shown the anion to be a regular octahedron. Greenwood and Straughan[37] came to this same conclusion in studying metal-halogen vibrations of simple octahedral ions containing selenium and tellurium. Interligand repulsions are sufficiently strong to overcome the stereochemical effect of the lone electron pair in the case of $SeCl_6^{2-}$ and $SeBr_6^{2-}$. K. J. Wynne[38] has studied the factors involved in the stereochemistry of $AX_6E$ systems (A=Sb, Bi, Se, Te; $X=Cl^-$, $Br^-$; E=lone pair) and explains the stereochemically inactive lone pair using the theory of hard and soft acids and bases (HSAB) proposed by Pearson[39]. Wynne considers two empirical rules concerning the stereochemistry of $AX_6E$ systems;

(1) Only the hardest donors (O,F) generally lead to the stereochemical activity of the lone pair.

(2) Soft donors generally lead to a stereochemically inert lone pair.

Complexes of Se(IV) in Hydrohalic acid:

The behaviour of Se(IV) in aqueous HF[40] and HCl[35,41,42] has been studied by Raman spectroscopy. In aqueous HF, the major components at high HF concentrations were found to be $SeOF_2$ and $HSeO_2F$[43]. Similarly in aqueous HCl (up to 12.17M) the following equilibrium occurs;

$$H_2SeO_3 + 2HCl = SeOCl_2 + 2H_2O$$

A solution of $SeO_2$ in $HCl_{aq}$ saturated with $HCl_g$ at 0°C (15M) indicates largely the presence of $SeCl_5^-$ due to the principal reaction occurring in this solution;

$$3HCl + SeOCl_2 = H_3O^+ + SeCl_5^-$$

In this solution, the presence of some hexachloroselenate(IV) ion, $SeCl_6^{2-}$, cannot be ruled out completely.

By the use of Raman spectroscopy Futekov and Specker[44] have reported that when selenious acid reacts with concentrated hydrobromic acid (7-8M), $SeOBr_2$, possibly as a dihydrate, is present as a reaction product. At higher concentrations, however, the equilibrium shifts towards $H_2SeBr_6$. Hendra and Jovic[35] have done a similar study and discuss the results in terms of an equilibrium between $SeBr_5^-$ and $SeBr_6^{2-}$ at high HBr concentrations;

$$SeBr_5^- + Br^- = SeBr_6^{2-}$$

The chemistry of Selenium-Bromine systems has not been studied extensively. Therefore, as part of the continuation of the research involving Se(IV) and its halo complexes, a number of bromoselenate(IV) complexes were prepared and their spectra in MeCN were used to identify anions present in the Se(IV)/$HBr_{aq}$ system.

# EXPERIMENTAL

## 1. Materials

Selenium dioxide (Alfa), tetramethylammonium bromide (Aldrich), tetraethylammonium bromide (Aldrich) and tetraphenylstibonium bromide (Alfa) were dried overnight on a vacuum line before use. Tetra-n-butylammonium bromide (Aldrich) was recrystallized from a 3:1 mixture of ethyl acetate: ethyl ether[45] and stored in a vacuum desiccator over $P_2O_5$.

Acetonitrile (Fisher) was dried by refluxing over $P_2O_5$ followed by distillation (B.Pt.81-82°C)

Seleninyl chloride (J.T. Baker, analyzed) was used after a single vacuum distillation.

Seleninyl bromide was prepared according to Lenher[46] and was purified by subliming onto a cold finger at 0°C under vacuo. Bright yellow crystals of $SeOBr_2$ were obtained.

Analysis. Calculated for $SeOBr_2$: Br, 62.73% Found: 62.43%.

Selenium tetrabromide was prepared according to Brauer[47].

Analysis. Calculated for $SeBr_4$: Br, 80.19% Found: 80.3%.

All materials were stored in a dry box.

Both hydrobromic and perchloric acids were standardized before use.

2. Chemical Analyses

Bromide analyses were done by the Volhard method. Selenium was determined iodometrically while carbon, hydrogen and nitrogen analyses were obtained from Canadian Microanalytical Service Limited.

3. Raman Spectra

Raman Spectra were recorded using a Jobin-Yvon grating monochromator in conjunction with PAR photon counting. Most spectra were excited with a Control Laser argon ion laser, using the 514.5nm line for both solids and solutions. Slit widths gave resolutions of 6-9 $cm^{-1}$ for solid samples and 11 $cm^{-1}$ for solutions at 500 $cm^{-1}$. Spectra were calibrated by means of the argon lines present when the spike filter was not used. Low wattages were used for the solids (100-350mw) to avoid decomposition of the sample. The spectra of $Me_4NSeOBr_3$, $n\text{-}Bu_4NSeOBr_3$, $(n\text{-}Bu_4N)_2\ SeOBr_4$, $(Me_4N)_2\ SeOBr_4$, the pentabromoselenates(IV) and the hexabromoselenates(IV) were taken using a Spectra Physics 125A He/Ne laser. The 632.8nm line was used and the spectra were calibrated by means of the Ne lines present when the spike filter was not used. Slit widths gave resolutions of 3-4 $cm^{-1}$ for solid samples and 5$cm^{-1}$ for solutions at 500 $cm^{-1}$. All samples were contained in pyrex melting point tubes. In the case of solution spectra, saturated solutions in MeCN were used.

For the solutions of $SeO_2$ in $HBr_{aq}$ the Raman spectra were taken using the He/Ne laser at 632.8 nm. The resolution for these spectra was the same as for the MeCN solutions. The spectra were taken in 1 cm path length cells designed for fluorescence spectroscopy which were held in a water-jacketed aluminium holder maintained at 25°C. All spectral intensities were normalized by comparison to perchloric acid solutions which were run after each selenium dioxide - hydrobromic acid solution. The normalization assumption was that the 925 $cm^{-1}$ band of perchloric acid for a 1M solution ($\nu_1$) had an area intensity of 1 $in^2$ (6.45 $cm^2$). A plot of the intensity of the 925 $cm^{-1}$ band against concentration was shown to be linear up to 5.76M $HClO_4$ (Fig.14). Peak intensities were measured with a Hruden planimeter. Slit width, time constant, laser power, photon counting rate, scan rate, and sample position were held constant for each series of runs.

4. Preparation of the Compounds

All preparations were carried out in a dry box except for those crystallized from aqueous solution.

$Ph_4SbSeO_2Br$: Tetraphenylstibonium monobromoselenate(IV) was prepared by dissolving stoichiometric amounts of $Ph_4SbBr$ and $SeO_2$ in a minimum amount of MeCN according to

$$MBr + SeO_2 = MSeO_2Br$$

The solution was cooled over dry ice, filtered and the light yellow crystals of $Ph_4SbSeO_2Br$ were pumped dry.

Analysis. Calculated for $Ph_4SbSeO_2Br$: C, 46.45%. H, 3.25%. Se, 12.72%. Br, 12.87%. Found: C, 46.25%. H, 3.25%. Se, 13.33%. Br, 13.25%.

n-$Bu_4NSeO_2Br$: Tetra-n-butylammonium monobromoselenate(IV) was considerably more soluble in MeCN than $Ph_4SbSeO_2Br$. It was prepared by dissolving stoichiometric amounts of n-$Bu_4NBr$ and $SeO_2$ in a minimum amount of MeCN and pumping to dryness. A bright yellow compound, n-$Bu_4NSeO_2Br$, was obtained.

$MSeOBr_3$: Tetramethylammonium, tetraethylammonium and tetraphenylstibonium oxotribromoselenates(IV) were all prepared by dissolving 1:1 mixtures of the bromide and $SeOBr_2$ in a minimum amount of MeCN, crystallizing over dry ice, filtering and pumping dry.

$$MBr + SeOBr_2 = MSeOBr_3$$

Analysis. Calculated for $Me_4NSeOBr_3$: C, 11.75%. H, 2.96%. N, 3.42%. Br, 58.63%. Found: C, 11.60%. H, 2.60%. N, 3.46%, Br, 59.06%. Calculated for $Et_4NSeOBr_3$: C, 20.66%. H, 4.33%. N, 3.01%. Se, 16.98%. Br, 51.56%. Found: C, 20.42%. H, 4.01%. N, 2.90%. Se, 16.77%. Br, 51.47%. Calculated for $Ph_4SbSeOBr_3$: C, 37.71%. H, 2.64%. Br, 31.36%. Found: C, 35.87%. H, 2.25%. Br, 30.95%.

Tetra-n-butylammonium oxotribromoselenate(IV) was very soluble in MeCN. It was prepared by dissolving a 1:1 mixture of $n\text{-}Bu_4NBr$ and $SeOBr_2$ in MeCN and pumping to dryness.

Tetraethylammonium oxotribromoselenate(IV) was also prepared from an aqueous hydrobromic acid solution. In the attempted preparation of $Et_4NSeBr_5$ from aqueous solution, $HBr_{aq}$ (4 moles) was added to a 1:1 mixture of $Et_4NBr$: $SeO_2$. An orange precipitate formed which was immediately dissolved in a minimum amount of $H_2O$, heated slightly, and placed over ice for crystallization. The yellow product obtained was filtered and pumped to dryness. The product was $Et_4NSeOBr_3$, according to

$$MBr + SeO_2 + 2HBr = MSeOBr_3 + H_2O$$

$\underline{M_2SeOBr_4}$: Tetra-n-butylammonium oxotetrabromoselenate(IV) was prepared by dissolving a 2:1 mixture of $n\text{-}Bu_4NBr$ and $SeOBr_2$ in MeCN. A yellow compound was obtained upon pumping to dryness.

Tetramethylammonium oxotetrabromoselenate(IV) was prepared by mixing stoichiometric amounts of $Me_4NBr$, $SeO_2$ and concentrated $HBr_{aq}$. Evaporating over $P_2O_5$ yielded the yellow-orange $(Me_4N)_2SeOBr_4$.

$$2MBr + SeO_2 + 2HBr = M_2SeOBr_4 + H_2O$$

Analysis. Calculated for $(Me_4N)_2SeOBr_4$: C, 17.05%. H, 4.29%. N, 4.97%. Br, 56.78%. Found: C, 16.82%. H, 4.17%. N, 4.17%. Br, 56.87%.

$MSeBr_5$: Tetra-n-butylammonium and tetramethylammonium pentabromoselenates(IV) were prepared by dissolving 1:1 mole ratios of the bromide and $SeBr_4$ in a minimum amount of MeCN. The solutions were placed over dry ice and the products which crystallized were filtered and pumped to dryness in the dry box.

Analysis. Calculated for $n\text{-}Bu_4NSeBr_5$: C, 26.25%. H, 5.03%. N, 1.94%. Se, 10.95%. Br, 55.41%. Found: C, 27.09%. H, 5.27%. N, 1.92%. Se, 10.94%. Br, 55.67%.

Calculated for $Me_4NSeBr_5$: Br, 72.3%. Found: 71.98%.

$M_2SeBr_6$: Caesium hexabromoselenate(IV) was prepared by adding a stoichiometric amount of $Cs_2CO_3$ (in excess $HBr_{aq}$) to a saturated solution of $SeO_2$ in $HBr_{aq}$. The orange product which precipitated was filtered and pumped to dryness in a vacuum desiccator over $P_2O_5$.

Tetraethylammonium hexabromoselenate(IV) was prepared by dissolving a 2:1 mixture of $Et_4NBr$ and $SeBr_4$ in MeCN. The dark orange product was crystallized over dry ice and let to dry in the dry box.

Analysis. Calculated for $Cs_2SeBr_6$: Br, 57.48%. Found: 58.17%.

Calculated for $(Et_4N)_2\ SeBr_6$: Br, 58.54%. Found: 58.02%.

## RESULTS AND DISCUSSION

### OXOBROMO COMPLEXES OF SELENIUM(IV)

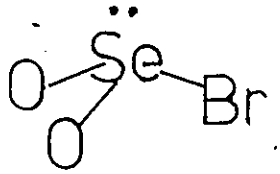
#### The monobromoselenate(IV) anion, $SeO_2Br^-$

Selenium dioxide is known to be polymeric[48] and insoluble in MeCN. However, it dissolves in this solvent in the presence of some soluble ionic bromide, according to:

$$SeO_2 + Br^- \underset{MeCN}{=} SeO_2Br^-$$

In this way, it behaves much like the corresponding fluorides[4,5] and chlorides[10].

The Raman spectra of $Ph_4SbSeO_2Br$, $n\text{-}Bu_4NSeO_2Br$ and $SeO_2Br^-$ in solution are listed along with the assignment, in Table I. The spectra of $n\text{-}Bu_4NSeO_2Br$ and $SeO_2Br^-$ in solution are shown in Figure 1. The $SeO_2Br^-$ ion is expected to have $C_s$ symmetry and six normal modes ($\Gamma = 4A' + 2A''$).




Of these, the four A' modes will be polarized. The Raman spectrum of $SeO_2Br^-$ in MeCN indicates three polarized modes at 139,249 and 888 $cm^{-1}$. The highest frequency band is readily assigned to the symmetric $SeO_2$ stretching vibration $\nu_1(A')$. The lowest frequency and highest intensity band at

139 $cm^{-1}$ is assigned to the SeBr stretching mode, $\nu_2(A')$. There are two remaining polarized bands but only one is seen in solution. Both of these bands are symmetric deformations. Of these deformations, the symmetric $SeO_2$ deformation, $\nu_3(A')$, is expected to have the highest frequency. Therefore, the lower frequency band at 249 $cm^{-1}$ is assigned to $\nu_4(A')$, the symmetric SeOBr deformation. The symmetric $SeO_2$ deformation is seen in both solids at 396 $cm^{-1}$ for $Ph_4SbSeO_2Br$ and 379 $cm^{-1}$ for n-$Bu_4NSeO_2Br$. Of the two remaining modes, the highest frequency one, 814 $cm^{-1}$ in $Ph_4SeO_2Br$, is assigned to the antisymmetric $SeO_2$ stretching vibration, $\nu_5(A")$. The last vibrational mode, 169 $cm^{-1}$ in n-$Bu_4NSeO_2Br$ and 172 $cm^{-1}$ in $Ph_4SbSeO_2Br$, is assigned to the antisymmetric SeOBr deformation, $\nu_6(A")$. All lower frequency bands in the solid spectra are due to lattice vibrations. This assignment is supported by the great similarity in the vibrational spectrum of $SeO_2Br^-$ to those of $SeO_2Cl^-$ [10] and $SeO_2F^-$ [5].

The shift to lower frequency of the symmetric and antisymmetric $SeO_2$ stretching modes in $Ph_4SbSeO_2Br$ and the difference in the intensities of these modes compared to what is observed in solution is an indication that there is probably some oxygen bridging present.

Table I. Raman spectra of the $SeO_2Br^-$ anion.

| $Ph_4SbSeO_2Br$ | $n\text{-}Bu_4NSeO_2Br$ | $SeO_2Br^-$ in MeCN[a] | Assignment | |
|---|---|---|---|---|
| | | | Mode No. | Description |
| 66(4) | - | - | ) | |
| | | | ) | Lattice Modes |
| 83(10) | - | - | ) | |
| - | 144(10) | 139(10,p) | $\nu_2(A')$ | $\nu_s(SeBr)$ |
| 172(9,br) | 169(1,sh) | - | $\nu_6(A'')$ | $\delta_{as}(SeOBr)$ |
| 214(6) | 253(1) | 249(1,p) | $\nu_4(A')$ | $\delta_s(SeOBr)$ |
| 396(0) | 379(0) | - | $\nu_3(A^1)$ | $\delta_s(SeO_2)$ |
| 814(1) | - | - | $\nu_5(A'')$ | $\nu_{as}(SeO_2)$ |
| 864(3) | 882(2) | 888(6,p) | $\nu_1(A')$ | $\nu_s(SeO_2)$ |

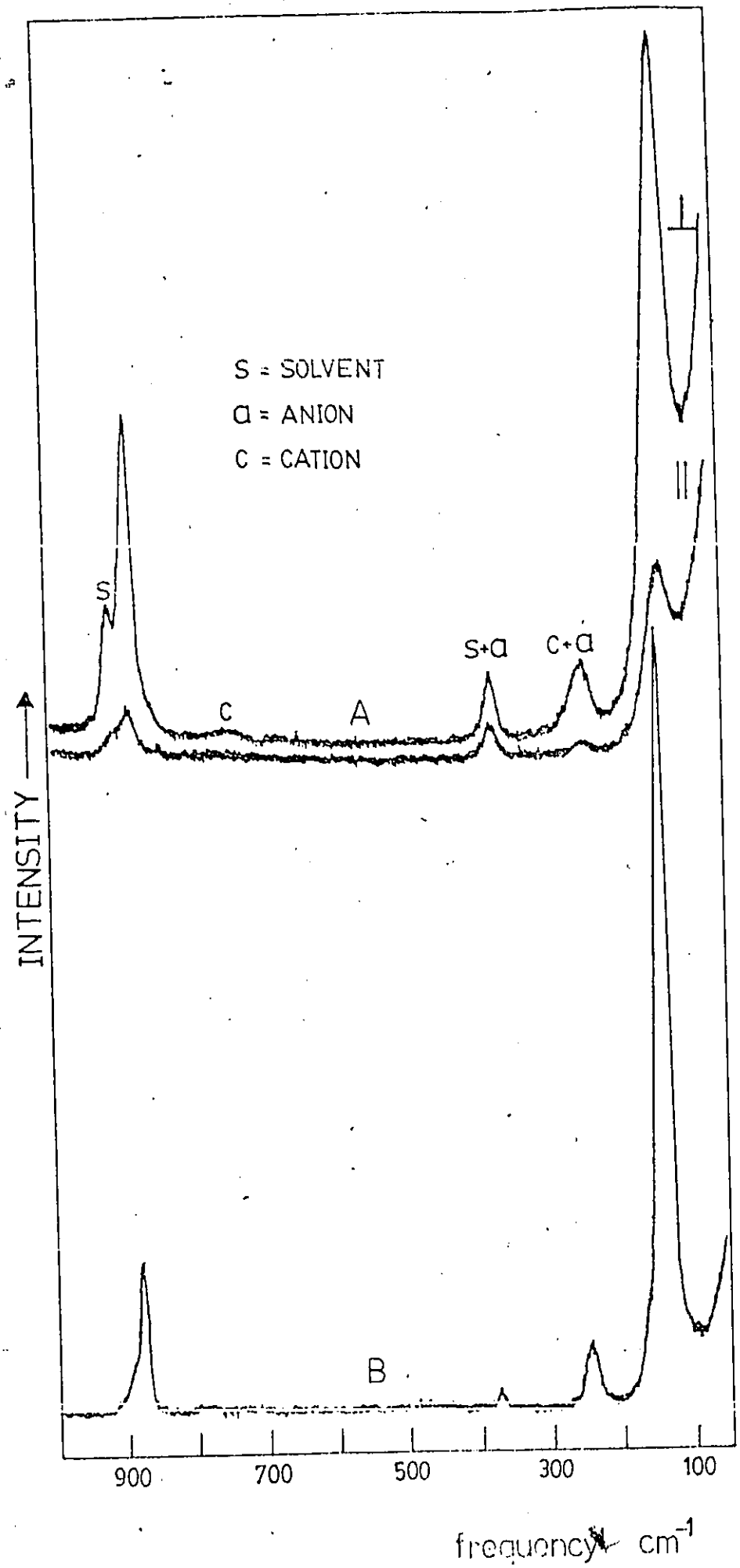
a. $n\text{-}Bu_4NSeO_2Br$

Figure 1

Raman Spectra of n-$Bu_4NSeO_2Br$

A in acetonitrile

B solid


S = SOLVENT
a = ANION
C = CATION
I
II
S
C
A
S+a
C+a
B
INTENSITY
900
700
500
300
100
frequency cm⁻¹

Solutions of $Br^-$: $SeO_2$ up to 4:1 mole ratio in MeCN showed no change in the Raman spectrum of the anion compared to a solution which is 1:1 bromide to $SeO_2$. Apparently, the formation constant of the dibromoselenate(IV) anion is very small compared to the monobromoselenate(IV) anion[10]. Wasif and Salama[9] have shown, via UV spectroscopy, that $SeO_2$, which is soluble in dimethyl sulfoxide (DMSO), forms a 1:1 complex with halide ion in DMSO. According to their stability constant, a 1M $SeO_2Br^-$ solution in DMSO is approximately 25% dissociated. No evidence of dissociation of the $SeO_2Br^-$ ion in MeCN has been found. This can be seen by the Raman spectrum and the absence of $SeO_2$, which is insoluble in MeCN.

