cm^{-1} are similar to a pair of bands at 13,200 and 15,900 cm^{-1} in the spectrum[1] of $W_2Cl_9^{3-}$. In the spectrum of the latter, however, there is also an intense band at 21,900 cm^{-1} which has no counterpart in the spectrum of $Mo_2Cl_9^{3-}$. Equivalent similarities and differences also occur in the spectra of $Mo_2Br_9^{3-}$ and $W_2Br_9^{3-}$.[3] Thus, the spectra of the enneahalodimolybdates possess certain features which resemble those of the corresponding MoX_6^{3-} and others which resemble those found in $W_2X_9^{3-}$. The only clear fact that emerges from this comparison is the enigmatic nature of these spectra.

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Infrared and Raman Spectra of the Se_4^{2+} Ion

BY R. J. GILLESPIE AND G. P. PEZ

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Infrared and Raman spectra have been recorded for a number of compounds that have been shown to contain the Se_4^{2+} ion. Characteristic vibrational frequencies for Se_4^{2+} were observed at 188 and 327 cm^{-1} in the Raman spectrum and at $\sim$306 cm^{-1} in the infrared spectrum. These have been assigned, respectively, to the B_{2g}, A_{1g}, and E_u fundamentals of a square-planar (D_{4h}) arrangement of selenium atoms. A normal-coordinate analysis based on a Urey–Bradley force field yields a value of 2.2 mdyn/Å for the Se–Se stretching force constant. A relatively novel technique for recording the infrared spectra of highly reactive solids is described.

Introduction

Selenium dissolves in sulfuric and fluorosulfuric acids in the presence of oxidizing agents to form intensely green or yellow solutions. Investigation of the yellow solutions by conductometric, cryoscopic, spectrophotometric, and magnetic methods has shown that the selenium is present as the polyatomic cation Se_4^{2+}.[1] A number of salts of Se_4^{2+} have been prepared and characterized: $Se_4(SO_3F)_2$ (I), $Se_4(HS_2O_7)_2$ (II), $Se_4(S_4O_{13})$ (III), and $Se_4(Sb_2F_{11})_2$ (IV).[2] Crystals of II have been examined by X-ray diffraction and have been found to be monoclinic, space group $P2_1/c$ (C_{2h}^5), containing two units of $Se_4(HS_2O_7)_2$ per unit cell. The Se_4^{2+} ion has been found to have a square-planar (D_{4h}) structure with an Se–Se separation of about 2.3 Å.[3] In this paper we report on the infrared and Raman spectra of compounds I–IV.

Experimental Section

Preparation of Materials.—Compounds I–IV were prepared as described in ref 2. They are bright orange to yellow solids and are extremely hygroscopic; they were prepared and handled in a dry nitrogen atmosphere. It was not possible to obtain solutions of I–IV in the usual spectroscopic solvents. For example, I and II are insoluble in CCl_4, C_6H_5F, BCl_3, and liquid SO_2. When mixed with CH_3NO_2, CH_3CN, $(CH_3)_2SO$, and CS_2, they are immediately reduced to selenium. All of the compounds are very soluble in the parent acids. Solutions of I–IV in fluorosulfuric acid or in dilute oleum were employed for Raman spectra.

Potassium hydrogen disulfate (KHS_2O_7) was made by dissolving "Analar" grade K_2SO_4 in hot 30% oleum (sulfuric acid containing 30% w/w of sulfur trioxide). Large columnar crystals appeared on cooling the solution. The crystals were washed with 10% oleum and subsequently with liquid SO_2 at −11° to remove any adhering acid. The dry material melted at 170–173° (mp 168°[4]); analyses for sulfur and for the sulfuric acid equivalent upon hydrolysis were within 0.7% of the values expected for KHS_2O_7.

Potassium fluorosulfate was prepared by carefully neutralizing ice-cold aqueous KOH with HSO_3F. The salt which separates out was recrystallized from hot (95°) water.

