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Raman Spectra and Structure of Bromine(I) Fluorosulfate and Bromine(I) Fluorosulfate Solutions of Alkali Metal Fluorosulfates

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Raman spectra of $BrOSO_2F$ and solutions of $BrOSO_2F$ in $S_2O_5F_2$ have been measured along with Raman spectra of $BrOSO_2F$ solutions of alkali metal fluorosulfates. Variations in the spectra of $BrOSO_2F$ and solutions in $S_2O_5F_2$ which depend upon solution concentration and temperature are interpreted in terms of association equilibria between $BrOSO_2F$ molecules. The gas-phase infrared spectrum is included to support the association interpretation. A number of spectral features which are not apparent in spectra of either the pure solute or the solvent are observed in spectra of $BrOSO_2F$ solutions of alkali metal fluorosulfates. These are interpreted in terms of various solvent–solvent and solute–solvent associations and complex formation between SO_3F^- ions and $BrOSO_2F$ molecules. Some structural models for the associations are suggested based upon the Raman spectra.

Introduction

In the course of some Raman studies of bromine(I) fluorosulfate solutions of alkali metal fluorosulfate salts, we found it necessary to understand more fully the Raman spectrum of bromine(I) fluorosulfate. During these studies some interesting changes were noticed in the band contours of the $BrOSO_2F$ spectrum upon dissolution of the fluorosulfate salts. The changes appear to involve an increase in the intensities of small shoulders which are on the major features in the room-temperature Raman spectrum of $BrOSO_2F$. Such spectral variations were subsequently observed in Raman measurements of $BrOSO_2F$ solutions in $S_2O_5F_2$. The contours of solute bands in the spectra of these solutions vary dramatically with concentration and to a lesser extent with temperature change between 0 and 60 °C. Careful study of the Raman spectrum of bromine(I) fluorosulfate and the solutions in $S_2O_5F_2$ was carried out in order to identify the features in the spectra of the fluorosulfate salt solutions in $BrOSO_2F$ which are due to the solvent and obtain structural information about liquid $BrOSO_2F$.

The Raman spectrum of bromine(I) fluorosulfate has been reported and assigned.[1,2] The present study involves details of the spectrum which have not been thoroughly explored. Interpretation of the details of Raman spectra of liquids often affords a good source of structural information. We believe that the present Raman measurements in conjunction with the gas-phase infrared spectrum and other physical data[3] indicate some interesting structural characteristics of liquid bromine(I) fluorosulfate and its alkali metal fluorosulfate solutions.

Many of the chemical and physical properties of bromine(I) fluorosulfate have been measured.[3,4,9] It is a deep red liquid which is thermally stable at ambient temperatures and up to about +150 °C and is not extensively disproportionated. The substance is known to be stable in $S_2O_5F_2$.[3] Some electrical and spectroscopic properties of $BrOSO_2F$ solutions in $S_2O_5F_2$ are reported in ref 3.

Experimental Section

Bromine(I) fluorosulfate was prepared by direct reaction of Br_2, J. T. Baker, Analyzed Reagent distilled from P_2O_5, and $S_2O_6F_2$, prepared by the method of Cady and Shreeve,[5] with the latter reactant in slight excess as described by Aubke and Gillespie.[3] Samples for Raman measurements were vacuum distilled into Pyrex tubes using a manifold with Fischer & Porter Lab Crest valves. The sample tube could be removed at a ground-glass joint. When removal was not provided for, the tubes were separated from the manifold by flame sealing. These procedures minimized contact of $BrOSO_2F$ with Kel-F grease which introduces traces of Br_2 and other impurities into the samples. The amounts of solvent and solute were determined by removing the sample tubes and weighing before and after each addition of liquid.

Solutions of alkali metal fluorosulfates were prepared in the manner described for the preparation of sodium and lithium bis(fluorosulfato)bromate(I) complexes.[1] Various concentrations were obtained by vacuum pumping bromine(I) fluorosulfate from the solutions at room temperature and collecting it in a trap at −183 °C. The amount of material removed was determined by periodically detaching and weighing the solution vessel, which also served as the cell for Raman measurements. The amount of solvent removed was checked occasionally by weighing the trap. Again, careful attention to keeping grease joints clean and the use of Fischer & Porter Lab Crest Valves essentially eliminated contamination of the samples by contact with vacuum grease.