Wasif and Salama[9] have concluded that $SeO_2$ acts as a hard Lewis acid and the stability of the $SeO_2X^-$ species is as follows;

$$SeO_2F^- > SeO_2Cl^- > SeO_2Br^-$$

which is also the order of decreasing halide base hardness[38,39]. This behaviour is reflected in the ease of preparation of the monofluoroselenate(IV) anion[5] with small cations such as $K^+$ and $Cs^+$ and the preparation of the monochloroselenate(IV) anion[10] with $Me_4N^+$ as cation compared to the limited capability of preparing the monobromoselenate(IV) complexes with such small cations. The attempted preparation of the monobromoselenate(IV) complexes with $Cs^+$, $Et_4N^+$ and $Me_4N^+$ yielded $SeO_2$ and the simple bromide upon cooling.

Seleninyl Bromide, $SeOBr_2$

The Raman spectrum of $SeOBr_2$ has been reported by two groups. The spectrum of Futekov and Specker[44] which has been partially assigned, has two bands, at 172 $cm^{-1}$ and 310 $cm^{-1}$ which do not appear in the spectrum of $SeOBr_2$ in the present work nor in that of Brockner and Demiray[19]. The present results, shown in Table II and Fig. 2, agree well with those of Brockner and Demiray although there are significant differences in the solid spectra. The spectrum they reported was taken at -196°C compared to 25°C for the present study. The differences are due, no doubt, to some phase change occurring between these two temperatures.

Only 5 of the 6 expected bands ( $\Gamma_{C_S} = 4A' + 2A''$) appear in the liquid[19] and solution spectra (Fig. 2). Since two strongly polarized bands appear between 200 and 300 $cm^{-1}$ and it is somewhat uncertain which is due to the symmetric SeBr stretch, $\nu_2(A')$ and which is the symmetric SeOBr deformation $\nu_3(A')$, a complete assignment of the $SeOBr_2$ spectrum is difficult. The highest and lowest frequency bands in the solution spectrum, 955 and 90 $cm^{-1}$, both of which are polarized, are readily assigned to $\nu_1(A')$, the SeO stretch and $\nu_4(A')$ the $SeBr_2$ deformation. The two remaining polarized modes belong to $\nu_2(A')$ and $\nu_3(A')$. Consideration of the SeOX symmetric deformations ($\nu_3$) in the spectra of

Table II. Solid and solution Raman spectra of seleninyl bromide.

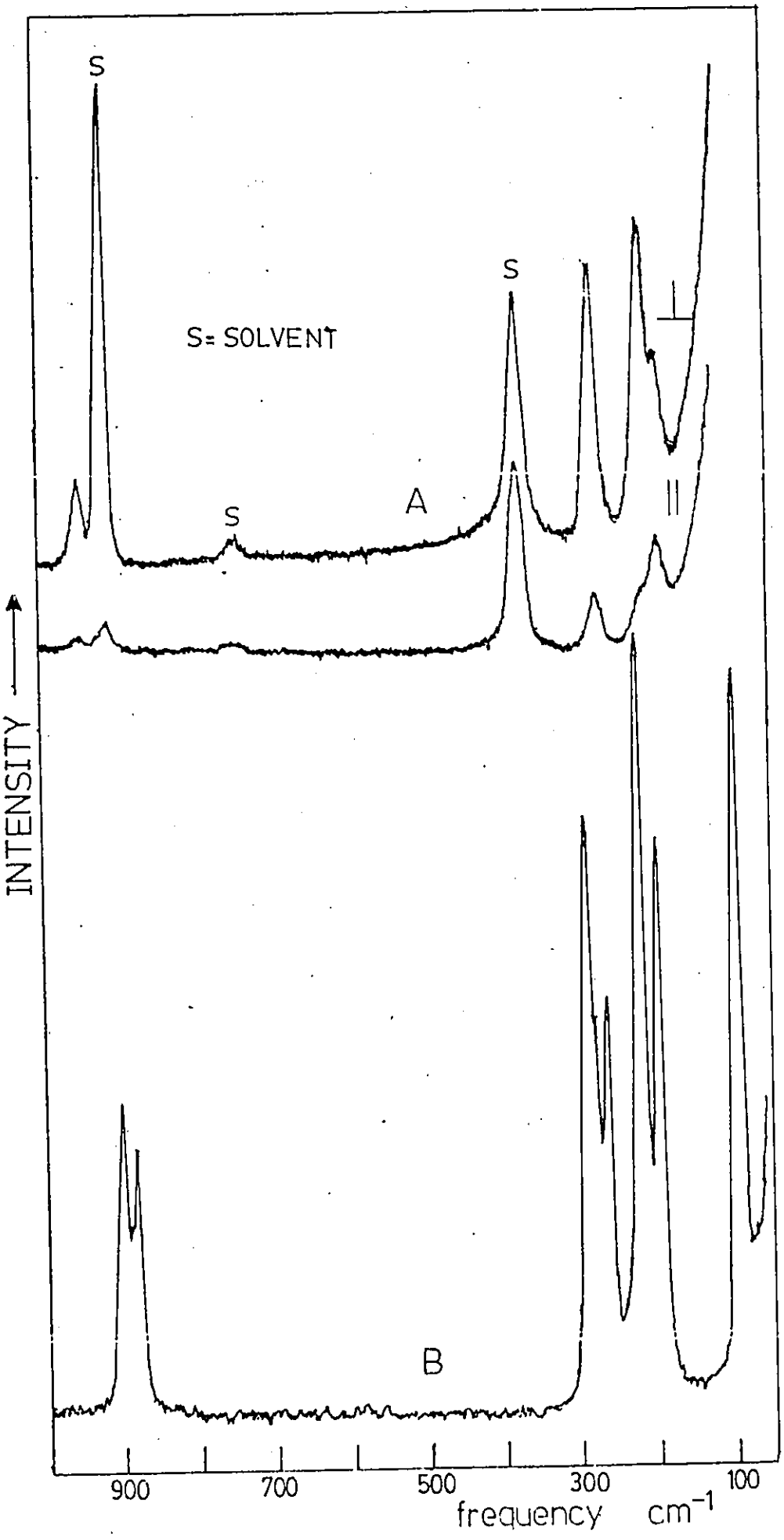
| $SeOBr_2$ at 25°C | $SeOBr_2$ in MeCN | Assignment Mode No. | Description |
|---|---|---|---|
| 97(10) | 90(7,p) | $\nu_4(A')$ | $\delta_s(SeBr_2)$ |
| 200(7) | 194(2,dp) | $\nu_6(A")$ | $\delta_{as}(SeOBr)$ |
| 222(10) | 218(10,p) | $\nu_3(A')$ | $\delta_s(SeOBr)$ |
| 265(5) | - | $\nu_5(A")$ | $\nu_{as}(SeBr_2)$ |
| 282(5,sh)<br>292(7) | 279(9,p) | $\nu_2(A')$ | $\nu_s(SeBr_2)$ |
| 883(3)<br>902(4) | 955(2,p) | $\nu_1(A')$ | $\nu_{(SeO)}$ |

Figure 2

Raman spectra of $SeOBr_2$

A in acetonitrile

B solid

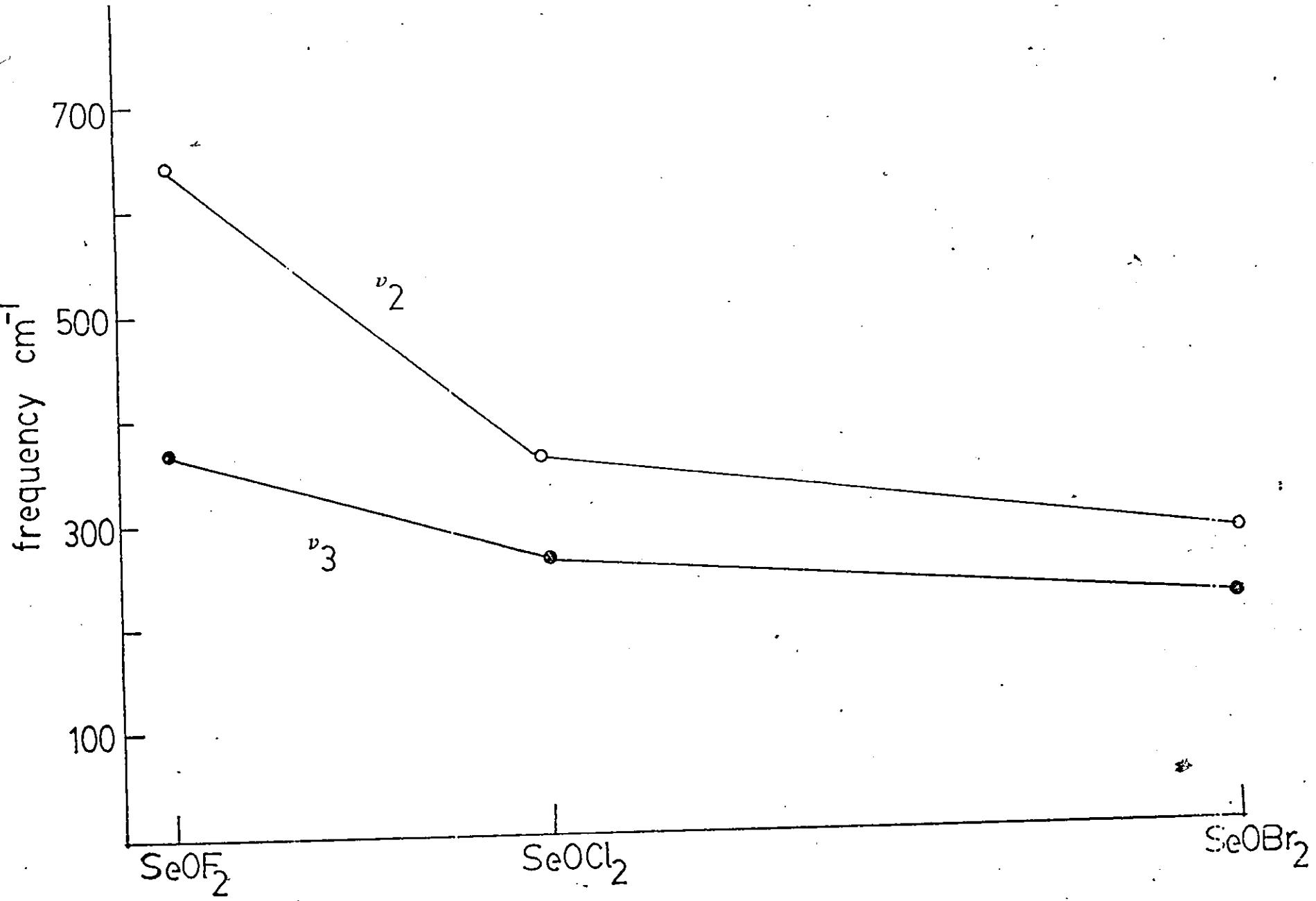

S
S= SOLVENT
S
S
A
II
INTENSITY
B
900
700
500
300
100
frequency cm⁻¹

$SeOF_2$[12,14] and $SeOCl_2$[13,16-18] shows that there is little change in frequency with change in mass of X (Fig. 3) and a frequency for $SeOBr_2$ can be quite reliably estimated to be 200 $cm^{-1}$. The SeOBr symmetric deformation is thus assigned to the mode at 218 $cm^{-1}$. The SeBr symmetric stretch, $\nu_2(A')$, is expected to be at higher frequency than $\nu_3(A')$, from comparison of $SeOF_2$ and $SeOCl_2$ liquid spectra, therefore the band at 279 $cm^{-1}$ is assigned to $\nu_2(A')$. This is supported by the fact that in the spectrum of $SeOBr_2$ in MeCN, the degree of polarization of the lower of the two bands is greater which is the expected situation judging from the spectrum of $SeOCl_2$ [41]. The two remaining bands to be assigned are A" modes, an SeBr antisymmetric stretch, $\nu_5(A")$, and an SeOBr antisymmetric deformation, $\nu_6(A")$. Only one depolarized band, at 194 $cm^{-1}$, is observed in the solution spectrum of $SeOBr_2$ but the sixth vibrational mode is observed in the solid spectrum at 265 $cm^{-1}$. This band is evidently masked in the solution spectrum by the stronger $\nu_2(A')$ band at 279 $cm^{-1}$. The two SeX stretching modes, A' and A", and the two SeOX deformations, also A' and A", make up two closely spaced pairs of bands in the case of liquid $SeOCl_2$ and $SeOF_2$. The two A" modes for $SeOBr_2$ are assigned consistent with this. Thus the band at 194 $cm^{-1}$ is assigned to $\nu_6(A")$, the antisymmetric SeOBr deformation mode, and the hidden band lying under the envelope at 279 $cm^{-1}$ is assigned

Figure 3

Plot of stretching frequencies

$\nu_2$ and $\nu_3$ in $SeOX_2$ species

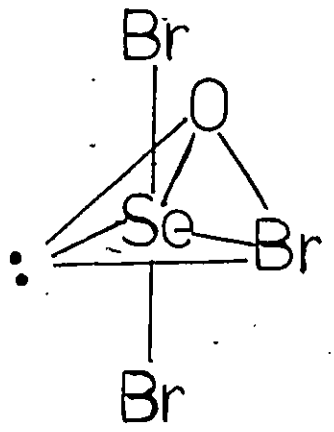

700
500
300
100
frequency cm$^{-1}$
$\nu_2$
$\nu_3$
$SeOF_2$
$SeOCl_2$
$SeOBr_2$

to $\nu_5(A")$, the antisymmetric SeBr stretching vibration. It should be noted that this assignment resembles that of Futekov and Specker[44], which has the SeBr stretching modes at higher frequency than the SeOBr deformations. The complete assignment is given in Table II.

Comparison of the solid and solution spectra of $SeOBr_2$ leads to conclusions concerning the structure similar to those for $SeOF_2$ and $SeOCl_2$. The solid shows evidence of oxygen bridging by the drop in frequency of the SeO stretching mode, going from solution to solid, and also by the fact that this mode is split, as it is in solid $SeOCl_2$[19] and solid $SeOF_2$[12]. However, contrary to $SeOCl_2$ and $SeOF_2$, we can only speculate that there may be some bromide bridging.

The oxotribromoselenate(IV) anion, $SeOBr_3^-$

The Raman spectra of $Et_4NSeOBr_3$ as a solid and $n\text{-}Bu_4NSeOBr_3$ in solution are shown in Fig. 4 and listed along with the spectra of $Me_4NSeOBr_3$, $Et_4NSeOBr_3$ and $Ph_4SbSeOBr_3$ in Table III. The Raman spectra of solid $Et_4NSeOBr_3$, $n\text{-}Bu_4NSeOBr_3$ and $Ph_4SbSeOBr_3$ are very similar to each other and to the spectrum of the $SeOBr_3^-$ion in MeCN solution and are consistent with an isolated $SeOBr_3^-$ion with $C_s$ symmetry ($\Gamma = 6A' + 3A"$).




This ion is expected to have nine bands in its Raman spectrum of which six will be polarized. Because of the greater bond strength of equatorial ligands compared to axial ligands in a trigonal bipyramidal structure, two sets of SeBr stretching vibrations are expected, a single mode at higher frequencies for the equatorial bromine and two bands, symmetric and antisymmetric, for the axial bromines. This situation exists in $SeOCl_3^-$ [10] where the SeCl equatorial stretch occurs at 336 $cm^{-1}$ while the SeCl axial symmetric and antisymmetric stretches occur at 248 and 228 $cm^{-1}$, respectively. In the spectrum of the $SeOBr_3^-$ anion the band at 936 $cm^{-1}$ is readily assigned to the symmetric SeO stretch, $\nu_1(A')$. In the spectrum of the $SeOCl_3^-$ anion the equatorial SeCl stretch, $\nu_2(A')$, occurs at 336 $cm^{-1}$ and is close to the mean of the SeCl stretching frequencies in the corresponding seleninyl halide, $SeOCl_2$, which is 353 $cm^{-1}$ [13]. On a similar basis, the polarized band at 265 $cm^{-1}$ for the $SeOBr_3^-$ anion is

Table III. Raman spectra of the oxotribromoselenate(IV) anion.

| $Me_4NSeOBr_3$ | $(Me_4N)_2SeOBr_4$ | $Et_4NSeOBr_3$ | n-$Bu_4NSeOBr_3$ | $Ph_4SbSeOBr_3$ | $SeOBr_3^-$ in MeCN[a] | Assignment Mode No. | Description |
|---|---|---|---|---|---|---|---|
| - | 70(1) | - | - | 74(1,sh) | - | | |
| 93(0) | 101(1) | 82(0) | - | 86(2) | - | | |
| 134(1,sh) | - | 114(1) | - | - | - | | |
| 150(10) | 131(7) | - | 154(9) | 140(10) | 138(10,p) | $\nu_5(A')$ | $\delta_s(SeOBr_{ax})$ |
| 165(5) | 143(2) | 164(10) | 173(10) | - | 155(8,dp) | $\nu_7(A'')$ | $\nu_{as}(SeBr_{ax})$ |
| 186(5) | - | - | 183( ,sh) | - | - | | |
| 198(1) | - | - | - | - | - | | |
| 215(4) | 179(6) | 194(7) | 198(10) | 195(2) | 194(8,p) | $\nu_3(A')$ | $\nu_s(SeBr_{ax})$ |
| 230(1) | - | - | - | - | - | | |
| 247(2) | 248(10) | 251(3) | 252(4) | 262(2) | 253(2,p?) | $\nu_4(A')$ | $\delta$(SeO, in plane) |
| 256(2) | 263(3) | 270(1) | 267(5) | 285(0) | 265(3,p) | $\nu_2(A')$ | $\nu(SeBr_{eq})$ |
| 265(1) | - | - | - | - | - | | |
| 296(1) | - | - | - | - | - | | |
| 907(0) | 926(1) | 936(2) | 939(1) | 928(1) | 936(1,p) | $\nu_1(A')$ | $\nu$(SeO) |

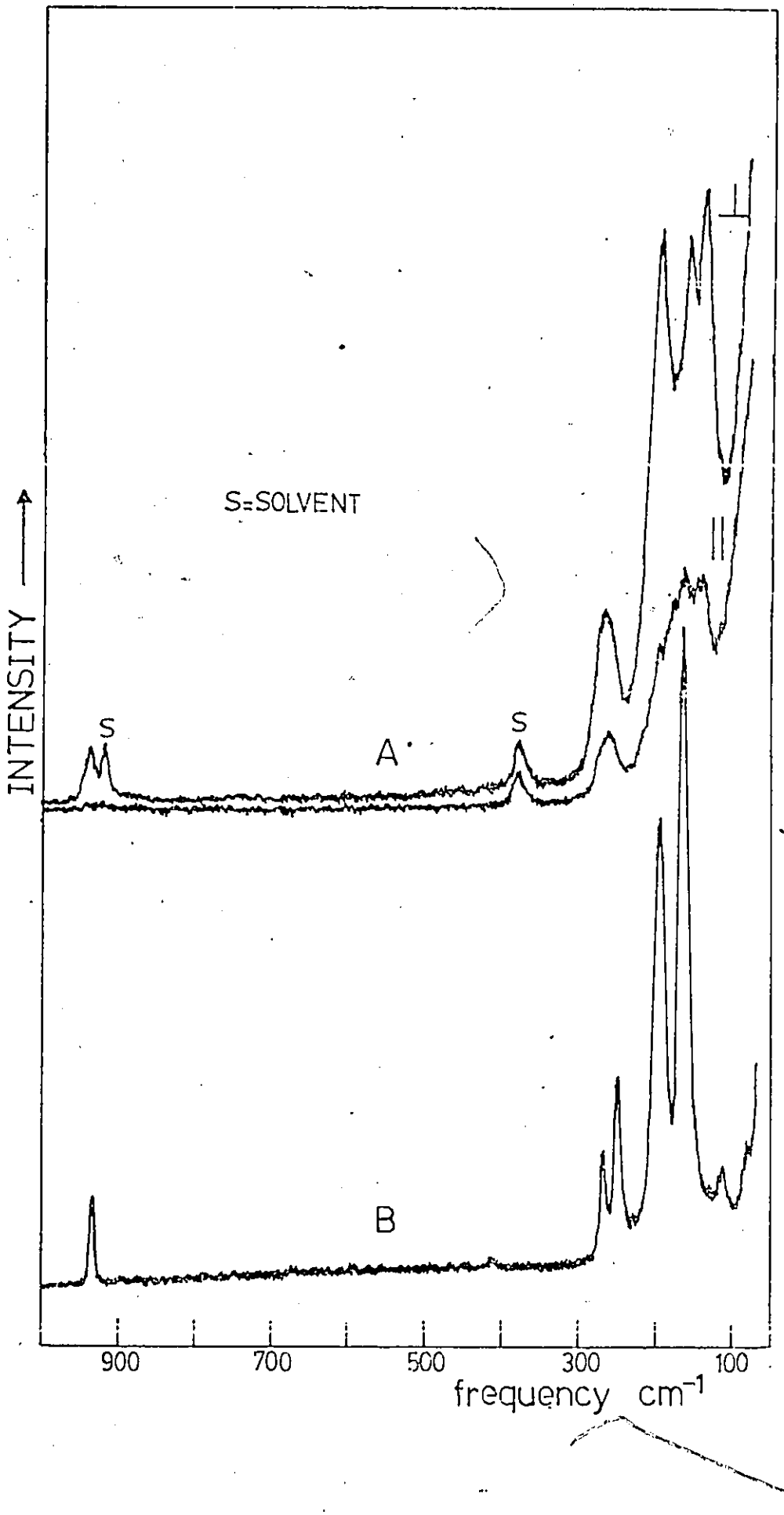
a. n - $Bu_4NSeOBr_3$

Figure 4

Raman Spectra of the $SeOBr_3^-$ ion

A in acetonitrile ($n\text{-}Bu_4NSeOBr_3$)

