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Oxofluoro Complex Anion Equilibria in Aqueous Hydrofluoric Acid. 3. Iodate(V) in Concentrated Hydrofluoric Acid (>26 M)

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The vibrational spectra of the IOF_4^- anion in $CsIOF_4$ and $KIOF_4$ and in solution in CH_3CN have been determined and assigned. Solutions of various ratios of IF_5 and H_2O in CH_3CN and of HIO_3 in hydrofluoric acid (48–100%) have been studied by Raman and ^{19}F NMR spectroscopy. The spectra of the acetonitrile solutions with up to a nearly equimolar ratio of H_2O to IF_5 are consistent with the presence of, in addition to the IOF_4^- ion, $HIOF_4$ and IF_5, while the spectra of the hydrofluoric acid solutions show the presence of $IO_2F_2^-$ ion, HIO_2F_2, $HIOF_4$, and IF_5.

Introduction

Recently the results of two studies of the behavior of iodine(V) in hydrofluoric acid have been reported.[1,2] El-Gad and Selig[1] showed that IF_5 is formed when I_2O_5 or $NaIO_3$ is dissolved in anhydrous HF. These authors found no evidence for the IF_6^- ion or for other oxofluoro or hydroxofluoro species in their solutions. Milne and Moffett[2] studied solutions of HIO_3 in aqueous hydrofluoric acid (<26 M) and found evidence for the species HIO_3, IO_3^-, and $IO_2F_2^-$. They evaluated the constant governing the equilibrium between IO_3^- and $IO_2F_2^-$. The region of HF concentration between 48 and 100% has not been thoroughly studied and forms the subject of this paper. Of particular interest was the possible existence of the IOF_4^- ion in these solutions. Compounds with this anion have been particularily elusive[3] although the x-ray crystal structure of $CsIOF_4$ has been reported[4] and the anion is a likely impurity in the preparations of hexafluoroiodate(V) compounds.[5,6]

Experimental Section

Materials. Iodic acid, 99% (BDH), potassium iodate (BDH), potassium fluoride, 98% (BDH), and cesium fluoride, 99% (Ozark-Mahoning), were dried by heating under vacuum for 12 h before use; hydrofluoric acid, 48% (J. T. Baker), was standardized against standard NaOH using phenolphthalein indicator before use. Anhydrous grade HF (Matheson) was used directly. Iodine pentafluoride, 98% (Matheson), was purified by distillation from NaF to remove HF and then from Hg to remove I_2. The distillation was carried out under vacuum in an all-glass break-seal apparatus. Acetonitrile, anhydrous (Eastman), was purified by distillation from P_2O_5.

Cesium iodate was prepared by crystallization from an aqueous solution of Cs_2CO_3 and HIO_3. Potassium difluoroiodate was prepared by the method of Helmholz and Rogers.[7] Three methods were tried for the preparation of the M^IIOF_4 compounds: (1) from a stoichiometric mixture of M^IIO_3, MF (M^I = K, Cs), and IF_5 according to the reaction

$$M^IIO_3 + 2M^IF + 2IF_5 = 3M^IIOF_4$$

(2) from a stoichiometric mixture of KIO_2F_2, KF, and IF_5 according to the reaction

$$KIO_2F_2 + KF + IF_5 = 2KIOF_4$$

and (3) by hydrolysis of hexafluoroiodate in acetonitrile

$$M^IIF_6 + H_2O = M^IIOF_4 + 2HF$$

Reactions were carried out in all-glass apparatus and transfers were done in a drybox. All of the methods produced M^IIOF_4 as indicated by ir spectra of the products, which showed the characteristic IO stretching mode of the IOF_4^- ion at 890 cm^{-1},[3,4] but none of the products was completely free of $M^IIO_2F_2$ impurity with moderately strong ir bands at 805–815 cm^{-1}.[2,8] Both acetonitrile and IF_5 were used as solvents for methods 1 and 2, but where the latter was used as solvent, an ir spectrum of the product showed that M^IIF_6, with characteristic bands in the region 605–655 cm^{-1},[5,9] was present. Neither $M^IIO_2F_2$ nor M^IIOF_4 produces bands in this spectral region. Recrystallization from acetonitrile gave a product which was free of M^IIF_6 but which consisted of $M^IIO_2F_2$ and M^IIOF_4.

