

In summary the large difference in reaction cross section for AsF_4^- and PF_4^- formation remains unexplained. Studies are in progress to determine the variation in reaction cross section for other congener pairs of groups V and VI non-metals.

The reaction cross section at 2.0-V repeller voltage for AsF_6^- formation *via* reaction 12 is greater by about a factor of 4 than the value measured⁵ for the formation of PF_6^- . For the group V pentafluorides the polarizability and size of the central atom must be the dominant parameter influencing the reaction since each molecule has a zero dipole moment. That the cross section for AsF_6^- formation is greater than that for PF_6^- production is consistent with the known¹⁶⁻¹⁸ Lewis acidities and reflects the significance of fluoride ion transfer processes in determining acidities of nonmetal fluorides.

The cross section for the reactions studied here exhibit a decrease in magnitude with increasing ion energy, an effect which is characteristic of exothermic reactions. The reactions involving SF_6^- are therefore shown to be exothermic, and thermochemical calculations of the approximate ionic heats of formation of the secondary ions may be carried out since $\Delta H(\text{reaction}) \geq 0$. However, since no measurements of internal energy or kinetic energy of the reactants or products were carried out in this study, the values obtained here represent upper limits.

The primary ion AsF_4^- is formed by reaction 5. From the appearance potential of AsF_4^- , $\text{AP} \approx 0$, the heat of formation of AsF_4^- is -315 kcal/mol. The value $\Delta H_f(\text{AsF}_4^-)$ may also be evaluated from an ion-molecule process (reaction 4). The heats of formation of SF_6^- and SF_5^- have been

previously evaluated⁵ as -289 and -234 kcal/mol, respectively. The heat of formation of the reactant AsF_3 is given³⁰ as -220.04 kcal/mol, so that $\Delta H_f(\text{AsF}_4^-) = -275$ kcal/mol. This latter value is more positive than the value calculated from reaction 5. That the $\Delta H_f(\text{AsF}_4^-)$ calculated from the ion-molecule reaction is greater than that evaluated from reaction 5 suggests that AsF_4^- is formed with significant excess energy in the ion-molecule process.

If the value $\Delta H_f(\text{AsF}_4^-) = -315$ kcal/mol is used in reaction 9, $\Delta H_f(\text{AsF}_6^-)$ is calculated to be -391 kcal/mol. On the other hand, $\Delta H_f(\text{AsF}_6^-)$ is evaluated as -351 kcal/mol from reaction 12. This result again suggests that in the ion-molecule reaction the products are produced with significant quantities of excess energy.

The gaseous heats of formation were obtained from the references cited (in kcal/mol): AsF_3 , -220 ;³⁰ AsF_5 , -296 ;¹⁵ SF_6^- , -289 ;⁵ SF_5^- , -234 ;⁵ F , 19 .³⁰

Experiments to measure the kinetic energies of primary and secondary ions are in progress so that more exact determinations of heats of formation of negative ions may be obtained.

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Registry No. SF_6^- , 12206-92-7; AsF_3 , 7784-35-2; AsF_4^- , 42847-14-3; AsF_5 , 7784-36-3.

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Interhalogen Fluorosulfates and Triatomic Interhalogen Cations of Iodine, Bromine, and Chlorine¹

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The synthesis of interhalogen fluorosulfates of the two types $\text{IX}_2\text{SO}_3\text{F}$ and $\text{I}_2\text{XSO}_3\text{F}$, with $\text{X} = \text{Br}$ or Cl , is accomplished by the oxidative addition of the corresponding halogen or interhalogen molecules to iodine(I) fluorosulfate. The vibrational spectra are interpreted in terms of ionic solids with evidence for strong anion-cation interaction. All compounds behave as strong bases in HSO_3F as shown by conductometric studies, giving rise to the solvated interhalogen cations ICl_2^+ , IBr_2^+ , I_2Cl^+ , and I_2Br^+ . The identity of these cations is confirmed by their electronic spectra in HSO_3F , HSO_3CF_3 , and 96% H_2SO_4 .

Introduction

Interhalogen cations have received considerable attention in previous years,² where they have been studied in the solid state or in solution of strong protonic acids. The abstraction of halide ions from interhalogens by suitable Lewis acids has been the main synthetic route to compounds containing such cations. Obviously this method is limited in its application by the number of known stable interhalogens and the small number of suitable Lewis acids strong enough to affect halide ion transfer without side reactions, such as halogen exchanges.

The route is very successful in the preparation of compounds containing fluoro cations, where BF_3 , SbF_5 , and AsF_5 can be used as Lewis acids. Of the cations formed by the heavier halogens Cl , Br , and I , only ICl_2^+ ³ and very recently I_2Cl^+ ^{4,5} and IBrCl^+ ^{5b} have been characterized as SbCl_6^- ^{3,5} or as AlCl_4^- salts.

In a recent preliminary communication⁶ we have drawn

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attention to an additional synthetic route, most suitable to obtain cations of the heavier halogens, even where the present interhalogen is unknown, as demonstrated by the synthesis of $\text{IBr}_2\text{SO}_3\text{F}$. This method suggests the addition of diatomic halogens to iodine(I) fluorosulfate⁷ according to $\text{ISO}_3\text{F} + \text{X}_2 \rightarrow \text{IX}_2\text{SO}_3\text{F}$, where $\text{X}_2 = \text{I}_2, \text{Br}_2, \text{or Cl}_2$. It appears one should be able to extend this method to the addition of diatomic interhalogens as well, such as ICl and IBr .

As demonstrated earlier,^{7,8} ISO_3F is quite capable of adding 1 or 3 mol of I_2 resulting in the formation of the polyhalogen fluorosulfates $\text{I}_3\text{SO}_3\text{F}$ ^{7,8} and $\text{I}_7\text{SO}_3\text{F}$.⁸ A rather impure $\text{ICl}_2\text{SO}_3\text{F}$ ⁷ was the only reported interhalogen fluorosulfate at the outset of this study.

These fluorosulfates should be excellent precursors for the formation of interhalogen cations in strong protonic acids, in particular HSO_3F which has the common anion. Previous solution work is confined mainly to polyhalogen cations. Only ICl_2^+ ^{9,10} and very recently IBr_2^+ ¹⁰ have been studied in sulfuric¹⁰ and disulfuric acid.⁹

The existence of the interhalogen cations I_2Br^+ and I_2Cl^+ in H_2SO_4 as components of rather complex mixtures had been suggested earlier,¹¹ however, no definitive evidence is provided. The cation I_2Cl^+ , which is a potential self-ionization ion in molten iodine monochloride, is claimed² to be possibly extensively disproportionated into I_3^+ and ICl_2^+ . Again, any experimental evidence is clearly lacking.

