Halogen and Interhalogen Cations

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In a previous review on halogen cations Arotsky and Symons[1] pointed out that for a long time there had been confusion in the literature over the terms 'positive halogen' and 'halogen cation'. In particular, the existence of many well-known compounds in which chlorine, bromine, and iodine are found in the +1 oxidation state led to the supposition that the cations Cl^+, Br^+, and I^+ are important as stable species or as reaction intermediates in many systems. For example, the fact that molten iodine has an appreciable electrical conductivity had been postulated as being due to the self-ionisation:

$$2I_2 \rightleftharpoons I^+ + I_3^-$$

The demonstration in the late 1940s that the nitronium ion was the reactive intermediate in aromatic nitration[2] led to the general assumption that other electrophilic substitution reactions involved similar cationic intermediates, *e.g.* Cl^+ in chlorination and I^+ in iodination. Although a considerable body of direct physical evidence was obtained for the nitronium ion, similar physical evidence for the simple halogen cations Cl^+, Br^+, and I^+ was not obtained. In the period 1957—1962 Symons and his co-workers assembled a large amount of evidence to support their suggestion that the intense blue coloured solutions obtained by dissolving iodine in 65% oleum contain the iodine cation I^+, and much of the earlier review by Arotsky and Symons was devoted to summarising this evidence. However, it was subsequently shown that this blue species is the I_2^+ cation and there is no evidence left standing for the I^+ cation,[3-5] nor is there any evidence for Cl^+ or Br^+ as stable species in solution or in the solid state. The I_2^+ cation is just one of a number of polyatomic halogen cations and interhalogen cations that have been discovered in recent years and which form the subject of this Review. We use the term 'halogen cation' to describe cations containing one or more atoms of only one of the halogens and the term 'interhalogen cation' to describe polyatomic cations containing at least two halogens. Cations containing one or more halogens and another element, *e.g.* oxygen, will not be considered. At the time of the previous review there was good evidence for only one halogen cation, I_3^+, and one interhalogen cation, ICl_2^+, whereas today ten halogen and

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[1] J. Arotsky and M. C. R. Symons, *Quart. Rev.*, 1962, **16**, 282.
[2] R. J. Gillespie and D. J. Millen, *Quart. Rev.*, 1948, **2**, 277.
[3] R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, 1966, **5**, 1577.
[4] R. J. Gillespie and K. C. Malhotra, *Inorg. Chem.*, 1969, **8**, 1751.
[5] R. D. W. Kemmitt, M. Murray, V. M. McRae, R. D. Peacock, and M. C. R. Symons, *J. Chem. Soc.*, 1968, 862.

interhalogen cations are definitely known and there is every reason to think that a number of others also exist as stable species.

As halogen cations are highly electrophilic species they can only exist in the presence of molecules and anions of very low basicity. Suitable media for the preparation and investigation of halogen cations are, therefore, extremely weakly basic solvents such as fluorosulphuric acid, disulphuric acid, antimony pentafluoride, iodine pentafluoride, and sulphur dioxide. Stable crystalline compounds of the halogen cations can similarly only be obtained with extremely weakly basic anions such as $Sb_3F_{16}^-$. It is not surprising, therefore, that the development of the chemistry of superacid systems in recent years has led to a rapid increase in the extent of our knowledge of the halogen and interhalogen cations.

1 Iodine Cations

A. The I_3^+ and I_5^+ Cations.—The first evidence for the existence of a stable iodine cation was obtained by Masson in 1938.[6] He postulated the presence of the I_3^+ and I_5^+ cations in solutions of iodine and iodosyl sulphate in concentrated sulphuric acid in order to explain the stoicheiometry of the reaction of such solutions with chlorobenzene to form both iodo and iodoso derivatives. He was unable to obtain evidence for I^+ and proposed that univalent positive iodine was extensively, if not completely, disproportionated to I_3^+, I_5^+, and IO^+. In 1962 Arotsky, Mishra, and Symons gave conductimetric evidence for I_3^+ formed from iodic acid and iodine in 100% sulphuric acid, and suggested that I_5^+ may be formed on the basis of changes in the u.v. and visible spectra when iodine is

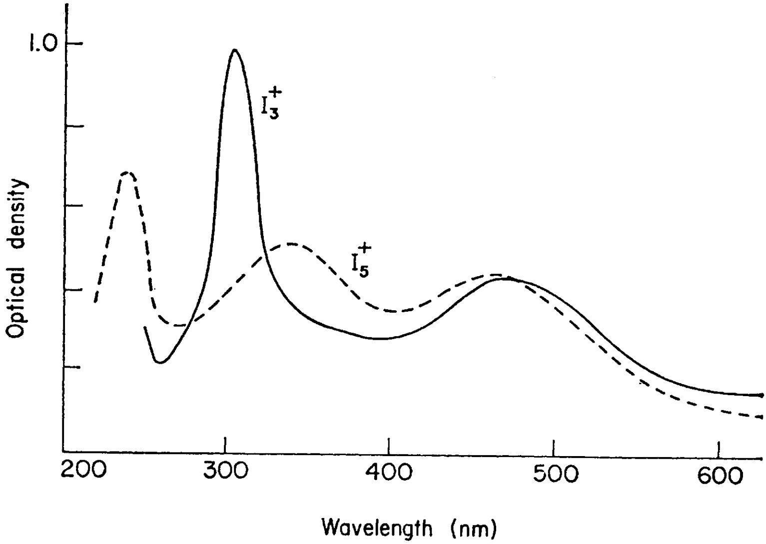

Figure 1 *Absorption spectra of solutions of* I_3^+ *and* I_5^+ in *fluorosulphuric acid at* 85 °C.

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[6] I. Masson, *J. Chem. Soc.*, 1938, 1708.

added to I_3^+ solutions.[7] Gillespie and co-workers confirmed the existence of I_3^+ and I_5^+ in 100% sulphuric acid by detailed conductimetric and cryoscopic measurements,[8] and also characterised the I_3^+ and I_5^+ cations in fluorosulphuric acid solutions.[9]

Figure 1 shows the u.v. and visible absorption spectra of the I_5^+ and I_3^+ cations in fluorosulphuric acid prepared by the reactions

$$3I_2 + S_2O_6F_2 \rightarrow 2I_3^+ + 2SO_3F^-$$
$$I_3^+ + I_2 \rightarrow I_5^+$$

The absorption spectrum of the dark brown solution of the I_5^+ cation in fluorosulphuric acid at −85 °C has peaks at 450, 345, 270, and 240 nm. At room temperature the I_5^+ cation is slowly oxidised by the solvent. Solutions of the red–brown I_3^+ cation have characteristic absorption maxima at 305 and 470 nm, with a molar extinction coefficient of 5200 at 305 nm. No data on the vibrational frequencies or the structures of these cations have been published. By analogy with the ICl_2^+ cation,[10] the I_3^+ cation may be presumed to have a bond angle close to 90°.