Ryan and Asprey[4] obtained crystals of $CsIOF_4$ from a mixture of CsI and IF_5 in acetonitrile. The oxygen source was not identified and could be either the glass reaction container itself or water adsorbed on the surface of the glass. It is interesting that XeF_6 reacts with Pyrex glass to give $XeOF_4$[10] and a similar reaction may occur with the isoelectronic IF_6^- ion: $2IF_6^- + SiO_2 = 2IOF_4^- + SiF_4$. To test this possibility a preparation of KIF_6 in CH_3CN was carried out in the presence of finely ground glass, which had been dried under vacuum, but the ir spectrum of the product showed only the presence of KIF_6 and SiO_2 in the product.

A typical preparation had 2.94 g of KF (0.05 mol), 5.41 g of KIO_3 (0.025 mol) and 11.15 g of IF_5 (0.05 mol). The mixture was shaken in 50 ml of dry acetonitrile for 24 h and then pumped dry under vacuum. The ir spectrum of the product could be accounted for by the presence of only KIO_2F_2 and $KIOF_4$. Anal. Calcd for $KIOF_4$: I, 49.19. Calcd for $KIOF_4$ containing 8% KIO_2F_2: I, 49.65. Found: I, 49.65. All products were analyzed for fluoride by titration with $La(NO_3)_3$, using a fluoride-sensitive electrode. Reasonably sharp end points were observed but the results were shown subsequently to be 15–20% high.[2] Using a correction factor of 0.85 estimated from the analysis of $M^IIO_2F_2$ compounds,[2] the fluoride content of the $KIOF_4$ product above was found to be 28% (calcd for $KIOF_4$, 29.46%; calcd for $KIOF_4$ containing 8% KIO_2F_2, 28.40%).

Methods. Analysis. Iodine was determined as iodate by reduction with excess KI and titration of liberated iodine with thiosulfate. The fluoride analysis has been discussed elsewhere.[2]

Spectroscopy. Ir spectra were taken as mulls in Nujol with CsBr plates using a Beckman IR20A spectrometer. Band positions were accurate to ±5 cm^{-1}. Raman spectra were taken on a Jarrell-Ash 300 spectrometer. All spectra were taken at 25 °C. The 4880-Å line of a Spectra Physics argon ion laser was used to excite the spectra and detection was by a cooled photomultiplier tube. A spike filter

Table I. Raman and Ir Spectra of $CsIOF_4$-$CsIO_2F_2$ and $KIOF_4$-KIO_2F_2 Products and of KIO_2F_2[a] (cm^{-1})

$CsIOF_4$-$CsIO_2F_2$		$KIOF_4$-KIO_2F_2	KIO_2F_2		$CsIOF_4$		$KIOF_4$
Raman	Ir	Ir	Raman	Ir[b]	Raman	Ir	Ir
888 vs	885 m	882 vs			888 vs	885 m	882 vs
835 mw, sh	845 w	850 w	838 m	851 m			
		845 w		845 m			
817 s	825 w	813 m	817 vs	819 vs			
810 s, sh		805 w	814 m, sh	805 w, sh			
533 vs	535 m, sh	529 s, sh			533 vs	535 m, sh	529 s, sh
[485 s]	[485 vs, br]	487 s, sh	479 s	485 s	485 s	485 vs, br	
475 m, sh		482 vs, br			475 m, sh		482 vs, br
461 w, sh	457 m, sh	441 w, sh	456 vw	440 m			
	405 w	421 w, sh		407 m			
365 ms	369 s	[361 m]			365 m	369 s	361 m
345 w			360 m	360 s			
				351 w, sh			
332 w	343 w, sh		346 w	345 s			
303 m			323 s				
273 w	275 m	280 w			273 w	275 m	280 w
214 w				220 m, sh	214 w		
			194 vw	197 s			
124 w, br							
[90 m]			90 br, sh		90 m		
75 m			58 m		75 m		

[a] Brackets indicate that the band has contributions from $IO_2F_2^-$ and IOF_4^-. [b] Reference 2.