The objectives of the present investigation are the synthesis of interhalogen fluorosulfates of the type $\text{X}_n\text{Y}_{(3-n)}\text{SO}_3\text{F}$, where X and Y represent the halogens Cl, Br, and I, by halogen or interhalogen addition to iodine(I) fluorosulfate, their structural characterization by ir and Raman spectra, where possible, and the study of their solution in HSO_3F by conductometric and spectrometric methods. Solution studies on the previously synthesized $\text{I}_3\text{SO}_3\text{F}$ ^{7,8} are included for comparison purposes, since the I_3^+ cation has been characterized previously in a number of protonic acids¹¹⁻¹⁵ by conductometric, cryoscopic, analytical, and spectrophotometric methods. In contrast to our approach, the cation had been produced *in situ* by the oxidation of molecular iodine.

Experimental Section

I. Chemicals. Resublimed iodine (Fisher Chemicals), bromine (BDH), distilled before use from P_2O_5 and KBr , and chlorine (Matheson of Canada Ltd.) of 99.5% purity, which was passed twice through 96% H_2SO_4 traps and finally P_2O_5 , were used in the addition reactions and in the synthesis of ISO_3F . The acids HSO_3F (technical grade) and H_2SO_4 (96.5-97.5% purity) as well as F_2 and SO_3 were obtained from Allied Chemicals. Fluorosulfuric acid was purified by double distillation at atmospheric pressure as described in the literature.¹⁶ Trifluoromethanesulfonic acid (Minnesota Mining and Manufacturing Co.) was distilled before use from ~100% H_2SO_4 under reduced pressure.

The chemicals ICl ,¹⁷ IBr ,¹⁸ $\text{S}_2\text{O}_6\text{F}_2$,¹⁹ and ISO_3F ^{5b} were synthesized according to published methods. Both ICl and IBr were re-

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crystallized before use. The purities of the univalent iodine compounds were checked by the melting points.

II. Instruments. Infrared spectra were obtained on a Perkin Elmer 457 grating spectrophotometer. Samples were run as fine films without the use of a mulling agent between BaF_2 , AgCl , and AgBr windows (all from Harshaw Chemicals).

Raman spectra were recorded on a Cary 81 spectrometer equipped with a Model 125 He-Ne gas laser (Spectra Physics Corp.). The samples were contained in 5-mm o.d. Pyrex tubes with flat bottom ends. ¹⁹F nmr spectra were recorded with a modified Varian Associates T60 nmr spectrometer. Freon 11 (CFCl_3) was used as external standard together with purified HSO_3F .

A Wayne-Kerr Universal Bridge No. B-221A was used for conductometric studies. A Sargent Thermonitor, Model ST, with a circulating and heating unit was used in the constant-temperature bath, held at $25.00 \pm 0.01^\circ$. The conductivity cells and the determination of cell constants have been described earlier.¹⁶

Uv-visible spectra were recorded with a Cary 14 spectrometer. The sample solutions were contained in 1- and 10-mm path length quartz cells (ISC Instruments Ltd.).

The solid starting materials and the interhalogen fluorosulfates were stored and handled in a "Dri-Lab" Model No. HE-43-2 (Vacuum Atmosphere Corp.) filled with purified dry nitrogen and equipped with "Dri-Train" Model No. HE-93B. A Mettler top loading balance Model P160 was used inside the drybox for the preparation of reaction mixtures and solutions.

Volatile reactants were manipulated in a Pyrex vacuum line fitted with Kontes Teflon stem stopcocks. Calibrated traps, made from Pyrex 1 and 2 ml measuring pipettes with 0.01-ml subdivisions and fitted with Teflon stem stopcocks and a ground glass joint, were used for quantitative additions of highly purified $\text{S}_2\text{O}_6\text{F}_2$. In addition all reactions were followed closely by weighing reactants and the reaction products where possible.

All reactions were carried out in one- or two-part Pyrex reactors of about 50-ml volume fitted with Teflon stem stopcocks.

III. Synthetic Reactions. (a) $\text{IBr}_2\text{SO}_3\text{F}$. In a typical preparation a large excess of dried and purified bromine was distilled *in vacuo* onto 0.856 g (3.79 mmol) of freshly prepared ISO_3F , contained in a one-part reaction vessel. The reaction mixture was warmed up to room temperature. All ISO_3F went into solution giving rise to a black-brown liquid. Subsequent heating to 85° for 30 min in a water bath produced a red-brownish solid. After removal of all excess Br_2 in a static vacuum with the reactor held at $+5^\circ$, 1.421 g of a rust-brown solid remained, later analyzed as $\text{IBr}_2\text{SO}_3\text{F}$ (3.68 mmol). Like all other interhalogen fluorosulfates $\text{IBr}_2\text{SO}_3\text{F}$ is extremely moisture sensitive and best stored under atmospheric pressure. The compound melts at $95-97^\circ$ with decomposition into Br_2 and a black liquid.

(b) $\text{ICl}_2\text{SO}_3\text{F}$. ISO_3F (2.514 g, 11.1 mmol), contained in a one-part room bottom Pyrex flask, was combined with a small excess of dried Cl_2 gas. Reaction took place when the temperature was gradually raised from -78° to room temperature; 3.288 g (11.1 mmol) of bright orange $\text{ICl}_2\text{SO}_3\text{F}$ was obtained after the removal of all excess chlorine where the reactor was held at $+5^\circ$. The solid melted at $41-42^\circ$ into a bright-red liquid without apparent decomposition.

(c) $\text{I}_2\text{ClSO}_3\text{F}$. Nearly stoichiometric amounts of finely powdered ISO_3F (6.590 g, 29.16 mmol) and ICl (4.741 g, 29.20 mmol) were combined into a two-part reactor. The mixture was stirred magnetically at $+50^\circ$ under atmospheric pressure (dry N_2) for 12 hr. A viscous black liquid formed, which crystallized to a black-brown solid on gradual cooling to room temperature. The solid left behind was analyzed as $\text{I}_2\text{ClSO}_3\text{F}$ (11.331 g, 29.18 mmol). The compound melts at $39-40^\circ$ with no apparent decomposition.