B solid $Et_4NSeOBr_3$


S=SOLVENT
INTENSITY
S
S
A
B
900
700
500
300
100
frequency cm⁻¹

assigned to $\nu_2(A')$, close to the mean of the SeBr stretching frequencies in $SeOBr_2$, which is 284 $cm^{-1}$. The SeBr equatorial stretch in the T-shaped $SeBr_3^-$ion[49], which is structually closely related to the $SeBr_3$ unit in the trigonal bipyramidal $SeOBr_3^-$ion, occurs at 264 $cm^{-1}$. The band at 155 $cm^{-1}$, which is depolarized, is assigned to the antisymmetric SeBr stretching mode, $\nu_7(A")$. The symmetric SeBr stretching mode is expected to lie at higher frequency than the corresponding antisymmetric mode[10]. Just as in the case of the $SeBr_3^-$ion a similar and very close parallel exists between $SeCl_3^-$ [49] and $SeOCl_3^-$. The three SeCl stretching modes and the analogous modes in $SeOCl_3^-$ are alike in their relative positions and their polarizations. The peak at 253 $cm^{-1}$, which appears to be polarized, is assigned to the symmetric SeO deformation, $\nu_4(A')$. The analogous deformation occurs at 268$cm^{-1}$ in $SeOCl_2$ [50] and 287 $cm^{-1}$ in $SeOCl_3^-$ [10]. The remaining polarized band at 138 $cm^{-1}$ is assigned to the last A' mode, the symmetric SeOBr deformation, $\nu_5(A')$. The other deformations, $\nu_6(A')$, $\nu_8(A")$ and $\nu_9(A")$, are not observed in solution and cannot justifiably be distinguished from lattice modes in the solids. They are expected to occur at frequencies lower than the SeBr stretching vibrations.

The Raman spectrum of $Me_4NSeOBr_3$ consists of 13 anion lines in the spectral region studied (50 - 1000 $cm^{-1}$), and the structure is apparently more complex than that of the isolated $SeOBr_3^-$ anion. As in the case of $KSeOCl_3$[10], which is polymeric, the shifts in some of the bands, particularly the SeO stretching vibration to lower frequency, and the increase in the number of bands in the SeO deformation region, seem to indicate that oxygen bridging is likely. Both halogen and oxygen bridging are observed in oxotrichloroselenates(IV)[10,23] and the smaller cation size favours anion bridging. Attempts to prepare $CsSeOBr_3$ from CsBr and $SeOBr_2$ in acetonitrile lead to the formation of $SeO_2$ and $Cs_2SeBr_6$.

The oxotetrabromoselenate(IV) anion, $SeOBr_4^{2-}$

The spectra of $(n\text{-}Bu_4N)_2SeOBr_4$ solid and in solution are shown in Fig. 5 and listed in Table IV. The addition of $n\text{-}Bu_4NBr$ to a 1M solution of $n\text{-}Bu_4NSeOBr_3$ in MeCN causes the strong peaks of the $SeOBr_3^-$ ion (138, 155 and 194 $cm^{-1}$) to be replaced by a single strong feature with a weak shoulder at 158 $cm^{-1}$. As in the case of the oxotetrachloroselenates(IV)[31], the oxotetrabromoselenate(IV) is formed,

$$SeOBr_3^- + Br^- \underset{MeCN}{=} SeOBr_4^{2-}$$

Evaporation of a 2:1 solution of n-$Bu_4NBr$: $SeOBr_2$ gave an orange product with a Raman spectrum quite similar to the solution spectrum. When a bromide with a smaller cation than n-$Bu_4N^+$, such as $Me_4N^+$ or $Et_4N^+$, was used in attempts to make the oxotetrabromoselenate(IV), oxotribromoselenates(IV) were formed. Apparently, the oxotribromoselenates(IV) of these smaller cations are less soluble than the oxotetrabromoselenates(IV) and the $SeOBr_4^{2-}$ ion is sufficiently dissociated to $SeOBr_3^-$ that the oxotetrabromoselenate(IV) cannot be prepared in this way. The Raman spectra of solutions where the bromide to $SeOBr_2$ molar ratio exceeds 2:1 show no changes compared to the 2:1 solution except for increases in cation bands. A series of solutions of 2:1 n-$Bu_4NBr$:$SeOBr_2$ in MeCN had Raman spectra that did not change in the range 1.0 to 0.1 molal. Only below 0.1 molal was the detection of some oxotribromoselenate(IV) possible indicating that the dissociation is completely repressed above 0.1 molal.

Since the Raman spectra of $(n\text{-}Bu_4N)_2SeOBr_4$ and $SeOBr_4^{2-}$ in MeCN are very similar to each other and much different from the $SeOBr_3^-$ ion indicates the presence of a new ion. The expected stereochemistry for this anion is that of a square pyramid with the oxygen axial and trans to the lone electron pair.

Table IV. Raman spectra of the oxotetrabromoselenate(IV) anion

| $(n\text{-}Bu_4N)_2SeOBr_4$ | $SeOBr_4^{2-}$ in MeCN[a] | Assignment | |
|---|---|---|---|
| | | Mode No. | Description |
| 89(2) | - | | deformations, Lattice Modes |
| 110(2) | - | | |
| 128(3) | 141 (5,p?) | $\nu_7(E_1)$ | $\nu_{as}(SeBr_4)$ |
| 156(10) | 158 (10,p) | $\nu_2(A_1)$ | $\nu_s(SeBr_4$, in phase) |
| 178(2) | 193(3,dp) | $\nu_4(B_1)$ | $\nu_s(SeBr_4$, out of phase) |
| 256(3) | 265(2,dp) | $\nu_8(E)$ | $\delta$(SeO, wag) |
| 941(1) | 932(1,p) | $\nu_1(A_1)$ | $\nu$(SeO) |

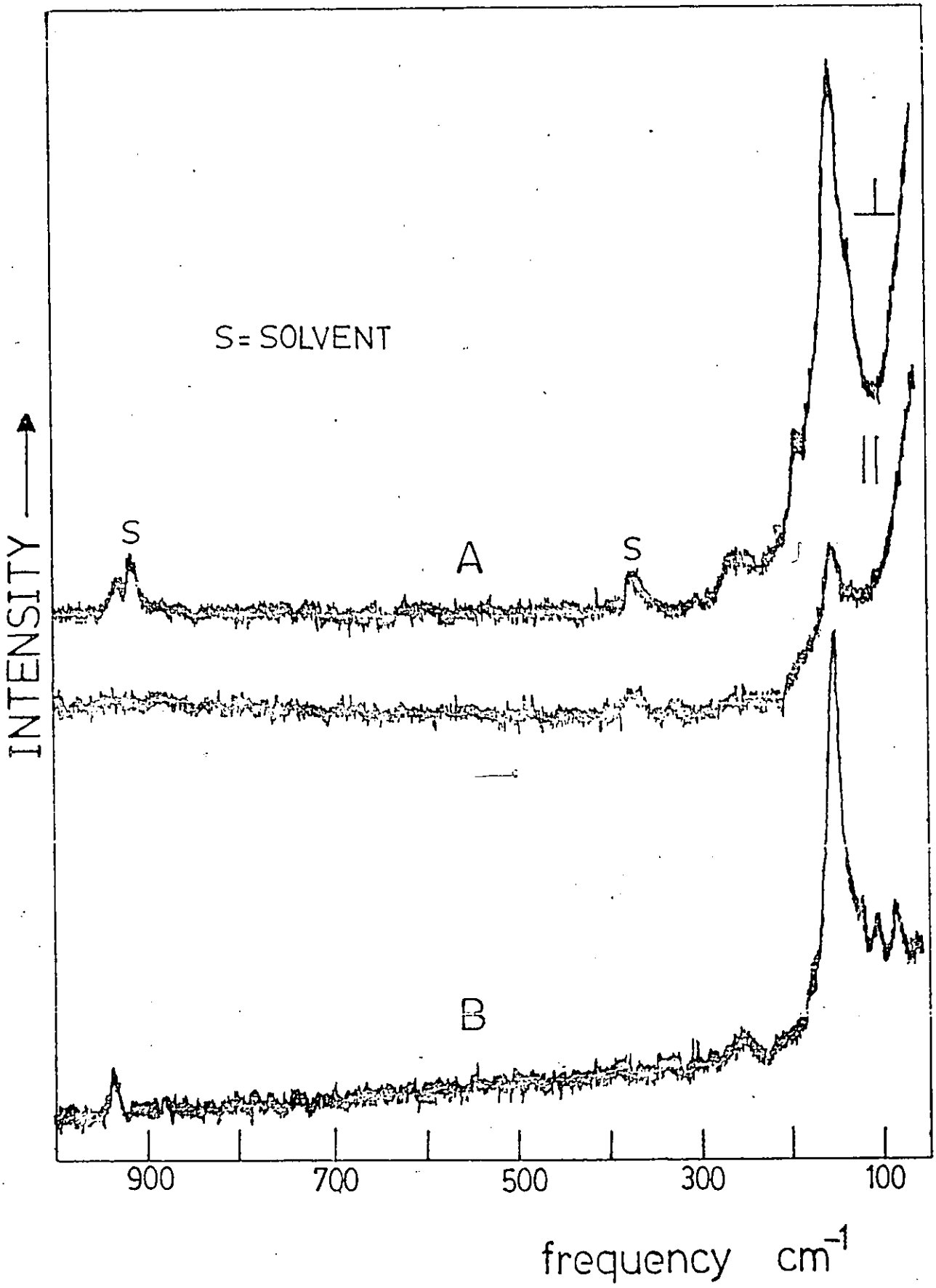
a. $(n\text{-}Bu_4N)_2SeOBr_4$

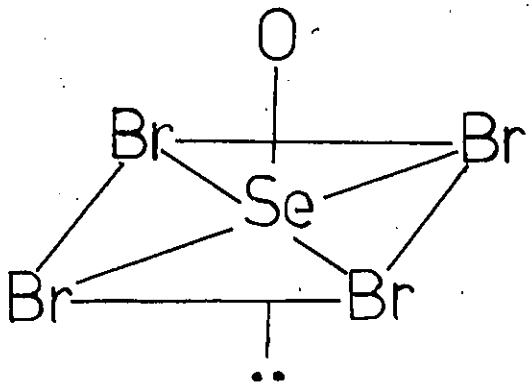
Figure 5

Raman Spectra of $(n\text{-}Bu_4N)_2SeOBr_4$

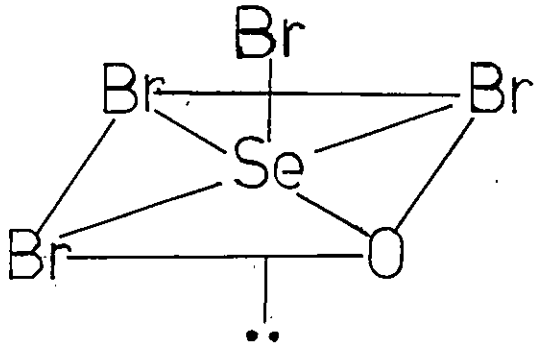
A in acetonitrile

B solid

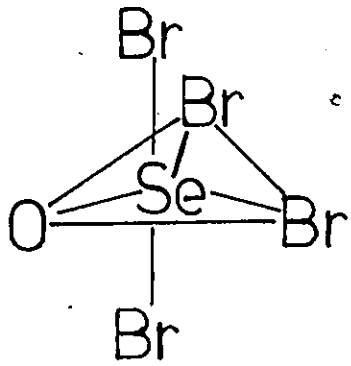

S= SOLVENT
INTENSITY
S
A
S
B
900
700
500
300
100
frequency cm⁻¹




For this $C_{4v}$ structure, nine normal modes are expected. ($\Gamma = 3A_1 + 2B_1 + B_2 + 3E$). The spectra in Fig. 5 show seven definite bands, of which two are clearly polarized. The spectra are more consistent with the $C_{4v}$ structure than with other possible structures such as a square pyramid with the oxygen in the energetically less favourable cis position (to the lone pair), giving this model $C_s$ symmetry with irreducible representation $\Gamma = 8A' + 4A''$.




If the electron pair is stereochemically inactive we could expect a trigonal bipyramidal structure with the oxygen equatorial.




In this case, the symmetry is $C_{2v}$ and 5 polarized bands are expected, $\Gamma = 5A_1 + A_2 + 3B_1 + 3B_2$. In both these latter cases, more polarized bands would be expected than are actually observed in the spectrum of $SeOBr_4^{2-}$ in MeCN.

A partial assignment under $C_{4v}$ symmetry is given in Table IV. On the basis of their intensity and polarization the bands at 932 and 158 $cm^{-1}$ are readily assigned to $\nu_1(A_1)$, the SeO stretching mode, and $\nu_2(A_1)$, the $SeBr_4$ symmetric in phase stretching mode, respectively. The broad peak near 260 $cm^{-1}$ consists of two peaks as shown by the spectrum with the polarization of the incident laser beam rotated 90°. The lower frequency band at 248 $cm^{-1}$ is polarized and belongs to the tetrabutylammonium cation while the band at higher frequency, 265 $cm^{-1}$, is assigned to the SeO deformation, $\nu_8(E)$. The position of this mode is comparable with that of the SeO deformations in $SeOBr_3^-$ (Table III), $SeOCl_3^-$ [10] and $SeOCl_4^{2-}$ [31]. It is difficult to decide whether the shoulder on the low frequency side of $\nu_2(A_1)$ at 141 $cm^{-1}$ is polarized or not but it is unlikely

that it is, since the only remaining $A_1$ mode is the $SeBr_4$ umbrella vibration, $\nu_3(A_1)$, which lies at 142 $cm^{-1}$ in the spectrum of $SeOCl_4^{2-}$ [31], and is expected to lie far below 141 $cm^{-1}$ in the $SeOBr_4^{2-}$ spectrum. The shoulders at 141 and 193 $cm^{-1}$ are assigned instead to the two remaining SeBr vibrations, $\nu_4(B_1)$ and $\nu_7(E)$. Since, in the spectra of the related species $SeCl_5^-$ [10], $TeOF_4^{2-}$ [8] and $TeCl_5^-$ [51], $\nu_4(B_1)$ lies at higher frequency than $\nu_7(E)$, the band at 141 $cm^{-1}$ is assigned to $\nu_7(E)$, the antisymmetric $SeBr_4$ stretching mode and the band at 193 $cm^{-1}$ is assigned to $\nu_4(B_1)$, the symmetric $SeBr_4$ out of phase stretch. The remaining bands at 89 and 110 $cm^{-1}$ may be due to anion deformations but due to their position no clear distinction can be made between these and lattice modes.

Attempts were made to prepare oxotetrabromoselenates(IV) from aqueous solution but only in the case of the tetramethylammonium bromide was a compound of the correct stoichiometry formed. The Raman spectrum of this compound resembles closely the spectrum of the oxotribromoselenate(IV) anion and is therefore listed in Table III. The compound is best formulated as $Me_4NSeOBr_3.Me_4NBr$. Similarly, dipyridinium oxotetrachloroselenate(IV)[30] has been found to be made up of $SeOCl_3^-$ anions with secondary bonding[52] to chloride ions which leaves the trigonal bipyramidal structure of the $SeOCl_3^-$ ion essentially unaltered.

## BROMOCOMPOUNDS OF SELENIUM(IV)

### The pentabromoselenate(IV) anion, $SeBr_5^-$

The spectra of the $SeBr_5^-$ anion show considerable variation in solids, melt and concentrated and dilute solutions in MeCN. The spectra of solid n-$Bu_4NSeBr_5$ and solid $Me_4NSeBr_5$ are shown in Fig. 6. The spectra of a melt of n-$Bu_4NSeBr_5$ and a saturated solution of n-$Bu_4NSeBr_5$ in MeCN are shown in Fig. 7. Fig. 8 shows the spectrum of $SeBr_5^-$ in MeCN. All spectra are listed in Table V. Over the concentration range 0.21 molal to 0.036 molal n-$Bu_4NSeBr_5$ in MeCN the normalized intensities (with respect to the 912 $cm^{-1}$ band of MeCN having an intensity of 1 cm) of the peaks at 150 and 250 $cm^{-1}$ show a linear dependence on concentration (Fig. 9), suggesting a single species in solution. The profile of the spectrum also remains the same. As the concentration of the solute is increased above 0.21 molal the peak at 250 $cm^{-1}$ grows in intensity relative to that at 150$cm^{-1}$ and shifts to lower energy. In addition, a band grows in at 183 $cm^{-1}$. The spectrum of molten n-$Bu_4NSeBr_5$, which melts in the range 58-60°C, is similar to that of the saturated solution although the band at 150 $cm^{-1}$ is much less intense. These changes are attributed to the condensation of the anion to form polymeric species like those formed in the case of $TeCl_5^-$ [53], $TeBr_5^-$ [54] and $BiBr_5^{2-}$ [55], which are all isoelectronic with $SeBr_5^-$ in valence electrons.

$$n SeBr_5^- = (SeBr_5)_n^{n-}$$

Some indication of the formation of bridged species has been found for the pentachloroselenate(IV) anion[10] as well.

Selenium tetrabromide is known to be fully dissociated[56] in a wide range of solvents to give an equilibrium mixture of selenium mono - and dibromides and elementary bromine. In the gas phase, $SeBr_4$ decomposes completely to $SeBr_2$ and $Br_2$. In MeCN, the same holds true according to the reaction,

$$SeBr_4 = SeBr_2 + Br_2(l)$$

Further decomposition to $Se_2Br_2$ is a minor reaction, if it occurs at all in MeCN. The pentabromoselenate (IV) anion may undergo related reactions,

$$SeBr_5^- = SeBr_3^- + Br_2 \quad (2)$$

or

$$SeBr_5^- = SeBr_2 + Br_3^- \quad (3)$$

Another possible decomposition reaction, which does not involve a change of valence of selenium is

$$2SeBr_5^- = SeBr_4 + SeBr_6^{2-} \quad (4)$$

followed by a subsequent decomposition according to (1). Solutions of $Br_2$ in MeCN where $[Br_2]$ = 2.43 molal indicate that the band due to bromine at 304 $cm^{-1}$ is approximately 8 times more intense than the 375 $cm^{-1}$ band of the solvent MeCN. If reactions (2) or (4) proceed to completion, the expected bromine concentrations for the 0.206 molal $SeBr_5^-$ solution, the spectrum of which is shown in Fig. 8, would be respectively 0.206 molal and 0.103 molal in bromine: At these concentrations any band due to bromine would be readily noticed. Since no band is observed at 304 $cm^{-1}$, bromine cannot be an important component. Equilibrium (3) could, however, be occuring in solutions of $n\text{-}Bu_4NSeBr_5$, since a peak at 280 $cm^{-1}$ is observed in Fig. 8, which is the frequency of the strongest band characteristic for $SeBr_2$ [57]. The concentration of $SeBr_2$ in this solution is estimated to be 0.05m on the basis of quantitative measurements of the Raman spectrum of $SeBr_2$ in MeCN[57]. The spectrum in Fig. 8 is, however, due for the most part to the $SeBr_5^-$ anion. Any bands due to $Br_3^-$ in this solution would be masked since they are not intense and occur at 160 and 190 $cm^{-1}$ [58].