Raman Spectra.—Raman spectra were taken with a Spex Industries Model 1400 spectrometer employing a 50-mW Spectra Physics Model 125 He–Ne laser source at 6328 Å, a double monochromator, and a photomultiplier detector followed by an electrometer amplifier and recorder. A convenient and particularly effective method of mounting samples was devised. Liquid, powdered, or crystalline samples were contained in 1.2-mm i.d. (melting point) capillary tubes mounted horizontally with their axes perpendicular to the collimated laser beam. The beam was focused near the center of the tube and the light scattered at 90° to the incident radiation and to the axis of the tube was focused on the slits of the monochromator. For liquid samples this arrangement gave Raman signals of better than 10 times the intensity obtained when using Supersil cuvettes of square cross section as sample containers. Also, by using capillary tubes, the size of sample and any absorption of the exciting radiation are kept to a minimum. Depolarization ratio measurements taken on CCl_4 lines compared favorably with depolarization data recorded with CCl_4 in the optically superior cuvettes. The readout of the monochromator was calibrated against emission lines of neon.

Infrared Spectra.—Compounds I–IV readily attack Nujol, polyethylene, and cesium iodide; hence the usual methods for taking infrared spectra could not be applied. A rather novel sampling technique was developed in which the compounds were supported as finely divided solids on a cold cesium iodide plate. This allowed coverage of the full CsI range ($\sim$180–4000 cm^{-1})

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[2] J. Barr, D. B. Crump, R. J. Gillespie, R. Kapoor, and P. K. Ummat, *ibid.*, **46**, 3607 (1968).

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without chemical reactivity problems and without background absorptions from mulling agents. The apparatus used was a variant of the dewar-type low-temperature cells normally employed for taking spectra of frozen gases and matrix isolation studies[5,6] (Figure 1).

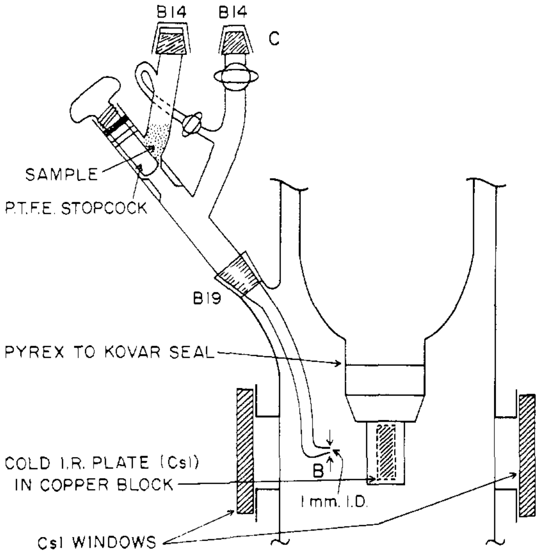

Figure 1.—Low-temperature infrared cell and injection system for powdered solids.

The solid (which must be finely powdered and very dry) was loaded into the sample compartment of the injection system. The latter was then attached to the dewar and the whole assembly was evacuated to $<1\ \mu$ pressure. The dewar was filled with liquid nitrogen and outlet C was connected to a supply of xenon. A small quantity of the solid was then caused to fall by gentle tapping into the horizontal section B at the extremity of the injection tube. Xenon gas (~ 10 cm^3 at 10 cm) was used to blow the solid onto the cold CsI plate. The xenon solidified and served to retain the finer particles of solid on the plate. This procedure was then repeated until the required spectral thickness was obtained. In our apparatus the CsI plate was not cold enough to retain the xenon on the plate for more than a few minutes. The sample, however, remained on the plate even after all of the xenon had sublimed to colder parts of the dewar.

Spectra were taken by mounting the cell directly in the sample compartment of a Beckman IR-12 spectrophotometer (range 200–4000 cm^{-1}). Tube B is moved out of the light path by a small rotation of the injection system about the B19 joint.