(d) $\text{I}_2\text{BrSO}_3\text{F}$. In the same fashion as described above 1.053 g of ISO_3F (4.66 mmol) and 0.965 g of IBr (4.67 mmol) were allowed to react first at $+50^\circ$ and later at $+75^\circ$ to produce, after cooling, a black solid which melted at $+70^\circ$ with slight decomposition (liberation of Br_2 and I_2) and analyzed as $\text{I}_2\text{BrSO}_3\text{F}$ (2.018 g, 4.66 mmol).

The synthesis of $\text{I}_3\text{SO}_3\text{F}$ from ISO_3F and I_2 has been described before.⁷ Direct synthesis from I_2 and $\text{S}_2\text{O}_6\text{F}_2$ can also be used. The obtained product melted at 104.0° in fairly good agreement with the value reported by Chung and Cady.⁸

IV. Analytical Data. Elemental analyses of the new interhalogen fluorosulfates were performed by Alfred Bernhard, Microanalytical Laboratory, Elbach, West Germany. The results are listed below.

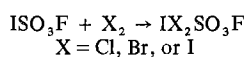
(a) *Anal.* Calcd for $\text{IBr}_2\text{SO}_3\text{F}$: I, 32.89; Br, 41.43; F, 4.92. Found: I, 33.14; Br, 41.08; F, 5.05.

(b) *Anal.* Calcd for $\text{I}_2\text{ClSO}_3\text{F}$: I, 65.36; Cl, 9.13; F, 4.89. Found: I, 65.29; Cl, 9.00; F, 4.95.

(c) *Anal.* Calcd for I_2BrSO_3F : I, 58.64; Br, 18.50; F, 4.39.
Found: I, 58.84; Br, 18.24; F, 4.36.

Results and Discussion

I. Synthesis. The halogens Cl_2 , Br_2 , and I_2 , when present in an excess, add quantitatively to ISO_3F according to



The reaction with chlorine proceeds spontaneously at room temperature, whereas the reactions with Br_2 and I_2 have to be initiated by heating the mixture to $\sim 85^\circ$. The solid reaction products are found to crystallize slowly from the melt and the excess halogen is easily removed by vacuum distillation, with the sample held slightly below room temperature. In contrast, the interhalogens ICl and IBr are best added in stoichiometric amounts to iodine(I) fluorosulfate. Both ICl and IBr are better ionizing solvents than the halogens,²⁰ and efforts to obtain crystalline products from the viscous solution formed with excess interhalogen proved rather difficult. All attempts to remove the excess ICl and IBr , respectively, resulted in impure products.

The described synthesis of the interhalogen fluorosulfates by a straightforward oxidative addition reaction and subsequent recrystallization is adopted from the standard preparative methods for ICl ¹⁷ and IBr .¹⁸ As is generally found in interhalogen chemistry, the synthesis is quantitative and appears to be simpler than the previously^{4,5} described routes to I_2Cl^+ compounds.

In all instances where an excess of Br_2 or Cl_2 was used, no evidence for compounds of the type IBr_4SO_3F or ICl_4SO_3F could be obtained. If either of these two is formed as intermediate, the thermal stability is probably very low.

Attempts to synthesize I_2BrSO_3F by a different route, the addition of bromine(I) fluorosulfate to an excess of iodine, failed. Instantaneous release of bromine from the reaction mixture was noted, suggesting the formation of iodine(I) fluorosulfate and/or I_3SO_3F . Interestingly, however, when the mixture was allowed to stand at room temperature, all bromine vapor had disappeared and seemingly reacted with iodine(I) fluorosulfate to give a rather complex mixture. It appears that addition is preceded by substitution and that only addition of halogen of the same or higher electronegativity onto a halogen(I) fluorosulfate is feasible.

Subsequent attempts to add Cl_2 to $BrSO_3F$ at room temperature failed. No evidence for $BrCl_2SO_3F$ could be obtained.

In contrast to observations on $I_2Cl^+SbCl_6^-$,⁵ the interhalogen fluorosulfates were found to be not sublimable. Heating *in vacuo* causes a reversal of the formation reaction. As expected, the most electropositive halogen remains bonded to the SO_3F group in contrast to the pyrolysis of salts containing trihalide anion,²¹ where the most electronegative halogen forms the counterion in the residual salt.

The observed melting or decomposition points of the interhalogen fluorosulfates and their thermal stability at room temperature rule out the possibility that they are merely mixtures of ISO_3F (mp $+50.2^\circ$) and the halogens Cl_2 and Br_2 or the interhalogens ICl and IBr . The possibility that I_2ClSO_3F and I_2BrSO_3F are completely or partly disproportionated into I_3SO_3F and ICl_2SO_3F or IBr_2SO_3F , respectively, exists and cannot be ruled out by similar arguments.

Of all interhalogen fluorosulfates described here, IBr_2SO_3F

is unique, because the parent interhalogen iodine tribromide is nonexistent. A parallel may be seen in the recently reported^{22,23} $ClF_6^+PtF_7^-$, where ClF_7 appears to be unknown.

The cation IBr_2^+ , formed by the interaction of stoichiometric amounts of I_2 , Br_2 , and HIO_3 in sulfuric acid has been identified previously¹⁰ by conductometry, cryoscopy, and electronic spectra; however, no solid compound was isolated. The presence of an IBr_2 group is also postulated in a compound of the composition $I_2Cl_4Br_2$,²⁴ but this interesting species is only identified by its ¹²⁹I Mossbauer spectrum.

Therefore, the existence of IBr_2SO_3F is not totally unexpected; the thermal stability up to $+90^\circ$ is, however, surprising.

II. Vibrational Spectra. Due to the high reactivity of all interhalogen fluorosulfates, only barium fluoride proved to be a satisfactory window material for infrared studies. Since no mulling agents could be used, the absorption bands which were obtained are generally fairly broad. The cut off for BaF_2 windows at $\sim 800\text{ cm}^{-1}$ permits only the study of sulfur-oxygen stretching vibrations. In certain cases the SF stretch might be observable in the transmission range of BaF_2 . In spite of these limitations, meaningful conclusions can be made regarding the structural conformation of the fluorosulfate group. The observed ir bands for the interhalogen fluorosulfates, I_3SO_3F , ISO_3F , and other relevant SO_3F compounds, exemplifying the five possible conformations of the fluorosulfate group, are listed in Table I and assigned as SO_3 or SF stretches, respectively.

