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Improved Synthesis of $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{16}^-]$ and Magnetic, Spectroscopic, and Some Chemical Properties of the Dihalogen Cations I_2^+ and Br_2^+

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The oxidation of Br_2 and I_2 by bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, at a 2:1 mole ratio followed by solvolysis in an excess of antimony(V) fluoride provides a simple, straightforward route to pure $[Br_2^+][Sb_3F_{16}^-]$ and $[I_2^+][Sb_2F_{11}^-]$. The dihalogen cations Br_2^+ and I_2^+ give resonance Raman spectra and provide suitable solutes for solution studies in fluorosulfuric acid and in superacid media. Magnetic susceptibilities in the range of 80–300 K indicate the presence of a temperature-independent paramagnetic contribution for both compounds. In addition antiferromagnetic interaction caused by an intermolecular iodine–iodine contact seems to occur in $[I_2^+][Sb_2F_{11}^-]$. While attempts to synthesize an IBr^+ species were unsuccessful, the cations $[BrCl_2^+]$ and $[Br_2Cl^+]$ are obtained in SbF_5 solution and characterized by spectroscopic techniques.

Introduction

The diatomic homonuclear halogen cations I_2^+[1] and Br_2^+[2,3] were identified and characterized some time ago, both in solutions of strong protonic acids like HSO_3F[1,4] and superacids,[3] as well as in solid compounds like $[I_2^+][Sb_2F_{11}^-]$,[5,6] $[I_2^+][TaF_6^-]$,[5] $[Br_2^+][Sb_3F_{16}^-]$,[2] and $[Br_2^+][AsF_6^-]$.[7] Ionic formulations were based on the molecular structures reported for $[Br_2^+][Sb_3F_{16}^-]$[2] and $[I_2^+][Sb_2F_{11}^-]$,[6] the observed paramagnetism, consistent with a ${}^2\Pi_{3/2_g}$ ground state, and the position of the Hal–Hal stretching frequency, easily detected on account of a strong resonance Raman effect.[2,3,6,8] A recent report[9] commenting on the observed electronic spectra[1,3] had pointed to a strong similarity between these ions, found in the condensed phase, and the transient $I_2^+(g)$ and $Br_2^+(g)$, detected by photoelectron spectroscopy of $I_2(g)$ and $Br_2(g)$, respectively.[10,11]

The principal synthetic routes to $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{16}^-]$ had been the comproportionation of a halogen fluoride like IF_5,[5] BrF_5,[2a] or BrF_3[2b] and stoichiometric amounts of I_2 or Br_2 in the presence of SbF_5 or the oxidation of the halogens by SbF_5, either in SO_2 solution[6] or in a large excess of SbF_5.[5] Even though these methods had yielded single crystals for X-ray diffraction studies, the bulk composition was often uncertain,[5] and elemental analysis[5,6] was rather unsatisfactory. An early study by Ruff,[12] who reported materials of the composition $(SbF_5)_2I$, $(SbF_5)I$, and $(SbF_5)Br$, may serve as an example for the materials formed by direct reaction of the halogens with SbF_5.

In the present study a simple synthetic route to both $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{16}^-]$ is described and the extension of this method to compounds containing the hitherto unknown diatomic heteronuclear halogen cation IBr^+ is explored. The results of a detailed magnetic and spectroscopic study on $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{16}^-]$ are discussed together with solution studies in strongly acidic protonic solvents. Some chemistry of $[Br_2^+][Sb_3F_{16}^-]$ is described. A preliminary account of the latter work has appeared recently.[13]

Experimental Section

(A) Chemicals. Resublimed iodine (Fisher Scientific), bromine (BDH), distilled before use from P_2O_5 and KBr, chlorine (Matheson of Canada Ltd.) of 99.5% purity which was passed twice through 96% H_2SO_4 traps and finally through P_2O_5, and stabilized sulfur trioxide (Allied Chemicals) were used. Fluorosulfuric acid (Allied Chemicals) of technical grade was purified by double distillation at atmospheric pressure as described.[14] Antimony pentafluoride (Ozark Mahoning) was purified by bubbling dry N_2 through the material in order to remove the bulk of the HF impurity. Subsequently a distillation at atmospheric pressure was followed by repeated distillation at 10^{-2} mmHg. The chemicals IBr,[15] ISO_3F,[16] IBr_2SO_3F,[17] $S_2O_6F_2$,[18] $I(SO_3F)_3$,[19] and $Br(SO_3F)_3$[19] were obtained according to published methods.

(B) Instrumentation. 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.

UV–visible and near-IR 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.). Magnetic susceptibilities were measured by using the Gouy apparatus described earlier.[20] The coil current of the magnet was regulated to give a field of approximately 4500 G. The temperature of the sample was controlled by the rate of evaporation of N_2 around the chamber. Calibration was achieved by using $HgCo(SCN)_4$.[21] Diamagnetic corrections used were as follows: Sb, 14; Br, 30.6; I, 44.6; F, 6.3 (all $\times 10^{-6}$ cm^3 mol^{-1}).