The isolated $SeBr_5^-$ anion is expected to have $C_{4v}$ symmetry ($\Gamma = 3A_1 + 2B_1 + B_2 + 3E$) just as is the case with $SeCl_5^-$ [10].

Figure 6.

Raman Spectra of solid $SeBr_5^-$ compounds

A $n\text{-}Bu_4NSeBr_5$

B $Me_4NSeBr_5$

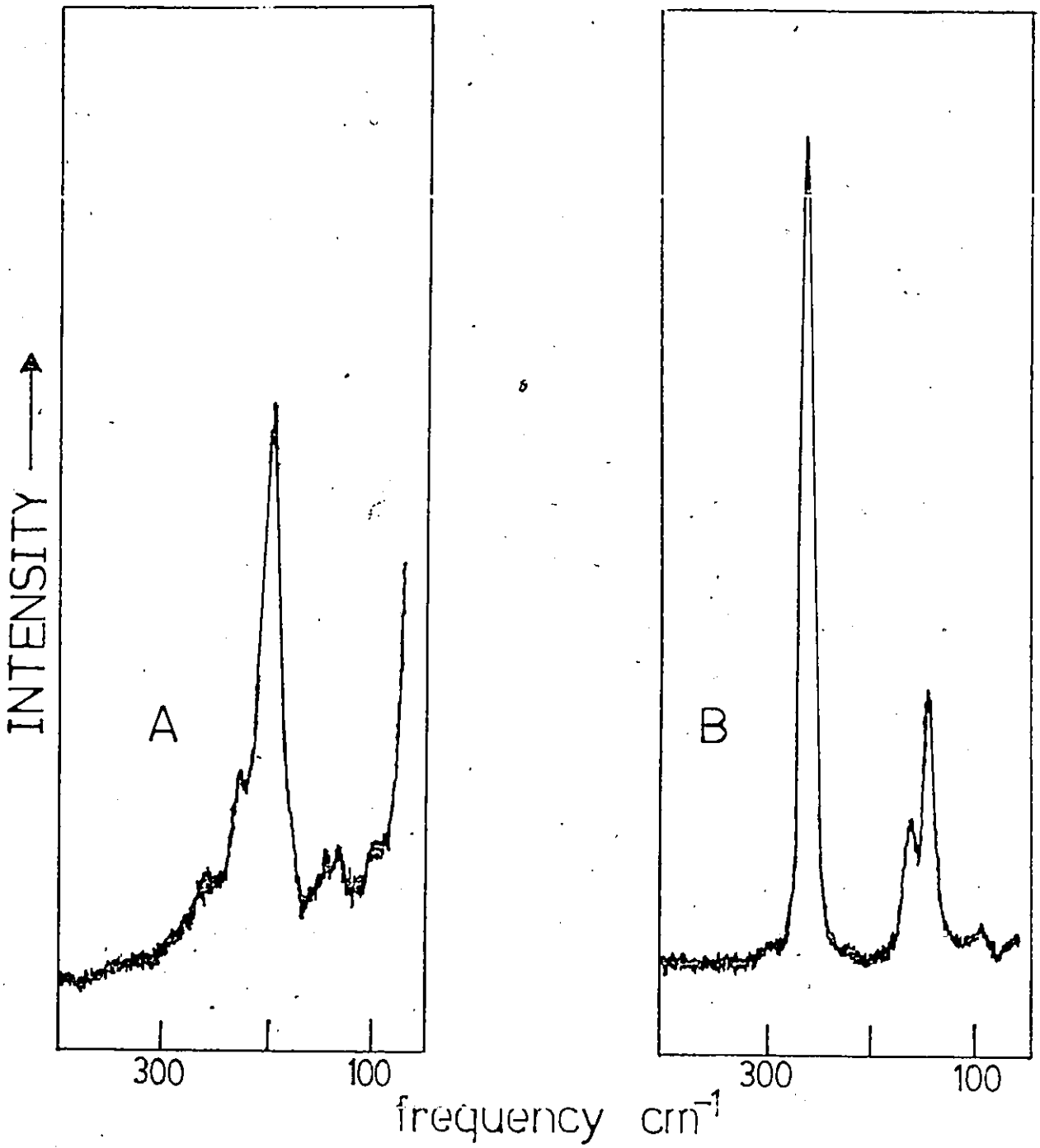

INTENSITY
A
B
300
100
300
100
frequency cm⁻¹

Figure 7

Raman Spectra of n-$Bu_4NSeBr_5$

A as a melt

B saturated in acetonitrile

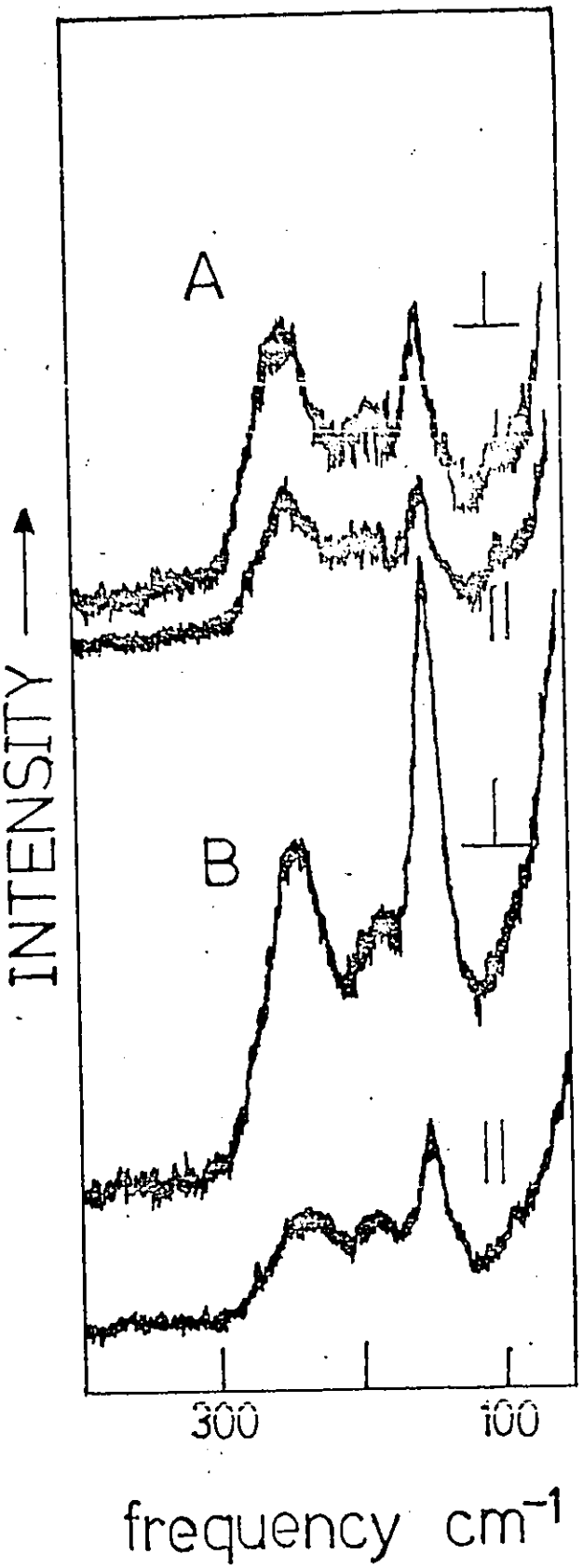

A
B
⊥
∥
⊥
∥
INTENSITY
300
100
frequency cm⁻¹

Figure 8

Raman Spectrum of $SeBr_5^-$ in acetonitrile

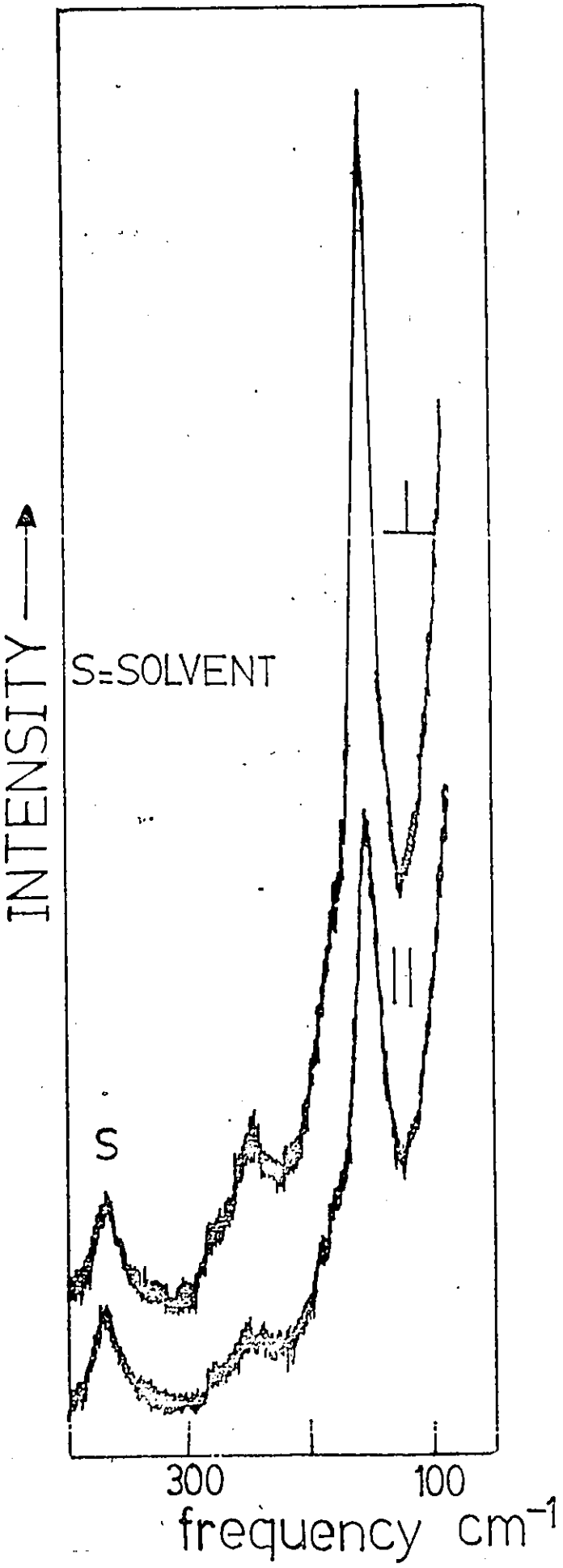
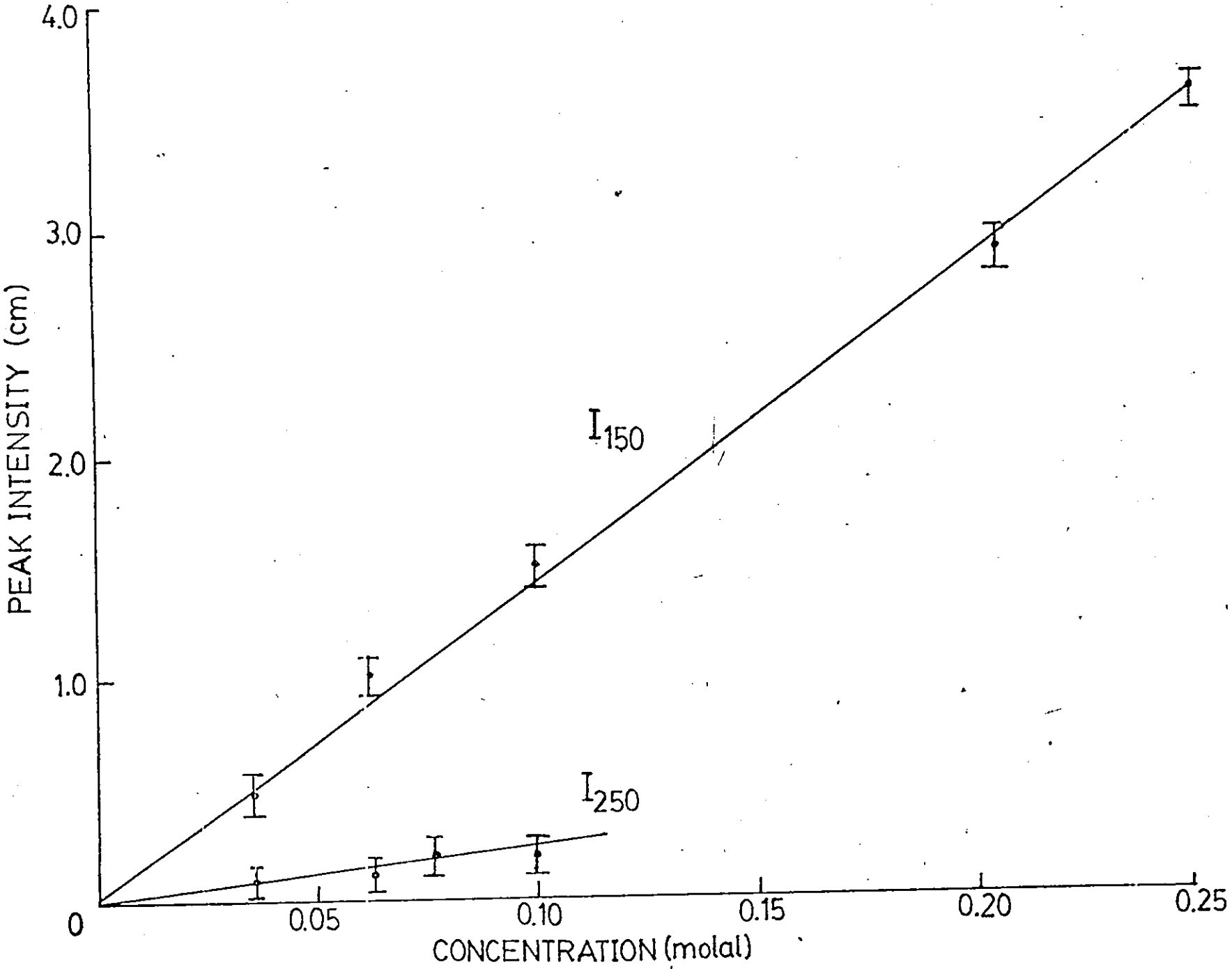
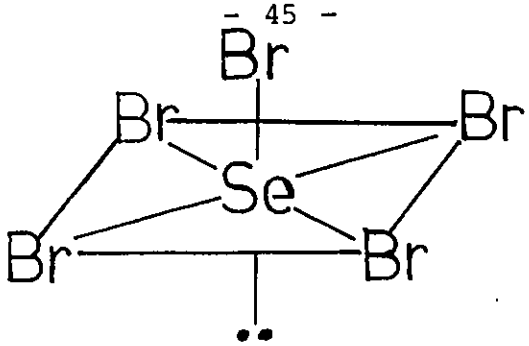

INTENSITY
S=SOLVENT
S
300
100
frequency cm⁻¹

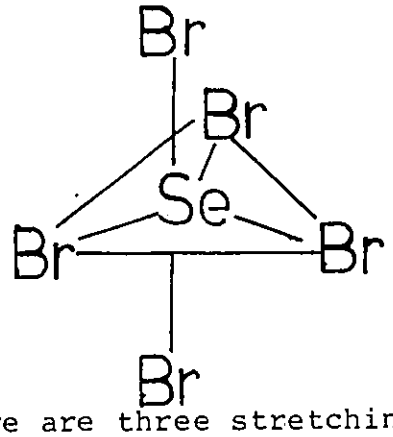
Figure 9

Plot of normalized intensities of the bands at 150 and 250 $cm^{-1}$ in $SeBr_5^-$ versus concentration


4.0
3.0
2.0
1.0
0
PEAK INTENSITY (cm)
I150
I250
0.05
0.10
0.15
0.20
0.25
CONCENTRATION (molal)




All nine vibrational modes will be active in the Raman spectrum and of these, three will be polarized. In the spectrum of $SeBr_5^-$ in MeCN, we find that there are 3 polarized bands and one single depolarized band. This observation is not consistent with a trigonal bipyramidal geometry ($D_{3h}$; $\Gamma = 2A_1 + 2A_2'' + 3E' + E''$) which would arise if the lone electron pair were stereochemically inactive.




In this model, there are three stretching modes active in the Raman effect, two of which are polarized, and all of the deformations are depolarized.

Thus, the spectra are more consistent with the $C_{4v}$ structure. In the spectrum of a square pyramidal species, the axial ligand stretching vibration, $\nu_1(A_1)$, has the highest frequency. In $SeBr_5^-$ this mode is assigned to the band at 247 $cm^{-1}$. The most intense band, at 151 $cm^{-1}$, which is also polarized, is readily assigned to the symmetric in

