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Raman Spectra and Structure of Bromine(I) Fluorosulfate and the Bromine(I) Difluorosulfato Anion

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The Raman spectra of bromine(I) fluorosulfate and cesium difluorosulfatobromate(I) are recorded. Eleven out of twelve fundamentals of $BrOSO_2F$ are found and assigned, and the point group C_s is suggested. $Cs[Br(OSO_2F)_2]$ is identified as a true complex with equivalently bonded fluorosulfate groups. The observed sulfur–oxygen and sulfur–fluorine stretching frequencies indicate a greater ionic character of the SO_3F group in the complex than in bromine(I) fluorosulfate.

Introduction

Bromine(I) fluorosulfate, first reported by Roberts and Cady,[1] is the only known unipositive bromine compound which is neither thermally unstable at room temperature as, *e.g.*, $BrONO_2$[2] and BrCl,[3] nor extensively disproportionated as BrF.[4] A thermal stability range up to +150° is reported for $BrOSO_2F$.[5] No information on its structure exists. All attempts to obtain infrared spectra resulted in extensive window attack. The reported uv–visible spectrum with a maximum at 3780 Å,[5] however, suggests that a Raman spectrum should be obtainable, when a helium–neon laser with an exciting line of 6328-Å wavelength is used.

In addition to some reported oxidation and substitution reactions, $BrOSO_3F$ has been found to form a complex with cesium fluorosulfate of the type $Cs[Br(OSO_2F)_2]$,[6] where in the absence of other structural information a Raman spectrum could be used to elucidate the nature and structure of the complex. Recently reported Raman spectra on $Br(OSO_2F)_3$ and the $Br(OSO_2F)_4^-$ ion[7] could be used for comparison and should allow some conclusions on the bonding in bromine fluorosulfate compounds.

Experimental Section

Bromine(I) fluorosulfate was prepared by direct reaction of Br_2 (BDH reagent grade) distilled from KBr[8] and P_2O_5 and $S_2O_6F_2$, prepared in a catalytic flow reaction,[9] with the latter in a slight excess as described previously.[5] Possible contaminants such as $S_2O_5F_2$, introduced as an impurity in $S_2O_6F_2$, and HSO_3F, formed by hydrolysis, can be removed by pumping or by using freshly prepared $BrOSO_2F$ for the Raman spectrum. It was found necessary to avoid any grease contact, which required filling of the Raman tubes in an all-glass vacuum line. The purity of the bromine(I) fluorosulfate was conveniently checked by the melting point.

Cesium difluorosulfatobromate(I) was prepared *via* two methods: the reactions of an excess of $BrOSO_2F$ with either CsCl or $CsSO_3F$, the latter being obtained from the reaction of cesium chloride and fluorosulfuric acid.[10] In both cases a yellow-orange solid was obtained as reported;[6] however, on prolonged pumping in order to remove all excess bromine(I) fluorosulfate, a slow decomposition was noted. As a consequence, all recorded Raman spectra were found to show weak impurity bands due to either $CsSO_3F$ or $BrOSO_2F$ which were easily recognizable since both infrared and Raman spectra of $CsSO_3F$ are known.[11] The approximate composition of the complex was determined by weight.

A Cary 81 Raman spectrophotometer was used, equipped with a Spectra Physics Model 125 He–Ne laser. The solid sample was contained in a flat-bottom Pyrex tube with a 6-mm o.d. Bromine(I) fluorosulfate was distilled into a flat-bottom Pyrex cell with a 6-mm o.d. of 50-mm length and a Pyrex rod sealed in as a spacer. The cell was flame sealed after distillation.

Results

The observed vibrational frequencies are listed in Table I together with the estimated intensities, the polarization ratios for $BrOSO_2F$, and the proposed assignments. Also listed are the previously reported frequency values for HSO_3F[12] and the $Br(OSO_2F)_4^-$[7] ion. The Raman spectrum of bromine(I) fluorosulfate is shown in Figure 1; the spectrum of $Cs[Br(OSO_2F)_2]$, in Figure 2. The band positions for the most intense bands in the range of 100–700 cm^{-1} were ascertained by recording the spectrum also in the anti-Stokes region for this range. The accuracy is judged to be ± 3.0 cm^{-1} or better.