All reactions were performed in Pyrex reaction vials of about 50-mL contents, fitted with Kontes Teflon stem valves. Volatile materials were handled by using vacuum-line techniques. Solids were handled in a Vacuum Atmospheres Corp. "Dri-Lab" Model No. HE-43-2, fitted with purified dry nitrogen and equipped with a "Dri-Train" Model No. HE-93-B circulating unit.

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(C) Preparations. (1) $[I_2^+][Sb_2F_{11}^-]$. To a Pyrex reaction vial was added 1.0241 g (4.0349 mmol) of finely ground I_2 in the drybox. Next, 0.4070 g (2.054 mmol) of $S_2O_6F_2$ was distilled in vacuo from the calibrated $S_2O_6F_2$-addition trap into the reactor. The mixture was heated to 90 °C to allow the reactants to combine for about 10 min before the reaction bulb and its contents were frozen to −196 °C. At this temperature, 6.7745 g (31.256 mmol) of SbF_5 was added to the 2:1 mixture of I_2:$S_2O_6F_2$ by distillation in vacuo. Heating to 50 °C subsequently produced a homogeneous dark blue-black liquid phase. For removal of any volatile materials, dynamic pumping in vacuo was applied to the sample which was kept at 25 °C for $^1/_2$ h, 60 °C for 15 h, and then 90 °C for 1 h. The volatile products were trapped in order to detect any colored material. This process yielded 2.8750 g (4.0706 mmol) of a dark blue-black solid which analyzed according to $[I_2^+][Sb_2F_{11}^-]$.

(2) $[Br_2^+][Sb_3F_{16}^-]$. First, 0.9825 g (6.148 mmol) of dry, purified Br_2 was distilled into a Pyrex reaction vial in vacuo. Then 0.6146 g (3.102 mmol) of $S_2O_6F_2$ was condensed in vacuo onto the Br_2, and the mixture was allowed to warm to room temperature. The reactants were held at room temperature and thoroughly mixed for 1 h. Next, 10.4156 g (48.055 mmol) of SbF_5 was distilled in vacuo into the reaction bulb and allowed to warm up to room temperature. Upon mixture of the reactants, a red solid was formed instantaneously, and subsequent pumping at RT for 3 h removed any volatile materials. This procedure resulted in 5.0387 g (6.078 mmol) of a bright red solid which analyzed as $[Br_2^+][Sb_3F_{16}^-]$.

(3) Formation of $[BrCl_2^+]$ in SbF_5. Into a Pyrex reaction vial were distilled 0.3727 g (2.083 mmol) of $BrOSO_2F$ and 0.1813 g (2.57 mmol) of Cl_2. After being allowed to warm up to room temperature, the reactants were mixed, but there was no apparent reaction. Next, 6.2948 g (29.043 mmol) of SbF_5 was distilled in vacuo into the reactor, resulting in the mole ratio 1.00:1.23:13.95 for $BrOSO_2F$:Cl_2:SbF_5. Upon warming of the solution to room temperature again, a visible reaction occurred and a cherry red intermediate was produced which eventually changed to a deep red viscous liquid phase. This phase separated upon standing at room temperature from a clear, colorless, somewhat viscous phase of lower specific gravity. A faint yellow gas (Cl_2), which could be removed in a static vacuum by condensation at −196 °C, remained above the two liquid phases. The separation of the two liquid phases was accomplished by pipetting in an inert atmosphere.

(4) Formation of $[Br_2Cl^+]$ in SbF_5. A sample (2.9881 g, 3.604 mmol) of $[Br_2^+][Sb_3F_{16}^-]$ in a Pyrex reaction vial was reacted with an excess (0.3775 g, 5.32 mmol) of Cl_2 at room temperature. When the excess Cl_2 was allowed to escape in an inert atmosphere, a dark red-brown material with a melting point at about room temperature was obtained. Attempts to remove some of the SbF_5 in order to obtain a solid reaction product resulted in thermal decomposition of the cation and formation of Br_2^+.

(D) Physical Properties and Chemical Analysis. Elemental analysis was performed by Analytical Laboratories (formerly A. Bernhardt), Gummersbach, West Germany.

$[I_2^+][Sb_2F_{11}^-]$ is a very hygroscopic, microcrystalline black-blue solid with a sharp melting point of 127 °C (lit.[6] mp 122–123 °C). The infrared spectrum shows the following bands (in cm^{-1}) with estimated intensities: ~680 s, sh, 640 vs, b, 600 m, sh, 535 m, sh, 495 m, 470 w, 420 w, sh. The Raman spectrum (Raman shifts in cm^{-1} and relative intensities with the highest intensity equal to 100 in parentheses) is as follows: ~1635 (0.5), ~1425 (3), 1193 (6), 951 (10), 718 (24), 480 (52), 439 (10), 370 (13), 277 sh, 242 (100), 162 (4). Anal. Calcd for $[I_2^+][Sb_2F_{11}^-]$: I, 35.94; F, 29.59. Found: I, 35.94; F, 29.23.