Table II. Raman and Ir Spectra of $XeOF_4$, IOF_4^-, and $TeOF_4^{2-}$ (cm^{-1})

		$XeOF_4$[a]		IOF_4^- [c]		$TeOF_4^{2-}$ [b]		
Class	Mode no.	Raman	Ir	Raman	Ir	Raman	Ir	Approx descripn of mode
A_1	ν_1	920 mw, p	926 s	888 vs	885 m	837 vs	840 s	$\nu(XO)$
	ν_2	567 s, p	576 m	533 vs	535 m, sh	461 m	480 m	$\nu_{sym}(XF_4)$ in phase
	ν_3	285 w, p	294 s	273 w	275 m		265 m	$\delta_{sym}(XF_4)$ umbrella
B_1	ν_4	527 m		475 m		390 m		$\nu_{sym}(XF_4)$ out of phase
	ν_5							$\delta_{asym}(XF_4)$ out of plane
B_2	ν_6	233 mw		214 w		190 w		$\delta_{sym}(XF_4)$ in plane
E	ν_7		608 vs	485 m, sh	485 vs, br	335 m	330–60 vs, br	$\nu_{asym}(XF_4)$
	ν_8	365 mw	361 s	365 ms	369 s			$\delta(OF_4)$ wag
	ν_9	161 m		124 w, br		129 w		$\delta_{asym}(XF_4)$ in plane

[a] Reference 14. [b] Reference 15. [c] $CsIOF_4$.

was used to remove plasma lines when recording the spectra of the solids. Solid samples were contained in 1-mm o.d. Pyrex tubes and the spectra of the solutions were taken using a cylindrical sapphire cell, 10 cm long × 5 mm i.d. (Tyco, Sapphikon Division) closed with a Kel-F needle valve which was attached by a Swagelock fitting. Slit widths were 5 cm^{-1} for the spectra of the solids and 10 cm^{-1} for the solutions. Solutions in aqueous hydrofluoric acid with HF greater than 48% were prepared on a Monel vacuum line equipped with Hoke valves, Kel-F traps (Argonne National Laboratory), and a Bourdon type pressure gauge (Helicord). Solutions were made up by weight and molarities were calculated using density data in ref 11.

^{19}F NMR spectra were taken on a Varian Associates HA 100 spectrometer operated at 94.1 MHz in unlocked mode. The 2500-Hz sidebands did not interfere with the spectra taken. Shifts were referenced to external $CFCl_3$ and determined by sideband techniques. The temperature was regulated by a Varian temperature controller and was accurate to ±5 °C. Samples were contained in Kel-F tubes which could be inserted into glass NMR tubes. The tubes were heat-sealed under vacuum.

Results and Discussion

Solids. The Raman spectrum of a mixture of $CsIO_2F_2$ and $CsIOF_4$ is given in Figure 1 along with the Raman spectrum of KIO_2F_2. The positions of the bands in the Raman and ir spectra of the mixture and those of KIO_2F_2 are given in Table I along with those for the ir spectrum of the mixture KIO_2F_2–$KIOF_4$ and the resultant bands attributed to $CsIOF_4$ and $KIOF_4$. The spectrum in Figure 1 shows that this product is free of both IO_3^- and IF_6^- ions by the absence of the strong Raman bands for these anions at 754 and 774 cm^{-1} [12] and 628 cm^{-1},[9] respectively. The spectrum of the IOF_4^- ion was obtained by subtraction of the bands due to $IO_2F_2^-$ ion from the Raman spectrum shown in Figure 1 and the ir spectra. We were unable to prepare anhydrous $CsIO_2F_2$ by standard methods[2] and the bands arising from the $IO_2F_2^-$ ion in Figure 1 show little resemblance to those in the spectrum of $CsIO_2F_2 \cdot {}^1/_3H_2O$[2] but there is a close similarity with the spectrum of KIO_2F_2. For this reason the Raman spectrum of KIO_2F_2 was used to subtract $IO_2F_2^-$ bands from the spectrum of the mixture and give the resultant IOF_4^- spectrum given in Table I. The Cs^+ cation is larger than the K^+ cation and therefore it is expected that the vibrational modes of the $IO_2F_2^-$ ion will occur at slightly lower frequencies in $CsIO_2F_2$ than in KIO_2F_2 due to expansion of the lattice.[13] This and the relative intensities of the bands have been taken into consideration in the establishment of the vibrational spectrum of the IOF_4^- ion.