B. The I_2^+ and I_4^{2+} Cations.—In 1965 Gillespie and Milne showed by conductimetric, spectrophotometric, and magnetic susceptibility measurements in fluorosulphuric acid that the blue iodine species is I_2^+ and not I^+.[3] Solutions of iodine in fluorosulphuric acid were oxidised with peroxydisulphuryl difluoride, and the concentration of the blue iodine cation was found to reach a maximum at the 2:1 mole ratio,

$$2I_2 + S_2O_6F_2 \rightarrow 2I_2^+ + 2SO_3F^-$$

rather than at the 1:1 mole ratio expected for the formation of I^+ according to the equation

$$I_2 + S_2O_6F_2 \rightarrow 2I^+ + 2SO_3F^-$$

Supporting evidence for the formation of I_2^+ was obtained from conductivity measurements which showed that the conductivity of a 1:1 $S_2O_6F_2$–I_2 solution was much less than that expected for the formation of I^+ and that 2:1 solutions had conductivities at low concentrations close to the conductivities of solutions of the same concentration of KSO_3F, indicating the formation of one mole of SO_3F^- per mole of I_2. Magnetic measurements showed that the blue solutions of iodine in fluorosulphuric acid or in oleum contain a paramagnetic species which has a magnetic moment of the 2·0 ± 0·1 B.M., as expected for the $^2\Pi_{\frac{3}{2}}$ ground state of the I_2^+ cation. The I_2^+ cation has characteristic peaks in its visible absorption spectrum at 640, 490, and 410 nm and has a molar extinction coefficient at 640 nm of 2560 (Figure 2).

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[7] J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 1962, 2582.
[8] R. A. Garrett, R. J. Gillespie, and J. B. Senior, *Inorg. Chem.*, 1965, **4**, 563.
[9] R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, 1966, **5**, 1236.
[10] C. G. Vonk and E. H. Wiebenga, *Acta Cryst.*, 1959, **12**, 859.

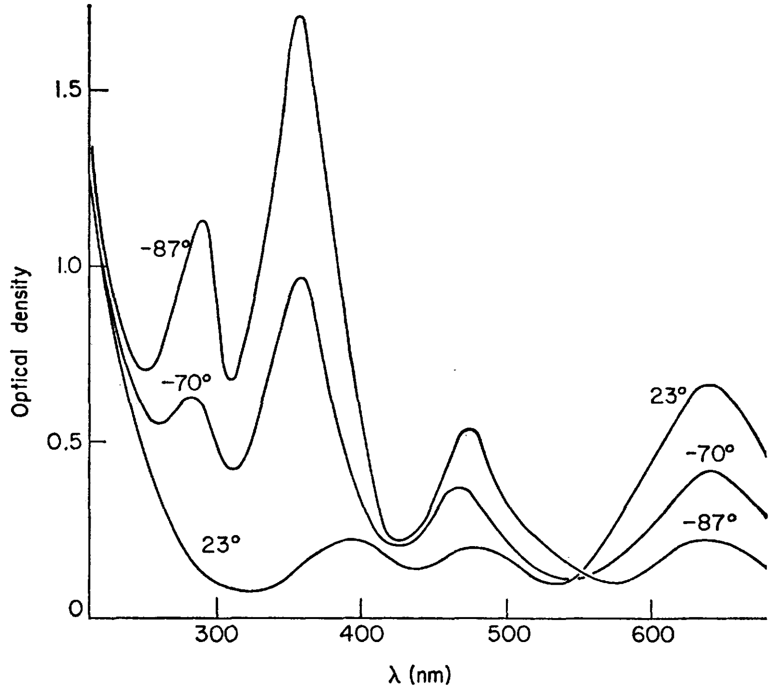

Figure 2 *Absorption spectra of* 1:1 I_2–$S_2O_6F_2$ *solutions in fluorosulphuric acid.* 23 °C (I_2^+), −86·5 °C (mainly I_4^{2+}).

The I_2^+ cation is not completely stable in fluorosulphuric acid and undergoes some disproportionation to the more stable I_3^+ and $I(SO_3F)_3$ according to the equation

$$8I_2^+ + 3SO_3F^- \rightleftharpoons I(SO_3F)_3 + 5I_3^+$$

as is shown, for example, by the appearance of the characteristic peak of the I_3^+ cation at 305 nm in solutions of $I_2^+SO_3F^-$ in fluorosulphuric acid and by conductivity measurements which show that there is less than one mole of SO_3F^- per mole of iodine as the concentration of iodine is increased. This disproportionation is largely prevented in a 1:1 I_2–$S_2O_6F_2$ solution in which $I(SO_3F)_3$ is formed,

$$5I_2 + 5S_2O_6F_2 \rightarrow 4I_2^+ + 4SO_3F^- + 2I(SO_3F)_3$$

and does not occur if the fluorosulphate ion concentration in the fluorosulphuric acid is lowered by the addition of antimony pentafluoride

$$SbF_5 + SO_3F^- \rightarrow SbF_5(SO_3F)^-$$

or in the less basic solvent 65% oleum.

In 100% H_2SO_4 the disproportionation of I_2^+ to I_3^+ and an iodine(III) species, probably $I(SO_4H)_3$, is essentially complete and only traces of I_2^+ can be detected by means of its resonance Raman spectrum.

The solutions of the blue iodine cation in oleums have been reinvestigated by conductimetric, spectrophotometric and cryoscopic methods, and these confirm that the I_2^+ cation is formed. In 65% oleum the oxidation of iodine to I_2^+ is rapid and complete according to the equation

$$2I_2 + 5SO_3 + H_2S_4O_{13} \rightarrow 2I_2^+ + 2HS_4O_{13}^- + SO_2$$

Kemmitt *et al.*[5] have prepared blue crystalline solids from iodine and antimony pentafluoride and tantalum pentafluoride, which they formulated as $I_2^+Sb_2F_{11}^-$ and $I_2^+Ta_2F_{11}^-$, respectively. They also studied the blue solutions of the iodine cation both in antimony pentafluoride, and with the Lewis acids SbF_5, TaF_5, NbF_5, AsF_5, and PF_5 in iodine pentafluoride, and have interpreted their results in terms of the I_2^+ cation. No e.s.r. spectra were obtained from any of these solutions in accordance with the expectation that strong spin–orbit coupling in the I_2^+ cation would broaden the spectrum beyond detection.

When the bright blue solutions of the iodine cation I_2^+ are cooled in fluorosulphuric acid, there is a rapid change of colour to an intense red near the freezing point. It has been shown by means of spectroscopic, cryoscopic, conductimetric, and magnetic susceptibility measurements carried out at low temperatures that the iodine cation dimerises to the I_4^{2+} cation, with $\Delta H_d = -10 \pm 2$ kcal.[11]

$$2I_2^+ \rightleftharpoons I_4^{2+}$$

The I_4^{2+} cation is diamagnetic and has intense visible absorption maxima at 470, 357, and 290 nm, with molal extinction coefficients at −86 °C of 11,000, 46,000, and 25,000, respectively (Figure 2).