$[Br_2^+][Sb_3F_{16}^-]$ is a bright red, moisture-sensitive, crystalline solid, which melts at 85.5 °C to a cherry red liquid (lit.[2] mp 69 °C). Infrared data in cm^{-1} are as follows: ~700 s, sh, 655 vs, 585 w, 560 w, 485 m, 425 vw. Observed Raman shifts with relative intensities are ~2150 (3), 1798 (10), 1447 (15), 1090 (28), 730 (57), 701 (11), 663 (9), 368 (3 × 100), and 302 (3) cm^{-1}. Anal. Calcd for $[Br_2^+][Sb_3F_{16}^-]$: Br, 19.28; F, 36.67. Found: Br, 19.12; F, 36.53.

$BrCl_2^+$ (as solution in SbF_5) is deep red and diamagnetic with the composition $BrCl_2SbF_6{\cdot}3.46SbF_5$. Halogen analysis indicates 7.03% Br and 6.24% Cl with the mole ratio of 1.00:2.00. Raman shifts ($\Delta\nu$ in cm^{-1}) are as follows: 709 m, 678 m, sh, 661 s, 598 w, 430 vs, 421 s, sh, 293 vw, 235 w, 167 m.

Br_2Cl^+ (as solution in SbF_5) is a dark red-brown, viscous, diamagnetic material of the composition $Br_2ClSb_3F_{16}$. Anal. Calcd for $Br_2ClSb_3F_{16}$: Br, 18.48; Cl, 4.10. Found: Br, 18.59; Cl, 3.88. Raman shifts ($\Delta\nu$ in cm^{-1}) are as follows: 700 vs, 655 s, 424 s, 298 ms.

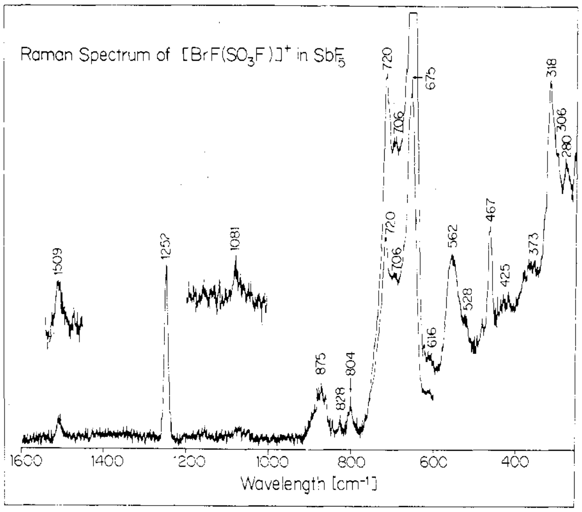

Figure 1.

The reaction (solvolysis) of $Br(SO_3F)_3$ in SbF_5 produces yellowish viscous oils. Analyses after removal of the volatile $Sb_2F_9(SO_3F)$ indicate 14.75% Br and 6.12% S, or a molar ratio of Br:S of 1.00:1.03, and the presence of $[BrF(SO_3F)^+]$ as the principal cation. A Raman spectrum of this sample is shown in Figure 1.

Results and Discussion

(A) Synthesis. While the earlier[2,5,6] studies indicate that the compounds $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{16}^-]$ do exist, it is clear from the synthetic methods employed that pure materials are not readily obtained. The comproportion reaction (see eq 1) employed to prepare $[Br_2^+][Sb_3F_{16}^-]$[2] requires a

$$9Br_2 + 2BrF_5 + 30SbF_5 \rightarrow 10[Br_2^+][Sb_3F_{16}^-] \qquad (1)$$

precise mole ratio of highly pure Br_2:BrF_5 = 9:2 in order to avoid the formation of cations like Br_3^+, BrF_2^+, or even BrF_4^+, with a Pyrex reaction vessel presenting additional problems by reacting with BrF_5.

The oxidation of I_2 by SbF_5 in SO_2, formulated by the authors[6] as eq 2, is said to allow easy separation of the reaction

$$2I_2 + 5SbF_5 \xrightarrow[20\ °C]{SO_2} [I_2^+][Sb_2F_{11}^-] + SbF_3 \qquad (2)$$

products by filtration, with SbF_3 insoluble in SO_2. However in the described reaction an excess of SbF_5 is used, which according to an earlier ^{19}F NMR study[22] causes appreciable solubility of SbF_3 in SO_2. Not surprisingly, the reported[6] elemental analysis indicates a rather impure material.