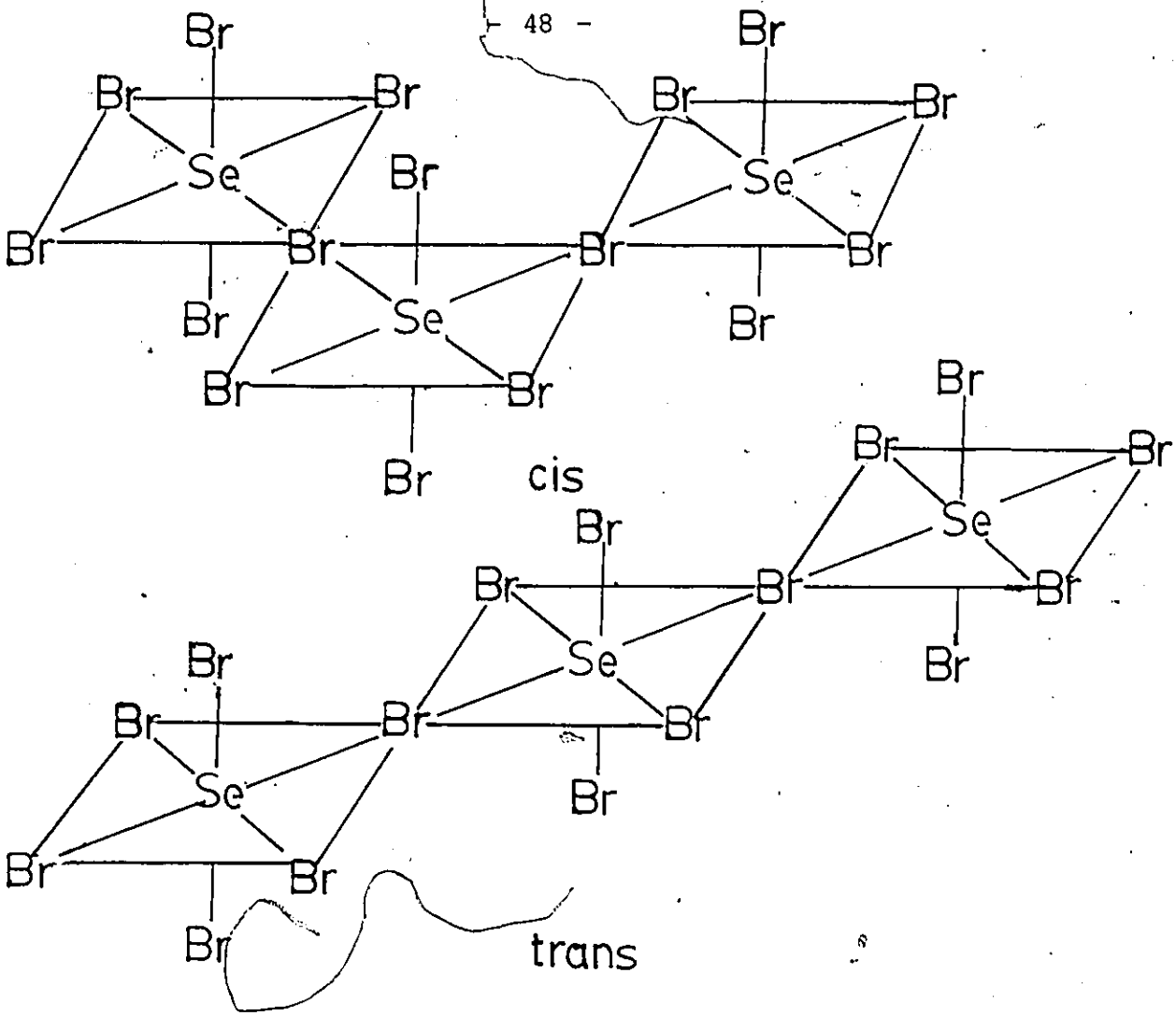
Table V. Raman spectra of the pentabromoselenate(IV) anion

| $Me_4NSeBr_5$ | $n\text{-}Bu_4NSeBr_5$ (solid) | $n\text{-}Bu_4NSeBr_5$ (molten, 60°C) | $n\text{-}Bu_4NSeBr_5$ (Sat'd in MeCN | $SeBr_5^-$ in MeCN[a] | Assignment Mode No. | Description |
|---|---|---|---|---|---|---|
| 95(0) | 98(0) | 98(1) | 95(0,br) | 112(1,p?) | $\nu_3(A_1)$ | $\delta_s(SeBr_4$, umbrella) |
| 147(3) | 132(1) | - | - | | | |
| 163(1) | 145(1) | 152(10,p) | 151(10,p) | 151(10,p) | $\nu_2(A_1)$ | $\nu(SeBr_4$, in phase) |
| - | 196(10) | 190(2) | 190(2) | 180(2,sh) | $\nu_4(B_1)$ | $\nu(SeBr_4$, out of phase) |
| 220(0) | 228(3) | - | - | | | |
| 261(10) | 257(2) | 248(10,p,br) | 243(7,p,br) | 247(2,p) | $\nu_1(A_1)$ | $\nu(SeBr_{ax})$ |
| 295(0) | - | 280(1,sh) | - | 280(1,sh) | | $\nu$(SeBr in $SeBr_2$) |

a. 0.21m $n\text{-}Bu_4NSeBr_5$

phase $SeBr_4$ stretching vibration, $\nu_2(A_1)$. The third polarized mode at 112 $cm^{-1}$ is assigned to the last $A_1$ mode, the umbrella deformation, $\nu_3(A_1)$. The only depolarized band, that at 180 $cm^{-1}$, is assigned to the symmetric out of phase $SeBr_4$ stretching vibration, $\nu_4(B_1)$. Since this is the only depolarized band seen and is expected to be more intense than the antisymmetric $SeBr_4$ stretching mode, $\nu_7(E)$, as in the case of $SeCl_5^-$ [10], this assignment is preferred over $\nu_7(E)$. In $SeCl_5^-$, the antisymmetric $SeCl_4$ stretching vibration, $\nu_7(E)$, lies very close to the symmetric out of phase stretch, $\nu_4(B_1)$, and in $SeOCl_4^{2-}$ [31] these two modes are coincident. However, in $SeOBr_4^{2-}$ the corresponding $\nu_7(E)$ mode is expected to lie at much lower frequency than $\nu_4(B_1)$ and hence $\nu_7(E)$ is not seen in the spectrum of $SeBr_5^-$. The $\nu_7(E)$ mode, since it lies at low frequency, may be lost in the Rayleigh scattered background (Fig. 8).

The spectra of solid $Me_4NSeBr_5$ and $n\text{-}Bu_4NSeBr_5$, listed in Table V and shown in Fig. 6, exhibit little parallel with each other or with the dilute solution spectra although the strongest peaks in the spectra of both solids are observed in the spectra of the saturated solution in MeCN and the melt of $n\text{-}Bu_4NSeBr_5$ (Fig. 7). Several structures may be adopted by the $SeBr_5^-$ anion in condensed form. The polymer may be cis or trans bridged.




The crystal structure of $PCl_4^+TeCl_5^-$ shows $[TeCl_5^-]_n$ chains with cis bridging and overall pseudooctahedral coordination of Te[53]. The chloride bridges in the structure are symmetric and have relatively long Te-Cl bonds while the Te-Cl bonds trans to the bridging chlorides and the Te-Cl bonds above and below the bridging plane are short. The cubane like $Te_4Br_{16}$ [54], which is isomorphous with $SeBr_4$, can be reacted with bromide to form monomeric and oligomeric halogenotellurates. The dimeric $Te_2Br_{10}^{2-}$ anion[54] consists of two distorted $TeBr_6$ octahedra sharing an edge. It is not possible to determine unequivocally between the two

structures proposed for $(SeBr_5)_n^{n-}$. The isoelectronic species, $BiBr_5^{2-}$ [59], has been studied by vibrational spectroscopy and found to have overall $C_{2v}$ site symmetry although it has pseudooctahedral coordination around bismuth and has two bridging bromines.

When dilute solutions of $Me_4NSeBr_5$ are made up in aqueous medium, some elemental bromine is expelled, as is indicated by the oxidation of iodide ion giving the $CCl_4$ layer a light reddish color upon vigorous shaking. This does not occur with n-$Bu_4NSeBr_5$. At first, it was thought that there may be some molecular bromine bridging as is the case in $Sb_2Br_9^{3-}$ [60]. However, when $Me_4NSeBr_5$ is dissolved in MeCN, a solvent which it is not very soluble in, no band due to elemental bromine is seen in the Raman spectrum. An attempt to form the isoelectronic analogue to $Sb_2Br_9^{3-}$, $Se_2Br_9^-$ in MeCN solution, leads only to an increase in the intensity of the bands at 280 $cm^{-1}$ and 304 $cm^{-1}$ relative to the bands due to $SeBr_5^-$, indicating the presence of $SeBr_4$ in equilibrium with $SeBr_2$ and $Br_2$ (equation 1). However, when concentrated solutions of $Me_4NSeBr_5$ in aqueous solution are made up, the presence of bromine is more obvious in the $CCl_4$ layer. Concentrated solutions yield low bromide analyses.

Possibly, in the case of $Me_4NSeBr_5$, an adduct exists as it does in Quinuclidinium Dodecabromantimon(III) antimon(V)ate-2-Dibromine, $(C_7H_{13}NH)_4Sb^{III}Sb^{V}Br_{12}.2Br_2$ [61].

The crystals of this compound consist of cations, $SbBr_6^{3-}$ and $SbBr_6^-$ anions and molecular bromine which bridges adjacent anions. We can only speculate that the larger cation stabilizes the $SeBr_5^-$ anion to a greater extent and that in $Me_4NSeBr_5$ some of the Se-Br bonds are more labile than in $n\text{-}Bu_4NSeBr_5$ leading to the evolution of elemental bromine when a large amount of $Me_4NSeBr_5$ is dissolved in aqueous medium.

The hexabromoselenate(IV) anion, $SeBr_6^{2-}$

A non-octahedral structure is predicted for $AX_6E$ molecules by the valence shell electron pair repulsion (VSEPR) theory[2]. The theory states that they should be based on a seven coordinate structure with a lone pair of electrons in one of the positions. Despite the prediction by VSEPR theory, many $AX_6E$ molecules exhibit octahedral symmetry. In fact, more examples are currently known where the lone pair is stereochemically inactive[38] than where it is active. However, one example, $XeF_6$ [38], is known to have a distorted structure. Gillespie explains the failure of VSEPR theory as due to ligand-ligand repulsions dominating the stereochemistry.

The Raman spectra of solid $Cs_2SeBr_6$ and $(Et_4N)_2SeBr_6$ are shown in Fig. 10. The spectrum of $(Et_4N)_2SeBr_6$ in MeCN is shown in Fig. 11 and all spectra are listed in Table VI. There is no evidence in the solution

Table VI. Raman spectra of the hexabromoselenate(IV) anion

| $Cs_2SeBr_6$[a] | $(Et_4N)_2SeBr_6$[a] | $SeBr_6^{2-}$ in MeCN[b,c] | Assignment |
|---|---|---|---|
| 98(7) | 90(3) | - | $\nu_5(T_{2g})$ |
| 145(5) | 143(10) | 153(10,p) | $\nu_1(A_{1g})$ |
| 162(10) | 160(7) | 165(2,sh) | $\nu_2(E_g)$ |

a. Exciting line 632.8nm

b. Exciting line 514.5nm

c. $(Et_4N)_2SeBr_6$

Figure 10

Raman Spectra of solid $SeBr_6^{2-}$ compounds

A $Cs_2SeBr_6$

B $(Et_4N)_2SeBr_6$

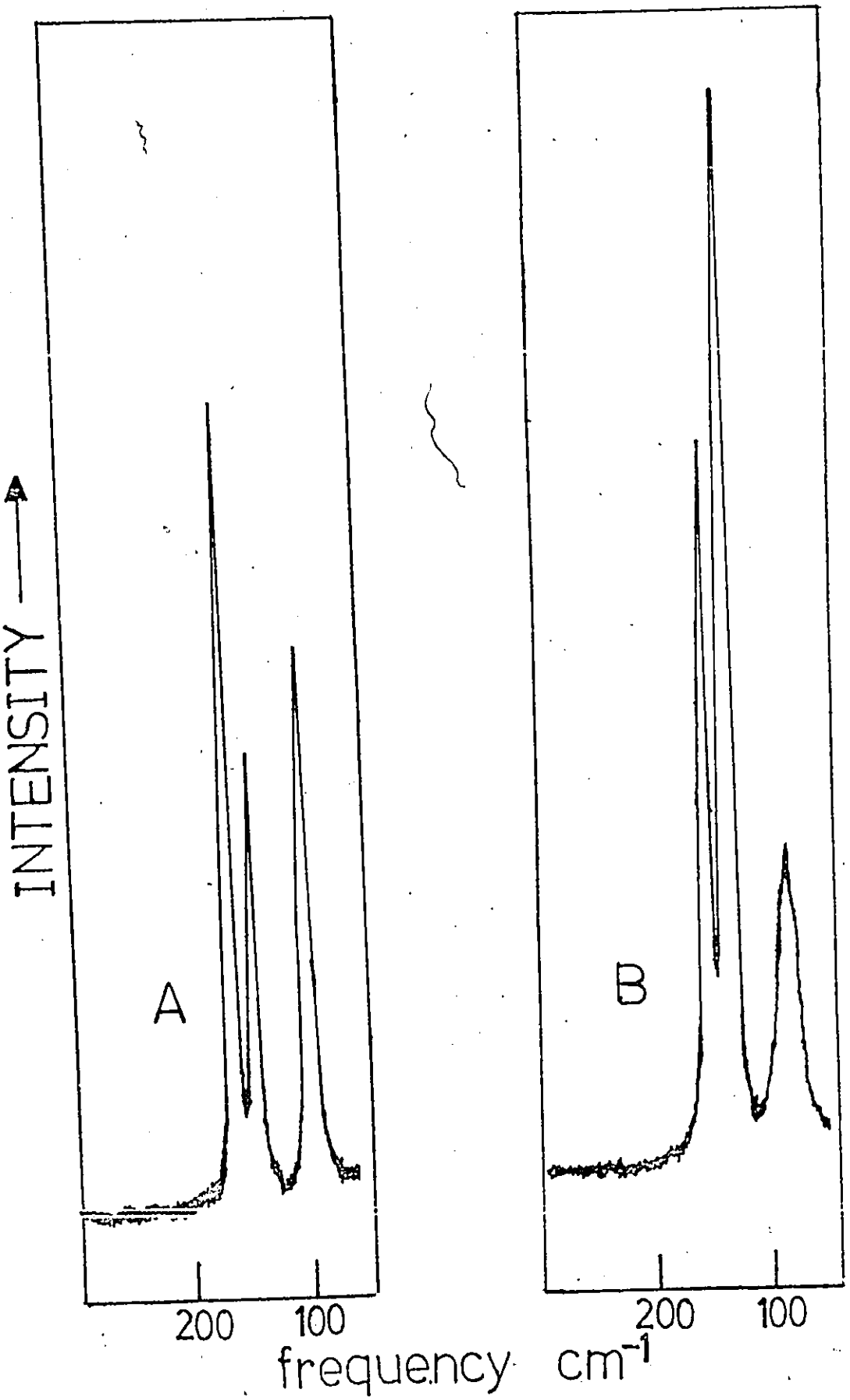
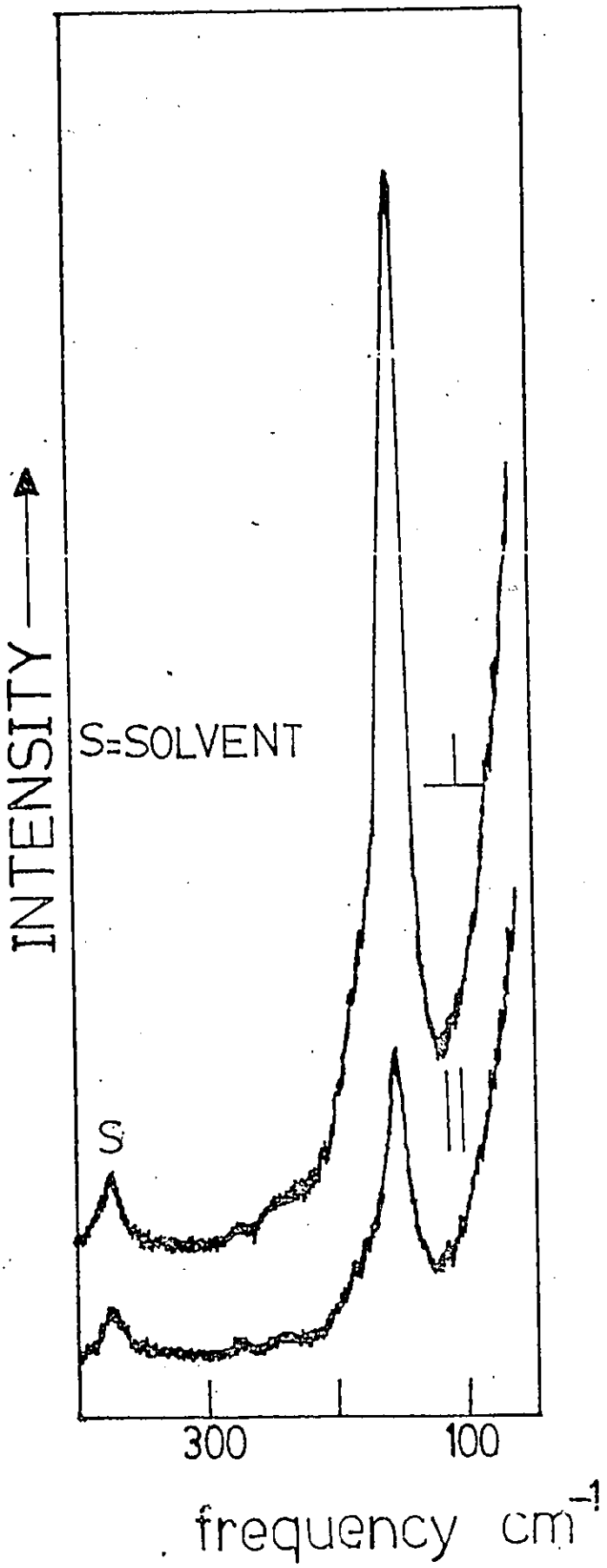

INTENSITY
A
B
200
100
200
100
frequency cm⁻¹

Figure 11

Raman spectrum of $(Et_4N)_2SeBr_6$

in acetonitrile


INTENSITY
S=SOLVENT
S
300
100
frequency cm⁻¹

spectrum for decomposition to Se(II) as observed for $SeBr_4$ and, to a lesser extent, $SeBr_5^-$ in MeCN. It seems that the most highly coordinated and symmetric a central atom is, the more stable the species is. The Raman spectrum of the $SeBr_6^{2-}$ anion has been reported by Hendra and Jovic[35], who assigned the stronger band in the spectrum of $Cs_2SeBr_6$ at 162 $cm^{-1}$ to $\nu_1(A_{1g})$ following the order of frequency $\nu_1(A_{1g}) > \nu_2(E_g)$ for all of the hexahalometallates which have been studied. In the high resolution spectrum of $(Et_4N)_2SeBr_6$ in MeCN there is a shoulder to high frequency of the strongest peak at 153 $cm^{-1}$. It is the band at 153 $cm^{-1}$ which is polarized and therefore belongs to $\nu_1(A_{1g})$ while the shoulder at 165 $cm^{-1}$ is $\nu_2(E_g)$. The relative intensities of these two bands remain the same in the spectrum of solid $(Et_4N)_2SeBr_6$ but the relative intensities are reversed in the spectrum of $Cs_2SeBr_6$. This cannot be due to intensity borrowing since the two modes are of different class. The observation of the $E_g$ mode a higher frequency than the $A_{1g}$ mode is truly an exception compared to previous assignments of hexahalometallates with octahedral symmetry[35,38].

## BROMOSELENATE(IV) EQUILIBRIA IN AQUEOUS HYDROBROMIC ACID

Seleninyl halides have been shown by Raman spectroscopy to be formed in solutions of selenium dioxide in hydrofluoric[40], hydrochloric[35,41,42] and hydrobromic[44] acids. In the case of seleninyl chloride[42], an equilibrium constant of $3.2 \times 10^{-6} mol^{-2} L^2$ has been determined for the equilibrium.

$$H_2SeO_3 + 2HCl = SeOCl_2 + 2H_2O$$

The Raman spectra of selenium dioxide in hydrobromic acid have been studied[35,44] and these solutions have shown to consist chiefly of $SeOBr_2$, $SeBr_5^-$ and $SeBr_6^{2-}$. However, no quantitative measurements have been made on these solutions. Morever, the spectra of the actual $SeO_2Br^-$, $SeOBr_3^-$, $SeOBr_4^{2-}$ and $SeBr_5^-$ anions were not considered in the earlier work, nor were polarization measurements made, which strengthen the interpretation. In view of this, the present study was undertaken to determine what species are present in these solutions on the basis of the information obtained on various bromoselenate(IV) anions in solids and aprotic media and also to determine quantitatively if equilibrium constants can be evaluated.

The Raman spectra of 1.0M solutions of selenium dioxide in hydrobromic acid over an HBr concentration range 0-8.9M, namely those at 8.9, 7.0, 5.0, 3.0 and OM HBr, are shown in Fig. 12 and the bands of the 8.9M hydrobromic acid

solution are listed in Table VII along with the bands belonging to $SeO_2Br^-$, $SeOBr_2$, $SeOBr_3^-$, $SeOBr_4^{2-}$, $SeBr_5^-$ and $SeBr_6^{2-}$ in acetonitrile and their relative intensities. The 1.0M $SeO_2$ in 8.9M HBr solution spectrum is listed in Table VII since this spectrum displays bands corresponding to all the different species which occur in these hydrobromic acid solutions and does not contain any selenious acid. This will become evident later in the chapter.