Several attempts were made to obtain infrared spectra of very concentrated solutions of II in fluorosulfuric acid. The solutions were contained in specially designed 0.05-mm path length cells with very thin (0.002-in.) Teflon windows. No absorptions that could be attributed to the solute were observed between 200 and 400 cm^{-1}. The intense background absorption of the acid solvent apparently obscured the relatively weak Se_4^{2+} vibrations in this region.

Results and Discussion

The infrared and Raman spectra of I–IV, KSO_3F, and $K(HS_2O_7)$ are reproduced in Figures 2 and 3; positions and relative intensities of band maxima are presented in Table I. Infrared spectra were scanned from 200 to 4000 cm^{-1} and Raman spectra were observed from 25 to 2000 cm^{-1}. However, we have only reported the spectral data to 500 cm^{-1}, since no vibrations characteristic of the Se_4^{2+} ion were noted at the higher frequencies. Frequencies listed in Table I are accurate to within ± 1 cm^{-1}, unless otherwise specified.

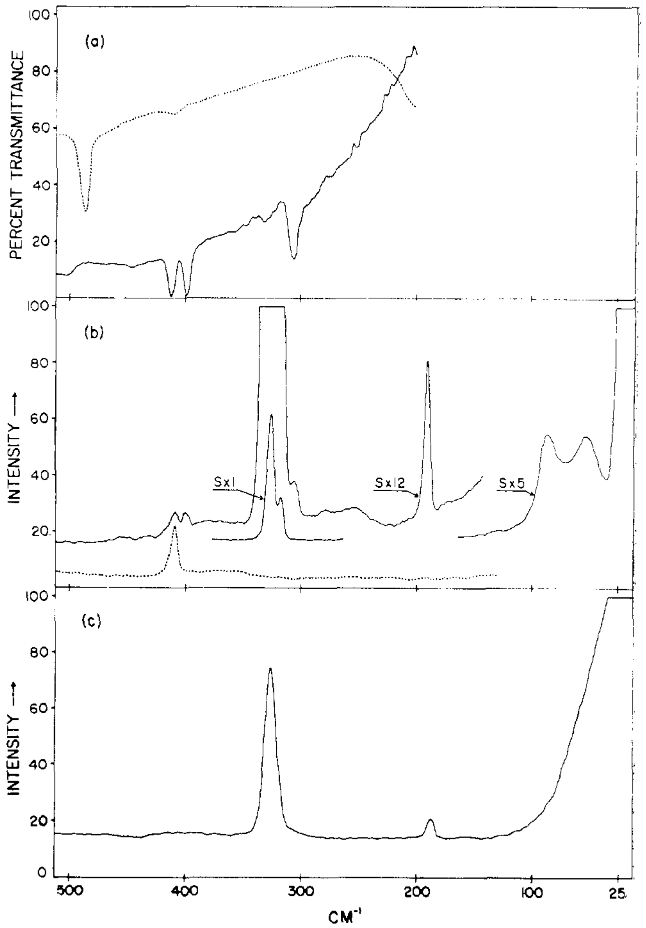

Figure 2.—(a) Infrared spectra of $Se_4(SO_3F)_2$ (solid line) and KSO_3F (broken line) at 90°K. (b) Raman spectra of $Se_4(SO_3F)_2$ (solid line) and KSO_3F (broken line) at 300°K. S indicates instrument sensitivity based on an arbitrary scale. (c) Raman spectrum of a 1 *m* solution of $Se_4(SO_3F)$ in fluorosulfuric acid at 300°K.

The Se_4^{2+} cation can initially be treated as an isolated ionic group of D_{4h} symmetry. Five fundamentals are predicted: $A_{1g} + B_{1g} + B_{2g} + B_{2u} + E_u$, the E_u mode being doubly degenerate. The mutual exclusion rule applies: A_{1g}, B_{1g}, and B_{2g} are Raman active and E_u is infrared active while B_{2u} is both infrared and Raman inactive (*cf.* Table II).