In order to obtain pure samples of $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{16}^-]$ in quantities of several grams, we used a different approach. Bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, can be obtained in very high purity, and its chemical and physical properties[23] allow easily controlled addition by vacuum distillation.[16] The compound oxidizes halogens, in particular iodine[24] and bromine,[19] according to

$$nI_2 + S_2O_6F_2 \rightarrow 2I_nSO_3F \quad n = 7, 3, \text{ or } 1 \qquad (3)$$

or

$$Br_2 + S_2O_6F_2 \rightarrow 2BrSO_3F \qquad (4)$$

with an excess of Br_2 soluble in bromine(I) fluorosulfate.[16] Hence the quantitative oxidation of 2 mol of I_2 or Br_2 by 1 mol of $S_2O_6F_2$ either will produce an equimolar mixture of

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[22] T. Birchall, P. A. W. Dean, B. DellaValle, and R. J. Gillespie, *Can. J. Chem.*, **51**, 667 (1973).

[23] F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 513 (1957).

[24] C. Chung and G. H. Cady, *Inorg. Chem.*, **11**, 2528 (1972).

ISO_3F and I_3SO_3F or will oxidize only 1 mol of Br_2 to give $BrSO_3F$.

Subsequent complete removal of the SO_3F group occurs via a solvolysis reaction in an excess of SbF_5 according to

$$Br_2 + 2BrSO_3F + 10SbF_5 \xrightarrow[25\ ^\circ C]{SbF_5} 2[Br_2^+][Sb_3F_{16}^-] + 2Sb_2F_9SO_3F \quad (5)$$

and

$$ISO_3F + I_3SO_3F + 8SbF_5 \xrightarrow[50\ ^\circ C]{SbF_5} 2[I_2^+][Sb_2F_{11}^-] + 2Sb_2F_9SO_3F \quad (6)$$

Precedents for the conversion of a fluorosulfate into a fluoroantimonate have been reported recently,[25,26] and the fluorosulfate-bridged compound $Sb_2F_9(SO_3F)$ had been found to have approximately 3–4 mmHg vapor pressure at room temperature,[27] allowing its removal in vacuo. Both conversions proceed rather smoothly, but while $[Br_2^+][Sb_3F_{16}^-]$ forms, as a crystalline precipitate, reaction 6 yields a homogeneous black-blue liquid mass. In the latter case complete removal of all volatiles in vacuo requires elevated temperatures. Excitation with the 632.8-nm He–Ne line produces excellent resonance Raman spectra for both solids. The observation of six overtones is possible in the Stokes region, and both fundamentals, 368 cm^{-1} for Br_2^+ and 242 cm^{-1} for I_2^+, are slightly higher than the solution values.[3,8]

Both compounds are obtained in reasonable quantities and in excellent purity, judged sufficient for a detailed magnetic study. Both melt sharply and not surprisingly at higher temperatures than reported previously. Vibrational spectra indicate complete absence of any fluorosulfate species.

Encouraged by the ease of the solvolysis reaction, an extension of this method in three directions is undertaken: (i) the search for materials containing a heteronuclear diatomic halogen cation, (ii) the solvolysis of the halogen tris(fluorosulfates) $I(SO_3F)_3$ and $Br(SO_3F)_3$, and (iii) the generation of the triatomic bromonium(III) cations Br_2Cl^+ and $BrCl_2^+$.

According to the reported[11] adiabatic first ionization potentials of IBr and ICl, with values of 9.58 and 9.80 eV, respectively, and lower than the corresponding value for Br_2 of 10.33 eV,[11] both IBr^+ and ICl^+ should be obtainable by chemical oxidation with bis(fluorosulfuryl) peroxide, with IBr^+ the more probable of the two. By use of the method of Herring and McLean[9] as previously applied to I_2^+ and Br_2^+, the main absorption bands of the electronic spectrum and the approximate position of the I–Br stretching frequency (~290 cm^{-1}) for IBr^+ may be predicted from the reported photoelectron spectrum[11,28] of IBr.

Besides the controlled oxidation of IBr with $S_2O_6F_2$ and subsequent solvolysis in antimony(V) fluoride according to eq 7 and 8, with n expected to be 2 or 3, two additional synthetic

$$2IBr + S_2O_6F_2 \rightarrow 2ISO_3F + Br_2 \quad (7)$$

$$2ISO_3F + Br_2 + 2(n + 2)SbF_5 \rightarrow 2IBrSb_nF_{5n+1} + 2Sb_2F_9SO_3F \quad (8)$$

approaches were attempted: the cosolvolysis of equimolar amounts of IBr_2SO_3F[17] and ISO_3F[16] in an excess of SbF_5 and a redistribution reaction between $[Br_2^+][Sb_3F_{16}^-]$ and $[I_2^+][Sb_2F_{11}^-]$ at a 1:1 mole ratio.

