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The Br_2^+ and Br_3^+ Cations: an Example of a Resonance Raman Spectrum

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Iodine can be oxidised in solution in a strong acid, such as H_2SO_4, HSO_3F, or $H_2S_2O_7$, either by the acid itself or by an added oxidising agent, *e.g.* $S_2O_6F_2$, to the cations I_3^+ and I_2^+. Evidence for I_3^+ was obtained thirty years ago[1] but the evidence for I_2^+ is more recent.[2] There has been no previous evidence for analogous stable cations of bromine but we now show that in media of sufficiently high acidity both Br_2^+ and Br_3^+ exist as stable species.

When bromine monofluorosulphate[3] is dissolved in the superacid[4] HSO_3F–SbF_5–$3SO_3$ (I) a new species is formed which is not obtained in fluorosulphuric acid alone. This species has a strong visible absorption at 510 mμ (Figure 1) and the Raman spectrum of its solution in the superacid solvent shows, in addition to weak peaks due to bromine monofluorosulphate and the solvent, a new intense fundamental band at 360 cm.$^{-1}$. That both spectra arise from the same species was confirmed by changing the Raman exciting wavelength from the 6328 Å laser line which gives a pre-resonance Raman spectrum to 5145 Å which gives a resonance Raman spectrum.[5] The intensity of the 360 cm.$^{-1}$ peak is considerably enhanced relative to the other peaks at the resonance frequency (Figure 2) and strong overtones are observed similar to those observed previously[6] in the resonance Raman spectrum of I_2^+. Decreasing the exciting wavelength further to 4880 Å caused a decrease in the intensity of the 360 cm.$^{-1}$ peak corresponding to the shift from the resonance condition (Figure 2). As iodine monofluorosulphate is completely disproportionated to I_2^+ and $I(SO_3F)_3$ when dissolved in fluorosulphuric acid,[2,7] it is reasonable to assume that $BrOSO_2F$ undergoes a similar disproportionation

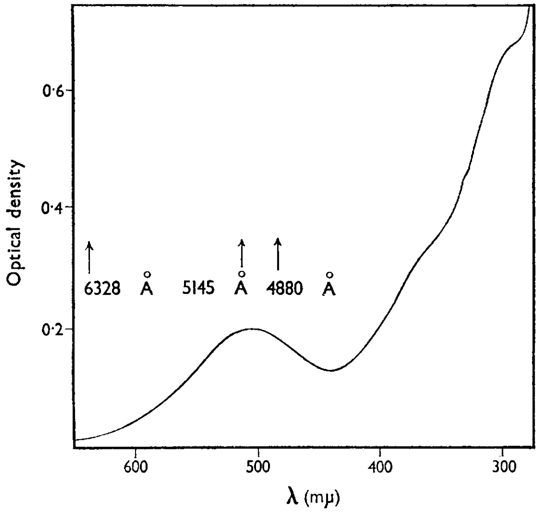

Figure 1. *Ultraviolet and visible spectrum of* 6·91 × 10^{-2} *molal* $BrSO_3F$ *and* 0·176 m SbF_5–$3SO_3$ *in* HSO_3F. *Path length* 0·0144 cm.

$$2BrOSO_2F \rightleftarrows 0{\cdot}8Br_2^+ + 0{\cdot}4Br(SO_3F)_3 + 0{\cdot}8SO_3F^- \quad (1)$$

The 510 mμ peak in the visible spectrum and the 360 cm.$^{-1}$ peak in the Raman spectrum may then be attributed to the Br_2^+ cation. In comparison

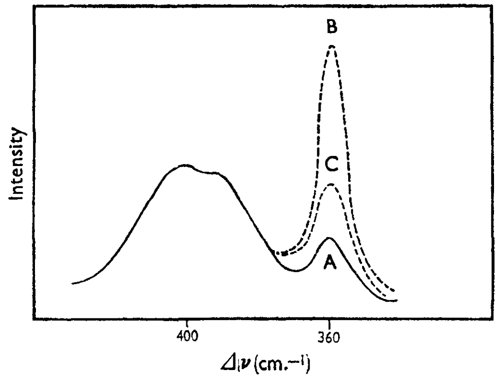

FIGURE 2. *Raman spectrum of* 360 cm.$^{-1}$ Br_2^+ *fundamental and* 400 cm.$^{-1}$ *solvent band in a* 1·30 × 10^{-2} m $BrSO_3F$ *and* 0·176 m SbF_5–$3SO_3$ *solution in* HSO_3F. *Excited by* A 6328 Å, B 5145 Å, C 4880 Å *laser.*

with the following data for I_2,I_2^+, and Br_2 these values are very reasonable for Br_2^+