Although crystalline solids containing the I_2^+ cation have been prepared, *e.g.* $I_2^+Sb_2F_{11}^-$, no *X*-ray crystallographic investigation has been carried out and hence the bond length is not known. The structure of the I_4^{2+} cation is not known.

Initial attempts to observe the vibrational frequency of the I_2^+ cation by Raman spectroscopy were unsuccessful owing to the absorption of the exciting radiation by the highly coloured solutions.[5] Recently, it has been shown[12] that the resonance Raman spectrum of the I_2^+ cation can be observed using 6328 Å He–Ne laser excitation and very dilute solutions. The resonance Raman spectrum of a 10^{-2} M solution of the I_2^+ cation in fluorosulphuric acid (Figure 3) shows, in addition to the fundamental at 238 cm^{-1}, intense overtones which become progressively broader and weaker. In this particular case the relatively weak Raman scattering from the fluorosulphuric acid solvent is completely absorbed by the solution. This intense resonance Raman spectrum obtained using exciting light with a wavelength close to the 640 nm visible absorption maximum of the I_2^+ cation can be used to detect the cation at a mole ratio as low as one in a

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[11] R. J. Gillespie, J. B. Milne, and M. J. Morton, *Inorg. Chem.*, 1968, **7**, 2221.

[12] R. J. Gillespie and M. J. Morton, *J. Mol. Spectroscopy*, 1969, **30**, 178.

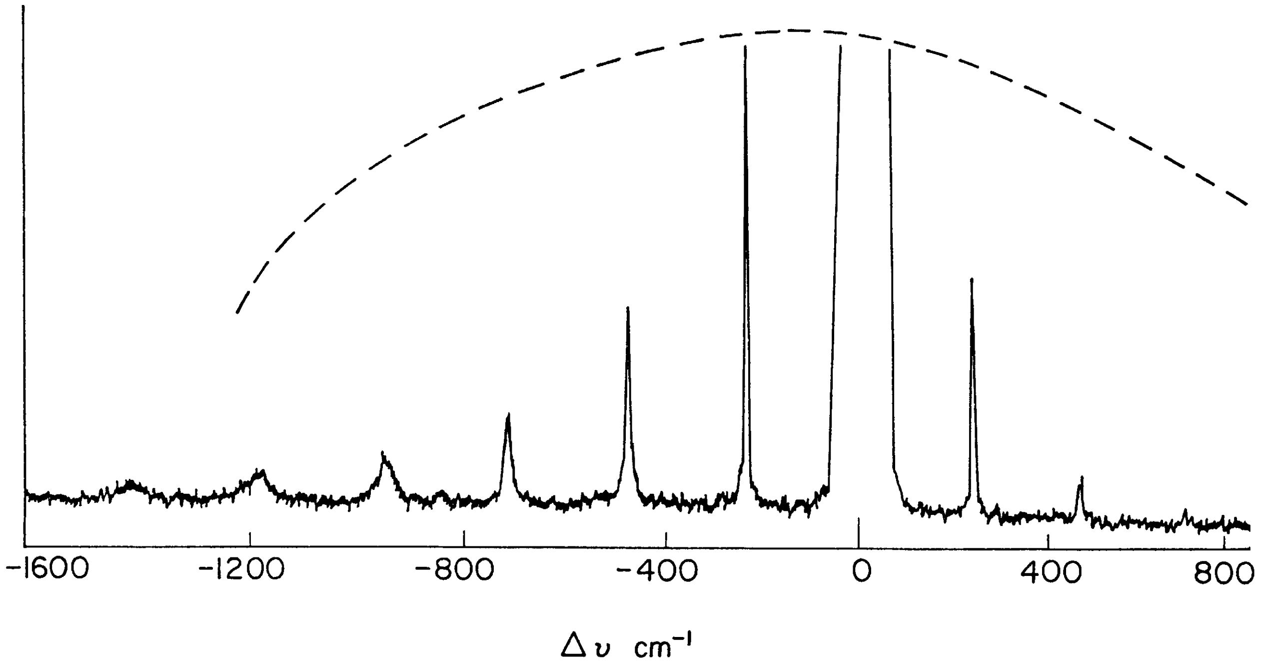

Figure 3 *Resonance Raman spectrum of* I_2^+. – – – *Absorption band maximum at* 6400 Å.

million in fluorosulphuric acid. The increase in the vibrational frequency from 215 cm^{-1} for the iodine molecule to 238 cm^{-1} for I_2^+ is consistent with the loss of an antibonding electron from I_2. Attempts to observe the vibrational frequencies of the I_3^+ cation have so far been unsuccessful.

2 Bromine Cations

A compound formulated as SbF_5Br was prepared by Ruff in 1906[13] by the reaction of Br_2 with SbF_5 but the nature of this compound remained a mystery. No further studies of the bromine–antimony pentafluoride system were made until 1966 when McRae[14] showed that the brown colour, λ_{max} (375 nm), in this system migrated to the cathode on electrolysis and on the basis of a vapour-pressure–mole-fraction curve, which showed a rise at a mole fraction of bromine of 0·3, suggested that bromine is oxidised by SbF_5 to the Br_3^+ cation. No compounds of definite composition were isolated from the mixture which presumably contained SbF_3. In 1968 Edwards *et al.*[15] reported the preparation and crystal structure of the paramagnetic scarlet salt $Br_2^+Sb_3F_{16}^-$ prepared from bromine, bromine pentafluoride, and antimony pentafluoride, and at the same time Gillespie and Morton reported[16] the characterisation of the Br_2^+ and Br_3^+ cations in the fluorosulphuric acid solvent system. This was followed shortly after by a report of the preparation of the compound $Br_3^+AsF_6^-$.[17]

Bromine cations differ from the analogous iodine cations in that a more weakly basic solvent is required to stabilise the more highly electrophilic bromine cations. Moreover, the +1 oxidation state of bromine is found in fluorosulphuric acid, in the form of covalent $BrSO_3F$,[18] whereas the hypothetical ISO_3F is completely disproportionated. The Br_3^+ cation is not completely stable in fluorosulphuric acid, but is in equilibrium with bromine and bromine monofluorosulphate.[16,19]

$$Br_2 + BrSO_3F \rightleftharpoons Br_3^+ + SO_3F^-$$

In the highly acidic SbF_5:$3SO_3$/HSO_3F system, however, the Br_3^+ cation is not disproportionated to any measurable extent. In this medium Br_3^+ can be further oxidised with $S_2O_6F_2$ and the solution turns from a brown to an intense cherry-red colour owing to the formation of the Br_2^+ cation, which is readily identified by means of its resonance Raman spectrum. Identical solutions can be obtained by dissolving $BrSO_3F$ in superacid SbF_5:$3SO_3$/HSO_3F, and the results of conductivity, u.v. and visible spectroscopy, Raman spectroscopy, and magnetic susceptibility measurements show that bromine monofluorosulphate