Raman spectra were recorded using an instrument centered around a Spex 1401 double-monochromator spectrometer with an ITT FW-130 thermoelectrically cooled phototube with S-20 response and a dc amplifier. The excitation source was a CRL Model 52 MG Ar^+, Kr^+ mixed-gas laser. Laser emissions at both 6471 and 5145 Å were used as exciting frequencies. Frequency calibration was carried out using Ar^+ and Kr^+ emission lines and known frequencies of CCl_4 and $CHCl_3$. Estimated maximum error in observed frequencies is ±3 cm^{-1} for sharp bands and ±5 cm^{-1} for broad bands. All measurements were done with a spectral slit width of 5–8 cm^{-1}.

Depolarization ratios were measured by rotating a Polaroid film analyzer in the scattered beam. The polarized radiation then passed through a polarization scrambler before entering the spectrometer.

Raman spectra were measured at various temperatures between 0 and 60 °C by training a continuous stream of hot air from a heater–blower or dry nitrogen passed through cooling coils onto the closed sample tube. The temperature was controlled by the flow rate and measured by a thermometer held beyond the sample tube in the stream of cool or warm nitrogen.

The gas-phase infrared spectra were measured on a Perkin-Elmer 225 grating infrared spectrometer. The samples were held in a 10 cm cylindrical glass cell with silicon windows and a side arm for containing the liquid. Bromine(I) fluorosulfate was transferred in a drybox to a container with a Teflon valve, attached to the vaccum line, and vacuum distilled into the side arm of the IR cell through a system with only Teflon valves. In one case, to ensure the absence of water, an ampule containing the $BrOSO_2F$ sample was broken inside the evacuated vacuum system. This distillation transfer was carried out for three separate experiments. The IR cell was separated from the vacuum line each time by flame sealing.

The mass spectrum of the gas from the IR cell was measured on an AEI MS-9 mass spectrometer by attaching the sample cell directly to the gas inlet system.

Results

Most of the bands in the Raman spectrum of bromine(I) fluorosulfate change in contour and shift in frequency when the substance is dissolved in $S_2O_5F_2$. Apparently, identical but much less pronounced Raman spectral changes are observed as the temperature of $BrOSO_2F$ is increased from 0 to 60 °C and similar shifts occur when fluorosulfate salts are dissolved in bromine(I) fluorosulfate.

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Table I. Vibrational Frequencies (cm^{-1}) of Bromine(I) Fluorosulfate in Various Conditions of Association[a]

	Raman in $S_2O_5F_2$						
IR of gas (1)	unassociated (2)	ρ	singly associated (4)	ρ	doubly associated (4)	ρ	approx assign
	202		172		(~172)		SO-Br bend
~280	298		314		(~314)		SO-Br wag
	(~388)		388		(~388)		SO_2 twist
430	(~462)		462		(~462)		SF wag
503	(~535)		535		(~535)		SO_2 rock
546	(~569)		569		(~569)		SO_2 bend
	636		656		(~656)		BrO str
822	812		834		846		SF str
858	~862		882		~904		S-OBr str
1240	1230	0.15 ± 0.08	1212	0.15 ± 0.08	1195	0.16 ± 0.06	SO_2 str
1472	1454	0.60 ± 0.08	1434	0.62 ± 0.06	1408	0.39 ± 0.08	SO_2 str

[a] Wavenumbers in parentheses are not observed as bands separate from those in the spectrum of liquid $BrOSO_2F$, but bands are expected near these values.