Discussion

Some general structural information on $BrOSO_2F$ can be obtained from the reported physical properties.[5] Molecular weight determination *via* the vapor density method indicates the presence of discrete $BrOSO_2F$ molecules in the gas phase, the Trouton constant of 25.5 indicates intermolecular association in the liquid phase, and the specific electrical conductivity of 7.21×10^{-4} ohm^{-1} cm^{-1} at 25°, together with a positive temperature coefficient of the specific conductance, indicates some ionic dissociation. The method of preparation and the observed ^{19}F nmr chemical shift of −34.6 ppm from $CFCl_3$ as external reference, well within the range of other covalent fluorosulfates,[13] are evidence of the presence of an SO_3F group, covalently bonded to bromine.

As discussed previously for the related molecule HSO_3F[12,14,15] C_s or C_1 symmetry is possible. Polariza-

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TABLE I

RAMAN FREQUENCIES FOR $BrOSO_2F$, $[Br(OSO_2F)_2]^-$, AND RELATED COMPOUNDS[a]

$BrOSO_2F$				$Cs[Br(OSO_2F)_2]$		$Cs[Br(OSO_2F)_4]$[b]		HSO_3F[c]
Δ, cm^{-1}	Intens	P	Approx description	Δ, cm^{-1}	Intens	Δ, cm^{-1}	Approx description	Δ, cm^{-1}
175	4	0.26	Br–O bend, A′					
317	10	0.34	SOBr wag, A′	261	4	239	F–SOX wag[d]	391
				349	0.2			
			($CsSO_3F$, ν_6)	(407)	0.2			
390	1, br	dep	SO_2 torsion, A″	398	1	406	SO_2 torsion	405
464	4	0.40	Br–O str, A′	437	4	447	Br–O sym str	
537	1	dep	SO_2 rock, A″	557	1	553	SO_2 rock	560
570	1	p	SF wag, A′	574	1	578	SF wag	
659	6	0.20	SO_2 bend, A′	618	10	615	SO_2 bend	
832	1	0.66	S–F str, A′	780	1, br	834	S–F str	850
884	2.5	0.62	S–OBr str, A′	1020	1	970	S–OX str[d]	960
							O–H bend	1178
			($CsSO_3F$, ν_1)	(1077)	2			
1206	4	0.24	SO_2 sym str, A′	1223	2.5	1220 1237	SO_2 sym str	1230
1438	2	dep	SO_2 asym str, A″	1378	1.5	1407 1424	SO_2 asym str	1445

[a] Explanation: P, polarization ratio; Δ, Raman frequency shift; sym, symmetric; asym, asymmetric; wag, wagging; str, stretch; br, broad; sh, shoulder; p, polarized; dep, depolarized. Impurity bands are listed in parentheses. [b] F. A. Hohorst and J. M. Shreeve, *Inorg. Chem.*, **5**, 2069 (1966). [c] S. M. Chackalackal and F. E. Stafford, *J. Amer. Chem. Soc.*, **88**, 4815 (1966). [d] X = Br or H.

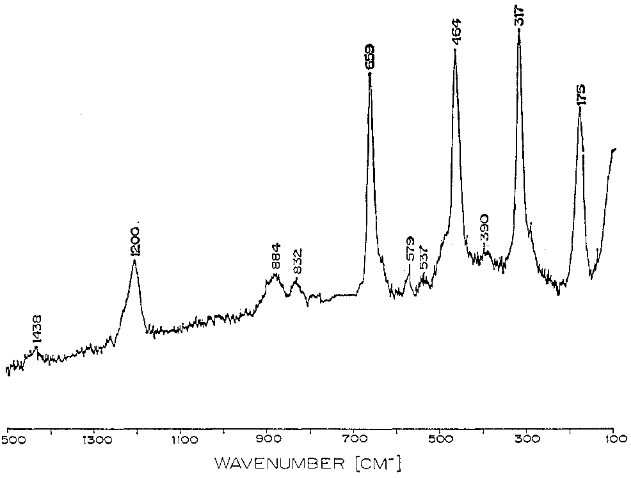

Figure 1.—The Raman spectrum of $BrOSO_2F$.