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[13] O. Ruff, H. Graf, W. Heller, and Knock, *Ber.*, 1906, **39**, 4310.
[14] V. M. McRae, Ph.D. Thesis, University of Melbourne, 1966.
[15] A. J. Edwards, G. R. Jones, and R. J. C. Sills, *Chem. Comm.*, 1968, 1527.
[16] R. J. Gillespie and M. J. Morton, *Chem. Comm.*, 1968, 1565.
[17] O. Glemser and A. Smale, *Angew. Chem. Internat. Edn.*, 1969, **8**, 517.
[18] F. Aubke and R. J. Gillespie, *Inorg. Chem.*, 1968, **7**, 599.
[19] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, in the press.

disproportionates according to the equilibria:

$$5BrSO_3F + 2H_2SO_3F^+ \rightleftharpoons 2Br_2^+ + Br(SO_3F)_3 + 4HSO_3F$$
$$4BrSO_3F + H_2SO_3F^+ \rightleftharpoons Br_3^+ + Br(SO_3F)_3 + 2HSO_3F$$

The u.v. and visible spectrum of a solution of $BrSO_3F$ in SbF_5:$3SO_3/HSO_3F$ given in Figure 4 shows the 510 nm peak due to the Br_2^+ cation, which has a molar extinction coefficient of 900, and the shoulder at 375 nm of the Br_3^+ cation. The Br_2^+ cation gives a resonance Raman spectrum with strong overtones and the intensity of the fundamental is proportional to the extinction coefficient of the 510 nm peak at the exciting wavelength. The vibrational frequency of the Br_2^+ cation in solution in SbF_5:$3SO_3/HSO_3F$ is 360 cm^{-1}. On cooling solutions of the Br_2^+ cation no certain evidence was obtained for the formation of the Br_4^{2+} cation.

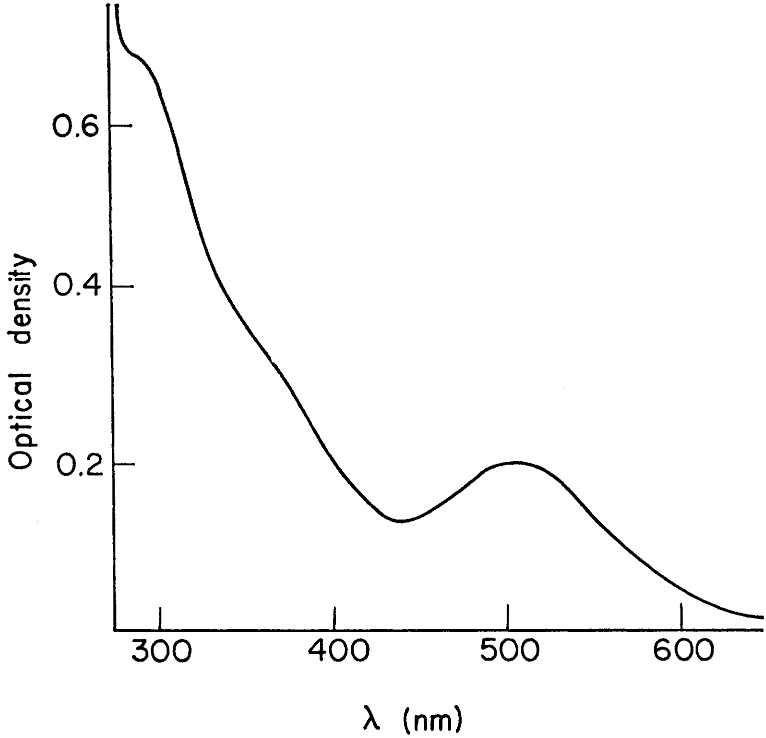

Figure 4 *Absorption spectrum of* $BrOSO_2F$ *in super acid.*

The compound $Br_2^+Sb_3F_{16}^-$ is a scarlet solid. The *X*-ray crystallographic study[15] showed the solid to consist of Br_2^+ ions with a bond length of 2·13 Å and $Sb_3F_{16}^-$ ions with a *trans*-fluorine-bridged structure (Figure 5). The bond

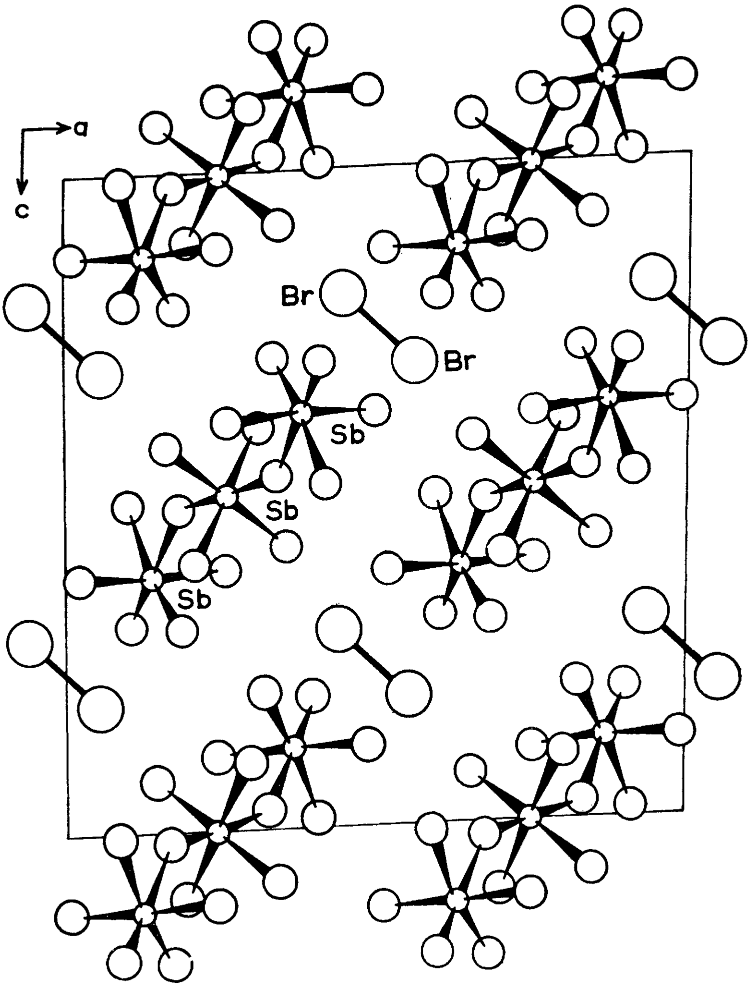

Figure 5 *Crystal structure of* $Br_2^+\ Sb_3F_{16}^-$.

length of 2·13 Å and the stretching frequency of 368 cm^{-1} when compared with the corresponding values for bromine of 2·27 Å and 320 cm^{-1} are consistent with an increase in bond order resulting from the loss of an antibonding electron.

The compound $Br_3^+AsF_6^-$ was prepared[17] by the oxidation of bromine with $O_2^+AsF_6^-$

$$2O_2^+AsF_6^- + 3Br_2 \rightarrow 2Br_3^+AsF_6^-$$

or by the reaction of bromine and arsenic pentafluoride with bromine trifluoride or bromine pentafluoride. It is described as a chocolate-brown solid at room temperature which becomes carmine red at liquid-nitrogen temperature.