The last reaction is particularly informative. Upon mixing of the reactants, an instantaneous exothermic reaction is noted, producing a blue-green viscous liquid. Removal of any volatile SbF_5 yields a green-black solid melting at 63–64 °C. Elemental analysis gives the composition $IBrSbF_6 \cdot 0.47SbF_5$, and magnetic susceptibility measurements over the temperature range 80–300 K reveal paramagnetism with μ_{eff} ranging from 1.24 to 1.33 μ_B depending on the temperature. However, the Raman spectrum of the solid or its solutions in HSO_3F or in superacid gives a resonance Raman spectrum typical for I_2^+,[8] while no Br_2^+ is detected. Similar black-green materials are formed by the other two methods.

Table I. Raman Frequencies for $[BrCl_2^+]$, $[Br_2Cl^+]$, and Related Molecules and Ions

species	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	ref
$[BrCl_2^+]$(l)	430	167	421	
$SeCl_2$(g)	415	153	377	32
BrCl(l)	434			a
$[Br_2Cl^+]$[b]	424	n.o.[d]	300	
Br_3^+	290	(140)[c]	290	31

[a] H. Stammreich, R. Forneris, and Y. Tavares, *Spectrochim. Acta*, 17, 1173 (1961). [b] ν_1 denotes the BrCl stretch, while ν_3 denotes the BrBr stretch. [c] Calculated value; see: R. J. Gillespie and J. Passmore, *Adv. Inorg. Chem. Radiochem.*, 17, 49 (1975). [d] Not observed.

It must be concluded that appreciable amounts of I_2^+ remain and may cause the observed paramagnetism and that stoichiometry of the redistribution reaction must be different from expectations. No attempt was subsequently made to obtain ICl^+-containing materials.

The solvolyses of $Br(SO_3F)_3$ and $I(SO_3F)_3$ are undertaken to obtain fluoroantimonates with the cations $[Br(SO_3F)_2^+]$ and $[I(SO_3F)_2^+]$. Both ions have been synthesized in complexes of the type $[Hal(SO_3F)_2]_2[Sn(SO_3F)_6]$,[29] with Hal = Br or I.

Again a different course of the solvolysis reaction is encountered: $I(SO_3F)_3$ in SbF_5 disproportionates extensively to yield dark blue solutions, characteristic of I_2^+. This is not totally surprising, since $I(SO_3F)_3$ is reported to disproportionate on gentle heating.[16] The solvolysis of $Br(SO_3F)_3$ in a large excess of SbF_5 will ultimately lead to solid $[BrF_2^+][SbF_6^-]$, identified by weight and its Raman spectrum,[30] after all volatiles are removed, with the overall reaction

$$Br(SO_3F)_3 + 7SbF_5 \rightarrow [BrF_2^+][SbF_6^-] + 3Sb_2F_9(SO_3F) \quad (9)$$

Yellowish viscous oils formed initially are thought to contain as intermediates both $[Br(SO_3F)_2^+]$ and $[BrF(SO_3F)^+]$.

Finally the bromonium cations $[Br_2Cl^+]$ and $[BrCl_2^+]$ are formed by the addition of chlorine to $[Br_2^+][Sb_3F_{16}^-]$ and by the solvolysis of $BrSO_3F$ in SbF_5 with an excess of chlorine present according to eq 10 and 11. Substitution of chlorine

$$2[Br_2^+][Sb_3F_{16}^-] + Cl_2 \rightarrow 2[Br_2Cl^+] + 2SbF_6^- + 4SbF_5 \quad (10)$$

$$BrSO_3F + Cl_2 + (n + 3)SbF_5 \rightarrow [BrCl_2^+] + SbF_6^- + nSbF_5 + Sb_2F_9(SO_3F) \quad (11)$$

by bromine in eq 10 and 11 will lead to similar Br_3^+-containing solutions, but solid materials are not obtained in all instances, because attempts to remove the excess of SbF_5 in vacuo with the sample at room temperature cause thermal degradation of the cation. The low thermal stability of all these ions, in particular of those with Br–Cl linkages, is not surprising. No precedents for either Br_2Cl^+ or $BrCl_2^+$ have been reported. Characterization of both ions is possible by Raman spectroscopy, and a vibrational assignment is shown in Table I.

