TABLE VI

SUMMARY OF THERMODYNAMIC PARAMETERS CALCULATED FOR THE HYDROLYSIS REACTION IN SCHEME II AT 25°[a]

Species	ΔH, kcal	ΔS, cal/deg	$\Delta H/y$, kcal	$\Delta S/y$, cal/deg	ΔC_p, cal/deg
A. Reaction: $x\mathrm{Al}^{3+} + y\mathrm{H_2O} = \mathrm{Al}_x(\mathrm{OH})_y{}^{(3x-y)+} + y\mathrm{H}^+$ Standard State: Hypothetical 1 *m* Solutions in 1 *m* KCl					
$Al_2(OH)_2{}^{4+}$	18.3 ± 2.6	27 ± 8	9.2 ± 1.3	14 ± 4	12 ± 44
$Al_3(OH)_4{}^{5+}$	30.9 ± 3.4	42 ± 11	7.7 ± 0.8	11 ± 3	90 ± 62
$Al_{14}(OH)_{34}{}^{8+}$	262.8 ± 1.9	377 ± 6	7.73 ± 0.06	11.1 ± 0.2	733 ± 42
B. Reaction: $x\mathrm{Al}^{3+} + y\mathrm{OH}^- = \mathrm{Al}_x(\mathrm{OH})_y{}^{(3x-y)+}$ Standard State: Hypothetical 1 *m* Solutions in 1 *m* KCl					
$Al_2(OH)_2{}^{4+}$	-9.0 ± 2.6	61 ± 8	-4.5 ± 1.3	31 ± 4	
$Al_3(OH)_4{}^{5+}$	-23.4 ± 3.4	111 ± 11	-5.8 ± 0.8	28 ± 3	
$Al_{14}(OH)_{34}{}^{8+}$	-201.6 ± 2.1	961 ± 7	-5.93 ± 0.06	28.3 ± 0.2	
C. Reaction: $x\mathrm{Al}^{3+} + y\mathrm{OH}^- = \mathrm{Al}_x(\mathrm{OH})_y{}^{(3x-y)+}$ Standard State: Hypothetical Mole Fraction Unity in 1 *m* KCl					
$Al_2(OH)_2{}^{4+}$	-9.0 ± 2.6	85 ± 8	-4.5 ± 1.3	43 ± 4	
$Al_3(OH)_4{}^{5+}$	-23.4 ± 3.4	159 ± 11	-5.8 ± 0.8	40 ± 3	
$Al_{14}(OH)_{34}{}^{8+}$	-201.6 ± 2.1	1339 ± 7	-5.93 ± 0.06	39.4 ± 0.2	

[a] Uncertainties include the covariance of ΔH, ΔS, and ΔC_p.

terms of mole fraction standard states as well as the molal standard states. Only in the former case (Table VIC) is the value of $\Delta S°$ independent of the change in the number of species in a reaction.

We see from Table V that, within the estimated uncertainties, the values of $\Delta H°/y$ and $\Delta S°/y$ each are constant for the three aluminum hydrolysis species of scheme II. Similar results have been observed previously[27] for a number of other sets of hydrolysis species, and this behavior may be generally true in cation hydrolysis. The $\Delta H°/y$ values for $Al_3(OH)_4{}^{5+}$ and $Al_{14}(OH)_{34}{}^{8+}$ in Table VIC are near the lower limit of the range of corresponding values for the other systems (-6.0 to -9.2). Th^{4+} ion—like Al^{3+}, a rare gas type ion—yields the most nearly similar values (-6.0, -6.2, and -6.0 kcal) for three polynuclear species. The $\Delta S°/y$ values for the aluminum species are near the value (37 cal deg^{-1}) predicted by the equation $\Delta S°/y = 28 + 1.0Z^2$ proposed previously.[27]

Species in Basic Solution.—The present results in basic solutions (Table III) are consistent with the observations of Brosset at 40°; *i.e.*, within the small uncertainties of the data they show the hydroxide-to-aluminum ratio to be equal to 4. This result, together with our observation of rapid kinetics and the reported solubility measurements,[15-17] suggests a mononuclear species with -1 charge. The Raman spectra of Moolenaar, *et al.*,[18] indicate that the species of this type formed at low temperatures is tetrahedral $Al(OH)_4{}^-$.

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Vibrational Spectra and Solution Studies on Iodyl Compounds

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Infrared and Raman spectra of the iodyl compounds IO_2F, IO_2AsF_6, and IO_2SO_3F are reported together with vibrational spectra for IOF_3 and KIO_2F_2. A polymeric structure with a bridging SO_3F group and discrete IO_2 groups are found for IO_2SO_3F. Solution studies of this compound in HSO_3F indicate incomplete ionization of the solute.