Support can be drawn from the Raman spectra, where for ICl_2SO_3F a well resolved spectrum was obtained, as shown in Figure 1. In addition IBr_2SO_3F gave a reasonably well resolved spectrum, whereas I_2ClSO_3F , I_2BrSO_3F , and I_3SO_3F gave less satisfactory results, undoubtedly caused by the dark coloration of these compounds. The results are listed in Table II. Deficiencies are found particularly in the SO_3 bending range ($560\text{--}610\text{ cm}^{-1}$), the peaks of which are of low intensity for ICl_2SO_3F . Also the highest frequency SO_3 stretch at $1280\text{--}1300\text{ cm}^{-1}$ is not observed for I_2BrSO_3F and I_2ClSO_3F . The Raman spectrum of I_3SO_3F is very fragmentary. We were unable to observe bands even in the halogen cation range.

Previously reported values for triatomic inter- and polyhalogen cations in solution of strong protonic acids or in solid state compounds, with AsF_6^- or $SbCl_6^-$ as counterions, are tabulated in Table III together with our assignments for these cations in the interhalogen fluorosulfates.

As can be seen from Table I for all interhalogen fluorosulfates as well as for ISO_3F and I_3SO_3F , three sulfur-oxygen stretching modes are observed and, except for iodine(I) fluorosulfate, the sulfur-fluorine stretching mode is not observed in the ir region. Therefore, any structural SO_3F conformation based on an unperturbed moiety with C_{3v} symmetry is unlikely. A monodentate OSO_2F appears as unlikely judging from the positions of the three SO_3 stretches. This leaves as feasible possibilities (a) a bidentate conformation with bonding through oxygen and (b) a SO_3F^- ion where C_{3v} symmetry is strongly perturbed, similar to findings for nitronium and nitrosonium fluorosulfate.²⁵ Except for ICl_2SO_3F , where a rather wide peak separation of the two highest frequency SO_3 stretches is observed, a fairly consistent

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Table I. Observed Stretching Frequencies for Some Fluorosulfates

Compd	SO ₃ F conformation and symmetry	S-O stretches			SF stretch	Additional struct evidence
M ^I SO ₃ F ^a M ^I = Li to Cs	Ionic C _{3v}	1280-1295	1072-1100	815-715	X-Ray diffr, KSO ₃ F, ^b NH ₄ SO ₃ F ^c	
NOSO ₃ F ^d NO ₂ SO ₃ F ^d	} Ionic (perturbed) C _{3v}	1278	1246	1077	755	
		1308	1286	1085	745	
XOSO ₃ F ^{e,f} X = F, Cl, Br	Monodentate C _s	1502-1438	1250-1206	788-884	857-832	Polarized ^e Raman spectra
R ₂ SnSO ₃ F, ^{g,h} R ₂ Sn(SO ₃ F) ₂ R = CH ₃ , C ₂ H ₅ , etc.	Bidentate bridging C _s	1355-1343	1205-1180	1076-1070	827-820	X-Ray diffr ⁱ (CH ₃) ₂ Sn(SO ₃ F) ₂ ¹¹⁹ Sn Mossbauer spectra ^{g,h,j}
X ₂ Sn(SO ₃ F) ₂ ^j X = Cl, Br, F		1360-1420	1130-1100	1080-1070	855-865	
Co ^{II} (SO ₃ F) ₂ ^k	Tridentate C _{3v}	1265	1108		850	Electronic ^k spectrum, magn prop
Ti ₃ Cl ₁₀ (SO ₃ F) ₂ ^l	Tetradentate C _{3v} (perturbed)	1260	1248	1082	650	
ISO ₃ F ^{m,n}		1395	1200	960	800-880	
I ₃ SO ₃ F ⁿ		{1315 1270	1200	1045		
I ₂ BrSO ₃ F ⁿ		1280	1200	1050		
IBr ₂ SO ₃ F ⁿ		1280	1225	1060		
I ₂ ClSO ₃ F ⁿ		{1310 1270	{1245 1205	{1100 1060		
ICl ₂ SO ₃ F ⁿ		1305	1245	1070		

^a Reference 30. ^b K. O' Sullivan, R. C. Thompson, and J. Trotter, *J. Chem. Soc.*, 2024 (1967). ^c K. O' Sullivan, R. C. Thompson, and J. Trotter, *ibid.*, 1814 (1970). ^d Reference 25. ^e Reference 28. ^f Reference 26. ^g Reference 31. ^h T. H. Tan, *et al.*, *Can. J. Chem.*, 50, 1843 (1972). ⁱ F. A. Allen, J. Lerbscher, and J. Trotter, *J. Chem. Soc. A*, 2507 (1971). ^j L. E. Levchuk, J. R. Sams, and F. Aubke, *Inorg. Chem.*, 11, 43 (1972). ^k J. M. Taylor and R. C. Thompson, *Can. J. Chem.*, 49, 511 (1971). ^l J. R. Dakziel, R. D. Klett, P. A. Yeats, and F. Aubke, *Can. J. Chem.*, submitted for publication. ^m Reference 8. ⁿ This work, all bands listed were observed as strong, moderately broad absorption bands.

Table II. Raman Spectra of Interhalogen Fluorosulfates^a (cm⁻¹)

ICl ₂ SO ₃ F	IBr ₂ SO ₃ F ^b	I ₂ BrSO ₃ F ^b	I ₂ ClSO ₃ F ^b	I ₃ SO ₃ F ^b
1320 mw	1280 vw			
1170 ms	1205 ms	1216 m	1210 mw	
1054 s	1063 s	1061 s	1062 ms	1059 ms
759 mw	805 m	805 mw	810 m	795 m
			795 m	
			600 m	
603 w	610 m		586 w	
580 mw	588 mw	585 mw	586 w	
565 w	569 vw, sh	571 w	570 w	
428 m	425 w	439 m	430 m	419 mw
399 w	369 ms	376 ms	369 s	364 mw
380 vs	256 vs ^c	258 ms	360 m	
360 vs	198 vw (imp) ^d	198 m, sh	198 mw, sh	
161 s	127 w, sh		126 m, sh	

^a Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. ^b Fluorescent sample with background shoulder ~490 cm⁻¹. ^c A value of 236 cm⁻¹ was erroneously reported in ref 6. ^d Trace impurity of I₂BrSO₃F.

pattern emerges for the remaining polyhalogen and interhalogen fluorosulfates. It is interesting that for I₂ClSO₃F a total of six SO₃ stretches is observed, which can be interpreted in terms of two slightly nonequivalent SO₃F groups in the solid. The two highest SO₃ bands are now separated by about 60 cm⁻¹, far less than for compounds where a bidentate SO₃F group is found and splittings between 140 and 290 cm⁻¹ are found.