The assignment of the spectrum of $CsIOF_4$ is given in Table II along with the spectrum of isoelectronic $XeOF_4$[14] and the $TeOF_4^{2-}$ ion.[15] The IOF_4^- ion is expected to have a square-pyramidal shape with the oxygen on the fourfold axis (C_{4v} symmetry). Of the expected nine normal modes (3 A_1

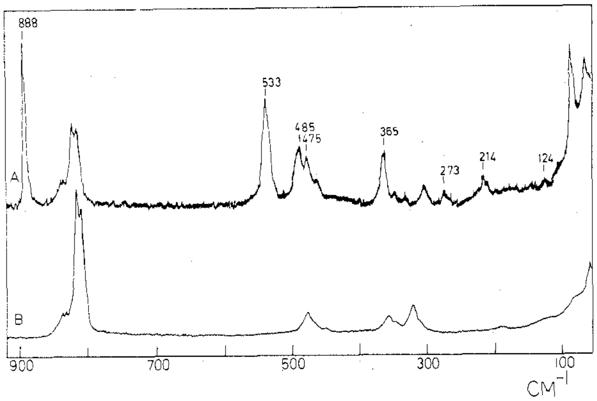

Figure 1. Raman spectrum of the solid $CsIOF_4$–$CsIO_2F_2$ mixture (A) and KIO_2F_2 (B). The frequencies for the $CsIOF_4$ bands are given in spectrum A.

Table III. Raman Spectra of IF_5 (cm^{-1})

Vapor (20 °C)[a]	HF soln[b]	CH_3CN soln	Mode
710 s, p	697 s, p	678 s, p	$\nu_1(A_1)$
631 sh			$\nu_7(E)$
614 vs, p	599 s, p	588 s, p	$\nu_2(A_1)$
602 sh	583 m	568 sh	$\nu_4(B_1)$
370 w	377 w	377[c]	$\nu_8(E)$
318 m, p	321 w, p	319 m, p	$\nu_3(A_1)$
274 w	273 w		$\nu_6(B_2)$
~200 w	191 vw		$\nu_9(E)$

[a] Reference 20. [b] Reference 1. [c] Band obscured by solvent.

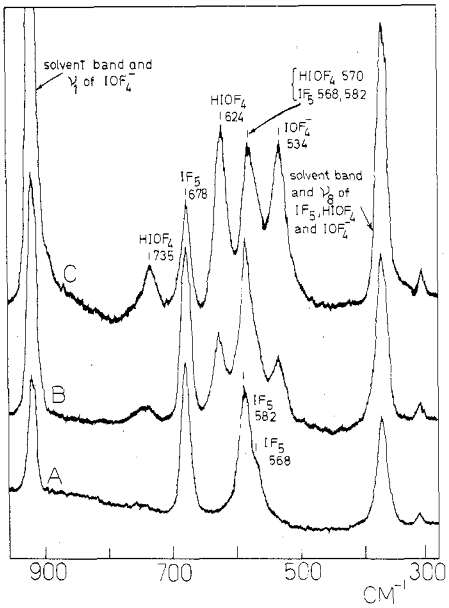

Figure 2. Raman spectra of IF_5–H_2O mixtures in CH_3CN: trace A, 1.50 M IF_5; trace B, 1.66 M IF_5 and 0.8 M H_2O; trace C, 1.66 M IF_5 and 1.20 M H_2O.

+ 2 B_1 + B_2 + 3 E) all are accounted for except ν_5, which is seldom observed in the spectra of related species with C_{4v} symmetry.[15,16] The normal modes of the IOF_4^- ion lie between those of $XeOF_4$ and $TeOF_4^{2-}$ in frequency. In the spectra of $XeOF_4$ ν_7, the antisymmetric XF_4 stretching mode, lies above ν_4, the symmetric out-of-phase stretching mode, while for $TeOF_4^{2-}$ the order is reversed. In the spectra of IOF_4^- the two modes virtually coincide. A similar crossing over of ν_4 and ν_7 arises in the series IF_5, TeF_5^-, and SbF_5^{2-}.[15]