The spectrum of the 1.0M $SeO_2$ in 0M HBr solution, shown in Fig. 12, is that of selenious acid. As the concentration of hydrobromic acid is increased, starting at 3.0M HBr, there is an increase in the intensity of the peaks in the region 100-300 $cm^{-1}$, the region of SeBr stretching modes. At concentrations of hydrobromic acid greater than 3.0M the intensity of the SeO single bond peak, at 695 $cm^{-1}$, falls as the SeBr bond intensity increases. The new bromo species present here has an SeO double bond, as can be seen by the increase of the SeO double bond stretch intensity, at 900 $cm^{-1}$, relative to the SeO single bond stretch intensity with increase in hydrobromic acid concentration, and is the major component in these solutions up to a hydrobromic acid concentration of 5.0M. Comparison of the spectrum of $SeOBr_2$ in MeCN, listed in Table VII, with that of the 1.0M $SeO_2$ in 5.0M HBr solution shows that $SeOBr_2$ is the principal species in the HBr solution. The possibility of having any

Figure 12

Raman Spectra of 1.0M $SeO_2$ solutions in aqueous HBr

A 1.0M $SeO_2$ in 8.9M HBr

B 1.0M $SeO_2$ in 7.0M HBr

C 1.0M $SeO_2$ in 5.0M HBr

D 1.0M $SeO_2$ in 3.0M HBr

E 1.0M $SeO_2$ in 0M HBr (1.0M $H_2SeO_3$)

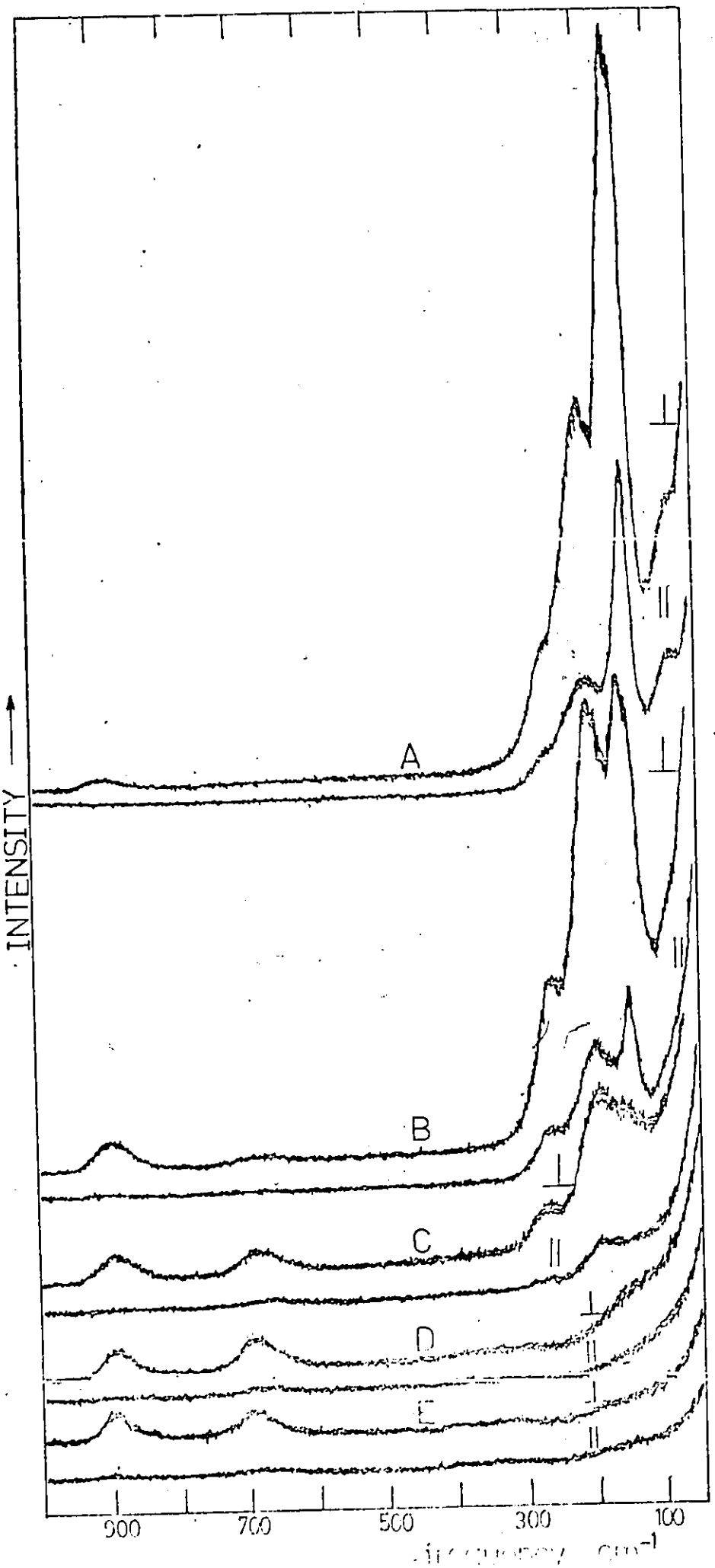

INTENSITY
A
B
C
D
E
⊥
∥
900
700
500
300
100

Table VII. Raman spectra of bromoselenium (IV) species[a].

| $SeO_2Br^-$ [b] | $SeOBr_3^-$ [c] | $SeOBr_4^{2-}$ [d] | $SeBr_5^-$ [e] | $SeBr_6^{2-}$ [f] | $SeOBr_2$ [g] | 1 Molar $SeO_2$ in 8.9MHBr |
|---|---|---|---|---|---|---|
| | | | | | 90(7,p) | 80(0,p?) |
| | | | 112(1,p?) | | | |
| 139(10,p) | 138(10,p) | 141(5,p?) | | | | |
| | | | 151(10,p) | | | 145(9,p) |
| | 155(8,dp) | 158(10,p) | | 153(10,p) | | 155(10,p) |
| | | | | 165(2,sh) | | |
| | | | 180(2,sh) | | | |
| | 194(8,p) | 193(3,dp) | | | 194(2,dp) | 190(5,p?) |
| | | | | | 218(10,p) | 205(6,p) |
| 249(1,p) | 253(2,p?) | | 247(2,p) | | | |
| | 265(3,p) | 265(2,dp) | 280(1,sh) | | 279(9,p) | 265(2,p) |
| 888(6,p) | 936(1,p) | 932(1,p) | | | 955(2,p) | 900(0,p) |

a. Solution spectra in MeCN
b. Table I
c. Table III
d. Table IV
e. Table V
f. Table VI
g. Table II

$SeO_2Br^-$ ion in the 1.0M $SeO_2$ in 5.0M HBr solution can be ruled out as an important species on the basis of the absence of a very prominent band at 139 $cm^{-1}$, due to the $\nu_2(A')$ (Table I) mode of this ion. We would also expect to see an antisymmetric SeO stretch at approximately 814 $cm^{-1}$. The Raman spectrum of the $SeOBr_3^-$ ion in acetonitrile is quite different from that of the 1.0M selenium dioxide in 5.0M hydrobromic acid solution, especially with respect to peak intensities and polarizations. If the highest frequency SeBr vibrational band in the 1.0M $SeO_2$ in 5.0M HBr solution, at 265 $cm^{-1}$, were due in part to the $SeOBr_3^-$ ion in this solution, a very intense polarized band at 138 $cm^{-1}$, $\nu_5(A')$ (Table III) would be expected. Since this band is not clearly distinguished in this spectrum, the presence of relatively large concentrations of the $SeOBr_3^-$ ion can be ruled out. Another strong band due to the $SeOBr_3^-$ anion at 194 $cm^{-1}$, $\nu_3(A')$ (Table III), which is polarized, would also be expected. Similarly, the band at 265 $cm^{-1}$ in the $SeO_2$ in HBr solution corresponds well in frequency with the band at 265 $cm^{-1}$ in the solution spectrum of the $SeOBr_4^{2-}$ ion (Fig. 5). However, in the spectrum of $SeOBr_4^{2-}$ in MeCN, the peak at 265 $cm^{-1}$ is due to the $\nu_8(E)$ (Table IV) mode and is depolarized, whereas in the HBr solution the band at 265 $cm^{-1}$ is polarized. In addition, if this band were due to the $SeOBr_4^{2-}$ ion in solution then,

along with a strong polarized band at 158 $cm^{-1}$, $\nu_2(A_1)$ (Table IV), we would expect a strongly depolarized band at 141 $cm^{-1}$ due to the $\nu_7(E)$ mode of $SeOBr_4^{2-}$ in MeCN. On this basis, the $SeOBr_4^{2-}$ ion cannot be present in significant quantities in this solution. The most intense peaks in the spectrum of the 1.0M $SeO_2$ in 8.9M HBr solution, at 145 and 155 $cm^{-1}$, can be shown to be due, respectively, to the $\nu_2(A_1)$ (Table V) mode of the $SeBr_5^-$ ion in MeCN and to the $\nu_1(A_{1g})$ (Table VI) mode of the $SeBr_6^{2-}$ ion in MeCN at 153 $cm^{-1}$. By comparison, these bands can be seen to be virtually non-existent in the 1.0M $SeO_2$ in 5.0M HBr solution. Therefore, the 1.0M $SeO_2$ in 5.0M HBr solution consists almost entirely of $SeOBr_2$ and $H_2SeO_3$. The equilibrium occurring in the 1.0M $SeO_2$ in 0 to 5.0M HBr solutions is

$$H_2SeO_3 + 2HBr = SeOBr_2 + 2H_2O \quad (1)$$

For purposes of determining the concentrations of the various Se(IV) species in hydrobromic acid solutions, it was necessary to measure the molar intensities of the SeO double and combined single bond stretching mode peaks (896 and 695 $cm^{-1}$, respectively) and the combined deformation modes (100 - 400 $cm^{-1}$) of selenious acid. In spite of the complex condensation equilibrium known to occur in these solutions[62], the dependence of intensity on concentration

for these peaks is known to be linear over the range 0 - 2.0 molar selenious acid in $H_2O$ (Fig. 13). It should be noted, as it was in the experimental section, that all spectral intensities were normalized by comparison to perchloric acid solutions which were run after each selenium dioxide-hydrobromic acid solution. The normalization assumption was that the 925 $cm^{-1}$ band of a 1.0M perchloric acid solution had an area intensity of $lin^2$ (6.45$cm^2$). A plot of the intensity of the 925 $cm^{-1}$ band of perchloric acid against concentration is shown to be linear up to 5.76M perchloric acid (Fig. 14). The measured normalized peak intensities for the SeBr stretching region (100 - 300 $cm^{-1}$), the SeO double bond and the SeO single bond frequencies for all $SeO_2$ in HBr solutions studied, are listed in Table VIII.

From the measurement of normalized peak intensities and a knowledge of molar peak intensities, the concentrations of the species present may be determined and the equilibrium constant calculated[63]. The equilibrium constant for equation 1 is given by

$$K = \frac{[SeOBr_2]\ a^2_w}{[H_2SeO_3]\ a^2_{HBr}} \qquad (2)$$

Figure 13

Plot of integrated peak intensities of the

896 and 695 $cm^{-1}$ bands in $H_2SeO_3$ versus concentration

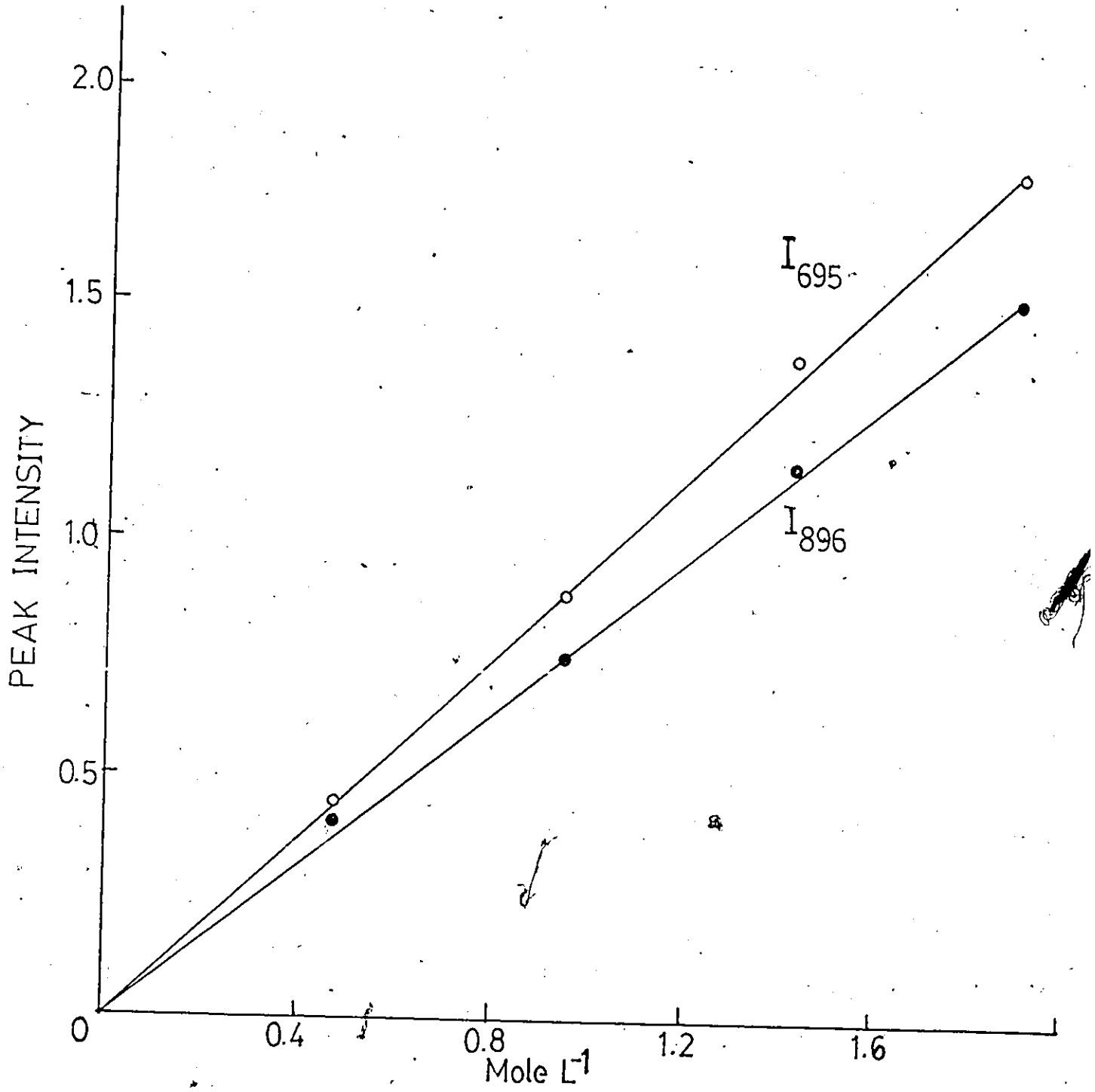

2.0
1.5
1.0
0.5
0
PEAK INTENSITY
$I_{695}$
$I_{896}$
0.4
0.8
1.2
1.6
Mole $L^{-1}$

Figure 14

Plot of Integrated Peak Intensities of the

925 $cm^{-1}$ band in $HClO_4$ versus concentration

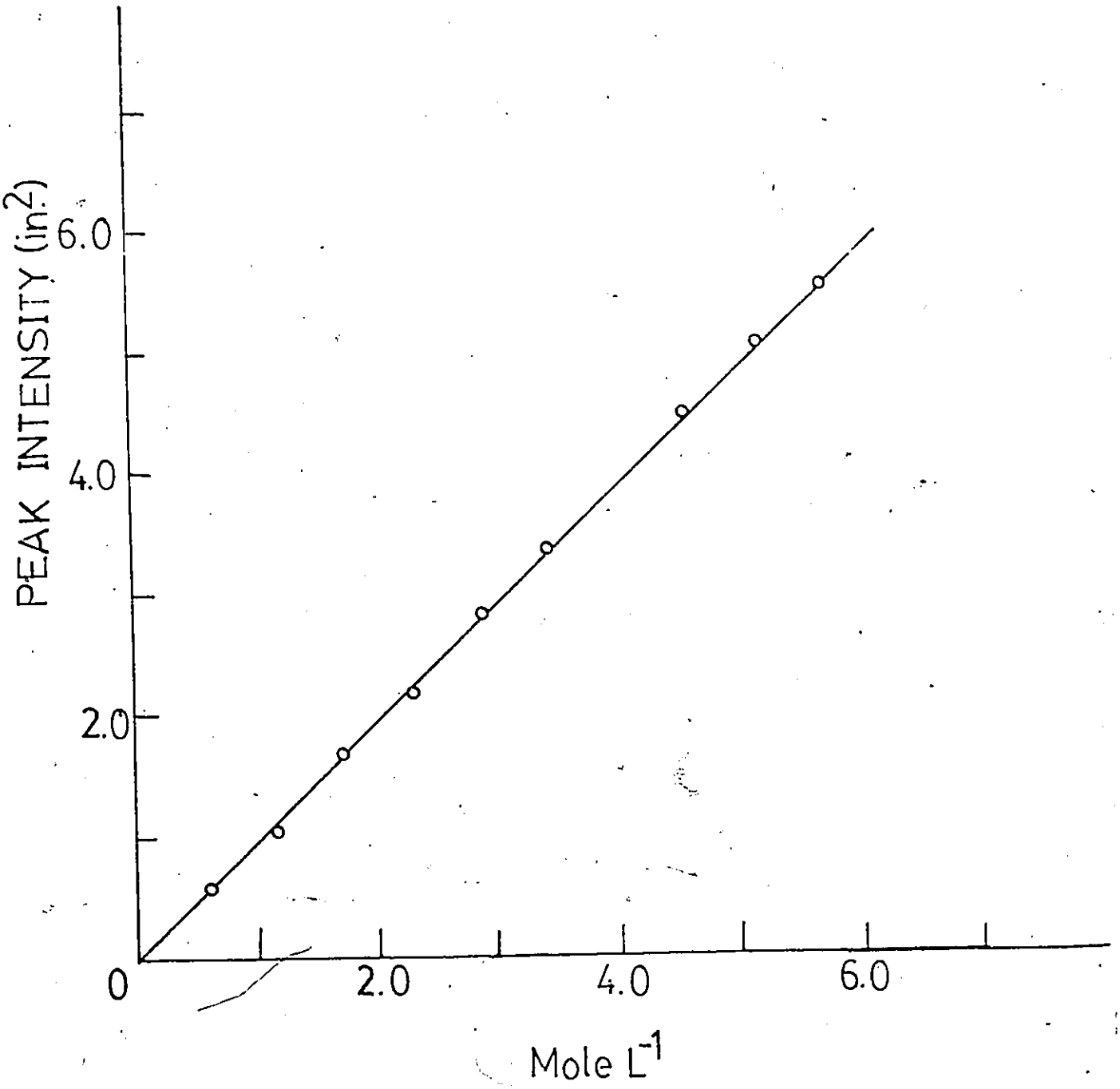

PEAK INTENSITY (in.2)
6.0
4.0
2.0
0
2.0
4.0
6.0
Mole L-1

Table VIII Values of Normalized Intensities for Solutions of Selenium Dioxide in Hydrobromic Acid

| Solution | $I_{SeBr}(cm^2)$ | $I_{Se=O}(cm^2)$ | $I_{Se-O}(cm^2)$ |
|---|---|---|---|
| 1.0M $SeO_2$ in 8.9M HBr | 194.78 | 2.99 | - |
| 1.0M $SeO_2$ in 8.0M HBr | 217.46 | 6.94 | - |
| 1.0M $SeO_2$ in 7.0M HBr | 181.43 | 8.95 | 3.05 |
| 1.0M $SeO_2$ in 6.0M HBr | 96.90 | 7.15 | 2.43 |
| 0.776M $SeO_2$ in 6.0M HBr | 92.71 | 6.67 | 3.41 |
| 0.513M $SeO_2$ in 6.0M HBr | 68.04 | 4.07 | 2.02 |
| 0.260M $SeO_2$ in 6.0M HBr | 49.33 | 2.96 | - |
| 1.0M $SeO_2$ in 5.0M HBr | 27.90 | 5.26 | 5.54 |
| 1.0M $SeO_2$ in 4.5M HBr | 17.39 | 6.00 | 6.20 |
| 1.0M $SeO_2$ in 4.0M HBr | 10.17 | 4.65 | 5.37 |
| 1.0M $SeO_2$ in 3.5M HBr | 8.81 | 5.43 | 7.73 |
| 1.0M $SeO_2$ in 3.0M HBr | 6.17 | 4.35 | 6.76 |
| 1.0M $SeO_2$ in 2.0M HBr | 5.28 | 4.26 | 5.22 |
| 1.0M $SeO_2$ in 1.0M HBr | 3.45 | 4.75 | 6.37 |

where $a_w$ is the rational activity of water and $a_{HBr}$ is the molar activity of hydrobromic acid. The activity coefficients of seleninyl bromide and selenious acid are assumed to be equal. From a knowledge of the concentration of seleninyl bromide or selenious acid and the solution stoichiometry, the concentration of all other species may be calculated. From the hydrobromic acid concentration both $a_{HBr}$ and $a_w$ may be obtained from data of Haase, Naas and Thumm[64]. The activities reported by these authors were given as molal activities of HBr and were converted to molar activities using density data[65]. The values of $C_{HBr}$ and $a_w$ are listed in Table IX. The concentration of selenious acid may be determined from the intensity of the band at 695 $cm^{-1}$, assuming no other bromoselenate(IV) in solution exhibits an SeO single bond stretch. Because of the low relative intensity of this peak and the complication which results from the selenious acid dimerization[62], this peak cannot be used to calculate values for K, in the hydrobromic acid concentration range studied (1.0M - 5.0M). Because of the greater intensity of the SeBr stretching bands in the spectra, they are better suited for the calculation of K. Allowance must, however, be made for the weak peaks due to $H_2SeO_3$ deformation modes, which lie in this region of the spectrum. The normalized molar intensities of the selenious acid vibrational modes are listed in Table X and the