When comparing the positions of the SO₃ bands for the interhalogen fluorosulfates to those for ISO₃F, it is apparent that a fundamental structural change has taken place when a halogen or an interhalogen is added to ISO₃F and that new compounds are indeed formed. The infrared spectrum of iodine(I) fluorosulfate shows in the SO and SF stretching range some remote similarity to the spectrum reported for BrOSO₂F²⁶ where a monodentate OSO₂F seems present but

Table III. Vibrational Frequencies of Triatomic Interhalogen Cations of the Halogens Iodine, Bromine, and Chlorine

Species	ν ₁ or ν _{I-X} , cm ⁻¹	ν ₂ or ν _{bend} , cm ⁻¹	ν ₃ or ν _{I-I} , cm ⁻¹	Ref
I ₃ ⁺ (solv)	207	114	233	a
Br ₃ ⁺ (solv)	290		290	b
Cl ₃ ⁺ AsF ₆ ⁻	490	225	508	c
ICl ₂ ⁺ SbCl ₆ ⁻	366	149	372	d
ICl ₂ SO ₃ F	360	161	380	This work
IBr ₂ SO ₃ F	256	124	256	This work
I ₂ Cl ⁺ SbCl ₆ ⁻	356	126	190	e
	350			
I ₂ ClSO ₃ F	360	126 ?	197	This work
I ₂ BrSO ₃ F	258		198	This work
ClIBr ⁺ SbCl ₆ ⁻	370	149	255 (ν _{IBr})	e

^a R. J. Gillespie and J. Sowa, unpublished results as quoted by R. J. Gillespie and J. Passmore, *Chem. Brit.*, 8, 475 (1972). ^b Reference 35. ^c R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 11, 591 (1972). ^d J. Shamir and R. Rafaeloff, *Spectrochim. Acta, Part A*, 29, 873 (1973). ^e Reference 5.

additional strong association in the liquid is evident from the physical properties²⁷ and the band positions when compared to the spectra obtained for other halogen fluorosulfates.²⁸ A polymeric structure not unlike the one reported for α-ICl₂²⁹ perhaps with discrete IOSO₂F molecules in the polymeric network, is most consistent with the reported diamagnetism⁷ and the electronic spectrum in a nonionizing solvent.²⁷

The Raman spectra, listed in Table II, reveal the same pattern and tend to favor model (b) involving a perturbed SO₃F⁻ ion even further. The sulfur-fluorine stretch is found at

(26) A. M. Qureshi and F. Aubke, *Inorg. Chem.*, 10, 1116 (1971).

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(28) A. M. Qureshi, L. E. Levchuk, and F. Aubke, *Can. J. Chem.*, 49, 2544 (1971).

(29) K. H. Boswijk, J. v. d. Heide, A. Vos, and E. H. Wiebenga, *Acta Crystallogr.*, 9, 274 (1956).

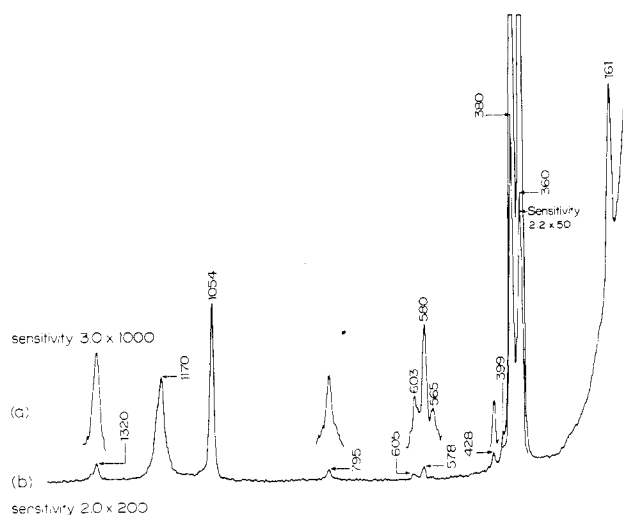


Figure 1. Raman spectrum of $\text{ICl}_2\text{SO}_3\text{F}$.

$\sim 800\text{ cm}^{-1}$, in the same region as alkali metal fluorosulfates of the strongly polarizing cations Li^+ and, to a lesser extent, Na^+ .³⁰ The observed splittings of the other E modes is again fairly small, much smaller than for compounds with bridging SO_3F groups,³¹ and no bonds assignable to halogen-oxygen stretching can be observed.

The bands assigned to cation vibrations are in good agreement with previous reports for ICl_2^+ , BrCl_2^+ , and I_2Cl^+ ,^{5b} or for isoelectronic molecules such as gaseous TeCl_2 .³² For IBr_2^+ only one stretching mode is observed. This finding would be consistent with a linear configuration, but since the Raman-forbidden bending mode is observed here, accidental coincidence of the two stretching modes as found previously for Br_3^+ ³³ and a bent cation appears to be more likely, in good agreement without findings for ICl_2^+ . For the cations I_2Cl^+ and I_2Br^+ an unsymmetrical configuration $(\text{I}-\text{I}-\text{X})^+$, with $\text{X} = \text{Cl}$ or Br , is preferred over a symmetrical configuration $(\text{I}-\text{X}-\text{I})^+$. The observation that for triatomic ions the heavier halogen occupies the central position appears to be a structural principle for both interhalogen cations² and anions.²¹

The perturbation of the SO_3F group appears to be caused by cation-anion interaction. X-Ray diffraction studies on interhalogen complexes such as BrF_2SbF_6 ,³⁴ ClF_2SbF_6 ,³⁵ ClF_2AsF_6 ,³⁶ $\text{BrF}_4\text{Sb}_2\text{F}_{11}$,³⁷ and $\text{ICl}_2\text{SbCl}_6$ ³⁸ or $\text{ICl}_2\text{AlCl}_4$ ³⁸ all indicate such interaction to a varying degree. Also vibrational spectra^{2,21} provide good evidence for such interaction whenever fluoro anions are present. As shown by the example of $\text{ICl}_2\text{SbCl}_6$,^{5b} chloro anions are rather insensitive in this respect, but here a far-infrared study would be needed to complement the picture. It must also be concluded that the SO_3F^- ion is a good indicator for such interaction. This was already apparent from our study on NO^+ and NO_2^+ fluorosulfates.²⁵

(30) A. Ruoff, J. B. Milne, G. Kaufmann, and M. Leroy, *Z. Anorg. Allg. Chem.*, **372**, 119 (1970).