A number of inorganic compounds containing the IO_2 group have been reported over the years. They include iodyl fluoride,[1-4] IO_2F, and its interaction products with the Lewis acids AsF_5 and BF_3,[5] commonly regarded as, *e.g.*, IO_2AsF_6[5,6] and not as $AsF_4{}^+IO_2F_2{}^-$[7] as assumed previously. The other known iodyl compounds can be regarded as salts of strong oxyacids and include the compounds $(IO_2)_2S_2O_7$,[8,9] IO_2SO_3F,[10] $IO_2CF_3CO_2$,[11] $(IO_2)_2SeO_4$, and $(IO_2)_2HSeO_4$.[12]

All these compounds are white or pale yellow nonvolatile compounds, previously thought to contain the

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iodonium cation IO_2^+. The existence of this cation had been postulated as a reactive intermediate.[13] However, the failure to establish the existence of such a cation in the sulfuric acid solvent system,[14] together with conclusions reached for the related iodosyl salts such as $(IO)_2SO_4$ and $(IO)_2SeO_4$,[15] where evidence from vibrational spectra points to an oxygen-bridged polymeric "IO^+" ion, has resulted in a preference for similar formulations[11,12,14] for the iodyl salts. Any structural proof for such postulated oxygen-bridged structures is clearly lacking. Except for an incomplete infrared spectrum on IO_2AsF_6[6] and a very recent brief report[16] of the ir spectrum of IO_2F, no detailed vibrational spectra of iodyl compounds appear to be reported.

It therefore seemed interesting to apply infrared and laser Raman spectroscopy to a systematic study of iodyl compounds. The selected examples IO_2F, IO_2AsF_6, and IO_2SO_3F were considered to be representative. It should be possible to decide whether a common structure for the iodyl group is found in all these compounds and whether such a group is polymerized *via* I–O–I bridges or exists as a discrete cation group with oxygen multiply bonded to iodine, as found in the formally related chloronium cation ClO_2^+. Anion–cation interaction as found for the latter[17,18] is also here a distinct possibility.

Inclusion of the related compounds IOF_3 and KIO_2F_2 in the vibrational study should help in the interpretation since for both compounds structural details are known[19,20] from X-ray diffraction studies. No detailed vibrational spectra appear to have been reported for these compounds.

Solution studies in fluorosulfuric acid were undertaken for three main reasons. (a) The study by Gillespie and Senior[14] used iodic acid as a solute in H_2SO_4. IO_2^+ ions, formed according to the net equation $HIO_3 + 2H_2SO_4 = IO_2{}^+{}_{solv} + H_3O^+{}_{solv} + 2HSO_4^-$, would have to coexist with the H_3O^+ ion. Solvolysis of solutes already containing the iodyl group would avoid the formation of the H_3O^+ ion and subsequent hydrolysis of IO_2^+. By analogy it is found that a solvated chloronium cation is formed not from solvolysis of metal chlorates or chloric acid but only from chloryl compounds.[17,21] (b) Fluorsulfuric acid is a stronger protonic acid than sulfuric acid and clearly better suited for the study of such highly electrophilic cations.[22] (c) The most suitable solute iodyl fluorosulfate was reported to be insoluble in HSO_3F.[10] It was found by us that the compound dissolves in HSO_3F at room temperature over several days to give clear solutions sufficiently concentrated for conductivity studies.

Experimental Section

Materials.—Iodine pentoxide (British Drug House, AR grade) was heated before use to ~150° and powderized in an inert-atmosphere box. Potassium iodate was obtained from Fisher Scientific Co. The volatile compounds IF_5, HF (both from Matheson of Canada Ltd.), and AsF_5 (Ozark Mahoning Co.) were distilled and manipulated in a Monel vacuum line fitted with Whitey valves. Technical grade fluorosulfuric acid (Allied Chemicals) was distilled twice before use in conductivity measurements, as described previously.[23] Literature methods were used for the preparations of peroxydisulfuryl difluoride[24] and KIO_2F_2.[25]

The method of Aynsley, *et al.*,[1] was used for the synthesis of IOF_3 and IO_2F (by thermal degradation of the former compound). The compound IO_2AsF_6 was formed in anhydrous hydrogen fluoride solution from IO_2F and AsF_5 according to the method of Schmeisser and Lang[4] using a Monel reactor. Attemps to prepare the compound by direct combination of both fluorides resulted in incomplete compound formation even under high pressure. Iodyl fluorosulfate was synthesized as reported previously[10] in a glass reaction vessel. Similar reaction flasks were used in the reaction of KIO_3 and $S_2O_6F_2$.