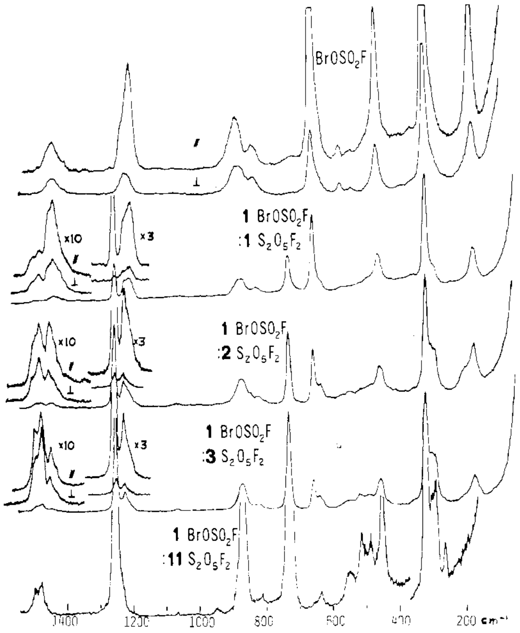

Figure 1. Raman spectra of $BrOSO_2F$ and solutions in $S_2O_5F_2$. Prominent bands in the 1:11 measurement indicate solvent frequencies.

The most readily identifiable constituents of the band contours in the Raman spectra of $BrOSO_2F$ are given in Table I. Column 2 lists Raman components which increase in intensity with increased temperature and solution dilution. Column 3 includes bands which are most intense in the Raman spectrum of $BrOSO_2F$ at room temperature and column 4 those which are least intense. Bands in columns 3 and 4 decrease in intensity with increased temperature and dilution. Intensities of bands in column 4 seem to decrease faster with temperature increase and dilution than those in column 3. The described intensity variations are illustrated in Figure 1.

Depolarization ratios were measured for selected bands to give additional support for the structural conclusions. The large error range indicated for these ratios may result from temperature variations due to local heating by the laser beam; this in turn leads to small relative intensity differences within the spectra taken with the two Polaroid orientations. This error does not destroy the usefulness of comparing depolarization ratio values within each of the spectra in Table I. Only C_1 symmetry is indicated since the SO_2 stretching assignments were never depolarized. An internal check of the polarization measurements of $BrOSO_2F$ solutions in $S_2O_5F_2$ is given by the adjacent higher frequency solvent bands. As expected, they are found to be depolarized.

Raman spectra of bromine(I) fluorosulfate solutions of lithium, sodium, potassium, rubidium, and cesium fluorosulfate with bromine(I) fluorosulfate to metal fluorosulfate mole ratios ranging from about 15 to <5 show similar frequency shifts and intensity changes. In each case the spectra become increasingly complex as the concentration is increased. Several bands in addition to those observed for $BrOSO_2F$ solutions in $S_2O_5F_2$ add to the complexity of the Raman contours for these solutions. Crystals of metal bis(fluorosulfato)bromate(I) begin to form in lithium, sodium, and cesium fluorosulfate solutions at solvent to solute mole ratios of 5.5, 4.0, and 1.3, respectively, and potassium and rubidium fluorosulfate remain undissolved at ratios of 3.0 and 2.5, respectively. The crystals formed were isolated and identified spectroscopically. Raman spectra of the $CsSO_3F$ solutions are illustrated in Figure 2.

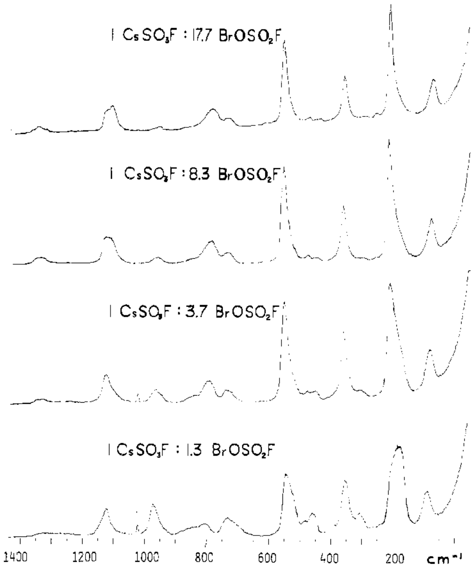

Figure 2. Selected examples indicating spectral variations dependent upon the concentration of $CsSO_3F$ in $BrOSO_2F$. Mole ratios are shown on the spectra. Frequencies are in cm^{-1}.