The structure of the Br_3^+ cation is not known but by analogy with the ICl_2^+ cation the bond angle is probably close to 90 °. One of the three expected Raman lines for Br_3^+ in solution has been observed at 290 cm^{-1}. Solutions of Br_3^+ absorb at 375 nm and 300 nm with a molar extinction coefficient of 900 at 375 nm.

3 Chlorine Cations

The Cl_2^+ ion has been identified in the gas phase at very low pressures and a value of ω_e of 645·3 cm^{-1} was obtained from the electronic absorption spectrum.[20] Recent papers by Olah and Comisarow claiming the identification of the Cl_2^+ and ClF^+ cations[21,22] in solution on the basis of e.s.r. spectra observed for solutions of chlorine fluorides in SbF_5, HSO_3F–SbF_5, or HF–SbF_5 have been criticised by several workers. Symons *et al.*[23] claim that the e.s.r. spectrum assigned to the ClF^+ cation arises from the $ClOF^+$ cation as the sum of the spin densities on chlorine and fluorine calculated from the observed spectrum is only 0·62, and the e.s.r. parameters fit in well with those of the isostructural FOO, ClOO, ClO_2, and NF_2 radicals. By analogy, they assign the e.s.r. spectrum assigned to Cl_2^+ by Olah and Comisarow to the $ClOCl^+$ cation. Christe and Muirhead[24] claim that radicals are not produced in the reaction of highly purified SbF_5 and ClF_3 or ClF_5 and that the radicals observed by Olah and Comisarow must have been due to impurities. Gillespie and Morton[25] observed an increase in intensity by a factor of several hundred in the e.s.r. signal previously assigned to the ClF^+ cation on adding a small amount of water to a sample of $ClF_2^+SbF_6^-$ in SbF_5. This supports the assignment to an oxy-radical which, they argue, is more likely to be the $FClO^+$ radical, isoelectronic with ClO_2, or the ClO_2F^+ radical, isoelectronic with ClO_3, rather than the $ClOF^+$ radical proposed by Symons and co-workers.[23]

Solid salts of the Cl_3^+ and Cl_2F^+ cations have, however, been prepared at −76 °C,[26] as is discussed below, but there is no evidence for the existence of the Cl_2^+ cation as a stable species in solution or in the solid state. Conductivity measurements and Raman spectra of solutions of chlorine monofluorosulphate and chlorine in the superacid SbF_5:$3SO_3$/HSO_3F have given no evidence for the formation of the Cl_3^+ or Cl_2^+ cations at 25 °C.[25] In view of the instability of the Cl_3^+ cation,[25] the existence of even trace quantities of the Cl_2^+ cation in these solutions would be surprising, as a comparison with the iodine and bromine cations demonstrates; thus, with iodine and bromine there is evidence for the

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[20] G. Herzberg, 'Molecular Spectra and Molecular Structure', Vol. 1, Van Nostrand, Princeton, New Jersey, 1960.

[21] G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, 1968, **90**, 5033.

[22] G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, 1969, **91**, 2172.

[23] R. S. Eachus, T. P. Sleight, and M. C. R. Symons, *Nature*, 1969, **222**, 769.

[24] K. O. Christe and J. S. Muirhead, *J. Amer. Chem. Soc.*, 1969, **91**, 7777.

[25] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, in the press.

[26] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 1970, **9**, 811.

X_2^+ cation only in solvents in which the X_3^+ cation is stable to disproportionation.

A simple calculation of the heats of formation of salts of the Cl_2^+ and O_2^+ cations based on the ionisation potentials and the lattice energies given by Kapustinskii's second equation[27] gives values for the Cl_2^+ salts some 3 kcal less favourable than for the corresponding O_2^+ salts with the hexafluoride anions.[28] Although this indicates that the salts $Cl_2^+PtF_6^-$ and $Cl_2^+Sb_2F_{11}^-$ are thermodynamically feasible, we expect no kinetic barrier to fluorination *via* fluorine bridging to give salts of the Cl_2F^+ cation,

e.g. $2Cl_2^+Sb_2F_{11}^- \rightarrow Cl_2F^+Sb_2F_{11}^- + Cl_2 + 2SbF_5$

In contrast to the corresponding reaction for the O_2^+ salt, the above reaction is probably exothermic as we can expect the Cl—F bond in the Cl_2F^+ cation to have a high bond energy. Thus, attempts to prepare salts of the Cl_2^+ cation are analogous to the attempts to prepare those of the Xe^+ cation in which the product has always been the XeF^+ cation.[29]

The yellow solid $Cl_3^+AsF_6^-$ has been prepared from chlorine, chlorine monofluoride, and arsenic pentafluoride at −76 °C. At room temperature the salt is completely decomposed to give Cl_2, ClF, and AsF_5.

$$Cl_2 + ClF + AsF_5 \rightarrow Cl_3^+AsF_6^-$$

The Raman spectrum shows the active bands of the AsF_6^- ion together with three relatively intense bands at 490 (split to 485 and 492), 225, and 508 cm^{-1} which are assigned to ν_1, ν_2, and ν_3, respectively, of the bent Cl_3^+ cation. The assigned frequencies are very close to the vibrational frequencies of the isoelectronic SCl_2 molecule (514, 208, and 525 cm^{-1}),[30] which has a bond angle of 103°, and it is concluded that the Cl_3^+ cation has a similar structure. Using a simple valence force field gives good agreement for the observed frequencies of the Cl_3^+ cation with a bond angle of 100°, a stretching force constant $b = 2{\cdot}5$ mdyn Å^{-1} and a bending force constant $d = 0{\cdot}36$ mdyn Å^{-1}.

The Cl_3^+ cation has also been identified by means of its Raman spectrum in the yellow solid which precipitates out of a solution of Cl_2 and ClF in HF–SbF_5 at −76 °C. At room temperature the Cl_3^+ cation is completely disproportionated in this solvent to give chlorine and ClF_2^+ salts. The salt $Cl_3^+BF_4^-$ is not formed from mixtures of chlorine, chlorine monofluoride, and boron trifluoride at temperatures down to −130 °C.

The stretching frequencies, absorption maxima and bond lengths of the halogen diatomic cations are summarised and compared with those of the halogens in Table 1.

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[27] A. F. Kapustinskii, *Quart. Rev.*, 1956, **10**, 284.
[28] N. Bartlett, S. P. Beaton, and N. K. Jha, *Chem. Comm.*, 1966, 168.
[29] V. M. McRae, R. D. Peacock, and D. R. Russel, *Chem. Comm.*, 1969, 62.
[30] H. Siebert, 'Anwendungen der Swingungsspcktroscopie in der Anorganischen Chemie Springer–Verlag, Berlin, 1966.