Solutions in Acetonitrile. Solutions of various mixtures of IF_5 and H_2O in CH_3CN were studied in order to assist in the identification of the species present in the aqueous HF solutions. Acetonitrile has been used as solvent for the study of the Raman spectrum of the IF_6^- ion,[18] for preparations involving IF_5[3,19] and $CsIOF_4$.[4] The spectra of IF_5 and various IF_5–H_2O mixtures dissolved in CH_3CN are shown in Figure 2. The bands observed for IF_5 are given along with those for IF_5 in HF[1] and gaseous IF_5[20] in Table III, and the bands for the hydrolysis products along with those for isoelectronic Te(IV) species are given in Table IV. Acetonitrile itself has Raman bands at 379 and 919 cm^{-1} [21] and these are obvious in the figure. Four normal modes of IF_5 are clearly observed in the Raman spectrum, trace A, with one band obscured by the solvent peak at 379 cm^{-1}. The three I–F stretching modes observed, ν_1, ν_2, and ν_4, are all shifted to significantly lower frequencies relative to those of IF_5 vapor, indicating that an adduct may be formed in solution similar to the solid adducts formed by IF_5 with donors such as pyridine[22] and the $BrF_5{\cdot}CH_3CN$ adduct.[23] Figure 2 shows that as H_2O is added to the solution, four new bands arise at 735, 624, 534, and 306 cm^{-1} and the bands at 678 and 319 cm^{-1} due to IF_5 decrease in relative intensity while the IF_5 band at 587 cm^{-1} appears to increase in intensity but shifts 10 cm^{-1} to lower wavenumber. Furthermore, the CH_3CN bands at 379 and 919 cm^{-1} increase in strength, indicating that the new species formed in solution also have bands at these frequencies. The new bands are best accounted for in terms of the reactions

$$\mathrm{IF_5 + H_2O \underset{CH_3CN}{=} HIOF_4 + HF}$$

$$\mathrm{H_2O + HIOF_4 \underset{CH_3CN}{=} H_3O^+ + IOF_4^-}$$

The presence of the IOF_4^- ion is shown by the characteristic IO stretching mode, ν_1, at 910 cm^{-1}, lying under the solvent peak at 919 cm^{-1} and the IF_4 symmetric in-phase stretching mode, ν_2, at 534 cm^{-1}. The growth of the solvent peak at 379 cm^{-1} is due in part to the underlying ν_8 of IOF_4^- at 365 cm^{-1}. The characteristically strong Raman bands for $IO_2F_2^-$ (840 and 483 cm^{-1} [2]) and IOF_3 (883, 657, and 550 cm^{-1} [24]) are not observed in the spectra. Thus, the three remaining new bands at 735, 624, and 306 cm^{-1} are attributed to the $HIOF_4$ molecule and may be assigned to ν_1, ν_2, and ν_3, respectively, in C_{4v} symmetry (OH group considered as one atom). The increase in intensity of the IF_5 peak at 582 cm^{-1}, relative to that at 682 cm^{-1}, and its shift to lower wavenumber as the H_2O concentration is increased indicate that a new band due to one of the hydrolysis products lies under this IF_5 peak. The IOF_4^- ion has no band here but the symmetric out-of-phase IF_4 stretch, ν_4, of $HIOF_4$ is expected to lie close to ν_4 of IF_5, judging from the close proximity of the two ν_4 bands in the

Table IV. Raman Spectra of I(V) Species Found in H_2O–IF_5 Solutions in Acetonitrile and Comparable Te(IV) Species[a] (cm^{-1})

IF_5	$HIOF_4$	IOF_4^-	TeF_5^- [a]	$Te(OH)F_4^-$ [a]	$TeOF_4^{2-}$ [a]	Mode
678 s, p	735 m, p	910[b] br, s, p	611 vs	697 vs	837 vs	ν_1
582 vs, p	624 vs, p	534 vs, p	504 s	502 vs	461 m	ν_2
318 w, p	306 w, p		282 mw	266 w		ν_3
568 sh	~570 m		472 s	465 m	390 m	ν_4
[379 s][b]	[379 s][b]	[379 s][b]	338 mw	378 w		ν_8
				342 w		

[a] Reference 16. [b] Obscured by solvent bands.

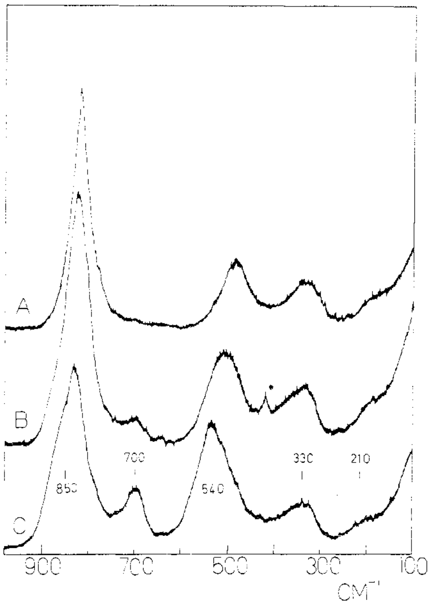

Figure 3. Raman spectra of 3 M HIO_3 solutions in hydrofluoric acid: trace A, 48% HF; trace B, 65% HF; trace C, 78% HF. Wavenumber assignments are given to the HIO_2F_2 peaks. Asterisk indicates sapphire peak.