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(30) H. A. Carter and F. Aubke, *Can. J. Chem.*, **48**, 2456 (1970).
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Table II. Electronic Solution Spectra (nm) of I_2^+(solv) and Br_2^+(solv)

	Br_2^+(solv)		$I_2^+(solv)^d$	
elec transitn	PES[a]	obsd	PES	obsd
$^2\Pi_{3/2g} \rightarrow {}^2\Pi_{1/2g}$	3180	3560	1823	1953 (75)[e]
$^2\Pi_{3/2g} \rightarrow {}^2\Pi_{3/2u}$	521	510 or 480[b]	712	638 (2192)
$^2\Pi_{3/2g} \rightarrow {}^2\Pi_{1/2u}$	475	n.o.[c]	490	486 (686)
$^2\Pi_{3/2g} \rightarrow {}^2\Delta_u$		355[b]		405 (686)
ν(Hal–Hal), cm^{-1}	220	242	360	368

[a] Data taken from ref 10 and 28. [b] Taken from Table IV, spectra obtained on SbF_5 solution. [c] Unresolved (see text). [d] Solvent HSO_3F + 0.21 *m* SbF_5; solute $[I_2^+][Sb_2F_{11}^-]$. [e] ϵ values in parentheses.

(B) Electronic Spectra. Both $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{11}^-]$ are very soluble in HSO_3F, as well as in the superacid systems HSO_3F/SbF_5 and $HSO_3F/3SO_3/SbF_5$. It must be assumed that both solutes act as sources for additional SbF_5. Therefore the acidity of fluorosulfuric acid should be enhanced[33] via, e.g., eq 12. The enhanced acidity in this solvent

$$2HSO_3F + SbF_5 \rightleftarrows [SbF_5(SO_3F)]^- + H_2SO_3F^+ \qquad (12)$$

does subsequently account for some observations, which seem to contradict previous reports: (i) The Br_2^+ cation is detectable by a band at ~500 nm. Previous work,[3] in particular a coulometric titration in HSO_3F,[34] had found no evidence for Br_2^+ in HSO_3F. (ii) Molar extinction coefficients for solutions of $[I_2^+][Sb_2F_{11}^-]$ in HSO_3F differ slightly from previously reported values,[1] primarily because the slight disproportionation of I_2^+(solv)[1] appears to be prevented in the more acidic solutions.

In agreement with previous reports on Br_2^+(solv),[3] this cation is best studied in the superacid media HSO_3/SbF_5 or better even in $HSO_3F/3SO_3/SbF_5$, but the intensity of the main absorption band at 510 nm indicates even here extensive disproportionation.[3] The formation of Br_3^+(solv) in such disproportionation reactions has prevented so far the observation of additional bands due to Br_2^+(solv). On the other hand, a complete assignment is available for all bands due to I_2^+(solv).[1,9]

The results of our spectroscopic study are summarized in Table II and compared to predictions from photoelectron spectra[10,28] by using the method of Herring and McLean.[9] The main features are the forbidden transitions $^2\Pi_{3/2_g} \rightarrow {}^2\Pi_{1/2_g}$ found at 1953 nm (ϵ 75) for I_2^+(solv) and at 3560 nm for Br_2^+(solv) (observed as a medium strong band in IR spectra). Both values are in good agreement with PES predictions,[10,28] and it appears that in both cases for the gaseous and the solvated cations the electronic ground state $^2\Pi_{3/2_g}$ is separated from the first excited state $^2\Pi_{1/2_g}$ by about 5120 and 2810 cm^{-1}, respectively, for I_2^+ and Br_2^+.[8]

PES predicts for Br_2^+(g) a spin–orbit coupling constant for $^2\Pi_{3/2_u}$ and $^2\Pi_{1/2_u}$ of 1850 cm^{-1}. The transitions $^2\Pi_{3/2_g} \rightarrow {}^2\Pi_{3/2_u}$ and $^2\Pi_{3/2_g} \rightarrow {}^2\Pi_{1/2_u}$ should give rise to bands separated by ~50 nm. It seems therefore reasonable that in the solution spectra these bands are not resolved and both transitions contribute to the intense band at 510 nm. Even in SbF_5 only one band is found in this region (see Table III).

The $^2\Pi_{3/2} \rightarrow {}^2\Delta_u$ transition (not predictable from PES data) is assigned to a band at 355 nm observed in liquid SbF_5. This band is obscured in protonic solvents by an intense band at ~375 nm due to Br_3^+(solv).

Table III. Electronic Spectra of Some Bromonium(III) Cations in SbF_5

species in SbF_5	λ_{max}, nm	abs, OD units
Cl_2	330	0.70
Br_2^+	480	0.36
	355	0.49
	247	2.92
Br_3^+	380	0.56
	~315 (sh)	~0.85
	292	0.87
	247	1.12
Br_2Cl^+	~370 (sh)	~0.75
	~305 (sh)	~1.20
	~285 (sh)	~1.30
	252	1.68
$BrCl_2^+$	~305	~0.60
	248	1.02

While Br_2^+(solv) is best studied in $HSO_3F/3SO_3/SbF_5$, I_2^+(solv) is gradually oxidized in this medium. Hence HSO_3F/SbF_5, where I_2^+(solv) is stable, becomes the solvent of choice to study the nature of the interaction between I_2^+(solv) and Br_2^+(solv), which is best monitored by measuring the intensity of the principal absorption band of I_2^+(solv) at 640 nm.