Methods.—Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer and covered the range 4000–250 cm^{-1}. The far-infrared spectrum of KIO_2F_2 was obtained on a Perkin-Elmer 301 spectrophotometer. Silver chloride and KSR-5 (Harshaw Chemicals) windows were used without any mulling agent in most cases, due to the reactivity of the compounds.

Raman spectra were obtained with a Cary 81 spectrophotometer equipped with a Spectro Physics 125 He–Ne laser. Light of 6328-Å wavelength was used for excitation. The samples were contained in 5-mm o.d. Pyrex or silica tubes, which were flame sealed except in the case of KIO_2F.

A Wayne-Kerr Universal Bridge No. B-221A was employed for the conductometeric studies. The conductivity cells and the determination of cell constants have been described previously.[23,26] A Sargent Thermonitor, Model ST, with circulating and heating unit was used in the constant-temperature bath, held at 25.00 ± 0.01°. All manipulations of the iodyl compounds were carried out in a Vacuum Atmosphere Corp. "Dri Lab."

Results

Well-resolved Raman spectra on the solid iodine–oxygen compounds were obtained in all cases except for IO_2AsF_6 where strong scattering occurred. Due to the extreme reactivity of the compounds no satisfactory infrared spectra could be obtained for IOF_3 and IO_2SO_3F.

The observed vibrational frequencies for IOF_3 and KIO_2F_2 are listed in Table I together with estimated

TABLE I[a]

VIBRATIONAL FREQUENCIES FOR IOF_3 AND KIO_2F_2

IOF_3		KIO_2F_2		
Raman freq, cm^{-1}	Approx character	Raman freq, cm^{-1}	Ir freq, cm^{-1}	Approx character
			855 m	
907 w	I–O str	830 w, sh	844 m	$\nu(IO)_{as}$
883 vs		808 vs	816 vs	$\nu(IO)_{sym}$
862 w			805 vs	
809 vw	IO_2F impurity	472 s	476 s	$\nu(IF_2)_{sym}$
716 vw	IO_2F impurity		434 s	$\nu(IF)_{asym}$
657 vs	$\nu(IF)_{eq}$			
550 vs	$\nu(IF)_{ax}$			
515 ms	$\nu(IF)_{ax}$			
351 m		363 ms	358 m, sh	$\delta(IO_2)$
		345 m, sh	340 s, sh	$\delta(IOF)$
302 ms				
295		319 s	322 m, sh	
			220 ms	$\delta(IF_2)$
		190 m, sh	196 ms	Rock

[a] Key for this table and Tables II and III: w, weak; m, medium; s, strong; b, broad; v, very; sym, symmetric; asym, asymmetric; eq, equatorial; ax, axial; str, stretching; rock, rocking; wag, wagging; bend, bending; def, deformation.

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TABLE II[a]
VIBRATIONAL FREQUENCIES FOR IO_2F, IO_2AsF_6, AND IO_2SO_3F

IO_2F			IO_2AsF_6		IO_2SO_3F			
Ir freq, cm^{-1}	Raman freq, cm^{-1}	Approx assignment	Ir freq, cm^{-1}	Approx assignment	Raman freq, cm^{-1}	Approx assignment	Raman freq, cm^{-1}	Approx assignment
858	866 w	I–O str modes	774 w, sh		1335 m	SO str	562 mw	SF wag
830 s	830 w, sh		718 s		1195 mw	SO_2 str	520 ms	I–O str
801 s	807 s		689 s	$\nu_3AsF_6^-$	1170 ms			
716 s	705 vs		614 mw				459 mw	SO_2 rock
557 vs	550 vs	I–F str def modes			1070 m	SO_2 str		
534 m, sh			394 m, sh		1030 m		428 s	IO_2 bend
356 s	364 w		384 s	$\nu_4AsF_6^-$	1010 mw			
337 s	328 s		376 m, sh		900 ms	IO_2 asym str	415 w	
300 ms	304 mw		350 w, sh		878 s		310 s	SO_2F torsion
	251		301 w		865 vs	IO_2 sym str	288 m	I–O bend
					843 m	SF str		
					685	SO wag		
					660 s	I–O str		
					615 w	SO_2 bend		
					603 s			
					592 m			
					582 w			

[a] For key see Table I.

intensities and suggested assignments. Table II contains vibrational frequencies of the iodyl compounds IO_2F, IO_2AsF_6, and IO_2SO_3F. Table III gives the vibrational frequencies for bridging SO_3F groups in $(CH_3)_2Sn(SO_3F_2)$ and IO_2SO_3F. The Raman spectrum of IO_2F is shown in Figure 1, and the Raman spectrum of IO_2SO_3F, in Figure 2.