(31) P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **11**, 2634 (1972).

(32) I. R. Beattie and R. O. Perry, *J. Chem. Soc. A*, 2429 (1970).

(33) R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, **11**, 585 (1972).

(34) A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 1467 (1969).

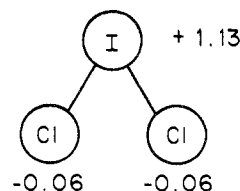
(35) A. J. Edwards and R. J. C. Sills, *J. Chem. Soc. A*, 2697 (1970).

(36) H. Lynton and J. Passmore, *Can. J. Chem.*, **49**, 2539 (1971).

(37) M. D. Lind and K. O. Christie, *Inorg. Chem.*, **11**, 608 (1972).

(38) C. G. Vonk and E. H. Wiebenga, *Acta Crystallogr.*, **12**, 859 (1959).

It is also not surprising that, of all the interhalogen cations, ICl_2^+ causes the strongest interaction. A calculation of charges in this ion using a modified Huckel theory³⁹ indicates the following pattern.



Replacement of chlorine by the less electronegative bromine and iodine should cause a decrease in positive charge on the central iodine atom and a reduction in anion polarization.

III. Solution Studies. The interhalogen fluorosulfates should be very convenient sources for interhalogen cations in solution of strong protonic acids. Fluorosulfuric acid⁴⁰ is an obvious choice for solution studies, because the SO_3F^- ion is one of the self-ionization ions in the equilibrium $2\text{HSO}_3\text{F} \rightleftharpoons \text{H}_2\text{SO}_3\text{F}^+ + \text{SO}_3\text{F}^-$, and conductometry in this solvent¹⁶ should allow one to follow the solution process. A number of polyiodine cations have been successfully studied in this solvent.⁴¹ In particular, one of the ions, I_3^+ , is well established in HSO_3F .

The results of the conductivity studies are shown in Tables IV and V for all triatomic poly- or interhalogen fluorosulfates, as well as iodine(I) fluorosulfate. Plots of specific conductance vs. concentration are shown in Figure 2 for the solutes $\text{IBr}_2\text{SO}_3\text{F}$ and ISO_3F together with the plot for the reference base, KSO_3F .

All interhalogen fluorosulfates behave as strong bases in HSO_3F . The γ values in Table V, indicative of the number of moles of SO_3F^- ion produced by a mole of solute, are very close to 1.0 in all instances and as shown in Figure 2 the plots for $\text{IBr}_2\text{SO}_3\text{F}$ and KSO_3F are indistinguishable. It can be concluded that dissociation is complete and the formation of SO_3F^- is further confirmed by additions of KSO_3F to the interhalogen fluorosulfate solutions resulting in a continued steep increase of the specific conductance. The ^{19}F nmr spectra of the interhalogen fluorosulfate solutions in HSO_3F are single lines shifted slightly upfield from the position for the pure acid, again indicating SO_3F^- formation. All solutions are stable over several days. Very dilute solutions of $\text{I}_2\text{BrSO}_3\text{F}$, $\text{I}_2\text{ClSO}_3\text{F}$, and $\text{I}_3\text{SO}_3\text{F}$ at concentrations of $1.5 \times 10^{-4}\text{ mol kg}^{-1}$ or lower show a light blue color, characteristic of the I_2^+ cation in HSO_3F . This cation was indeed identified by its electronic spectrum (*vide infra*), and it is presumably formed by solvent oxidation.

The conductivity results appear not to be affected by this interference. In fact, conductances of ISO_3F solutions at similar concentrations have γ values approaching unity (see Figure 2). Agreement with earlier conductivity studies of I_3^+ in HSO_3F ,¹⁵ where the cation is formed *in situ* by the oxidation of iodine by $\text{S}_2\text{O}_6\text{F}_2$, is very good. The γ values of about 1.0 indicate very similar ion mobilities for solvated K^+ and the interhalogen cation. Due to the low viscosity of HSO_3F at 25°C ,⁴⁰ cation mobilities contribute noticeably to the conductivity.

As shown in Figure 2 at concentrations greater than $1 \times 10^{-2}\text{ M}$, ISO_3F is far less conducting. The observed slope

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Table IV. Experimental Concentrations and Specific Conductivities for Various Iodine-Containing Fluorosulfate Compounds in HSO₃F

ISO ₃ F		ICl ₂ SO ₃ F		IBr ₂ SO ₃ F		I ₃ SO ₃ F		I ₂ BrSO ₃ F		I ₂ ClSO ₃ F	
10 ³ m ^a	10 ³ Ω ⁻¹ cm ⁻¹	10 ³ m ^a	10 ³ Ω ⁻¹ cm ⁻¹	10 ³ m ^a	10 ³ Ω ⁻¹ cm ⁻¹	10 ³ m ^a	10 ³ Ω ⁻¹ cm ⁻¹	10 ³ m ^a	10 ³ Ω ⁻¹ cm ⁻¹	10 ³ m ^a	10 ³ Ω ⁻¹ cm ⁻¹
0.00	0.12	0.00	0.11	0.00	0.12	0.00	0.13	0.00	0.11	0.00	0.13
0.73	0.15	2.71	0.72	0.73	0.19	0.45	0.25	0.56	0.20	0.15	0.16
2.78	0.58	5.01	1.29	2.78	0.67	1.55	0.52	5.29	1.38	0.43	0.22
3.79	0.85	7.59	1.91	5.77	1.42	2.93	0.87	10.15	2.59	3.63	1.04
4.90	1.10	11.71	2.89	12.81	3.16	5.20	1.44	14.33	3.61	5.40	1.49
7.19	1.73	16.84	4.07	18.52	4.55	9.86	2.59	18.31	4.56	7.13	1.93
10.61	2.36	24.70	5.79	24.96	6.07	15.29	3.89	24.78	6.09	9.98	2.64
13.05	2.54	30.96	7.15	32.07	7.71	21.46	5.35	31.27	7.59	14.07	3.64
15.15	2.84	36.73	8.38	38.75	9.18	28.26	6.92	37.47	8.99	17.50	4.46
19.42	3.12	41.98	9.52	45.37	10.67	35.64	8.58	45.39	10.74	23.12	5.77
24.42	3.39	46.93	10.57	51.89	12.17	42.45	10.09	52.13	12.21	28.83	7.07
29.81	3.66	51.05	11.68	56.51	13.13	48.47	11.41	58.51	13.57	35.13	8.48
33.65	3.87	55.12	12.56	61.37	14.23	53.51	12.49	64.05	14.74	41.39	9.88
39.05	4.14	58.68	13.36	65.91	15.34	58.52	13.56	68.35	15.63	47.31	11.23
44.76	4.43	61.97	14.12	69.09	16.07	62.80	14.49	72.62	16.50	52.61	12.43
49.85	4.69	64.82	14.78	71.25	16.63	66.65	15.45	76.56	17.32	58.76	13.80
55.18	4.98	67.14	15.43			69.94	16.32			65.14	15.34
59.83	5.25										
64.92	5.56										
69.67	5.87										