Spectra produced by oxidation of IBr by $S_2O_6F_2$ at a 2:1 molar ratio are identical with those produced by a 1:1 molar mixture of I_2^+(solv) and Br_2^+(solv). Monitoring the intensity of the 640-nm band for I_2^+(solv) indicates consumption of this species upon further addition of Br_2^+(solv), until at a I_2^+(solv) to Br_2^+(solv) ratio of about 5:9 a new spectrum emerges with three bands of rather low intensity: λ_{max} 560 nm (ϵ ~84), 455 (154), 360 (602). Both band positions and intensities identify this species as the previously reported $[IBr_2^+]$(solv).[17] No resonance Raman band due to either I_2^+(solv) or Br_2^+(solv) is observed at this mole ratio, and the overall reaction may be formulated as a redox reaction rather than the intended halogen distribution:

$$5I_2^+(\text{solv}) + 9Br_2^+(\text{solv}) \xrightarrow{HSO_3F/SbF_5} 9IBr_2^+(\text{solv}) + I^{5+} \text{ species} \qquad (13)$$

The nature of the I(V) species is unknown, and attempts to identify this species by Raman or ^{19}F NMR spectra were unsuccessful.

Not unexpectedly both the 640-nm absorption and the resonance Raman band at 242 cm^{-1} are also absent when $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{16}^-]$ are combined at a 5:9 molar ratio to give a black-brown liquid. This indicates a similar redox reaction takes place in SbF_5 solution, and again $[IBr_2^+]$(solv) is favored over $[IBr^+]$(solv).

Finally the results of some qualitative measurements of UV–visible spectra of bromonium(III) cations in SbF_5 are shown in Table III. While the spectra produced by Br_3^+(solv) and $[Br_2Cl^+]$(solv) are somewhat similar, a few general points may be made: (i) Free Cl_2, which has a similar λ_{max} value as in Cl_2(g) when dissolved in SbF_5, seems to be absent in the spectra of $[Br_2Cl^+]$(solv) and $[BrCl_2^+]$(solv), and extensive dissociation does not seem to occur. (ii) The absence of Br_2^+(solv) in the spectra of the two new cations also speaks against dissociation or disproportionation of $[Br_2Cl^+]$(solv) or $[BrCl_2^+]$(solv). (iii) Two absorption bands are found for Br_2^+(solv) in SbF_5. No disproportionation seems to occur. I_2^+(solv), in agreement with previous work,[5] gives in SbF_5 a three-band spectrum identical with the one observed in protonic solvents. (iv) An intense UV band at ~250 nm occurs in all spectra of bromonium ions in SbF_5. This band is tentatively assigned to the solvated SbF_6^- anion.

(C) Magnetic Susceptibilities. As mentioned previously, both I_2^+ and Br_2^+ have $^2\Pi_{3/2_g}$ ground states with the first excited states $^2\Pi_{1/2_g}$ at approximately 5100 and 2800 cm^{-1},

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Table IV. Magnetic Data

$[I_2^+][Sb_2F_{11}^-]$				$[Br_2^+][Sb_3F_{16}^-]$			
	$10^6\chi_M$,	μ_{eff},[a] μ_B			$10^6\chi_M$,	μ_{eff},[a] μ_B	
T, K	cm^3 mol^{-1}	a	b	T, K	cm^3 mol^{-1}	a	b
295	1962	2.15	2.00	297	1790	2.06	2.00
274	2075	2.13	1.99	275	1934	2.06	2.00
253	2199	2.11	1.98	255	2084	2.06	2.01
237	2309	2.09	1.97	235	2250	2.06	2.01
232	2332	2.08	1.96	213	2454	2.05	2.00
210	2486	2.04	1.93	193	2703	2.04	2.00
191	2677	2.02	1.92	172	2999	2.03	2.00
170	2892	1.98	1.89	151	3354	2.01	1.98
149	3145	1.94	1.85	131	3822	2.00	1.97
131	3429	1.90	1.82	116	4427	2.02	2.00
112	3782	1.84	1.78	104	4835	2.01	1.98
103	3924	1.80	1.74	80	6054	1.96	1.95
81	4360	1.68	1.63				

[a] μ_{eff} calculated from (a) $\mu_{eff} = 2.828(\chi_M T)^{1/2}$ and (b) $\mu_{eff} = 2.828[(\chi_M - \mathrm{TIP})T]^{1/2}$ when TIP = 260×10^{-6} and 100×10^{-6} cm^3 mol^{-1} for $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{16}^-]$, respectively.

respectively, both in the gas phase[28] and in solution. The magnetic moment in both cases is expected to be 2.0 μ_B[35] and, because of the absence of thermally accessible states, should be temperature independent.[35]

Magnetic susceptibility data obtained for $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{16}^-]$ are given in Table IV. In both instances the magnetic moments around room temperature are in excess of 2.0 μ_B and moreover they decrease with decreasing temperature. While thermal population of excited states is not possible in these molecular ions, the mixing of excited states with the ground state via the second-order Zeeman effect is possible. This would give rise to a contribution to the magnetic susceptibility which is independent of temperature (TIP). Subtracting a relatively modest TIP contribution of 100×10^{-6} cm^3 mol^{-1} from the data for $[Br_2^+][Sb_3F_{16}^-]$ gives, to within experimental error, the theoretically predicted 2.0 μ_B over the entire temperature range 80–300 K.