TABLE III[a]
VIBRATIONAL FREQUENCIES FOR BRIDGING SO_3F GROUPS IN $(CH_3)_2Sn(SO_3F)_2$ AND IO_2SO_3F

	$(CH_3)_2Sn(SO_3F)_2$ Ir freq, cm^{-1}	IO_2SO_3F Raman freq, cm^{-1}	Approx description
ν_7	1360	1335	SO str (A″)
ν_1	1180	1195, 1170	SO_2 str asym (A′)
ν_2	1088, 1072	1070, 1030, 1010	SO_2 str sym (A′)
ν_3	825	843	SF str (A′)
ν_8	618	615	SO wag (A″)
ν_4	589	603	SO_2 bend (A′)
ν_5	554	562	SF wag (A′)
ν_9	417	459	SO_2 rock (A″)
ν_6	304	310	Torsion (A′)

[a] For key see Table I.

The interpolated and measured specific conductivities for solutions of IO_2SO_3F in HSO_3F at 25° are listed in Table IV. A plot of specific conductance *vs.* molality is shown in Figure 3.

TABLE IV
Specific Conductivities of IO_2SO_3F in HSO_3F at 25.00°

		KSO_3F additions	
$10^2[IO_2SO_3F]$, *M*	$10^4\kappa$, ohm^{-1} cm^{-1}	$10^2[KSO_3F]$, *m*	$10^4\kappa$, ohm^{-1} cm^{-1}
0.0000	1.125	0.0429	31.45
0.0536	1.912	0.3477	36.45
0.2882	5.728	1.210	51.86
1.026	13.83	2.796	83.01
1.541	18.07	3.725	101.6
2.071	21.68	4.911	125.5
2.778	25.92		
3.196	28.49		
3.635	30.77		

Interpolated Specific Conductivities

Concn × 10^2, *m*	$10^4\kappa$, ohm^{-1} cm^{-1}		Concn × 10^2, *m*	$10^4\kappa$, ohm^{-1} cm^{-1}	
	KSO_3F	IO_2SO_3F		KSO_3F	IO_2SO_3F
0.00	1.085	1.125	2.00	50.0	21.5
0.25	7.0	4.9	2.50	62.5	24.8
0.50	13.61	8.0	3.00	72.7	27.7
0.75	19.7	10.8	3.50	84.9	30.1
1.00	25.8	12.4	4.00	97.0	31.9
1.50	38.0	17.7			