Table 1 *Stretching frequencies, absorption maxima, and bond lengths of the halogens and the diatomic halogen cations*

	Stretching frequency (cm^{-1})	*Principal absorption* (nm)	*Bond length* (Å)
Cl_2	564·9^a	330	1·98
Cl_2^+	645·3^a	—	—
Br_2	320	410	2·27
Br_2^+	360	510	2·13
I_2	215	500	2·66
I_2^+	238	646	—

$^a\omega_e$ from ref. 20.

4 Triatomic Interhalogen Cations

The following are the possible triatomic interhalogen cations: ClF_2^+, BrF_2^+, IF_2^+, Cl_2F^+, Br_2F^+, I_2F^+, $ClBrF^+$, $ClIF^+$, $BrIF^+$, $BrCl_2^+$, ICl_2^+, Br_2Cl^+, I_2Cl^+, $BrICl^+$, IBr_2^+, and I_2Br^+. It seems reasonable to assume that the least electronegative halogen occupies the central position, where it carries a formal positive charge. Of these sixteen cations, only ClF_2^+, BrF_2^+, IF_2^+, Cl_2F^+, and ICl_2^+ have so far been definitely established, and crystal structure determinations have been published only for ICl_2^+, BrF_2^+, and ClF_2^+. All three ions have been found to have angular structures in accordance with the fact that their valency shells have four electron pairs, which would be expected to have a tetrahedral arrangement.

A. ClF_2^+.—Adducts of ClF_3 with AsF_5, SbF_5, and BF_3 have been known for some time[31] and more recently it was established by i.r. and Raman spectra studies that these compounds are best formulated as salts of the ClF_2^+ cation, *e.g.* $ClF_2^+AsF_6^-$.[32,33] The spectroscopic data indicate a bent structure. Vibrational frequencies and force constants are listed in Table 2. The strong splitting of ν_2 of the AsF_6^- anion, and its appearance as a strong band in the i.r. as well as in the Raman spectrum contrary to the mutual exclusion rule has been attributed to a lowering of symmetry of the octahedral AsF_6^- as a consequence of fluorine bridging between AsF_6^- and the ClF_2^+ cation.[33] Very recently the crystal structure of $ClF_2^+SbF_6^-$ has been determined[34] (Figure 6). The ClF_2^+ ion has a bond angle of 95·9 ° and a bond length of 1·58 Å. There is indeed strong fluorine bridging between the anion and the cation, and the two fluorine bridges formed by each ClF_2^+ give rise to a very approximately square co-ordination of fluorine around chlorine, which is the geometry predicted by the valence shell electron pair repulsion theory for AX_4E_2 co-ordination (where X is a ligand and E a lone pair). It is interesting to note that the SbF_6^- ion in this structure forms

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[31] 'Halogen Chemistry', ed. V. Gutman, Academic Press, London and New York, 1967.
[32] K. O. Christe and W. Sawodny, *Inorg. Chem.*, 1967, **6**, 313.
[33] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 1970, **9**, 811.
[34] A. J. Edwards and R. J. C. Sills, *J. Chem. Soc.*, 1970, 2697.

Table 2 *Vibrational frequencies* (cm^{-1}) *and force constants of the* ClF_2^+ *and* BrF_2^+ *cations*

		$ClF_2^+SbF_6^-$	$ClF_2^+AsF_6^-$		$ClF_2^+BF_4^-$	
		Raman	*Raman*	*I.r.*	*Raman*	*I.r.*
	ν_1	805 809	806 809	810	788 798	798
	ν_2	387	384		373 394	
	ν_3	830	821	818	808	813
Simple valence force field force constants (mdyn Å^{-1})	f	4·8	4·7		4·6	
	d	0·63	0·6		0·61	

		$BrF_2^+SbF_6^-$		$BrF_2^+AsF_6^-$	
		Raman	*I.r.*	*Raman*	*I.r.*
	ν_1	705	705	706	713
	ν_2	362	—	360	—
	ν_3	702	692	703	698
Modified valence force field constants $f r\alpha$ = 0 and α = 95 °	fr	4·60			
	frr	0·21			
	$f\alpha$	0·47			

trans bridges rather than the *cis* bridges that have been observed in related structures.

B. BrF_2^+.—The 1:1 adduct of BrF_3 with SbF_5 has been shown by *X*-ray crystallography[35] to contain BrF_2^+ and SbF_6^- ions held together by fluorine bridging in such a way that bromine acquires a very approximately square planar configuration (Figure 7). Each bromine atom has two fluorine atoms at 1·69 Å, making an angle of 93·5 ° at bromine, and two other neighbouring fluorine atoms at 2·29 Å which form part of the distorted octahedral co-ordination of the antimony atoms. The two fluorine bridges formed by SbF_5^- are *cis* rather than *trans*, as in the unusual $ClF_2^+SbF_6^-$ structure.

The i.r. and Raman spectra of BrF_3,SbF_5, BrF_3,AsF_5, and $(BrF_3)_2GeF_4$ have been reported very recently.[36,37] The vibrational frequencies given by Christe and Schack[36] for the BrF_2^+ ion are given in Table 2. There is, however, some

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[35] A. J. Edwards and G. R. Jones, *J. Chem. Soc.*, 1969, 1467.

[36] K. O. Christe and C. J. Schack, *Inorg. Chem.*, 1970, **9**, 2296.

[37] T. Surles, H. H. Hyman, L. A. Quarterman, and A. I. Popov, *Inorg. Chem.*, 1970, **9**, 2726.