	λ_{max}(mμ)	ν(cm.$^{-1}$)
I_2	520	215
I_2^+	640	238
Br_2	410	320
Br_2^+	510	360

A solution of Br_2–$S_2O_6F_2$ in the mole ratio 3:1 in solution in the superacid (I) gave a spectrum which had an intense absorption at 300 mμ with a shoulder at 375 mμ and no absorption at 510 mμ. Conductivity measurements on such solutions are in agreement with the quantitative formation of Br_3^+. Since the superacid solvent has a high conductivity due to the highly conducting $H_2SO_3F^+$ ion,[4] the ionisation of a substance that behaves as a base of the fluorosulphuric acid solvent system may be investigated by following the decrease in conductivity, when the basic solute neutralises the $H_2SO_3F^+$ ion in the superacid, and comparing this decrease in conductivity with that caused by the strong base KSO_3F. In this way, γ, the number of moles of fluorosulphate ions formed by one mole of solute, was found to be 0·7 for the 3:1 Br_2–$S_2O_6F_2$ solution which is consistent with the formation of the Br_3^+ cation according to the equation.

$$3Br_2 + S_2O_6F_2 \rightarrow 2Br_3^+ + 2SO_3F^- \qquad (2)$$

The visible spectrum attributed to Br_3^+ can also be obtained in fluorosulphuric acid. Figure 3 shows the spectrum of bromine in fluorosulphuric acid and also the changes that occur in the spectrum on addition of $S_2O_6F_2$ to give the mole ratios $S_2O_6F_2$:Br_2 = 1:3, 1:1, 3:1, and 5:1. These ratios

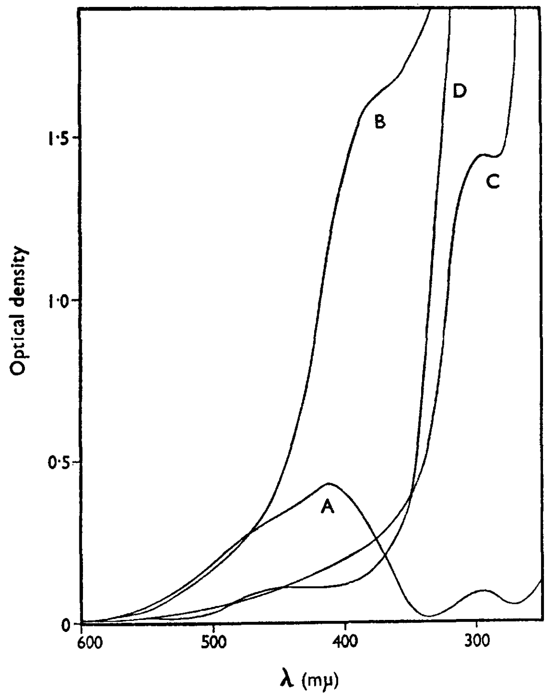

FIGURE 3. *Ultraviolet and visible spectra in* HSO_3F. *Path length* 0·100 cm. Br_2 = 1·422 × 10^{-2} m; ratio Br_2–$S_2O_6F_2$: A, 1 : 0; B, 1 : 0·33; C, 1 : 1; D, 1 : 3 and 1 : 5.

correspond to oxidation to Br_3^+, $BrOSO_2F$, and $Br(SO_3F)_3$ respectively. Apparently $Br(SO_3F)_3$ is not further oxidised by excess $S_2O_6F_2$ and we note also that there is no trace of the 510 mμ peak due to the red Br_2^+ ion.

A solution of Br_2–$S_2O_6F_2$ in the mole ratio 1:1 has exactly the same visible and Raman spectra as the solution of $BrOSO_2F$ in the superacid (I). The 300 mμ and 375 mμ peaks attributed to Br_3^+ are also present in the absorption spectrum of this solution implying that, in addition to the disproportionation (1), it is also disproportionated to some extent according to the following equation:

$$4BrOSO_2F \rightleftarrows Br_3^+ + Br(SO_3F)_3 + SO_3F^- \qquad (3)$$

Still another equilibrium is involved in these systems as conductivity measurements show that $Br(SO_3F)_3$ behaves as a base in the superacid system and is approximately 75% ionised according to the equation:

$$Br(SO_3F)_3 + H_2SO_3F^+ \rightleftarrows Br(SO_3F)_2^+ + 2HSO_3F \qquad (4)$$

It is noteworthy that although the I_3^+ cation is stabilised by the acidity of sulphuric acid, the I_2^+

cation is almost completely disproportionated in this solvent and it needs the greater acidity of fluorosulphuric acid to enable it to exist in any appreciable concentration. The bromine cations are still less stable and Br_3^+ can be obtained in fluorosulphuric acid although not in sulphuric acid, while the Br_2^+ cation exists as a stable species only in the superacid (I).

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