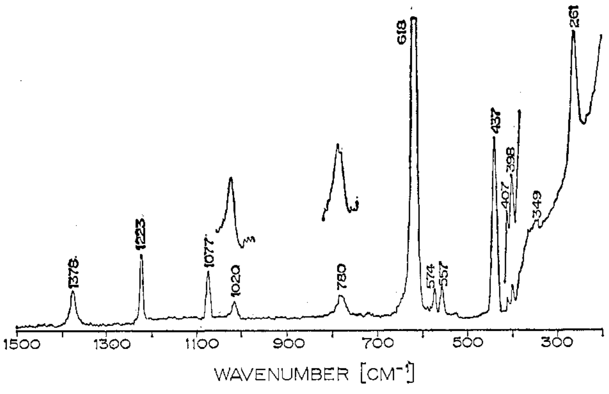

Figure 2.—The Raman spectrum of $Cs[Br(OSO_2F)_2]$.

tion measurements indicate the presence of three depolarized modes with the missing Br–O torsion mode expected to be depolarized too, thus ruling out C_1 symmetry.

Point group C_s for $BrOSO_2F$ would mean either that the Br–O–S group is linear or, if it is bent, that it is in one plane with the fluorine whereby cis and trans isomers are possible. A nonlinear configuration is preferred by us for the following reasons. The reported low-temperature infrared spectrum of Br_2O[16] is interpreted in terms of a bent molecule with C_{2v} symmetry. A linear configuration would violate the Gillespie–Nyholm[17] valence-shell electron-pair repulsion model and could only be achieved by assuming extensive lone-pair delocalization from oxygen into bromine and/or sulfur d orbitals with appreciable multiple-bond character. The observed S–OX stretch at 884 cm^{-1}, however, is lower than the corresponding frequency in HSO_3F[12] where C_s symmetry and a bent H–O–S group are postulated.[12,14] The Br–O stretching mode is assigned to a strong polarized band at 464 cm^{-1}, considerably lower than the Cl–O stretch in $ClOSO_2F$[18,19] assigned at 700 cm^{-1} but in good agreement with the assignment for $Br(OSO_2F)_4^-$[7] and for ν(Se–O) in $SeO(OSO_2F)_2$[20] found at 446 and 452 cm^{-1}. For Br_2O[16] slightly higher values of 587 and 504 cm^{-1} are reported for the asymmetric and symmetric bromine–oxygen stretch, again favoring the bent model for $BrOSO_2F$.

The remaining frequencies in the Raman spectrum are easily assigned in analogy to HSO_3F[14] and the $Br(OSO_2F)_4^-$ anion.

In $Cs[Br(OSO_2F)_2]$ bromine(I) fluorosulfate can be regarded as a fluorosulfate ion acceptor. Quite in analogy to a large number of trihalide anions[21] a linear or nearly linear configuration of the O–Br–O group would be expected. The observed thermal instability of the complex results in the occurrence of very weak-intensity bands in the Raman spectrum due to the parent molecules $CsSO_3F$. A tentative assignment is nevertheless possible for the remaining bands, indicating that a complex is indeed formed as reported.[6] The spectrum is shown in Figure 2. Only one type of fluorosulfate group seems to be present as judged by the number of observed bands. As can be seen, the

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splitting between the symmetric and asymmetric SO_2 stretches has decreased from 232 cm^{-1} in $BrOSO_2F$ to only 154 cm^{-1}. This indicates a trend toward a more ionic SO_3F group in the anionic complex. This is further indicated by a strong upward shift of the S–OBr stretching mode from 884 cm^{-1} in $BrOSO_2F$ to 1022 cm^{-1}. The corresponding SO stretching modes for $Br(OSO_2F)_4^-$[7] show a similar trend. In addition, the sulfur–fluorine stretch, which has been found to be very sensitive toward changes in the covalent bond strength,[22] is found at 781 cm^{-1}, exactly between the S–F stretching frequencies for $BrOSO_2F$ and $CsSO_3F$.[11] The symmetric SO_2 bending vibration is found at 618 cm^{-1}, again higher than any other bending mode but noticeably reduced from the position in the spectrum of bromine(I) fluorosulfate.