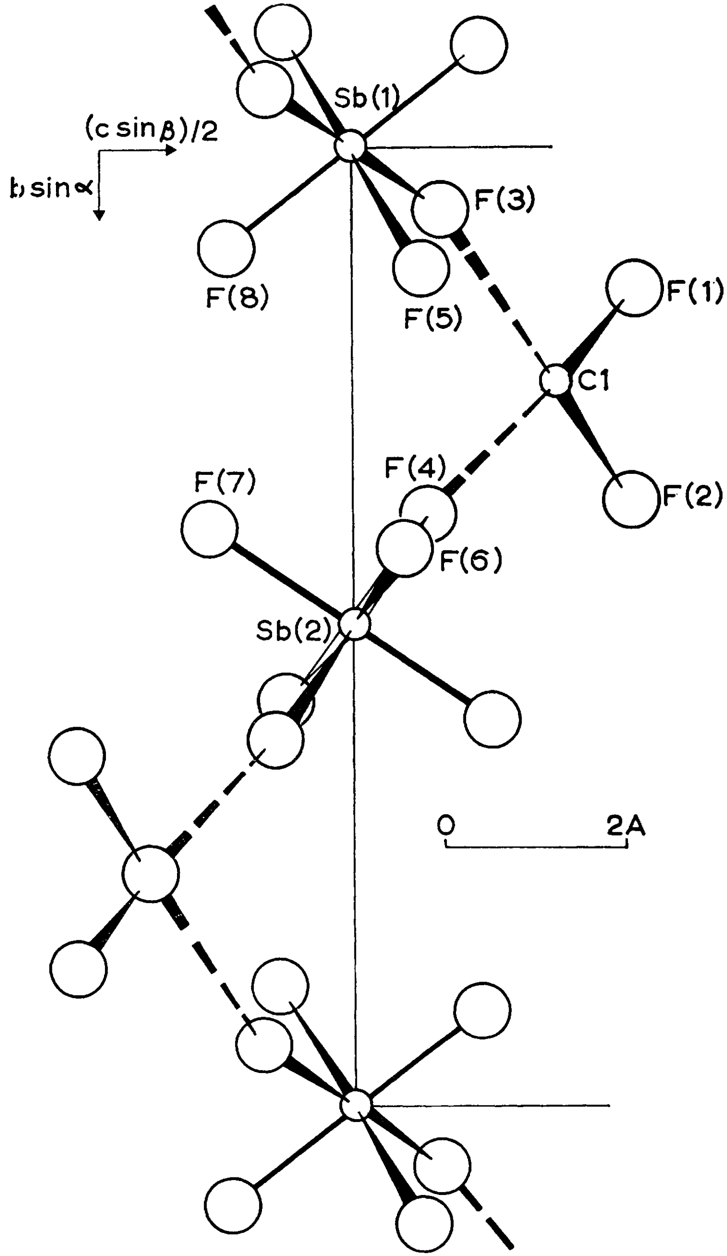

Figure 6 *Crystal structure of* ClF_2^+ SbF_6^-.

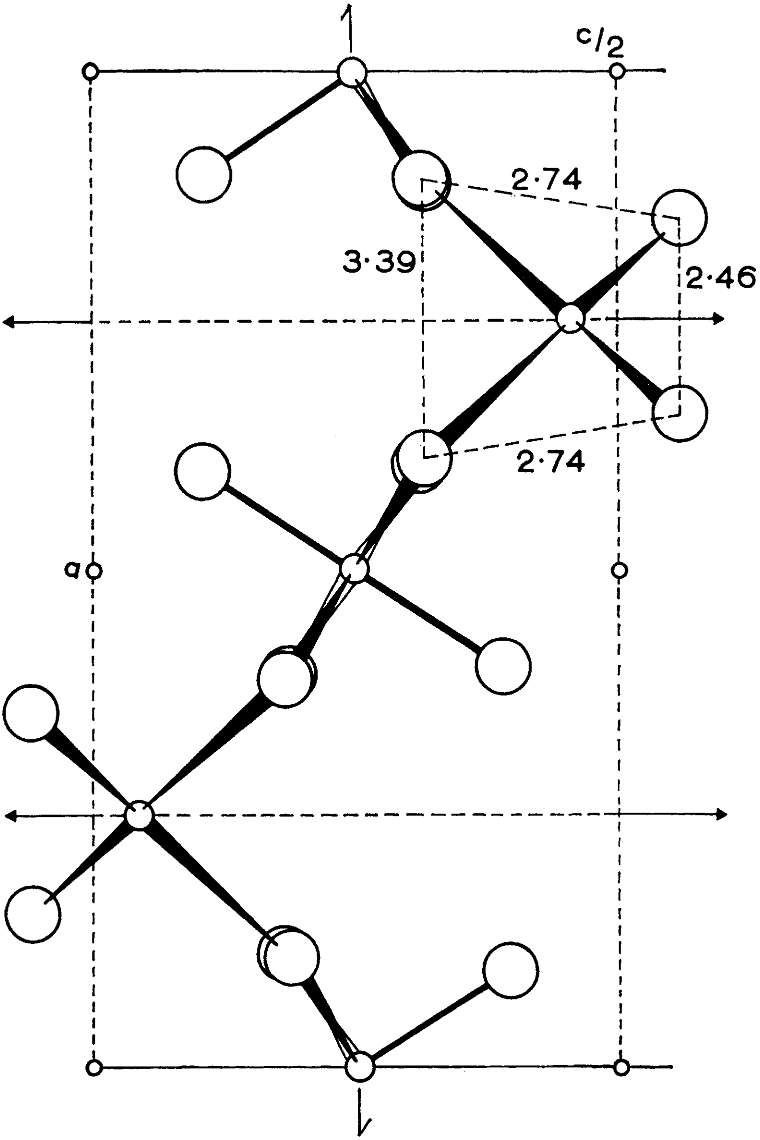

Figure 7 *Crystal structure of* BrF_2^+ SbF_6^-.

disagreement between this work and that of Surles *et al.*[37] and the latter authors tentatively assign a frequency of 308 cm^{-1} to the bending mode ν_2. The bands in the spectrum of $(BrF_3)_2GeF_4$ that are apparently due to the Br—F stretching modes are shifted to the lower frequencies of 690 and 657 cm^{-1}, which is presumably due to a change in the fluorine bridging strength or simply to the fact that the stoicheiometry necessitates a different structure for the crystalline solid. It is interesting to note that Surles *et al.*[37] found an even larger shift to 635 and 625 cm^{-1} for the stretching frequencies of the BrF_2^+ ion in solution in BrF_3. They attributed this shift to strong solvation of the BrF_2^+ ion.

The electrical conductivity of liquid bromine trifluoride[38] (specific conductance = 8×10^{-3} ohm^{-1} cm^{-1}) may be attributed to the self-ionisation $2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$.

C. IF_2^+.—The salts $IF_2^+AsF_6^-$ and $IF_2^+SbF_6^-$ have been prepared from IF_3 and AsF_5, and from IF_3 and SbF_5 in AsF_5 as solvent at −70 °C.[39] The compound $IF_2^+SbF_6^-$ is stable to 45 °C and the solid gives two broad overlapping ^{19}F n.m.r. signals whose relative intensities were estimated to be 1:2·6, and which were assumed to arise, therefore, from fluorine on iodine and fluorine on antimony, respectively. $IF_2^+AsF_6^-$ was found to be stable only to −20 °C.

D. Cl_2F^+.—Raman spectra of the adducts $AsF_5,2ClF$ and $BF_3,2ClF$ have established that these compounds contain the unsymmetrical $ClClF^+$ cation[26] and not the symmetrical $ClFCl^+$ cation previously reported on the basis of the i.r. spectrum alone.[40] The vibrational frequencies and assignments are listed in Table 3 and, as with the salt $ClF_2^+AsF_6^-$, the splitting of ν_2 of AsF_6^- and its appearance in the i.r. can reasonably be attributed to fluorine bridging. Table 4 shows how the frequency ν_1 and the splitting of ν_2 of the AsF_6^- ion vary in the series $Cl_3^+AsF_6^-$, $Cl_2F^+AsF_6^-$, and $ClF_2^+AsF_6^-$ in which an increasingly strong fluorine bridging is expected.