In crystalline $Se_4(HS_2O_7)_2$ the C_{2h}^5 space group requires that each of the two cations occupy a site of C_i symmetry in the unit cell. When the analysis is based on site symmetry selection rules, the E_u degeneracy in D_{4h} is lost and all vibrations fall under the A_g and A_u species of C_i. Since there are two Se_4^{2+} ions in the unit cell, the total number of possible vibrations is doubled. Vibrations from the two ions may give rise to identical frequencies, but, if there is any vibrational interaction between them, the degeneracy is removed and a splitting of bands (*i.e.*, "factor group splitting"[7,8]) may occur.

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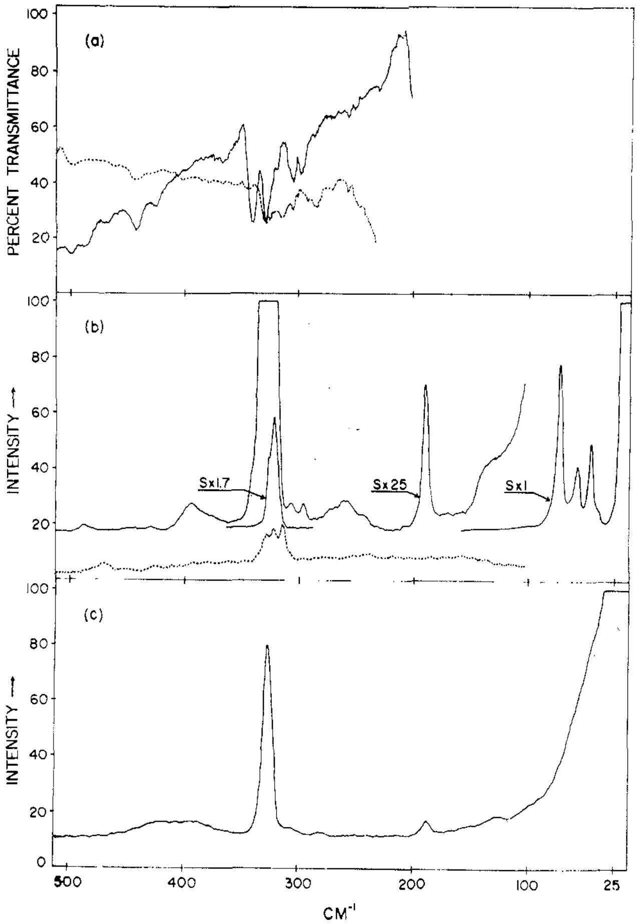

Figure 3.—(a) Infrared spectra of $Se_4(HS_2O_7)_2$ (solid line) and $K(HS_2O_7)$ (broken line) at 90°K. (b) Raman spectra of $Se_4(HS_2O_7)_2$ (solid line) and $K(HS_2O_7)$ broken line at 300°K. (c) Raman spectrum of a 0.2 *m* solution of $Se_4(HS_2O_7)_2$ in 2–5% oleum at 300°K.

The factor group or unit cell symmetry in $Se_4(HS_2O_7)_2$ is C_{2h}. In a factor group analysis the same number of vibrations is expected as under C_i, but the vibrations will now be more restricted by the higher symmetry of the unit cell. The correlation between the D_{4h}, C_i, and C_{2h} groups for Se_4^{2+} in $Se_4(HS_2O_7)_2$ is given in Table II.

The identification of Se_4^{2+} vibrations in the spectra of I–IV is complicated by overlapping bands from the anions and by crystal lattice effects which for compounds I, III, and IV cannot be predicted because of lack of structural data. In the Raman spectra the prominent features are bands at ~327 and ~188 cm^{-1} which are observed for all of the compounds I–IV and their solutions in HSO_3F and oleum. The bands are assigned to the A_{1g} and B_{2g} vibrations, respectively. (The Se–Se stretching mode appears at 292 cm^{-1} in Se_2Cl_2, at 286 cm^{-1} in Se_2Br_2,[9] and at 286 cm^{-1} in $(CH_3)_2Se_2$.[10]) The mutual exclusion selection rules are not strictly obeyed; thus A_{1g} appears as a weak band in the infrared spectra of I, III, and IV and with moderate intensity in II (*cf.* Table I).