The situation in regard to $[I_2^+][Sb_2F_{11}^-]$ is not as simple. A much greater TIP contribution of 260×10^{-6} cm^3 mol^{-1} is required to bring the room-temperature moment into agreement with theory. However, this correction, applied over the entire temperature range, does not remove the significant drop in the magnetic moment which is observed on decreasing the temperature to 80 K (see Table IV). The phenomenon which seems likely to account for this drop is interaction of an antiferromagnetic nature between contiguous I_2^+ cations in the solid lattice.

The possibility of such interaction is supported by the crystal structure,[6] which shows I_2^+ cations, not insulated by intervening diamagnetic atoms, aligned in chains along the c axis of monoclinic crystals. The closest intermolecular I···I distance is 4.29 Å.[36]

The crystal structure of $[Br_2^+][Sb_3F_{16}^-]$[2] on the other hand shows greater separation between individual cations (with the closest intermolecular Br···Br distance 6.445 Å[36]) and insulation by the intervening anions, consistent with the absence of significant magnetic concentration in this compound.

Except for the report of a rather low magnetic moment at room temperature of 1.6 μ_B[2] for $[Br_2^+][Sb_3F_{16}^-]$, previous magnetic susceptibility studies on these cations are limited to I_2^+. Gillespie and Milne[1] report the magnetic moment of I_2^+ in solution of HSO_3F to be 2.0 ± 0.1 μ_B. This result is in reasonable agreement with our findings, as we would expect a moment of the order of 2.15 μ_B (including TIP) in solution, where no possibility of magnetic interaction exists. Kemmitt et al.[5] report magnetic susceptibility studies on $(SbF_5)_2I$, a material thought to contain the I_2^+ cation. These authors find magnetic moments ranging from 2.25 μ_B at room temperature to 2.05 μ_B at 100 K. Considering the uncertainty in the chemical composition of their material, not much significance should be attached to the absolute magnitude of the magnetic moments. A similar temperature variation to that obtained for $[I_2^+][Sb_2F_{11}^-]$ is observed however, and contrary to the statement by these authors that cooperative effects are unimportant, it seems likely that in the $(SbF_5)_2I$ system, too, there is antiferromagnetic interaction between I_2^+ cations in the solid state.

The occurrence of both temperature-independent paramagnetism and antiferromagnetic coupling is not unprecedented for paramagnetic molecules. A TIP of 19.8×10^{-6} cm^3 mol^{-1} is reported for solid NO,[37] and strong antiferromagnetic coupling, reportedly caused by interionic contact, is found for NaO_2;[38] however, the situation here may be somewhat obscured by two phase transitions at low temperatures.[39]

(D) Conclusion. While the solvolysis of halogen fluorosulfates or of their mixtures with halogens in an excess of SbF_5 provides a clean and facile route to pure $[I_2^+][Sb_2F_{11}^-]$ and $[Br_2^+][Sb_3F_{16}^-]$ or the cation $[BrCl_2^+]$, an attempted extension of this synthetic method to the generation of a novel diatomic heteronuclear cation $[IBr^+]$ fails, resulting eventually in the formation of $[IBr_2^+]$ as the main product. It is hence not surprising that no conclusive evidence for a stable heteronuclear dihalogen cation has been reported, even though the rather low first ionization potentials of IBr[11] and ICl[11] in particular suggest their existence.

Agreement in respect to electronic structure between transient I_2^+(g) and Br_2^+(g), as observed by PES, and the solvated cations is rather good. The expected simple magnetic behavior is somewhat complicated both for I_2^+ and Br_2^+ by temperature-independent paramagnetism and for the case of I_2^+ by antiferromagnetic coupling in the solid lattice.

Antimony(V) fluoride is found to be a very suitable solvent for these strong electrophiles, even though the high viscosity, the corrosiveness, and the lack of volatility present serious drawbacks, in particular where thermally unstable cations are encountered.

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Registry No. $[I_2^+][Sb_2F_{11}^-]$, 53108-64-8; $[Br_2^+][Sb_3F_{16}^-]$, 11088-93-0; $S_2O_6F_2$, 13709-32-5; $BrCl_2^+$, 55426-81-8; Br_2Cl^+, 56488-80-3; IBr^+, 73002-69-4; Cl_2, 7782-50-5; Br_3^+, 33105-86-1.

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