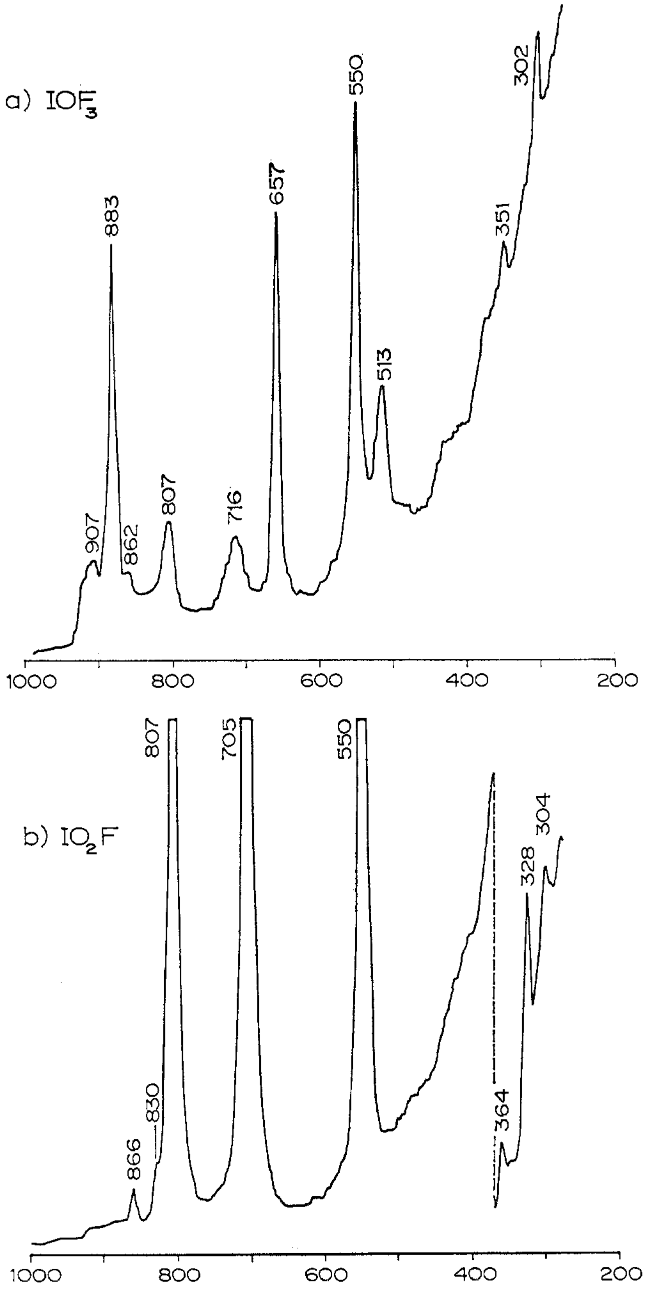

Figure 1.—Raman spectra of IOF_3 and IO_2F.

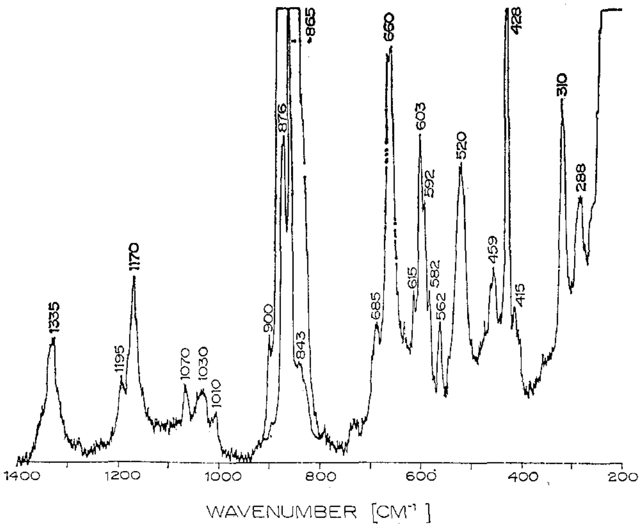

Figure 2.—Raman spectrum of IO_2SO_3F.

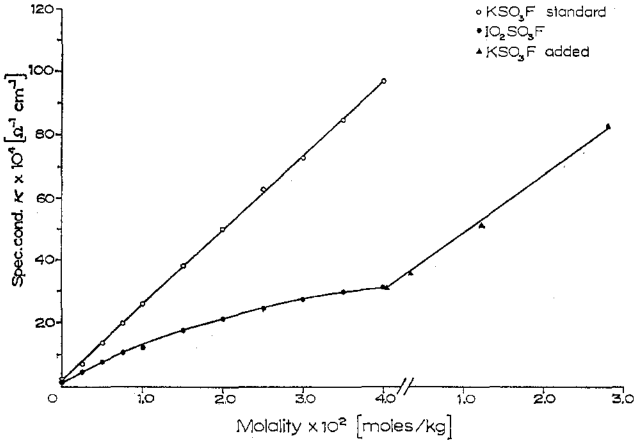

Figure 3.—Electrical conductivity of IO_2SO_3F in HSO_3F at 25°.

Discussion

It seemed reasonable to start the vibrational spectroscopic study with two compounds where the existence of discrete, nonbriding iodine–oxygen groups had been established by X-ray diffraction studies. Both IOF_3[19] and the $IO_2F_2^-$ ion in KIO_2F_2[20] are found to have related configurations, derived from a trigonal bipyramid with a stereochemically active lone pair on the central atom. The axial positions are occupied by two fluorine atoms whereas oxygen, the lone pair, and the third fluorine in IOF_3 occupy the equatorial position. As observed generally for this structural type,[26] equatorial bonds are shorter and stronger than axial ones, resulting in $r_{I-F,\text{axial}} > r_{I-F,\text{equatorial}}$.

Additional features are substantial distortions from the ideal structure as reflected by the observed bond angles and generally shorter bonds for IOF_3 than for $IO_2F_2^-$, even though an exact comparison is difficult due to large error limits reported for the latter. Evidence for strong intermolecular interaction *via* I···F and I···O contacts can be seen in the unequal I–F axial bond distances in IOF_3 and nonbonding I···F and I···O distances which are shorter than the sum of the van der Waals radii.