An absorption which appears with medium intensity at 306 cm^{-1} in the infrared spectrum of I and as a doublet (304, 297 cm^{-1}) in the spectrum of II is most likely the infrared-allowed E_u mode. The doublet could come from the removal of the E_u degeneracy by the lower symmetry of the site or factor groups in $Se_4(HS_2O_7)_2$. Again, coincident lines are observed in the Raman spectra but they have very low intensities. It is difficult to give a more definite assignment of the $Se_4(HS_2O_7)_2$ lines between 280 and 340 cm^{-1} since $HS_2O_7^-$ ion vibrations contribute to the spectrum, especially in the infrared region (*cf.* KHS_2O_7 spectra). Interference from the anion becomes even more severe in spectra of III and IV. In IV, very strong absorptions are found between 250 and 315 cm^{-1} and presumably overshadow the relatively weak Se_4^{2+} E_u band. The Raman spectrum of $CsSb_2F_{11}$ displays a broad band of moderate intensity at ~290 cm^{-1}.[11]

The normal-coordinate analysis discussed later shows that the remaining B_{1g} mode is expected to appear between 300 and 330 cm^{-1}, but it has not been definitely identified. In the Raman spectrum of I, the shoulder which appears on the low-frequency side of A_{1g} at 319 cm^{-1} could be attributed to B_{1g}. The relative intensities of the 327-cm^{-1} (A_{1g}) and 319-cm^{-1} lines are unchanged down to 120°K; hence the latter cannot be a hot band overlapping with A_{1g}. Components to the low-frequency side of A_{1g} are also found in the Raman spectra of II and III. It is possible, however, that the observed lines between 315 and 330 cm^{-1} arise from a factor group splitting of A_{1g}, at least in $Se_4(HS_2O_7)_2$. In this event, the very weak Raman lines at 307 cm^{-1} in I, at 304 and 297 cm^{-1} in II, and at 307 cm^{-1} in III could be attributed to the B_{1g} mode.

The A_{1g} bands in II and III are modulated on either side by broad features at 260 and 393 cm^{-1} and at ~260 and 390 cm^{-1}, respectively. These are assigned to sum and difference combination bands of A_{1g} with a lattice mode of A_g or B_g symmetry at ~65 cm^{-1}. No overtone or combination bands of the four Se_4^{2+} fundamentals were observed. Anharmonicity effects in the vibrations of such a system of heavy atoms are predictably small.

Raman lines in I–IV below 180 cm^{-1} do not appear in the solution spectra and have been arbitrarily assigned to lattice modes. The B_{1u}, Se_4^{2+} ring-puckering mode should appear in the infrared spectrum of crystalline $Se_4(HS_2O_7)_2$ at very low frequencies, *e.g.*, below 100 cm^{-1}. In spectra of Figures 2(c) and 3(c) the broad bands at ~400 cm^{-1} are characteristic of the acid solvents.[12,13] The very weak lines in Figure 3(c) at 120, 281, and 307 cm^{-1} presumably come from the oleum solvent or the solvated anion; they are unlikely to arise from the Se_4^{2+} ion since they have no counterpart in the HSO_3F solution spectra (Figure 2(c)).