^a m = molality ≡ moles of solute/kg of solvent.

Table V. Interpolated Concentrations and Calculated γ Values for Some Iodine-Containing Fluorosulfate Compounds

10 ³ m ^a	γ Values				
	ICl ₂ SO ₃ F	IBr ₂ SO ₃ F	I ₃ SO ₃ F	I ₂ BrSO ₃ F	I ₂ ClSO ₃ F
5.0	0.99	1.00	1.04	1.03	1.06
10.0	0.98	0.98	1.01	0.98	1.04
15.0	0.97	0.97	1.01	0.98	1.03
20.0	0.96	0.98	1.01	0.99	1.01
25.0	0.96	0.99	1.00	0.98	1.01
30.0	0.96	0.99	1.00	0.99	1.01
35.0	0.96	0.98	0.99	0.99	1.00
40.0	0.96	0.98	0.99	1.00	1.00
45.0	0.96	0.99	0.99	1.00	1.00
50.0	0.96	0.99	0.99	0.99	1.00
55.0	0.97	0.99	0.99	0.99	1.00
60.0	0.97	1.00	1.00	0.99	1.00
65.0	0.98	1.00	1.00	0.99	1.01
γ _{av}	0.97	0.99	1.00	0.99	1.01

^a m = molality ≡ moles of solute/kg of solvent.

and the blue-green color of the solution point to similar equilibria as postulated earlier^{15,42} for 1:1 mixtures of I₂ and S₂O₆F₂ in HSO₃F, involving the ions I₂⁺, I₄²⁺, and [(SO₃F)₄]⁻.

It must be pointed out that the conductivity studies can strictly only be used to deduce the number of SO₃F⁻ ions per mole of solute. Unsymmetrical interhalogen cations such as I₂Br⁺ and I₂Cl⁺ may still undergo disproportionation to form the symmetrical ions I₃⁺, IBr₂⁺, and ICl₂⁺ which have all been detected previously^{2,9,10,41} in strong protonic acids.

Electronic spectra should distinguish whether such disproportionation does take place. Spectra of I₃⁺ in HSO₃F^{7,15} and H₂SO₄^{7,14} and of ICl₂⁺ and IBr₂⁺ in H₂SO₄¹⁰ are reported in the literature.

During the course of this study it was found that HSO₃F is not a very suitable solvent for spectroscopic studies in very dilute solution. Solutions of I₂ClSO₃F and I₂BrSO₃F as well as, to a lesser extent, I₃SO₃F gave strong indications of I₂⁺. Since the intensity of the characteristic absorption band at ~640 nm decreased drastically in HSO₃CF₃, it must be concluded that oxidation in HSO₃F occurs. Whether SO₃

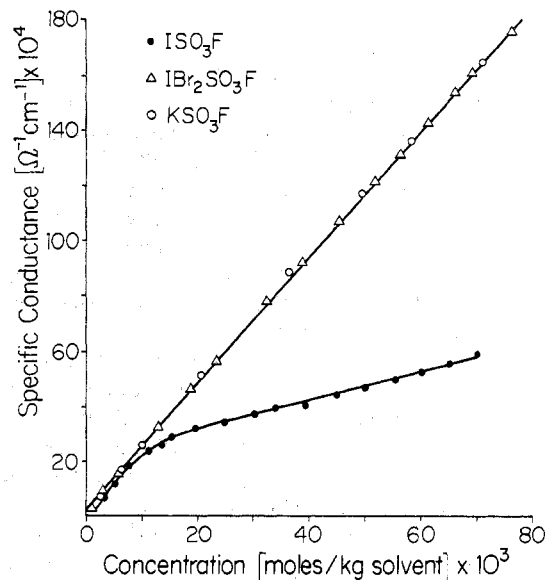
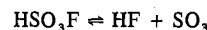


Figure 2. Specific conductivities in HSO₃F of IBr₂SO₃F, ISO₃F, and KSO₃F at 25.0°.

is present as an impurity found even in highly purified acid,^{40,43} or produced by a dissociation according to



as claimed very recently,^{44,45} is unimportant in this case.

A simple and convenient solvent was found in reagent grade H₂SO₄ (~96%), a solvent in which the I₂⁺ ion is not capable of existence. The interhalogen cations appear to be stable indefinitely in this solvent. The sensitivity of the cations to reduction by trace impurities of SO₂ became apparent, when a spectrum of IBr₂SO₃F was recorded in 100% H₂SO₄. The spectrum changed slowly over a period of 24 hr until it became identical with a spectrum of IBr in this solvent.

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(45) J. Badoz-Lambling, M. Herlem, A. Thiebault, and G. Adhami, *Anal. Lett.*, **5**, 305 (1972).