Disregarding all these irregularities, the expected symmetry would be C_s for IOF_3 and C_{2v} for the $IO_2F_2^-$ ion. This should result in nine Raman-active vibrations for both and also nine infrared-active modes for IOF_3 but only eight ir modes for $IO_2F_2^-$. The described structural type is rather unusual in the chemistry of main group elements; only for the related ionic species $SeOF_3^-$ [27] and for the xenon oxyfluoride XeO_2F_2[28] are vibrational spectra reported which reveal a certain structural similarity.

As shown in Table I, a total of seven vibrational modes are found for iodine oxide trifluoride and are tentatively assigned. The remaining two modes are deformation bands which should occur at low frequencies and are probably obscured by strong background scattering from the exciting light. For KIO_2F_2 such low-frequency vibrations are indeed found in the far-infrared spectrum at 220 and 196 cm⁻¹; however an assignment here can only be rather tentative because lattice vibrations can occur in this spectral region.

A tentative assignment of the vibrational frequencies for IOF_3 can also in part be based on the vibrational assignment for IOF_5,[29] where polarization measurements on the liquid and the observed combination bands in the infrared spectrum have allowed a more rigorous assignment.

As indicated by the reported structure, a discrete I–O group exists in IOF_3 and the observed band at 883 cm⁻¹ is best described as an I–O stretching vibration. As found for a number of spectra on solid iodine–oxygen compounds, additional bands are found at 907 and at 862 cm⁻¹, both of lower intensity. The main band is slightly lower in frequency than the corresponding mode in IOF_5, where a value of 927 cm⁻¹ is found.

Iodine–fluorine stretching vibrations are found at 657, 550, and 515 cm⁻¹, again lower than in IOF_5 indicating some intermolecular interaction. The positions suggest that the 657-cm⁻¹ band is mainly due to the equatorial fluorine whereas the lower vibrations are due to the axial iodine–fluorine groups. Only tentative assignments are possible for the bending modes.

The recorded vibrational frequencies for the $IO_2F_2^-$ ion in KIO_2F_2 agree very well with previous reports.[6] Again the I–O stretching modes are split; both the iodine–oxygen and the iodine–fluorine stretching modes are noticeably reduced when compared to the values for IOF_3. In particular the iodine–fluorine vibrations are found quite low and only one band at 472 cm⁻¹ is observed in the Raman spectrum indicating a nearly linear F–I–F arrangement. The asymmetric iodine–fluorine stretch is assumed to be too low in intensity to be detected in the Raman spectrum. The high intensity of the second ir-active band in the I–F region, however, does not indicate a combination band and bending modes should not occur at such high frequencies.

A similar spread of element–oxygen and element–fluorine stretching vibrations is found for the $SeOF_3^-$ ion,[27] where both types of stretching modes are reduced compared to the corresponding bands in $SeOF_2$. Only a tentative assignment is presented by the author.[30]

It can be concluded that discrete IO_2^- groups in iodyl compounds are expected to exhibit stretching

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frequencies in the 800–900-cm^{-1} range. This is supported by the reported value of 810 cm^{-1} [31] for the symmetric stretching mode of the TeO_2 molecule, isoelectronic with IO_2^+, as determined by a vibrational analysis of the electronic spectrum.

Such discrete IO_2 groups seem to be present for iodyl fluoride as evidenced by the observed bands in the expected region. Again very good agreement with the previously reported infrared spectrum[16] is observed; the iodine–oxygen stretching modes in the Raman spectrum are partly of very high intensity and found at 807, 866, 830, and 705 cm^{-1}. Only one band is assignable to iodine–fluorine stretching. The observed complexity is in contrast to the rather simple vibrational spectrum observed for IOF_5[29] and the formally related chloryl fluoride ClO_2F[32] where the symmetry is C_s.

The complexity of the vibrational spectra in the stretching region indicates extensive vibrational coupling between different vibrational modes. This allows only an approximate description of the bands in the attempted assignment. A polymeric structure, already indicated by the lack of volatility even at elevated temperatures, appears likely; however it is not possible to decide between molecular association over oxygen or over fluorine, or the presence of both.