Only one absorption mode is found in the bromine–oxygen region, a strong band at 437 cm^{-1}, tentatively assigned as a symmetric bromine–oxygen stretch. The absence of any other vibrations in this region is consistent with a linear O–Br–O grouping, where neither the asymmetric stretch nor the O–Br–O bend is expected to be Raman active.

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Raman Intensity Measurements on Group IV Tetrahalides

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The intensities of the totally symmetric stretching modes of the tetrachlorides, tetrabromides, and tetraiodides of carbon, silicon, germanium, tin, and titanium (MX_4) have been determined relative to the 806-cm^{-1} band of cyclohexane as internal standard. The measurements were made, wherever possible, using four different exciting lines. The results indicate that the relative intensities of these modes depend, in most cases, strongly on the exciting line used and in particular on the energy gap between the exciting frequency and the frequency of the first allowed electronic transition of each halide. The data have been used to determine bond polarizability derivatives ($\bar{\alpha}'_{MX}$) at zero exciting frequency (infinite frequency for the first electronic transition) for each halide. These quantities, which vary in the order MCl < MBr < MI and CX $\sim$ SiX < GeX < SnX < TiX, are discussed with reference to the degree of covalent character of the metal–halogen bonds and, more specifically, with the δ function potential model for absolute Raman intensities. The a_1 bands of the tetrachlorides have all been studied under high resolution, both as neat liquids and in cyclohexane solutions, and the variations in the structures of these bands from their expected isotopic pattern are discussed. In particular, the spectra of neat $SiCl_4$ and neat $TiCl_4$ have been obtained in the solid state and in the liquid state at three temperatures and the data have been interpreted to rule out a previous suggestion that these molecules are dimeric in the liquid state. The halogen-exchange reaction between $TiCl_4$ and $TiBr_4$ has been studied by monitoring the intensities of the a_1 peaks of both the parent tetrahalides as well as those of the mixed halides $TiCl_3Br$, $TiCl_2Br_2$, and $TiClBr_3$. By studying the spectra of mixtures of $TiCl_4$ and $TiBr_4$ with widely varying mole ratios, it is concluded that the mixtures consist of an almost random distribution of the five species.

Introduction

The key quantity which, according to the Placzek theory,[1] determines the intensity and state of polarization of a Raman line is the derived polarizability tensor α', where $\alpha' = (\delta\alpha/\delta Q)_0$, the rate of change of the polarizability, α, with respect to the normal coordinate Q at the equilibrium configuration. Like α, this tensor possesses the invariants $\bar{\alpha}'$ and γ', which are its mean value and anisotropy

$$\bar{\alpha}' = {}^1/_3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$(\gamma')^2 = {}^1/_2[(\alpha'_{xx} - \alpha'_{yy})^2 + (\alpha'_{yy} - \alpha'_{zz})^2 + (\alpha'_{zz} - \alpha'_{xx})^2 + 6(\alpha'^2_{xy} + \alpha'^2_{yz} + \alpha'^2_{zx})]$$

The theory leads to the result that for an assemblage of freely rotating molecules irradiated with polarized light, the total intensity, I, and the degree of depolarization ratio, ρ, of the Raman light scattered at right angles to the incident direction are

$$I = (\text{constant})[45(\bar{\alpha}')^2 + 7(\gamma')^2]$$

$$\rho = \frac{3(\gamma')^2}{45(\bar{\alpha}')^2 + 4(\gamma')^2}$$

In the special case of an isotropic molecule, $\gamma = 0$, and so for the symmetric stretching mode $\gamma' = 0$. Hence the Raman intensity of this mode is directly related to $(\bar{\alpha}')^2$ and the depolarization ratio is zero. As the molecular group IV tetrahalides are isotropic, they form an ideal set of molecules for which to determine mean polarizability derivatives and bond polarizability derivatives ($\bar{\alpha}'_{MX}$) and thus any relationship between the latter and bond character. An initial study along these lines was carried out by Woodward and Long[2] for five tetrachlorides and two tetrabromides of group IV, from which they concluded that their observed $\bar{\alpha}'_{MX}$ values agreed, with one exception, with values calculated from the empirical equation $\bar{\alpha}'_{emp} =$

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