Our vibrational assignments are summarized in Table I. Unassigned frequencies in this table are assumed to arise from anion vibrations; their counterpart can generally be seen in the spectra of the potassium salts. Infrared and Raman spectra of I and II from 500 to

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TABLE I

Assignment of Se_4^{2+} fundamentals (species in D_{4h})	$Se_4(SO_3F)_2$ (I)			$K(SO_3F)$		$Se_4(HS_2O_7)_2$ (II)			$K(HS_2O_7)$		$Se_4(S_4O_{13})$ (III)			$Se_4(Sb_2F_{11})_2$ (IV)		
	Solid		HSO_3F soln. (1 *M*)	Solid		Solid		2.5% oleum soln (0.2 *M*)	Solid		Solid		10% oleum soln	Solid		HSO_3F Soln
	Ir	Raman	Raman	Ir	Raman	Ir	Raman	Raman	Ir	Raman	Ir	Raman	Raman	Ir	Raman	Raman
↑							46 (15)					42 (8)				
Lattice		52 (5.5)					58 (11)					65 (12)				
modes																
							73 (30)					73 (8)				
↓		87 (7.5)						120^c				81 (7)				
B_{2g}		192 $(1)^b$	189 (1) dp (ρ = 0.7 ± 0.1^a)				191 (1)	188 (1) dp				191 (1)	~188 dp		186 (1)	~188 dp
							~260 (1.16)					~260 (0.06)		225, 237 s		
											272 m			264 vs		
								281^c			291 w			272 vs		
						297 m	296 (0.12)		285 m		298 m			285 vs	289 (0.5)	
E_u	306 m	307 (0.23)				304 m	307 (0.11)	307^c		314 (7)		307 (0.33)				
B_{1g}		319 (4.8)					324 (12)		320 m	321 (6)	314 w	318 (5.5)		~323 w		
A_{1g}	330 w	327 (14)	326 pol (ρ = 0.36 ± 0.1)			329 m	328 (7.5)	327 pol		327 (5)	329 w	324 (15)	~327	328 w	328 (5.7)	~327 pol
						340 m					342 w	340 (13)		339 m		
	399 m	399 (0.10)	380–420^c					380–420^c			356 s		380–420^c			380–420^c
							~393 (0.16)					~390 (0.05)			418 (0.1)	
	413 m	409 (0.11)			409				443 w		465 vs					
							487 (0.04)			472 (1)	483 vs			485 s		
				486 m												

[a] ρ_{max} for incident polarized light is 0.75. [b] For I–IV the B_{1g} Raman line intensity is arbitrarily taken as 1. [c] Solvent bands; see text.

TABLE II

CORRELATION OF IONIC SYMMETRY OF Se_4^{2+} WITH SITE AND FACTOR GROUP SYMMETRY IN $Se_4(HS_2O_7)_2$

Type of vibration	Ionic group (D_{4h})			Site group (C_i)			Factor group (C_{2h})		
	Selection rules	N^a	Species	Selection rules	Species	N^a	N^a	Species	Selection rules
Totally sym ring str	Raman	1	A_{1g}	Raman	A_g	3 × 2^b	3	A_g	Raman
Ring str	Raman	1	B_{1g}						
Ring bend (in plane)	Raman	1	B_{2g}				3	B_g	Raman
Ring bend (out of plane)	Inactive	1	B_{1u}	Ir	A_u	3 × 2^b	3	A_u	Ir
Ring def	Ir	1	E_u				3	B_u	Ir

[a] Number of normal vibrations (fundamentals) in each symmetry species. [b] The factor 2 occurs because there are two $Se_4(HS_2O_7)_2$ units per unit cell.

2000 cm^{-1} bear a 1:1 correspondence with the spectra of KSO_3F and $K(HS_2O_7)$, respectively.

Normal-Coordinate Analysis.—A normal-coordinate analysis was performed for the Se_4^{2+} D_{4h} model using Wilson's *FG*-matrix method.[14]

The symmetry coordinates are

$$S_r^{A_{1g}} = {}^1/_2(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

$$S_r^{B_{1g}} = {}^1/_2(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_\alpha^{B_{2g}} = {}^1/_2(\Delta \alpha_1 - \Delta \alpha_2 + \Delta \alpha_3 - \Delta \alpha_4)$$

$$S_r^{E} = \frac{1}{\sqrt{}}(\Delta r_1 - \Delta r_3)$$

$$S_\alpha^{E_u} = \frac{1}{\sqrt{2}}(\Delta \alpha_1 - \Delta \alpha_3)$$

where the Δr and $\Delta \alpha$ terms refer to small increments in the Se–Se bond lengths and the SeSeSe angles, respectively.