In analogy to the behavior of other oxyfluorides, *e.g.*, ClO_2F,[33–35] the reaction of IO_2F with strong Lewis acids such as AsF_5 and BF_3 should possibly lead to fluoride ion abstraction and IO_2^+ formation. An alternative formulation of the reaction product with AsF_5 as $AsF_4^+IO_2F_2^-$ has been ruled out previously.[6] However, the recorded infrared spectrum of IO_2AsF_6 does not show any absorption bands in the 800-cm^{-1} region. Bands at 689 and 384 cm^{-1}, respectively, are in the expected region for the two infrared-active bands of the AsF_6^- ion $\nu_3[F_{1u}]$ and $\nu_4[F_{1u}]$ but the highest observed band is a weak shoulder at 774 cm^{-1}.

Two possible explanations can be offered for the observed spectrum. The first is complex formation between polymeric IO_2F and AsF_5 *via* oxygen, as recently observed for $SeOF_2 \cdot NbF_5$.[36] In this case it would be however surprising to find AsF stretching and bending modes corresponding to those expected for the AsF_6^- ion. The second explanation is the formation of an I–O–I bridged polymeric cation with AsF_6^- as counterion. Vibrational bands at 614 and 535 cm^{-1} could be attributed to such bridging iodine–oxygen groups; other I–O stretching modes may be obscured by strong absorption bands in the arsenic–fluorine regions of the spectrum at 774 and 718 cm^{-1}. The failure to obtain a Raman spectrum for this species does not permit a better assignment and a clear distinction between the alternatives; however it seems to be safe to conclude that a discrete monomeric IO_2^+ cation is absent in IO_2AsF_6.

The Raman spectrum of IO_2SO_3F shown in Figure 2 seems to indicate a different structural type for this compound. Very intense absorption bands are found in the iodine–oxygen stretching region at 876 and 865 cm^{-1}; however a simple ionic formulation such as $IO_2^+SO_3F$ must be excluded since far too many absorption bands are observed even if allowance is made for factor group splitting. In the sulfur–oxygen stretching region three main bands are found at ~1335, ~1170, and ~1030 cm^{-1} with extensive splitting for the latter two bands. This and corresponding observations for the bending and deformation region of the SO_3F group can be taken as a good indication of a lowering of the symmetry from C_{3v} to C_s which is expected to increase the number of vibrational modes from 6 to 9, all infrared and Raman active. The point group C_s is expected for SO_3F when the group acts as either a monodentate or a bidentate group where bridging occurs through oxygen only. A bridging or a chelating arrangement is possible in the latter case. Evidence from vibrational spectra for a bidentate bridging configuration has been found only very recently,[37,38] for a number of tin(IV) fluorosulfates, *e.g.*, for $(CH_3)_2Sn(SO_3F)_2$, where confirmation from a detailed X-ray diffraction study has been obtained.[39] A bidentate SO_3F has also been found for the halogen tris(fluorosulfates) $Br(SO_3F)_3$ and $I(SO_3F)_3$ [40] where monodentate SO_3F groups are also found.

The vibrational frequencies for IO_2SO_3F, which are due to the fluorosulfate group, are listed separately in Table III and are compared to the corresponding modes for $(CH_3)_2Sn(SO_3F)_2$.[41] As can be seen, excellent agreement exists for the stretching and the deformation modes. It is on this evidence that we assign the fluorosulfate vibrations to a bidentate fluorosulfate group. The observed physical properties, *e.g.*, the lack of volatility and the solution behavior in HSO_3F—to be discussed below—favor a bidentate bridging group over a bidentate chelating arrangement, resulting in a polymeric structure.

Assignments for the iodyl group vibrations can be made quite easily. The bands at 900 and 876 cm^{-1} are assigned to the asymmetric stretching mode with the corresponding symmetric stretch at 865 cm^{-1}. The fact that both stretching modes appear in the Raman spectrum may be interpreted in terms of a nonlinear IO_2 group. The IO_2 bending mode is assigned to a band at 428 cm^{-1}.

Iodine–oxygen single bonds give rise to the two bands at 660 and 520 cm^{-1}, respectively. The presented assignment suggests a polymeric structure with discrete IO_2 groups, where the iodine–oxygen bonds appear to have multiple-bond character and where polymerization through bridging anionic groups occurs rather than *via* I–O–I groups. A trigonal-bipyramidal configuration with one lone pair and both oxygen atoms in the equatorial position and the bridging SO_3F groups in the axial position appears to be a reasonable structural model. A principal structural difference between IO_2AsF_6 and IO_2SO_3F is apparent. The tendency toward intermolecular association which was apparent from the reported structures for the neutral IOF_3 and

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the $IO_2F_2^-$ ion seems to increase when a formal positive charge is placed on iodine in iodyl compounds and polymerization may occur not only *via* polycation formation as speculated previously[11,14,21] but also *via* bridging anionic groups. It is obvious that under such circumstances the calculation of iodine–oxygen stretching force constants is not too meaningful.