isoelectronic pair $Te(OH)F_4^-$ and TeF_5^- (Table IV). The spectra of all species and their assignments are given in Table IV. The bands for $HIOF_4$ have been assigned in C_{4v} symmetry. Except for the shoulder at 568 cm^{-1} due to ν_4 of IF_5 and ν_4 of $HIOF_4$ at 570 cm^{-1}, all of the bands observed are polarized in agreement with the proposed assignment, and the relationship between the spectra of the three species is similar to that between the spectra of the isoelectronic series, TeF_5^-, $Te(OH)F_4^-$, and $TeOF_4^{2-}$,[15] as shown in Table IV. An exception is ν_2 which is virtually the same in $KTeF_5$ and $KTe(OH)F_4$ but which lies some 40 cm^{-1} lower in IF_5 compared to its position in $HIOF_4$. The relatively low value for IF_5 in CH_3CN is no doubt due to complex formation.

The ^{19}F NMR spectrum of a 5.24 M IF_5 solution in CH_3CN which was 2.37 M in H_2O showed, upon cooling to 10 °C, the typical doublet and quintet pattern of IF_5[25] (δ_{CFCl_3} −4.9 ppm (doublet), −47.3 ppm (quintet), $J_{FF'}$ = 80 Hz) in addition to a broad resonance at δ_{CFCl_3} +40.2 ppm which may be assigned to HF, $HIOF_4$, and IOF_4^- undergoing rapid exchange on the NMR time scale. Cooling to −45 °C, at which point the solution froze, failed to stop this exchange. It is interesting that the exchange does not take place via IF_5 and rapid proton exchange cannot account for the single exchanging peak observed. Exchange may be occurring via IOF_3

$$HF + IOF_4^- \underset{CH_3CN}{\rightleftarrows} IOF_3 + HF_2^-$$

$$HIOF_4 \underset{CH_3CN}{\rightleftarrows} IOF_3 + HF$$

Integration showed a ratio of exchanging peak area to total area of IF_5 peaks of 0.72. Using the stoichiometry of the mixture and assuming complete reaction to give $HIOF_4$ and IOF_4^-, a theoretical ratio of 0.83 is calculated. The low observed ratio shows that not all of the water causes hydrolysis of IF_5 but some is protonated by the acid $HIOF_4$.

Solutions in Aqueous HF. Solutions of HIO_3 in 0–48% HF have been shown to contain varying amounts of HIO_3, IO_3^-, and $IO_2F_2^-$.[2] A solution of 3.0 M HIO_3 in 48% HF gives only the spectrum of the $IO_2F_2^-$ ion but in 65 and 78% HF bands due to a new species are found as shown in Figure 3. Both the symmetric IO_2 stretching band at 840 cm^{-1} and the IF_2 stretching band at 483 cm^{-1} of $IO_2F_2^-$ shift to higher frequency and a new band appears at 700 cm^{-1}. These changes cannot be accounted for by any of the species identified in the acetonitrile solutions but are consistent with the formation of HIO_2F_2 in the more strongly acidic HF solutions

Table V. Raman Spectrum of the HIO_2F_2 Molecule

Freq, cm^{-1}	Approx descripn of mode	Freq, cm^{-1}	Approx descripn of mode
700 m, p	ν_{I-OH}	210 w, p(?)	$\delta_{IF_2,sym}$
850 s, br, p	ν_{IO}	330 m, p(?)	$\delta_{I(OH)O,sym}$
540 s, p	$\nu_{IF_2,sym}$		

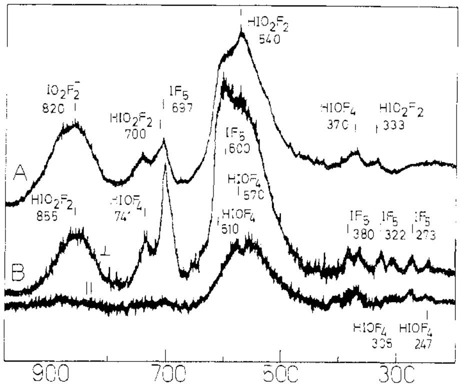

Figure 4. Raman spectra of 3 M HIO_3 solutions in hydrofluoric acid: trace A, 90% HF; trace B, 100% HF.