Table IX. Values of Concentrations and Activities of HBr (Molar) and Activities of Water

| $c_{HBr}$ | $a_w$ | $a_{HBr}$ |
|---|---|---|
| 0.1 | 0.997 | 0.0803 |
| 0.2 | 0.993 | 0.1560 |
| 0.3 | 0.990 | 0.2325 |
| 0.4 | 0.986 | 0.3116 |
| 0.5 | 0.982 | 0.3935 |
| 0.6 | 0.978 | 0.4794 |
| 0.7 | 0.974 | 0.5691 |
| 0.8 | 0.970 | 0.6640 |
| 0.9 | 0.967 | 0.7632 |
| 1.0 | 0.962 | 0.8690 |
| 1.20 | 0.953 | 1.0968 |
| 1.39 | 0.944 | 1.3525 |
| 1.58 | 0.934 | 1.6416 |
| 1.77 | 0.924 | 1.9346 |
| 1.96 | 0.913 | 2.3285 |
| 2.83 | 0.853 | 5.006 |
| 3.69 | 0.782 | 10.210 |
| 4.46 | 0.703 | 19.040 |
| 5.21 | 0.619 | 34.428 |
| 5.96 | 0.536 | 62.991 |
| 6.65 | 0.460 | 111.753 |
| 7.30 | 0.390 | 199.217 |
| 7.93 | 0.332 | 350.577 |
| 8.56 | 0.277 | 552.796 |

corrected and normalized intensities of the SeBr stretching region (100 - 300 $cm^{-1}$) are listed in Table XI. An estimate of the molar intensity of the SeBr peaks for $SeOBr_2$ (100 - 300 $cm^{-1}$) may be calculated from the intensities in the spectrum for the 5.0M hydrobromic acid solution and a knowledge of the concentration of selenious acid and the total Se(IV) concentration.

$$C_{\text{total Se(IV)}} = [H_2SeO_3] + [SeOBr_2] \qquad (3)$$

In order to make this initial estimate, the selenious acid concentration was calculated using the molar intensity for the SeO single bond peak given in Table X and the intensity of the peak at 695 $cm^{-1}$. The molar intensity of the SeBr bands for $SeOBr_2$ was found in this way to be 205 $cm^2$. For the calculation of K, the following procedure was used. By use of the molar intensity of $SeOBr_2$, a preliminary value for the concentration of seleninyl bromide was calculated, the selenious acid concentration was determined using equation 3 and a correction of the SeBr envelope could then be made to allow for selenious acid deformations lying under the SeBr peaks. The molar intensity of the selenious acid deformations is given in Table X. The concentration of hydrobromic acid was then calculated from

Figure 15

Raman Spectra of solutions used to calculate K

A 1.0M $SeO_2$ in 5.0M HBr

B 1.0M $SeO_2$ in 4.5M HBr

C 1.0M $SeO_2$ in 4.0M HBr

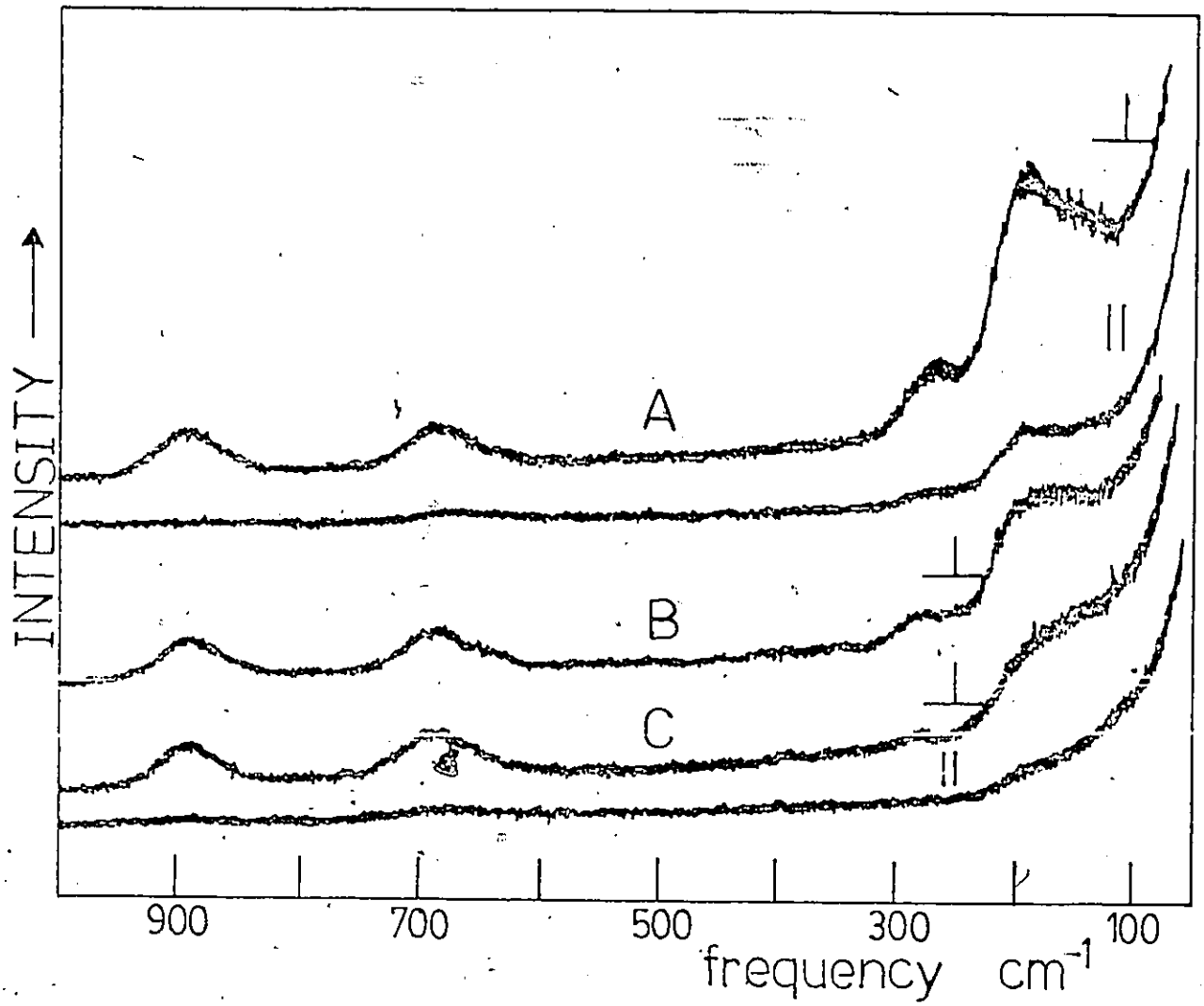

INTENSITY
A
B
C
⊥
∥
900
700
500
300
100
frequency cm⁻¹

Table X. Molar Intensities of Selenious Acid Bands

| freq. ($cm^{-1}$) | mode description | molar intensity ($cm^2$) |
|---|---|---|
| 100 - 400 | deformations | 2.50 |
| 695 | SeO single bond stretch | 6.34 |
| 896 | SeO double bond stretch | 5.12 |

Table XI. Normalized Intensities of SeBr Peaks, Concentrations and Equilibrium Constants for Seleninyl Bromide Formation

| $C_{HBr}$ | ISeBr($cm^2$) | $[SeOBr_2]$ | $[H_2SeO_3]$ | [HBr] | $a_w$ | $a_{HBr}$ | $10^{-4}K(mol^{-2}L^2)$ |
|---|---|---|---|---|---|---|---|
| 4.02 | 8.34 | 0.0407 | 0.9593 | 3.938 | 0.757 | 13.00 | 1.4 |
| 4.505 | 15.03 | 0.0734 | 0.9266 | 4.358 | 0.677 | 23.50 | 1.3 |
| 5.0 | 25.83 | 0.1262 | 0.8738 | 4.747 | 0.640 | 30.5 | 1.2 |

NOTE: All concentrations are in molar terms.
ISeBr values are corrected for $H_2SeO_3$ deformations

Kavg = 1.3 $X10^{-4}$ $mol^{-2}L^2$

$$[HBr] = C_{HBr} - 2[SeOBr_2] \qquad (4)$$

From this information, $a_{HBr}$ and $a_w$ could be obtained (Table IX), and the equilibrium constant, K, could be calculated using equation 2. Peak intensities, concentrations, activities and equilibrium constants are listed in Table XI. The spectra of the solutions used are shown in Fig. 15. The estimated molar intensity of the SeBr bands for $SeOBr_2$, 205 $cm^2$, gave the best constancy of K over the range of concentrations studied without need of adjusting it as was done in the case of the equilibrium constant calculation for the Se (IV)/HCl system[41]. The average value for K was found to be 1.3 X $10^{-4} mol^{-2} L^2$. The solutions of selenium dioxide in hydrobromic acid where the hydrobromic acid concentration was less than 4.0M gave values of K which were 2 to 5 times larger. This can only be attributed to the difficulty in measuring the SeBr stretching region intensity to a good degree of certainty, since this region was not much more intense than the selenious acid deformation region. The solutions which were used for the final determination of K where those of 1.0M $SeO_2$ in 4.0, 4.5 and 5.0M HBr.

## Solutions of Selenium Dioxide in Hydrobromic Acid at Concentrations of HBr greater than 5.0 Molar

Comparison of the Raman spectrum of selenium dioxide in 5.0M hydrobromic acid to that in 6.0M HBr (Fig. 16) reveals bands at 145 $cm^{-1}$ and 155 $cm^{-1}$, which are due to the presence of the $SeBr_5^-$ and $SeBr_6^{2-}$ ions. These bands are due to the $\nu_2(A_1)$ (Table V) mode of the $SeBr_5^-$ ion on MeCN and to the $\nu_1(A_{1g})$ (Table VI) mode of the $SeBr_6^{2-}$ ion on MeCN, 151 and 153 $cm^{-1}$ respectively (Table VII). This is particularly clear in the spectrum with 90° rotation of the plane of polarization. Assuming that these SeBr stretching modes, in the 6.0M HBr solution, are due to the presence of the $SeBr_5^-$ ion alone, an attempt can be made to calculate the concentration of $SeBr_5^-$ in this solution. Assuming that the molar intensity of the SeO double bond is due only to $SeOBr_2$ and $H_2SeO_3$ and assuming that the selenious acid concentration can be calculated from the SeO single bond intensity, it was thought possible to calculate the $SeBr_5^-$ concentration. However, the molar intensity of the SeO double bond, corrected for the $H_2SeO_3$ contribution yielded values of $[SeOBr_2]$, which resulted in

$$[H_2SeO_3] + [SeOBr_2] > C_{\text{total Se(IV)}}$$

and thus the $SeBr_5^-$ concentration could not be calculated. A list of values for SeO double bond intensities (from Table VIII), corrected SeO double bond intensities, $H_2SeO_3$ and $SeOBr_2$ concentrations are given in Table XII. The high

concentrations of $SeOBr_2$ can be accounted for by the possible presence of other bromoselenate(IV) species which contribute to the SeO double bond intensity. For this reason, the presence of the $SeOBr_3^-$ ion appears likely. Also the $SeOBr_4^{2-}$ anion may be present in small proportions. It should be noted that oxotribromoselenate(IV) compounds could be prepared from aqueous solution but oxotetrabromoselenate(IV) compounds could not. The values for total concentration of Se(IV) given in Table XII show that, as the hydrobromic acid concentration increases (from 6.0 to 7.0 molar), the excess concentration of Se(IV) gets larger. For the 1.0M $SeO_2$ in 7.0M HBr the total Se(IV) concentration is calculated to be 53% higher than it actually is. Since $SeOBr_3^-$ is the only species which could contribute to the SeO double bond molar intensity, it would have to be present in appreciable amounts. However, as was discussed earlier, the presence of $SeOBr_3^-$ in low concentrations is possible but substantial amounts cannot be accounted for reasonably in the solution spectra (Fig. 12 and Table VII) of 1.0M $SeO_2$ in HBr. Furthermore, at concentrations of HBr greater than 5.0 molar, the SeO single bond intensities are quite small and large errors could be involved in the measurement of their intensities. This would cause large variations in the selenious acid concentrations which in turn would change the values of seleninyl bromide

Figure 16

Raman Spectra of 1.0M $SeO_2$ in concentrated aqueous HBr solutions

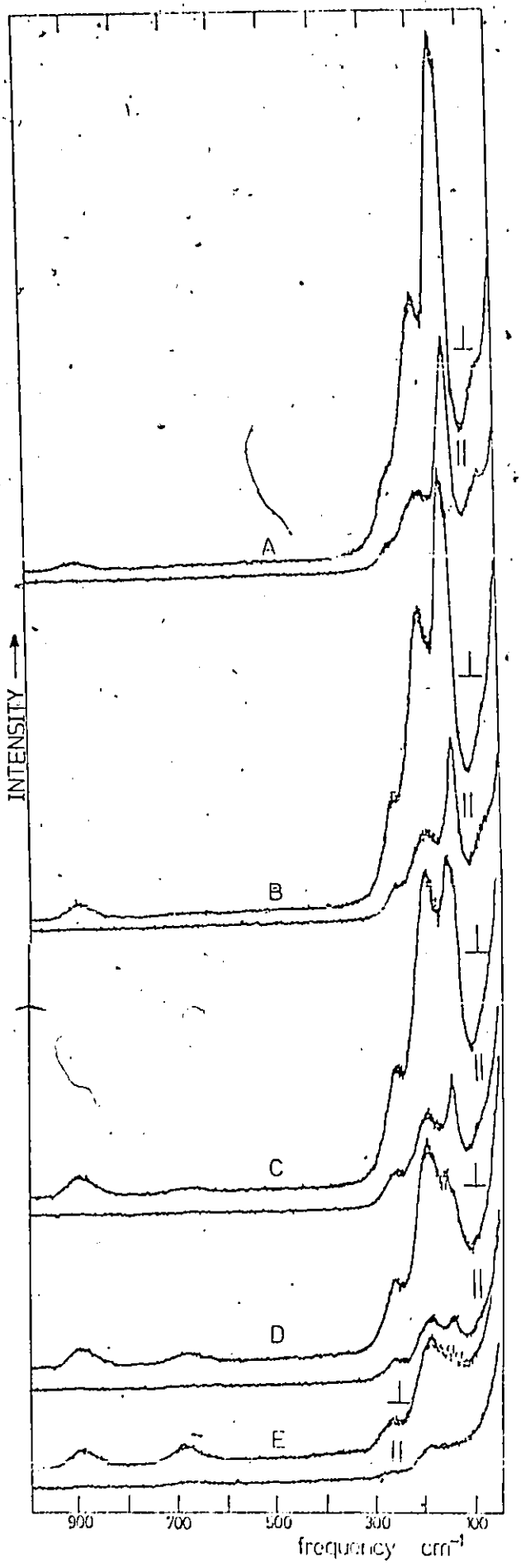
A 1.0M $SeO_2$ in 8.9M HBr

B 1.0M $SeO_2$ in 8.0M HBr

C 1.0M $SeO_2$ in 7.0M HBr

D 1.0M $SeO_2$ in 6.0M HBr

E 1.0M $SeO_2$ in 5.0M HBr


INTENSITY
A
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D
E
⊥
∥
900
700
500
300
100
frequency cm⁻¹

Table XII. SeO double bond Corrected and Uncorrected Intensities, and Concentrations of $H_2SeO_3$ and $SeOBr_2$

| Solution | ISe=0 [a] | ISe-0 | $[H_2SeO_3]$ [b] | ISe=0 [c] | $[SeOBr_2]$ | Total Se(IV) conc. |
|---|---|---|---|---|---|---|
| .513M $SeO_2$ in 6M HBr | 4.07 | 2.02 | 0.3186 | 2.44 | 0.3948 | 0.7134 |
| .776M $SeO_2$ in 6M HBr | 6.67 | 3.41 | 0.5378 | 3.92 | 0.6343 | 1.1721 |
| 1.0M $SeO_2$ in 6M HBr | 7.15 | 2.43 | 0.3833 | 5.19 | 0.8398 | 1.2231 |
| 1.0M $SeO_2$ in 7M HBr | 8.95 | 3.05 | 0.4810 | 6.49 | 1.0502 | 1.5312 |

a. Intensities are in $cm^2$

b. Concentrations in molar terms

c. Corrected for $H_2SeO_3$ double bond

concentrations. Therefore, we can say that the errors on the values of the SeO single bond intensities are more likely to be the reason for the excess calculated value of total Se(IV) concentration.

The Raman spectra of the 1.0M selenium dioxide in 5.0, 6.0, 7.0, 8.0 and 8.9 molar hydrobromic acid solutions are shown in Fig. 16. These spectra show that, as the hydrobromic acid concentration is increased, the intensities of the bands due to the $SeBr_5^-$ and $SeBr_6^{2-}$ ions, 145 and 155 $cm^{-1}$ respectively, increase relative to those for $SeOBr_2$. At a concentration of 5.0M HBr, $SeOBr_2$ is seen as being the only bromo species present in this solution and at a concentration of hydrobromic acid of 6.0M, the contribution due to $SeOBr_2$ is greater than that of the other bromo species. In the 1.0M $SeO_2$ in 7.0M HBr solution the highest intensity band for $SeOBr_2$ at 205 $cm^{-1}$, is almost equal in intensity to the bands in the 150 $cm^{-1}$ region due to the $SeBr_5^-$ and $SeBr_6^{2-}$ ions and finally at a concentration of hydrobromic acid of 8.9M the bands due to the $SeBr_5^-$ and $SeBr_6^{2-}$ are seen to be approximately twice as intense as the band at 205 $cm^{-1}$ due to $SeOBr_2$.