Assignments in Table I are in agreement with the assignments in ref 2. The columns of spectra in Table I are arranged from left to right in order of increasing degree of association or complexity of the species to which they are attributed.

The infrared spectrum of gas-phase $BrOSO_2F$ is shown in Figure 3 and the wavenumber values are listed in column 1 of Table I.

Discussion

Bromine(I) Fluorosulfate Solutions in Pyrosulfuryl Difluoride. The observed variations of the band contours in Raman spectra of $BrOSO_2F$ solutions in $S_2O_5F_2$ with changes in concentration and temperature are due to variations of the

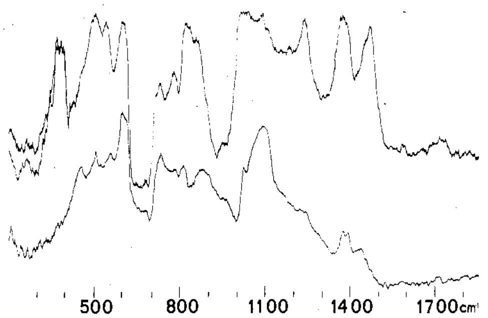

Figure 3. Infrared spectra of gaseous $BrOSO_2F$. Bands at about 390 and 1020 cm^{-1} indicate formation of SiF_4 in the cell. The lower spectrum is of the cell with gaseous contents frozen into the side arm. The intense band at 1368 cm^{-1} and the feature at 778 cm^{-1} are apparently due to $BrOSO_2F$ and may be explained as combination bands, e.g., 822 + 546 cm^{-1}.

intensities of the components within groups of overlapped bands. The components of the band groups are all at frequencies near the major features in the Raman spectrum of liquid $BrOSO_2F$. Sets of bands, including one from each group, which show corresponding intensity changes as a function of concentration can be easily selected. These sets of Raman bands, which have most of their frequencies slightly shifted in relation to the liquid $BrOSO_2F$ frequencies, are essentially complete spectra of $BrOSO_2F$. The band sets are listed in columns 2–4 of Table I. The close frequencies and similar relative intensities indicate that no changes in molecular structure have occurred. Accordingly, the variations can be attributed to equilibria between $BrOSO_2F$ molecules in different states of association. Explanation of the variations in terms of solute alone instead of solute–solvent interactions is further supported by the similar but much less dramatic variations observed as a function of temperature in spectra of liquid $BrOSO_2F$.

Moreover, species of the type $Br(OSO_2F)_3$ and $Br(OSO_2F)_4^-$ which may result from reaction with impurities or autooxidation may be ruled out by comparison with their known Raman spectra.[6] The extent of self-ionization is known to be too small to account for the observed variations.[3] The presence of $Br(OSO_2F)_2^-$, SO_3F^-, or Br_2^+ ions is also detectable based upon their known Raman and resonance Raman spectra.[1,2,8]

Previous physical measurements, including a Trouton constant of 25.75, have indicated strong intermolecular association in liquid bromine(I) fluorosulfate.[3] Our interpretation of the Raman spectra is in keeping with this previous indication.

The variations observed in the Raman spectra of $BrOSO_2F$ solutions in $S_2O_5F_2$ can be explained based on the plausible model for intermolecular association shown in Figure 4. The most important result of association to bromine should be found in variations of the O–Br stretching frequency, and association to oxygen will cause the largest change in the coupled SO_2 stretching frequencies. Moreover, association between two $BrOSO_2F$ molecules affects only the O–Br vibration frequencies of one and the SO_2 frequencies of the other. That is, the changes observed in bands assigned to SO_2 vibrations are not due to the same molecule which gives rise to the changed O–Br frequencies. These bonds are too far separated in the molecule to be appreciably coupled. Most of the other vibrations are more likely to be affected by association through oxygen than through bromine since oxygen is one bond closer to most of the bonds in the $BrOSO_2F$ molecule than is the bromine atom. Consequently, only one complete additional vibration spectrum would be observed for the associations diagrammed in Figure 4a. The vibration spectrum of the molecule labeled 2 is not distinguishable from one of the two spectra given by those labeled 1 and 3. The second of the latter spectra would be essentially the same as the spectrum given by an unassociated molecule in solution.