$$2HF + IO_2F_2^- \rightleftarrows HIO_2F_2 + HF_2^-$$

This protonation is consistent with the steep fall in the Hammett acidity function, H_0, of 4 units from 48 to 65% HF.[26] The modes ν_{I-OH}, ν_{IO}, and $\nu_{IF_2,sym}$ in the Raman spectrum of HIO_2F_2 are expected to be strong. The band observed at 700 cm^{-1} lies in the range of I–OH stretching modes ($\nu_4(HIO_3)$ 644 cm^{-1};[2] $\nu_1(HIOF_4)$ 735 cm^{-1}). The frequency lies between those for HIO_3 and $HIOF_4$ as expected on electronegativity grounds. The symmetric IF_2 stretching mode for HIO_2F_2 is expected to lie at higher frequencies than that for the $IO_2F_2^-$ ion because of the change in ion charge. A comparable change is observed in the spectra of $TeOF_4^{2-}$ and $Te(OH)F_4^-$ where ν_2, the symmetric TeF_4 stretch, increases by 40 cm^{-1} upon protonation (Table IV). For the same reason ν_{IO} is expected to lie at higher frequencies than the symmetric IO_2 stretch, ν_1, in the spectrum of $IO_2F_2^-$.[2] In a comparable example, a shift of +20 cm^{-1} is observed on going from the $HSeO_3^-$ ion to H_2SeO_3.[27] In Figure 3, trace C, the relatively sharp ν_1 mode of the $IO_2F_2^-$ ion at ~820 cm^{-1} can still be observed sitting on top of the IO stretch of HIO_2F_2. Thus, the Raman spectrum of HIO_2F_2 cannot be completely determined from the traces in Figure 3 due to overlap with $IO_2F_2^-$ bands, but the three modes which can be assigned with reasonable certainty and their approximate description are given in Table V. If the OH group is assumed to be freely rotating or if the hydrogen lies in the plane of the IO_2 group, then the molecule has C_s symmetry and all of the modes observed have A′ symmetry.

As the HF concentration is increased, new species are formed and further changes occur in the spectrum. The Raman spectra of 3.0 M HIO_3 solutions in 90 and 100% HF are shown in Figure 4. In the spectrum of the solution in 90% HF (trace A in Figure 4) the bands due to the $IO_2F_2^-$ ion have virtually disappeared with the slight asymmetry of the peak at 855 cm^{-1} caused by ν_1 of $IO_2F_2^-$ (820 cm^{-1}) being the only remaining evidence for this ion. The spectrum shows, in addition to bands due to HIO_2F_2, (1) a second I–OH stretch at 741 cm^{-1}, (2) a sharp peak sitting on top of the I–OH stretch of HIO_2F_2 at 700 cm^{-1}, (3) a considerably enhanced shoulder on the high-wavenumber side of the symmetric IF_2 stretch of HIO_2F_2 at 540 cm^{-1}, which appears to be made up of a peak at 571 cm^{-1} and a strong shoulder centered near 600 cm^{-1}, and finally (4) a new peak at 370 cm^{-1}. The spectrum observed is best interpreted in terms of a mixture of HIO_2F_2, $HIOF_4$, and IF_5. The presence of HIO_2F_2 is indicated by the strong band at 855 cm^{-1}, the strong shift in the 500–600-cm^{-1} region, the broad shift underlying the sharp peak at 697 cm^{-1}, and the peak at 333 cm^{-1}. The evidence for the presence of $HIOF_4$ consists of the I–OH stretching mode at 741 cm^{-1} (ν_1, 735 cm^{-1} in acetonitrile, Table IV), the relatively strong shoulder at 610 cm^{-1}, which is also in part due to ν_2 of IF_5, the peak at 571 cm^{-1} (ν_4, 570 cm^{-1} in acetonitrile), and the small peak at 370 cm^{-1} (ν_8, 379 cm^{-1} in acetonitrile). The presence of IF_5 is shown by the sharp peak at 697 cm^{-1} and the shoulder at 600 cm^{-1}. These peaks arise from ν_1 and ν_2 of IF_5, which are reported by El-Gad and Selig to come at 697 and 599 cm^{-1} in HF solution.[1]