A study was also done where the hydrobromic acid concentration was kept constant, at 6.0 molar, but the selenium dioxide concentration varied from 1.0M to 0.26M. These spectra are shown in Fig. 17. As the concentration of

Figure 17

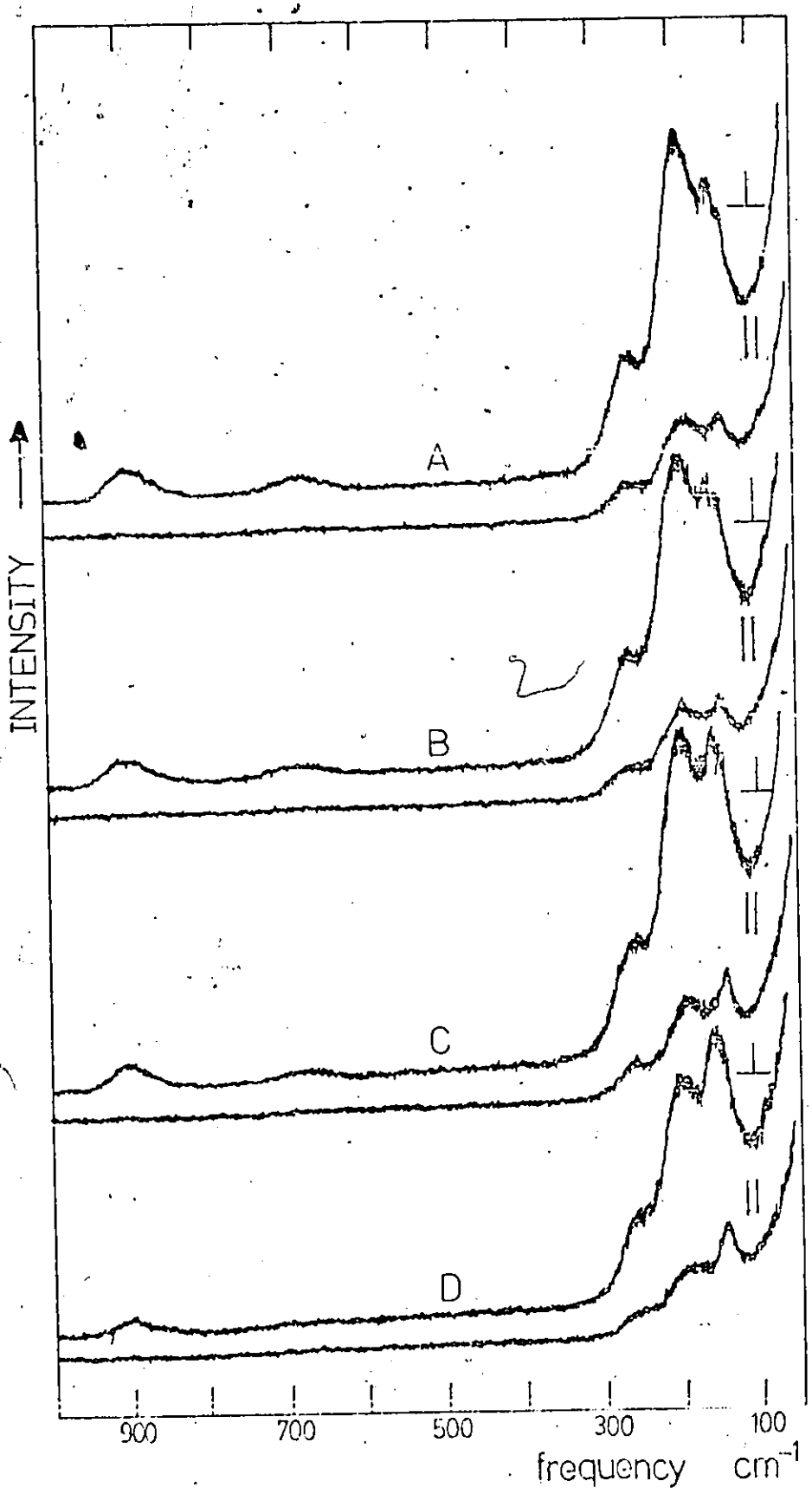
Raman Spectra of $SeO_2$ solutions in 6.0M HBr

A 1.0M $SeO_2$

B 0.776M $SeO_2$

C 0.513M $SeO_2$

D 0.26M $SeO_2$


INTENSITY
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frequency cm⁻¹

$SeO_2$ falls from 1.0M to 0.26M, the opposite effect to what was seen in the solutions shown in Fig. 12 (1.0M $SeO_2$ in 0 - 8.9M HBr) and Fig. 16 occurs. There is not much change in the solution spectra of 1.0M $SeO_2$ in 6.0M HBr compared to that of the 0.776M $SeO_2$ in 6.0M HBr solution. However, at a selenium dioxide concentration of 0.513M the spectrum can be seen to display intensities of the $SeBr_5^-$ and $SeBr_6^{2-}$ ions, 145 and 155 $cm^{-1}$ respectively, which are almost identical in intensity to the 205 $cm^{-1}$ band of $SeOBr_2$. The SeO single bond intensity, at 695 $cm^{-1}$, also falls relative to the SeBr envelope and to the SeO double bond intensity, at 900 $cm^{-1}$, until it disappears completely at a concentration of 0.26M $SeO_2$. This effect can be accounted for reasonably by the fact that as more $SeO_2$ is added to the hydrobromic acid solution more HBr is consumed, to form the bromoselenate(IV) species observed. Thus more $H_2O$ is formed and oxobromo species, mainly $SeOBr_2$, are favoured. These observations are further justified by the changes in the spectra with 90° rotation of the plane of polarization. In the 0.26M $SeO_2$ in 6.0M HBr solution, no $H_2SeO_3$ is present and we could expect, as was explained before, that at lower $SeO_2$ concentrations the spectra would indicate largely the presence of the $SeBr_5^-$ and $SeBr_6^{2-}$ ions and smaller contributions due to $SeOBr_2$.

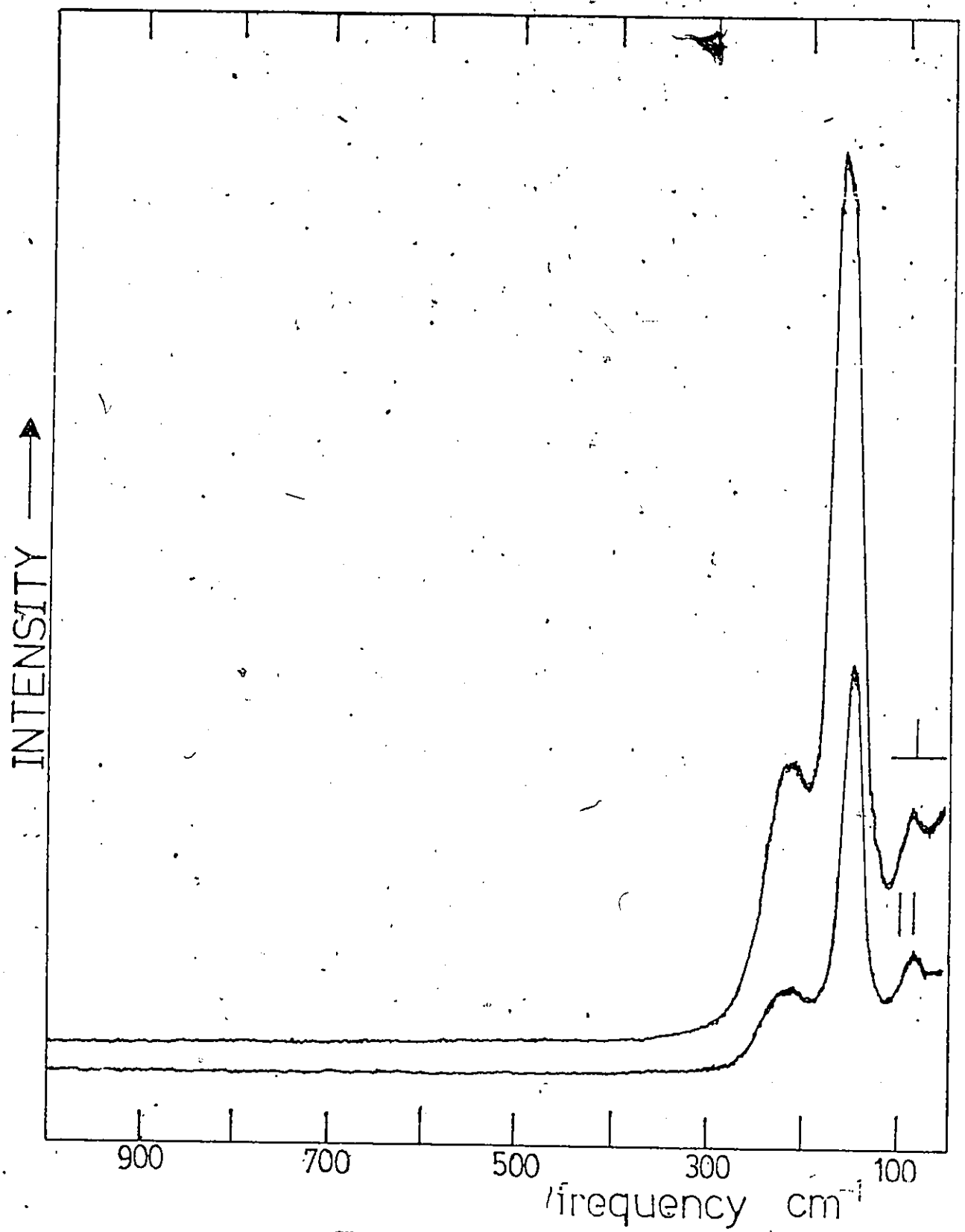
## Selenium Dioxide in Hydrobromic Acid Saturated with Hydrogen Bromide at 0°C

The Raman spectrum of a 1.0M selenium dioxide solution in hydrobromic acid saturated with hydrogen bromide is shown in Fig. 18. The hydrogen bromide concentration of an aqueous solution saturated at 0°C is 15.74M[65,66], calculated using density data taken at 4°C. The densities of aqueous HBr solutions at 0°C were not available, hence those measured at 4°C were used. It was estimated that this introduced an error in the molarity of approximately 1% which is far within the experimental error of the measurement of peak intensities (±5%). On comparing the spectrum of the saturated HBr solution with that of the 1.0M selenium dioxide in 8.9M hydrobromic acid solution (Fig. 12 and Fig. 16) it can be seen that the two spectra are quite similar. However, the saturated solution spectrum shows a larger contribution at 145 and 155 $cm^{-1}$, due to the $SeBr_5^-$ and $SeBr_6^{2-}$ ions respectively, compared to the band at 212 $cm^{-1}$. The spectrum in Fig. 18 provides no evidence for the presence of $SeOBr_2$ or $SeOBr_3^-$ since there is no SeO double bond stretch observable. Although the band at 212 $cm^{-1}$ is close in frequency to what we would expect for the most intense band of $SeOBr_2$, 205 $cm^{-1}$, it cannot be due to $SeOBr_2$. Therefore, the band at 212 $cm^{-1}$ is most likely due to condensation of the $SeBr_5^-$ ion to a dimeric or

Figure 18

Raman Spectrum of 1.0M $SeO_2$ in

15.74M HBr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polymeric anion as was observed in the case of $n\text{-}Bu_4NSeBr_5$ in acetonitrile at high concentration. The band at 212 $cm^{-1}$ could be interpreted in terms of the shifts of the bands at 180 $cm^{-1}$ to higher frequency, and 247 $cm^{-1}$ to lower frequency as was observed in the saturated solution of $SeBr_5^-$ in MeCN (Table V). Therefore, the spectrum of 1.0M $SeO_2$ in 15.47M HBr can be interpreted as being due to the $SeBr_6^{2-}$ ion and to a high concentration of $SeBr_5^-$ ion.

When the 1.0M selenium dioxide in 8.9M hydrobromic acid solution was saturated with hydrogen bromide at 0°C, a reddish-brown precipitate would form depending on how long the hydrogen bromide gas was allowed to pass through the solution once saturation was complete. For the solution used in Raman spectral study, the hydrogen bromide gas was passed through the solution at a slow rate and careful observation made it possible to cease the saturation before the point of precipitation. However, when the HBr gas was allowed to flow rapidly through the 1.0M $SeO_2$ solution at 0°C, a dark red-brown precipitate would form after a short period of time. Krebs and Hein[67] have identified this compound as being the hydrate of hexabromoselenic(IV) acid, $H_2SeBr_6.8H_2O$. This further justifies the presence of $SeBr_6^{2-}$ in solutions of $SeO_2$ in HBr.

## CONCLUSION

The Raman spectral study of the compounds prepared in this thesis indicated structures of the isolated anions $SeO_2Br^-$, $SeOBr_3^-$, $SeOBr_4^{2-}$ and $SeBr_5^-$ (in low concentration solutions in MeCN) to obey the predictions of VSEPR theory. The $SeBr_6^{2-}$ anion is known to possess octahedral symmetry, contrary to the expected geometry from VSEPR theory and is therefore exceptional in this series. Seleninyl bromide, $SeOBr_2$, showed evidence of oxygen bridging in the solid but bromide bridging was not as evident as the chloride bridging is in solid seleninyl chloride. In solution, $SeOBr_2$ was best approximated as having $C_s$ symmetry, as is predicted by VSEPR theory.

Although $SeBr_4$ decomposes to $SeBr_2$ and $Br_2$ in MeCN, it was shown that addition of bromide ion stabilizes Se(IV) in acetonitrile. The $SeBr_5^-$ compounds indicated bridging in their solid Raman spectra and in the Raman spectra of concentrated solutions. However, we could only speculate, from what is known about isoelectronic species, as to the type of bridging occurring. The Raman spectra of dilute solutions of $SeBr_5^-$ in MeCN indicated the decomposition of this anion to $SeBr_2$ and $Br_3^-$, however, these spectra were due, for the most part, to the $SeBr_5^-$ ion.

The spectra of the new bromoselenate(IV) anions $SeO_2Br^-$, $SeOBr_3^-$, $SeOBr_4^{2-}$ and $SeBr_5^-$ were considered in interpreting the spectra of Se(IV) in aqueous HBr. The spectra of these solutions taken when the plane of

polarization was rotated 90° also helped in clarifying the presence of the different bromo species. The species $H_2SeO_3$, $SeOBr_2$, $SeBr_5^-$ and $SeBr_6^{2-}$ were definitely identified in these solutions. $Se^{77}$ N.M.R. could help in confirming the conclusions of the Raman work as well as identifying species which may be present in small amounts, such as $SeOBr_3^-$, $SeOBr_4^{2-}$ and $SeBr_2$. By varying the Se(IV) concentration in solutions of $SeO_2$ in hydrobromic acid saturated with hydrogen bromide, the condensation of $SeBr_5^-$ to polymeric species would become more evident by the increase of the intensity of the band at 212 $cm^{-1}$ relative to that at 145 $cm^{-1}$ with increasing Se(IV) concentration.

The equilibrium constant determined for the equilibrium:

$$H_2SeO_3 + 2HBr = SeOBr_2 + 2H_2O$$

is of the order of 100 times larger than the corresponding equilibrium constant for the chloride system which demonstrates that, in aqueous solution, seleninyl bromide is more stable than seleninyl chloride. This is further supported by the fact that $SeOBr_3^-$ compounds could be prepared from aqueous solution.

## REFERENCES


1. J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Longmans, Green, Vol. X, 1930.

2. R. J. Gillespie, "Molecular Geometry", Van Nostrand-Reinhold, London, 1972.

3. R. Paetzold and K. Aurich, Z. Anorg. Allg. Chem., 335, 281 (1965).

4. R. J. Gillespie, P. Spekkens, J. B. Milne and D. Moffett, J. Fluorine Chem., 7, 43 (1976).

5. J. B. Milne, Inorg. Chem., 17, 3592 (1978).

6. K. O. Christe and E. C. Curtis, Inorg. Chem., 11, 35 (1972).

7. A. Finch, P. N. Gates and M. A. Jenkinson, J. Flourine Chem., 2, 111 (1972/73).

8. J. B. Milne and D. Moffett, Inorg. Chem., 12, 2240 (1973).

9. S. Wasif and S. B. Salama, J. Chem. Soc., Daton Trans., 2239 (1975).

10. P. Lahaie and J. B. Milne, Inorg. Chem., 18, 632 (1979).

11. E. E. Aynsley, R. D. Peacock and P. L. Robinson, J. Chem. Soc., 1231 (1952).

12. L. E. Alexander and I. R. Beattie, J. Chem. Soc., Dalton Trans., 1745 (1972).

13. R. Paetzold, Z. Chem., 4, 272 (1964).

14. J. A. Rolfe and L. A. Woodward, Trans. Far. Soc., 51, 778 (1955).

15. J. C. Dewan and A. J. Edwards, J. Chem. Soc., Dalton Trans., 2433 (1976).

16. V. W. Bues, W. Brockner and A. F. Demiray, Z. Anorg. Allg. Chem., 434, 249 (1977).

17. H. Gerding, E. Smit and R. Westrik, Recueil Trav. Chim. Pays-Bas, 60, 513 (1941).

18. F. H. Westphal and F. Rosenburger, J. Mol. Spec., 83, 355 (1980).

19. W. Brockner and A. F. Demiray, Monat. Chem., 110, 525 (1979).

20. R. Paetzold and K. Aurich, Z. Anorg. Allg. Chem., 348, 94 (1966).

21. C. R. Wise, J. Amer. Chem. Soc., 45, 1233 (1923).

22. J. J. Jackson and G. B. L. Smith, J. Amer. Chem. Soc., 62, 545 (1940).

23. A. W. Cordes, Inorg. Chem., 6, 1204 (1967).

24. I. Lindgquist and G. Nahringbauer, Acta Cryst., 12, 638 (1959).

25. P. Gregory, L. Hargittai and M. Kolonits, J. Mol. Structure, 31, 261 (1976).

26. J. D. McCullough and G. Hamburger, J. Amer. Chem. Soc., 64, 508 (1942).

27. J. D. McCullough and R. E. Marsh, Acta Cryst., 3, 41 (1950).

28. Y. Hermodsson, Acta Chem. Scand., 21, 1313 (1967).

29. Y. Hermodsson, Acta Cryst., 13, 656 (1960).

30. A. W. Cordes and Bi-Cheng Wang, Inorg. Chem., 9, 1643 (1970).

31. J. B. Milne, Inorg. Chem., 18, 2924 (1979).

32. K. O. Christe, E. C. Curtis, C. J. Shack and D. Pilipovich. Inorg. Chem., 11, 1679 (1972).

33. F. Seel and H. Massat, Z. Anorg. Allg. Chem., 280, 186 (1955).

34. E. E. Aynsley, G. Hetherington and P. L. Robinson, J. Chem. Soc., 1119 (1954).

35. P. J. Hendra and Z. Jovic, J. Chem. Soc., 600 (1968).

36. G. Engel, Z. Krist., 90, 341 (1935).

37. N. N. Greenwood and B. P. Straughan, J. Chem. Soc., 962 (1966).

38. K. J. Wynne, J. Chem. Ed., 50, 328 (1973).

39. R. G. Pearson, Chem. in Britain, 3, 103 (1967).

40. H. Selig and U. El-Gad, J. Inorg. Nucl. Chem. Suppl., 233 (1976).

41. P. Lahaie and J. B. Milne, Inorg. Chem., 18, 3180 (1979).

42. L. Futekov and N. Jordanov, Izv. Fiz., Inst. ANEB, Bulg. Akad. Nauk., 21, 289 (1971).

43. D. Moffett, Ph.D. Thesis, University of Ottawa (1974).

44. L. Futekov and H. Specker, Z. Anal. Chem., 276, 41 (1975).

45. B. E. Conway, R. E. Verrall and J. E. Desnoyers, Trans. Far. Soc., 62, 2738 (1966).

46. V. Lenher, J. Amer. Chem. Soc., 44, 1668 (1922).

47. G. Brauer, "Handbook of Preparative Inorganic Chemistry", Riley N.Y. 1963 - 1965.

48. J. D. McCullough, J. Amer. Chem. Soc., 59, 789 (1937).

49. K. J. Wynne and J. Golen, Inorg. Chem., 13, 185 (1974).

50. J. B. Milne, Submitted for Publication in Spectrochimica Acta A.

51. Y. Hermodsson, Acta Chem. Scand., 21, 1328 (1967).

52. N. W. Alcock, Advances in Inorganic Chemistry and Radiochemistry, 15, 1 (1972).

53. P. H. Collins and M. Webster, Acta Cryst., Sec. B, 28, 1260 (1972).

54. B. Krebs and K. Büscher, Z. Anorg. Allg. Chem., 463, 56 (1980).

55. W. G. Macpherson and E. A. Meyers, J. Phys. Chem., 72, 532 (1968).

56. J. W. George and N. Katsaros, Inorg. Chem., 8, 759 (1969)

57. L. Frost and J. B. Milne, Unpublished Results.

58. W. B. Person, G. R. Anderson and J. N. Fordemwalt, J. Chem. Phys., 33, 908 (1961).

59. J. Laane and P. W. Jagodzinski, Inorg. Chem., 19, 44 (1980).

60. R. A. Jacobson and C. R. Hubbard, Inorg. Chem., 11, 2247 (1972).

61. R. A. Jacobson and S. L. Lawton, Inorg. Chem., 10, 709 (1971).

62. L. Barcza and L. G. Sillen, Acta Chem. Scand., 25, 1250 (1971).

63. J. B. Milne and D. Moffett, Inorg. Chem., 13, 2750 (1974).

64. R. Haase, H. Naas and H. Thumm, Z. Phys. Chem. Neue Folge, 37, 210 (1963).

65. International Critical Tables, 3, 55 (1928).

66. A. Seidell; W. F. Linke, "Solubities of Inorganic and Metal Organic Compounds", Amer. Chem. Soc., Vol. 1, 1102 (1958 - 1965).

67. B. Krebs and M. Hein, Z. Naturforsch., 34b, 1666 (1979).