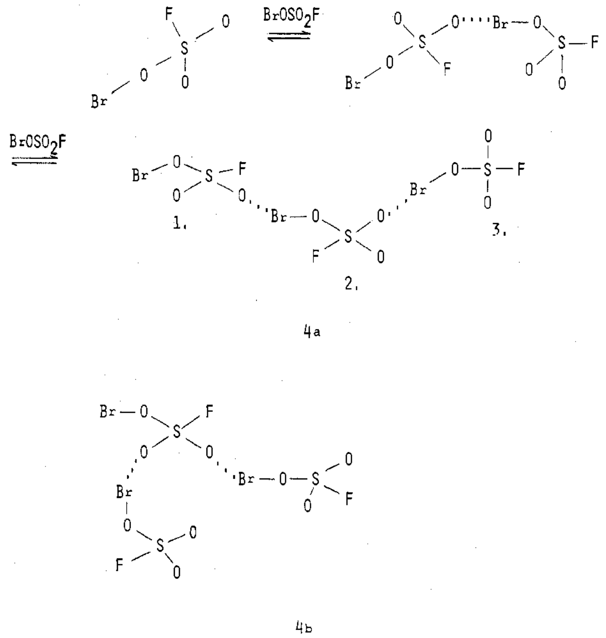

Figure 4.

An indication of the changes expected in the vibrational frequencies of $BrOSO_2F$ upon intermolecular association is given by comparing the frequencies assigned to corresponding vibrations of monodentate and bidentate OSO_2F^- in the spectrum of $Br(OSO_2F)_3$.[6] Relative to the monodentate ligand, the SO_2 stretching frequencies are lowered and the S–F and S–OBr stretching frequencies are increased in the spectrum of the bidentate group. The band pairs assigned to SO_2 and SO–Br angle deformation modes are coalesced in the spectrum of the bidentate ligand relative to the assignments for monodentate fluorosulfate. For example, the SO_2 stretching frequencies assigned to monodentate and bidentate groups in the spectrum of $Br(OSO_2F)_3$ are 1490 and 1241 and 1372 and 1168 cm^{-1}, respectively. The same spectral variations are observed if the halogen bound to OSO_2F^- is replaced by a less electronegative atom.[2] These changes in the vibrational spectra are generally considered to be due to variations in the degree of multiple bonding due to polarization of the bonding electrons. For example, the alterations described above apparently reduce the multiple character of the SO_2 bonds in $XOSO_2F$ compounds, thus lowering both stretching frequencies and, to a lesser extent, decoupling them so that their separation is decreased.[2,6]

With these considerations in mind, the Raman spectra can be readily related to the model shown in Figure 4. The most intense bands in the Raman spectrum of bromine(I) fluorosulfate, Table I, column 3, which decrease in intensity with increased temperature and dilution, are most likely due to associated $BrOSO_2F$ molecules. The second spectrum, column 2 in Table I, has its relative intensities continuously increased with dilution and temperature elevation and has its highest relative intensity for bands observable in the most dilute solutions. For example, bands from this spectrum at 636 and 812 cm^{-1} are observed singly, that is, in the absence of bands due to corresponding vibrations of any other $BrOSO_2F$ species, in the spectrum of a 1:11 mole ratio solution in $S_2O_5F_2$, Figure 1. The latter set is assigned to molecules which are not associated with another $BrOSO_2F$ molecule. The spectra of monomer and associated $BrOSO_2F$ species in columns 2 and 3 of Table I show the expected frequency differences and are readily accounted for by the simple equilibrium model shown in Figure 4a.

It is furthermore interesting to note that the O–Br stretching frequency, like the S–F stretching frequency, is increased in the spectrum of the associated molecule relative to the unassociated molecule values.