Table 3 *Vibrational frequencies (cm^{-1}) and assignments of the* Cl_2F^+ *cation*

	$Cl_2F^+AsF_6^-$		$Cl_2F^+BF_4^-$	
Assignment	*Raman*	*I.r.*	*Raman*	*I.r.*
ν_1 (Cl–F str)	744		743	
				511 *
ν_2 (Cl—Cl str)	528	527	516	519
	535	535	540	528
				532
ν_3 (bend)	293	293	296	
	299			

* These bands contain ν_4 of BF_4^-, which appears at 519, 529 cm^{-1} in the ClF_2^+ salt, as well as ν_2 of the Cl_2F^+ cation.

The Cl_2F^+ ion appears to be unstable in solution and was found to be completely disproportionated in SbF_5–HF even at −76 °C.

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[38] A. A. Banks, H. J. Emeleus, and A. A. Woolf, *J. Chem. Soc.*, 1949, 2861.
[39] M. Schmeisser, W. Ludovici, D. Naumann, P. Sartori, and E. Scharf, *Ber.*, 1968, **101**, 4214.
[40] K. O. Christe and W. Sawodny, *Inorg. Chem.*, 1969, **8**, 212.

$$2Cl_2F^+ = ClF_2^+ + Cl_3^+$$

The Cl_3^+ cation disproportionates further at room temperature to give chlorine and ClF_2^+.[25]

Table 4 *Variation of the frequencies of* ν_1 *and* ν_2 *for the* AsF_6^- *ion with the nature of the cation*

	$ClF_2^+AsF_6^-$	$Cl_2F^+AsF_6^-$	$Cl_3^+AsF_6^-$
ν_1	693	685	674
ν_2	544 602	563 581	571

E. ICl_2^+.—*X*-Ray crystallographic investigations[10] of the adducts of ICl_3 with $SbCl_5$ and $AlCl_3$ have shown that these may be regarded as ionic compounds, *i.e.* $ICl_2^+SbCl_6^-$ and $ICl_2^+AlCl_4^-$, although there is considerable interaction between the two ions *via* two bridging chlorines, which give an approximately square planar arrangement of four chlorines around the iodine atom, similar to the arrangement of fluorines around bromine and chlorine in $BrF_2^+SbF_6^-$ and $ClF_2^+SbF_6^-$. The bond angle and bond length for ICl_2^+ were found to be 92·5° and 2·31 Å in $ICl_2^+SbCl_6^-$ and 96·7° and 2·28 Å in $ICl_2^+AlCl_4^-$.

The electrical conductivity of liquid ICl_3 (specific conductance = $9{\cdot}85 \times 10^{-3}$ ohm^{-1} cm^{-1})[41] can be attributed to the self-ionisation:

$$2ICl_3 \rightarrow ICl_2^+ + ICl_4^-$$

F. I_2Cl^+.—There is no certain evidence for the I_2Cl^+ cation but presumably the electrical conductivity of liquid ICl (specific conductance = $4{\cdot}52 \times 10^{-3}$ ohm^{-1} cm^{-1} at 31 °C)[41] which has previously been ascribed to the self-ionisation:

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

is in fact due to a self-ionisation which produces the I_2Cl^+ ion according to the equation:

$$3ICl \rightleftharpoons I_2Cl^+ + ICl_2^-$$

The I_2Cl^+ cation, however, is possibly extensively disproportionated to give the known I_3^+ and ICl_2^+ cations

$$2I_2Cl^+ \rightleftharpoons I_3^+ + ICl_2^+$$

5 Penta- and Hepta-atomic Halogen Fluoride Cations

Chlorine pentafluoride forms 1:1 adducts with AsF_5 and SbF_5 and a preliminary interpretation of the Raman spectra of these compounds indicates that they can probably be formulated as $ClF_4^+AsF_6^-$ and $ClF_4^+SbF_6^-$.[42] Bromine penta-

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[41] N. N. Greenwood and H. J. Emeleus, *J. Chem. Soc.*, 1950, 987.

[42] K. O. Christe and D. Pilipovich, *Inorg. Chem.*, 1969, **8**, 391.

fluoride forms the adducts $BrF_5,2SbF_5$ and BrF_5,SO_3.[43] These may, presumably, be formulated as $BrF_4{}^+Sb_2F_{11}{}^-$ and $BrF_4{}^+SO_3F^-$ although the latter compound might be the covalent BrF_4SO_3F. Iodine pentafluoride forms 1:1 adducts with SbF_5[44] and PtF_5.[45] There has been a preliminary report[46] of the crystal structure of IF_5,SbF_5 which is shown to be $IF_4{}^+SbF_6{}^-$. The $IF_4{}^+$ has a structure like SF_4 with two fluorines occupying the axial positions of a trigonal bipyramid and two fluorines and a lone pair occupying the equatorial positions. The electrical conductivity of liquid IF_5 (specific conductance = $2{\cdot}30 \times 10^{-5}$ ohm^{-1} cm^{-1})[41] can presumably be attributed to the self-ionisation

$$2IF_5 = IF_4{}^+ + IF_6{}^-$$

In the Raman spectrum of $IF_4{}^+SbF_6{}^-$ nine lines have been assigned to the $IF_4{}^+$ cation[47] which is consistent with a C_{2v} structure found by *X*-ray crystallography.

Iodine heptafluoride has been shown to form the complexes IF_7,AsF_5 and $IF_7,3SbF_5$.[48] The Raman and i.r. spectra of IF_7,AsF_5 in the solid state and in solution in HF show that it should be formulated as $IF_6{}^+AsF_6{}^-$.[49,50] Vibrational assignments and force constants are listed in Table 5.

Because the highest interhalogen chlorides and bromides are ICl_3 and IBr it seems unlikely that any penta-atomic chloride or bromide cations will exist, with the possible exception of $ICl_4{}^+$.

Table 5 *Vibrational frequencies and assignments of the* $IF_6{}^+$ *cation* in $IF_6{}^+AsF_6{}^-$

Assignment	*Observed frequency* (cm^{-1})	
	Raman	*I.r.*
ν_1 (A_{1g})	708	
ν_2 (E_g)	732	
ν_3 (F_{1u})		797 790
ν_4 (F_{1u})		404
ν_5 (F_{2g})	340	

Valence force constants (mdyn Å^{-1})
f_r, 5·60; f_{rr}, $-0{\cdot}06$; $f_{rr'}$, 0·27

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[43] M. Schmeisser and E. Pammer, *Angew. Chem.*, 1957, **69**, 281.
[44] A. A. Woolf, *J. Chem. Soc.*, 1950, 3678.
[45] N. Bartlett and D. H. Lohman, *J. Chem. Soc.*, 1962, 8253; 1964, 619.
[46] H. W. Baird and H. F. Giles, *Acta Cryst.*, 1969, **A25**, S115.
[47] J. Shamir and I. Yaroslavsky, *Israel J. Chem.*, 1969, **7**, 495.
[48] F. Seel and O. Detmer, *Angew. Chem.*, 1958, **70**, 163; *Z. anorg. Chem.*, 1959, **301**, 113.
[49] K. O. Christe and W. Sawodny, *Inorg. Chem.*, 1967, **6**, 1783.
[50] K. O. Christe, *Inorg. Chem.*, 1970, **9**, 2801.