A Urey–Bradley (UB) force field was employed since there is not sufficient vibrational data for evaluating a general potential function. The UB potential is given by

$$2V = \sum_i [2K'r\Delta r_i + K(\Delta r_i)^2] + \sum_{i<j} [2H'r^2\Delta\alpha_{ij} + Hr^2(\Delta\alpha_{ij})^2] + \sum_{i<j}[2F'q\Delta q_{ij} + F(\Delta q_{ij})^2]$$

where K and H are the bond stretching and valence angle bending force constants, respectively. F and F' are the UB interaction constants associated with the displacements (Δq_{ij}) in the equilibrium distance[9] between adjacent nonbonded atoms. The linear displacement constants K' and H' can be neglected because of the equilibrium condition that $\partial V/\partial r = 0$ and $\partial V/\partial \alpha = 0$. The F-matrix elements in Wilson's method were expressed in terms of K, H, and F (F' was put equal to $-0.1F$) using the technique described by Overend and Scherer.[15] Four linear equations are obtained relating the force constants to the vibrational frequencies, any three of which can be solved directly for K, H, and F.

From the data for A_{1g} (327 cm^{-1}), E_u (306 cm^{-1}), and B_{2g} (188 cm^{-1}) we arrive at $K = 2.2$, $H = 0.12$, and $F = 0.15$ mdyn/Å. The B_{1g} mode is then predicted to occur at 306 cm^{-1} which is in reasonable agreement with either of the assignments discussed for this vibration.

As far as we are aware, the only other Se–Se stretching force constants available for comparison are those for the $^{80}Se_2$ molecule ($k = 3.498$ mdyn/Å, $r_e = 2.1661$ Å)[16] and for dimethyl diselenide. For $(CH_3)_2Se_2$, the value of $k = 1.674$ mdyn/Å has been estimated on the basis of a modified valence force field calculation. We feel that our value of 2.2 mdyn/Å is significantly larger despite the fact that it relates to a different potential function. This presumably indicates that there is some degree of multiple bonding in the Se_4^{2+} ion. A simple Hückel-type MO calculation gives an Se–Se bond order of 1.5.[3] The UB constants H and F may be compared with those for ClSSCl ($H_{SSCl} = 0.21$, $F_{SCl} = 0.19$ mdyn/Å) and BrSSBr ($H_{SSBr} = 0.15$, $F_{SBr} = 0.16$ mdyn/Å).[17]

Acknowledgment.—We thank the National Research Council of Canada for financial support of this work.

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The Fluorosulfuric Acid Solvent System. VII. The Behavior of Some Extremely Weak Bases in the Superacid System HSO_3F–SbF_5–SO_3

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Nitrogen, oxygen, neon, xenon, hydrogen, nitrogen trifluoride, and carbon monoxide all have a very small solubility in the HSO_3F–SbF_5–SO_3 system and do not appear to be protonated. Carbon dioxide has a moderate solubility and sulfur dioxide has a high solubility in this superacid solvent but neither is protonated to any significant extent. The very weak base 1,3,5-trinitrobenzene appears to be completely protonated.

Introduction

Considerable use has been made in the past few years of the extremely high acidity of solutions of antimony pentafluoride in fluorosulfuric acid in the study of the protonation of a variety of weak organic bases.[1-3] Conductivity and nmr measurements[4] have shown that these solutions contain the acid $H[SbF_5(SO_3F)]$ which is partly ionized according to

$$H[SbF_5(SO_3F)] + HSO_3F \rightleftharpoons H_2SO_3F^+ + SbF_5(SO_3F)^-$$

thus giving a moderately high concentration of the fluorosulfuric acidium ion $H_2SO_3F^+$ and consequently a rather highly acidic medium. It has also been shown that the high acidity of this system can be further in-

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