The third set of bands, which shows corresponding intensity variation, is listed in column 4 of Table I. It is the least intense in the Raman spectrum of $BrOSO_2F$ and the intensity decreases with dilution and increased temperature. The relevant frequencies of this spectrum are shifted in the same directions from those assigned to the unassociated molecules as the bands due to the associated species in Figure 4a; however, the shifts are about twice as large. For example, the SO_2 stretching frequencies are lowered from 1454 and 1230 cm^{-1} to 1408 and 1195 cm^{-1}, respectively, and the S–F stretching frequency is raised from 812 to 846 cm^{-1}. These observations suggest the presence of a less abundant but more extensively associated species which is similar to the principal associated species already described, Figure 4a. A likely structure involves $BrOSO_2F$ molecules which have both the SO_2 oxygens independently associated with two other $BrOSO_2F$ molecules. The model which accounts for the observations is shown in Figure 4b.

The IR spectrum of the unassociated gas-phase $BrOSO_2F$ molecules lends strong support to the present interpretation of the liquid and solution spectra. The observed gas-phase wavenumber values are nearest to those assigned to unassociated liquid-phase $BrOSO_2F$ molecules. They are shifted farther from the correspondingly assigned associated molecule wavenumber values than are the frequencies of the unassociated liquid-phase molecules and in the same directions. See column 1 of Table I and Figure 3. These are the expected differences between the liquid- and gas-phase measurements.

It should be noted that gaseous $BrOSO_2F$ reacts slowly with the silicon cell windows. The rate of reaction is increased at elevated temperatures. Some of the products of this reaction were determined from the IR, visible, and Raman spectra of the condensed gases and the mass spectrum of the product gases to be SO_3, SO_2, SiF_4, $S_2O_5F_2$, Br_2, and probably Br_3OSO_2F.

Liquid $ClOSO_2F$ and $IOSO_2F$ are also suggested to be associated[13] and may display the same type of equilibria. A comparative study of these compounds may yield further information concerning structural details of the liquids.

Alkali Metal Fluorosulfate Solutions. Formation of crystalline cesium,[9] lithium, and sodium[10] bis(fluorosulfato)bromate(I) compounds by direct interaction of the metal fluorosulfate with bromine(I) fluorosulfate has already been accomplished, and the Raman spectra have been reported.[1,10] The substantial decrease in the rate of removal of $BrOSO_2F$ from bromine(I) fluorosulfate solutions of alkali metal fluorosulfates at solvent to solute mole ratios greater than 1 under dynamic vacuum suggests the formation of higher order bromine(I) fluorosulfate complexes.[9,10] Further indications of the nature of this complex formation are found in the Raman spectra of $BrOSO_2F$ solutions of alkali metal fluorosulfates.

Comparative examination of Figures 1 and 2 indicates a greater broadening of the Raman bands of $BrOSO_2F$ accompanying dissolution of $M^+SO_3F^-$ than that observed dependent upon varying the concentration of $BrOSO_2F$ in $S_2O_5F_2$. Some of the intensity alterations which lead to broadening of features in spectra of the former solutions are the same as those observed in spectra of the latter. Raman bands corresponding to frequencies of $Br(OSO_2F)_2^-$ can be identified in spectra of the more concentrated alkali metal fluorosulfate solutions, i.e., ≥1:4 mole ratio of MSO_3F to $BrOSO_2F$. The Raman spectrum of a supersaturated solution of $CsSO_3F$ in $BrOSO_2F$ prepared by slowly cooling a 1:1.07 mole ratio solution from 50 °C to room temperature shows these bands distinctly. The Raman spectrum of this solution is compared with that of a mixture of the same ratio including crystals of $CsBr(OSO_2F)_2$ in Figure 5. The indication is that $Br(OSO_2F)_2^-$ is one of the ions in solution and that the additional broadening of the Raman bands in spectra of the alkali metal fluorosulfate solutions can be reasonably attributed to solute–solvent associations and complex formation. The similar observations in the spectra of the two systems suggest that some of the structural variations are the same.