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Table VI. Electronic Spectra of Solutions of Some Interhalogen Fluorosulfates in Strong Protonic Acids at +25^oa

Compd	HSO ₃ F		HSO ₃ CF ₃		H ₂ SO ₄ 96%	
	λ_{\max} , nm	ϵ_{\max}	λ_{\max} , nm	ϵ_{\max}	λ_{\max} , nm	ϵ_{\max}
I ₃ SO ₃ F	635*	~440				
	472	1580	462	2430	459	2200
	300	4580	295	5810	290	6070
I ₂ BrSO ₃ F	635*	~250	620*	very weak		
	414	790	418	1070	490	1000
	300*	~1920	300*	~2610	300*	~2610
	260*	4080	260*	4600	255*	~7000
I ₂ ClSO ₃ F	635*	~250	630*	~140		
	461	543	450	661	438	810
	300	1220	315	1350	295	2400
	~230		235	1460		
IBr ₂ SO ₃ F	~560*	~80	~545	~96	~535*	~94
	455*	~160	453*	~200		
	361	560	360	598	355	630
	232	5600	~260	~1410	260	1600
ICl ₂ SO ₃ F	486	48	471	48	448	51
	395	64	374	70	355*	~88
	275*	~470	310	146	318	142

a * denotes shoulder, extinction coefficient value is very approximate.

The results of the spectrophotometric measurements are listed in Table VI for the solvents HSO₃F, HSO₃CF₃, and H₂SO₄ (96%) together with the observed extinction coefficients. In addition, Figure 3 shows the absorption bands for I₃SO₃F, I₂BrSO₃F, and IBr₂SO₃F each in 96% H₂SO₄. Beer's law was obeyed in all cases. To record absorption bands below 300 nm, optical density filters were used. The recorded extinction coefficients for these bands may not be very accurate. A shift to shorter wavelengths for the three solvents may not be very significant considering the broad absorption bands. The strongest frequency shift was noted for ICl₂⁺, which as pointed out earlier, is most capable of interacting with the anion in the solid state and may also interact with the solvent. The fact that slightly lower γ values were found for this species is consistent with our views. A puzzling situation is found for IBr₂⁺. In both HSO₃F and HSO₃CF₃ a fairly intense shoulder at 455 nm is observed. In H₂SO₄ this shoulder is not observed and the two low-energy bands listed agree well with those reported by Senior and Grover¹⁰ in 100% H₂SO₄.

A close inspection of the λ_{\max} values and the corresponding extinction coefficients for both I₂Cl⁺ and I₂Br⁺ does not indicate extensive disproportionation into the symmetric inter- and polyhalogen cations. It must be concluded that both ions can exist in strongly acidic medium, provided interference from oxidizing or reducing agents is avoided.

Some attempts were made to obtain Raman spectra of the ICl₂⁺ cation in HSO₃F solution because the solutions are not nearly as deeply colored as for the other cations, but unfortunately only the peaks due to HSO₃F could be found, with a rather broad absorption band at 380–400 cm⁻¹ as the only departure from the findings for HSO₃F.²⁸

Attempts to ascertain the existence of the interhalogen cations in the solid fluorosulfates by recording their electronic spectra in fluorolube oil mulls were successful only for ICl₂SO₃F where good correspondence to the solution spectra could be found. Both IBr₂SO₃F and I₃SO₃F were found to interact with the fluorolube oil, giving rise to IBr and I₂, respectively.

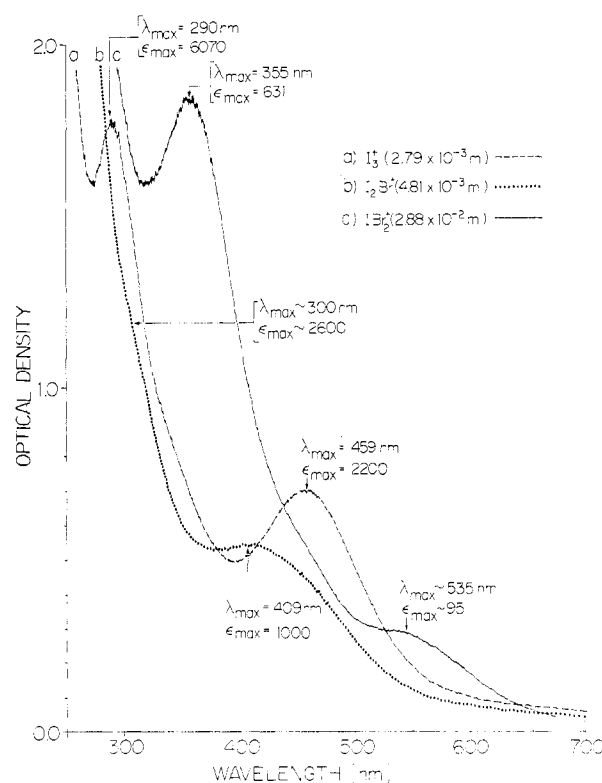


Figure 3. Electronic absorption spectra from 700 to 250 nm of I₃SO₃F, I₂BrSO₃F, and IBr₂SO₃F in H₂SO₄ (96%) at 25°.

IV. General Conclusion. The evidence presented here indicates that the interhalogen fluorosulfates, obtained by oxidative addition of I₂, Br₂, Cl₂, IBr, and ICl to iodine(I) fluorosulfate, may be regarded as interhalogen cation derivatives, if allowance is made for varying degrees of cation-anion interaction. A final decision will require X-ray diffraction studies. Supporting evidence is expected from detailed nqr studies, currently underway. Preliminary results⁴⁶ for ³⁵Cl nqr in ICl₂SO₃F, with resonances at 37.902 and 38.343 MHz at 77°K, indicate some difference to earlier work⁴⁷ on ICl₂AlCl₄ at 297°K, which may be due partly to different degrees of anion-cation interaction in both compounds and partly to the difference in the temperature of the measurement. Similar differences are found for the ³⁵Cl resonances of I₂Cl₆^{47,48} at these two temperatures.

Disappointingly I₂ClSO₃F did not give a ³⁵Cl resonance, precluding a comparison with recent reports on I₂ClAlCl₄.⁴

Acknowledgment. We are very grateful to the National Research Council of Canada for financial support. Mr. P. A. Yeats is thanked for his assistance in the solution studies and Mrs. B. Krizan for the technical drawings. We are also grateful to Drs. W. R. Cullen and M. C. L. Gerry and Mr. L. S. Chia for the use of the nqr spectrometer.

Registry No. Br₂, 7726-95-6; Cl₂, 7782-50-5; ICl, 7790-99-0; IBr, 7789-33-5; I₃SO₃F, 13537-34-3; ICl₂SO₃F, 13933-20-5; IBr₂SO₃F, 42996-24-7; I₂BrSO₃F, 42996-25-8; I₂ClSO₃F, 42996-26-9; I₃SO₃F, 13537-36-5.

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