An additional difference in chemical behavior between IO_2F and IO_2SO_3F was found when attempts were made to prepare the KIO_2F_2 analog $KIO_2(SO_3F)_2$ *via* the reaction $KIO_3 + S_2O_6F_2 \rightarrow KIO_2(SO_3F) + 0.5O_2$. Even though a reaction took place and the white reaction product obtained analyzed as $KIO_2(SO_3F)_2$, the recorded Raman spectrum revealed the presence of a stoichiometric mixture of KSO_3F and IO_2SO_3F. This indicates that IO_2SO_3F does not act as an SO_3F^- acceptor. This conclusion should have some bearing on the interpretation of the conductometric results.

It became interesting to see whether a strongly ionizing solvent as HSO_3F would be capable of breaking up the polymeric structure of IO_2SO_3F. Quite in contrast to other fluorosulfates which have been studied by us, iodyl fluorosulfate dissolves extremely slowly. Even for small amounts, several hours is required before a clear solution is formed. A similar observation was made when the polymeric solute $Sn(SO_3F)_4$[38] was dissolved, indicating a slow breaking up of a polymeric species.

The solutions of IO_2SO_3F were found to be conducting and the maximum concentration was about 4×10^{-2} mol/kg, comparable to the concentration range studied by Gillespie and Senior.[14] The resulting experimental and interpolated electrical specific conductivities are listed in Table IV for both IO_2SO_3F and the reference base KSO_3F. A specific conductivity plot *vs.* molality is shown in Figure 3. The following features are noteworthy. Compared to KSO_3F and ClO_2SO_3F,[21] iodyl fluorosulfate is not completely dissociated into $IO_2{}^+{}_{solv}$ and SO_3F^-, even at very low concentrations. The observed κ values indicate a more extensive ionic dissociation than observed for HIO_3 in H_2SO_4,[14] which may well be due to the higher acidity of HSO_3F. The specific conductance *vs.* molality plot shows appreciable curvature. Even though addition of KSO_3F results in an immediate increase in specific conductance—no minimum is observed—the slope of the resulting curve is less steep than that found for KSO_3F itself, indicating some uptake of SO_3F^- and a repression of the original ionic dissociation presumably under formation of SO_3F-bridged polymeric cationic fragments.

In conclusion our experimental findings are in good agreement with previous work by Gillespie and Senior.[14] In addition to the proposed polymeric oxygen-bridged structures,[14] a structural model where discrete IO_2 groups are bridged by bidentate fluorosulfate groups becomes a possible alternative, which can account for the observed conductivities. Unfortunately no meaningful Raman spectra could be obtained on such dilute solutions.

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The Crystal Structure of β-Ytterbium Triantimonide, a Low-Temperature Phase[1]

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A previously reported phase Yb_5Sb_2 is shown to be a low-temperature polymorph of Yb_5Sb_3. β-Yb_5Sb_3 crystallizes in the orthorhombic system, space group *Pnma*, $a_0 = 12.398$ (2) Å, $b_0 = 9.562$ (2) Å, and $c_0 = 8.246$ (2) Å, $Z = 4$, $\rho_{calcd} = 8.343$ g/cm^3. Molybdenum radiation was used to measure the integrated intensities of 1555 independent reflections with a scintillation counter and a four-circle diffractometer. The parameters were refined by least squares to $R = 0.0797$ for 1252 reflections greater than σ using anisotropic temperature factors. The structure consists of trigonal prisms formed by Yb whose centers are occupied by Sb. The prisms articulate by edge sharing into hexagons, and by face sharing they form hexagonal columns parallel to [010]. Within the columns are rhombs formed by two Yb and two Sb, and the Sb atoms are shared with the next rhombs to produce an infinite chain. The structure is very closely related to Rh_5Ge_3. The shortest Yb–Yb bond length is 3.543 Å and the shortest Yb–Sb distance is 3.044 Å. There is only a tenuous relationship between the structures of the high-temperature α form and the low-temperature β form.

Introduction

Seven intermediate phases have been reported to exist in the Yb–Sb phase diagram,[2] and five had known crystal structures. The stoichiometries of the two phases whose structures were new were given as Yb_5Sb_4 and Yb_5Sb_2. A single-crystal structure determination showed that the former compound had the composition $Yb_{11}Sb_{10}$ and was isostructural with $Ho_{11}Ge_{10}$.[3,4] A pre-

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