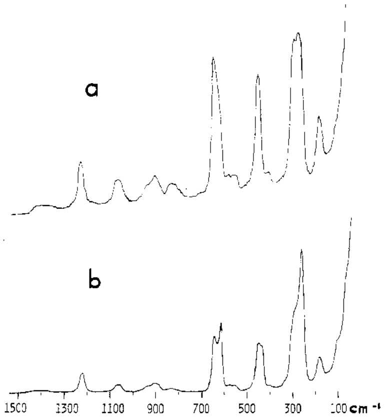

Figure 5. Comparison of the Raman spectrum of a supersaturated solution of $CsSO_3F$ in $BrOSO_2F$, 1:1.07 mole ratio (a), and the mixture after crystals of $CsBr(OSO_2F)_2$ are formed (b).

The apparent intensity changes of the bands due to $BrOSO_2F$ indicate destruction of the intermolecular association with increased $M^+SO_3F^-$ concentration. Decreased association is the expected change as the atoms through which $BrOSO_2F$ molecules are associated solvate the M^+ and SO_3F^- ions. While solvent–solvent interactions decrease with increased salt concentration, complex ion and contact-ion-pair formation through solute–solvent and solute–solute interactions are expected to increase. Thus, the similar spectroscopic observations with dilution of $BrOSO_2F$ solutions and increasing concentration of metal fluorosulfate are quite reasonable and support the proposed association models. The described initial structure-breaking effect of MSO_3F dissolved in $BrOSO_2F$ is similar to that observed when many salts are dissolved in water.[11]

Bands which are due to the fluorosulfate anion are identified by their positions and relative intensity variation with increasing salt concentrations.[12] Note that the intense band at 1072 cm^{-1}, assigned to the SO_3 symmetric stretching mode, includes at least three components in the Raman spectra of bromine(I) fluorosulfate solutions of $CsSO_3F$: ca. 1072, 1055, and 1032 cm^{-1}, Figure 2. These are probably due to various types of solvation associations. The remaining SO_3F^- bands at 408, 553, 578, 786, 1287, and 1300 cm^{-1} are weak or overlapped with bands due to the solvent.

A number of further observations are of interest with regard to structural indications of solvent–solute interactions. Changes in the contours which are assigned to S–O stretching are particularly instructive. A broad feature appears at ~1340 cm^{-1} and increases in intensity with increasing salt concentration to almost the size of the 1430-cm^{-1} band of bromine(I) fluorosulfate in the spectrum of the 30 mol % solution. With further increase in concentration, the intensity between these two features at ~1380 cm^{-1} grows. The 1220-cm^{-1} contour becomes more complex with increasing salt concentration by the appearance of weak bands at ~1155 and 1175 cm^{-1}. The S–OBr stretching frequency, ~900 cm^{-1}, shows increased complexity at higher wavenumbers. Several bands around 950 cm^{-1} increase in intensity with increasing salt concentration, Figure 2.

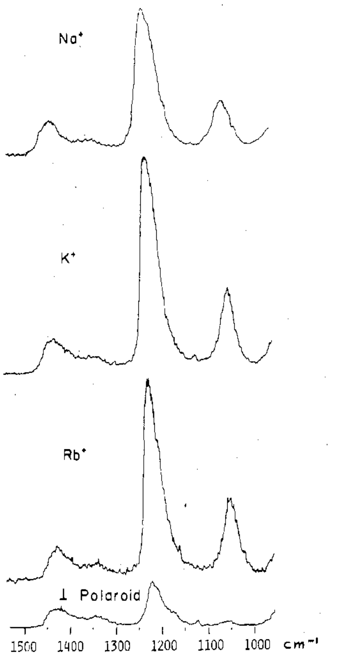

Figure 6. Comparison of 1:4 solute to solvent mole ratio spectra above 1000 cm^{-1} for various alkali metal fluorosulfate salts dissolved in $BrOSO_2F$. The Cs^+ system may be included by comparing the spectra in Figure 6 with the 1:3.7 spectrum in Figure 2. The lithium solution is in equilibrium with $LiBr(OSO_2F)_2$ crystals at a mole ratio of 1:4 and is consequently not included in Figure 6.