In the spectrum of the solution of 3 M HIO_3 in 100% HF (trace B, Figure 4), the bands due to IF_5 at 697, 600, 380, 322, and 273 cm^{-1} are much more obvious. The positions of these bands agree well with those reported for IF_5 in HF but are shifted to slightly higher wavenumber from those for IF_5 in CH_3CN (Table IV). The peaks due to HIO_2F_2 (855, 540, and 333 cm^{-1}) and $HIOF_4$ (741, 610, 571, and 370 cm^{-1}) are still present. In the absence of interfering species, ν_1 and ν_2 of IF_5 are of nearly equal strength (Figure 2, trace A; ref 1) but in trace A of Figure 4 the band at 600 cm^{-1} is much stronger than that at 697 cm^{-1}. Moreover, the peak at 600 cm^{-1} has a shoulder on the high-frequency side. This is evidence for the presence of the symmetric in-phase IF stretching mode, ν_2, of $HIOF_4$ in this region of the spectrum. The spectrum taken with incident light polarized parallel to the viewing direction shows bands at 577, 555, and ~375 cm^{-1}. These bands arise principally from the depolarized modes, ν_4 and ν_8, of IF_5 and $HIOF_4$.

El-Gad and Selig[1] found that only IF_5 was observed in HF solutions when a ratio of HF to I(V) (as I_2O_5) of 15:1 was reached. In our solutions HIO_2F_2 and $HIOF_4$ were still observed at a ratio of 17:1. However, our I(V) solute, HIO_3, produces 20% more H_2O than does I_2O_5 upon reaction with HF, and this accounts for the difference between the two solutions

$$I_2O_5 + 20HF \rightleftarrows 2IF_5 + 5H_3O^+ + 5HF_2^-$$

$$2HIO_3 + 22HF \rightleftarrows 2IF_5 + 6H_3O^+ + 6HF_2^-$$

It is surprising that El-Gad and Selig did not observe any of the oxofluoroiodate(V) species in their study of the solutes I_2O_5 and $NaIO_3$.[1]

The ^{19}F NMR spectrum of a 2.2 M HIO_3 solution in 26 M aqueous HF (45%) at 25 °C gives a single broad shift arising from exchange of all species. Upon cooling to −58 °C, a second shift appeared at δ_{CFCl_3} −0.7 ppm while the solvent shift was found at δ_{CFCl_3} +152 ppm. On the basis of the Raman evidence this new peak must arise from the $IO_2F_2^-$ ion. Integration of the spectra gave the intensity ratio for I(V) species to solvent of 1:4.91. Calculation based upon stoichiometry gives, assuming $IO_2F_2^-$ to be the I(V) species, a theoretical intensity ratio of 1:4.95. Solutions of HIO_3 in 71 and 83% aqueous HF gave a single broad exchanging peak down to the freezing point of the solutions at −20 °C. A 6.4 M HIO_3 solution in 100% HF gave, upon cooling to −60 °C, the typical doublet–quintet pattern of IF_5 (δ_{CFCl_3} −3.1 ppm (doublet), −52.9 ppm (quintet), $J_{FF'}$ = 78 Hz) in addition to the HF solvent shift at δ_{CFCl_3} 94.8 ppm. The NMR parameters are close to those observed by El-Gad and Selig[1] for a solution of I_2O_5 in 100% HF but these authors were able to observe their spectrum at 25 °C. Their solution was made up in a large excess of 100% HF and contained IF_5 as the only I(V) species present, according to their Raman spectrum. Exchange in our solutions is apparently occurring via $HIOF_4$ and/or HIO_2F_2 rather than via IF_6^- ion inasmuch as the solutions studied in both laboratories contained comparable amounts of HF_2^- ion and exchange via IF_6^- ion would be equally favorable at room temperature.

Upon cooling of this 6.4 M HIO_3 solution to −70 °C an additional shift at δ_{CFCl_3} 0.3 ppm was observed. Whether this peak is due to HIO_2F_2, $HIOF_4$, or both is not certain and further studies will be needed to clarify this point.

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Registry No. KIO_2F_2, 16087-90-4; $CsIOF_4$, 36374-06-8; $KIOF_4$, 59654-71-6; IF_5, 7783-66-6; $HIOF_4$, 59654-72-7; HIO_2F_2, 59654-73-8.

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