Interpretation of the above spectral alterations is greatly assisted by concurrent observation of some relevant physical properties. Upon addition of alkali metal fluorosulfate to bromine(I) fluorosulfate, the color changes from deep red to orange. The solutions became more distinctly yellow-orange with increasing salt concentration. We note that the crystalline compounds identified as Li-, Na-, and $CsBr(OSO_2F)_2$[1,10] all are yellow-orange. Thus, an alteration in the environment around the bromine atom in $BrOSO_2F$ to one similar to that found in the crystalline $MBr(OSO_2F)_2$ compounds is indicated. Furthermore, the viscosity of the solutions increases with increasing salt concentration. The most concentrated solutions flowed extremely slowly in ~6 mm i.d. Pyrex tubes and appeared to vitrify upon cooling. Finally, the rate of removal of solvent by vacuum pumping at constant temperature shows a sharp decrease at solvent to solute mole ratios of ~2 or 3.[9,10]

The combined observations suggest complex formation and contact-ion pairing. The details of the Raman spectra support complex formation; however, the slight dependence of a few frequencies on the metal involved could be due to contact-ion pairing or may be correctly attributed to the effect of solvating the metal ions. The appearance of S–O stretching frequencies at ~1340, ~1150–1180, and ~940–970 cm^{-1}, and S–F at 840 cm^{-1}, may be accounted for in terms of bridging SO_3F^- groups.[7] A likely explanation is the formation of complexes of the type $FSO_3(BrOSO_2F)_2^-$ and $FSO_3(BrOSO_2F)_3^-$ in addition to the known $Br(OSO_2F)_2^-$ ion. Addition of another SO_3F^- to $Br(OSO_2F)_2^-$ to give dinegative $Br(OSO_2F)_3^{2-}$ is unlikely.

Several further observations support particular aspects of the above contentions. First, the very weak band at ~1155 cm^{-1} and the shoulder at ~1175 cm^{-1}, Figure 6, have much higher depolarization ratios (~0.50) than the components of the 1220-cm^{-1} envelope in Raman spectra of $BrOSO_2F$ (~0.15). Also, the intensities of the 1155- and 1175-cm^{-1} bands are comparable to the intensity of the 1340-cm^{-1} group whereas the 1220-cm^{-1} contour for $BrOSO_2F$ is about 10 times more intense than that at 1430 cm^{-1}. These are expected variations for S–O stretching frequencies of bridging SO_3F^- since the 1150–1180-cm^{-1} bands would correlate with an asymmetric motion under higher symmetry and 1340 cm^{-1} would correlate with frequencies due to a symmetric motion. Raman intensity in the 1150–1180-cm^{-1} region may also be assigned to asymmetric SO_3 stretching of triply associated SO_3F^- which has C_{3v} symmetry.[14] Second, the intensity of the composite assigned to S–OBr stretching shifts to higher wavenumbers as the MSO_3F concentration is increased. Noting that this motion is assigned at 1018 cm^{-1} for crystalline $CsBr(OSO_2F)_2$ and 880 cm^{-1} for $BrOSO_2F$, the frequency for three and two $BrOSO_2F$ molecules associated with SO_3F^- might be expected at an intermediate frequency and could account for the observed intensity shift. Third, the intensity between 1340 and 1430 cm^{-1} is increased in the Raman spectra of the most concentrated solutions. This increased intensity is probably due to formation of $Br(OSO_2F)_2^-$ ions with increasing SO_3F^- concentration. The comparable band is at 1373 cm^{-1} in the spectrum of crystalline $CsBr(OSO_2F)_2$. Finally, the complexity of the 830-cm^{-1} band due to S–F stretching and the 880-cm^{-1} band assigned to S–OBr stretching is further indication of the highly and variously associated nature of these solutions.

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Registry No. $BrOSO_2F$, 13997-93-8; $CsSO_3F$, 13530-70-6; $NaSO_3F$, 14483-63-7; KSO_3F, 13455-22-6; $RbSO_3F$, 15587-05-0; $CsBr(OSO_2F)_2$, 32715-56-3.

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