

# Homopolyatomic and Heteropolyatomic Halogen Cations

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## ABSTRACT

*This review is not exhaustive in scope but rather focuses on the most recent years of work in the field of cationic halogens, covering the literature up to mid 1992. This area is still currently developing. The review summarizes structure, preparation, and reactivity of cationic halogens. Modern theoretical aspects (ab initio MO calculations) as well as the energetics (thermodynamics) of these species are also included. In particular, the symmetric and unsymmetric structures of heteropolyatomic cations, the charge delocalization and bond lengths alternation in  $n\pi\pi-n\pi\pi$  species ( $n < 2$ ), and the dimerization by  $\pi^*-\pi^*$  interactions are discussed.*

## INTRODUCTION

Usually, metals are associated with cation formation and nonmetals with anion formation. In fact, the most important and most common oxidation state for all the halogens is  $-1$ . However, it has been known for many years that iodine dissolves in strongly oxidizing solvents, such as oleum ( $\text{H}_2\text{SO}_4/\text{SO}_3$ ), to give bright blue paramagnetic solutions; and it was in 1966 that this behavior was shown to be due to the formation of the diiodine cation,  $\text{I}_2^+$  [1]. Meanwhile, not only homopolyatomic halogen cations ( $\text{X}_n^+$ ) ( $n = 2,3,5$ ) but also numerous polyhalonium cations of the type  $\text{XY}_{2n}^+$  ( $n = 1,2,3$ ) have been prepared and fully characterized [2]. Although claims have been made for the

preparation of salts of monoatomic nonmetal cations,  $\text{X}^+$  [3], none have been conclusively identified.

A comprehensive review covering the area of homopolyatomic cations with an excellent discussion of the preparative, structural, and thermodynamic aspects by Burford et al. [4] was preceded by four earlier reviews [5–8]. In a more specific account in 1979, Gillespie focuses on the structural features of polychalcogen cations [9] and seeks to rationalize the observed geometries in the context of the extended VSEPR model. A physical basis for the VSEPR model has been presented by Bader et al. [10]. In 1976, Corbett reviewed the preparation of polyhalogen cations using  $\text{AlCl}_3$  melts [11]. Three years later, Shamir reviewed the extensive series of polyhalogen cations, including both homo- and heteroatomic cations [12].

Although this review directs its attention primarily to stable compounds (that can be isolated), some aspects on the energetics of ions that are unstable in the solid state have also been included (e.g.,  $\text{F}_3^+$ ). We intend to establish perspective with respect to earlier work and to contemporary research to evaluate the present state of the subject and to cast a glance to the future.

## HOMOPOLYATOMIC CATIONS

The homopolyatomic halogen cations that have either been characterized by X-ray diffraction studies or have been reasonably structurally characterized on the basis of vibrational spectral data (Raman) are summarized in Table 1. It can be stated that (except for fluorine) all the elements of group 17 form stable homopolyatomic cations in the solid state (N.B.  $\text{Cl}_3^+$  is stable at low temperatures only).

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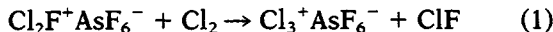
**TABLE 1** Homopolyatomic Cations of Elements of Group 17, Structurally Characterized by X-Ray except Cl<sub>3</sub><sup>+</sup> by Raman Spectroscopy

F	Cl	Br	I
		Br <sub>2</sub> <sup>+</sup> [13]	l <sub>2</sub> <sup>+</sup> [17,18] l <sub>4</sub> <sup>2+</sup> [19,20]
	Cl <sub>3</sub> <sup>+</sup> [13]	Br <sub>3</sub> <sup>+</sup> [14] Br <sub>5</sub> <sup>+</sup> [15,16]	l <sub>3</sub> <sup>+</sup> [21] l <sub>15</sub> <sup>+</sup> [22] l <sub>15</sub> <sup>3+</sup> [23]

### Fluorine and Chlorine Cations

There are no stable homopolyatomic fluorine cations in the solid state. This, of course, is due to the extremely high ionization potential of fluorine ( $I_p$ ,  $F_2 = 363.2$  kcal/mol) [4] compared even with the strongest oxidizers known (e.g.,  $E_A$ ,  $PtF_6 = 185.0$  kcal/mol) [24]. Moreover, there is only one chlorine cation, Cl<sub>3</sub><sup>+</sup>, which has been obtained on a preparative scale [25].

The AsF<sub>6</sub><sup>-</sup> salt of Cl<sub>3</sub><sup>+</sup>, has been prepared by warming Cl<sub>3</sub>F<sup>+</sup>AsF<sub>6</sub><sup>-</sup> (see the Triatomic Species section) in the presence of excess chlorine until all of the solid has vaporized and then recooling to Dry Ice temperature and pumping off the excess gases [25].



Cl<sub>3</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> is a yellow solid completely dissociating to Cl<sub>2</sub>, ClF, and AsF<sub>5</sub> at room temperature. The low-temperature Raman and IR spectra show that Cl<sub>3</sub><sup>+</sup> has C<sub>2v</sub> symmetry [25–27]. The valence force constants have been calculated [25]. The geometries and relative energies of the singlet and triplet state of Cl<sub>3</sub><sup>+</sup> were studied with ab initio MO calculations at the UHF/6-31G\* level [28]. The triatomic cation has a singlet ground state ( $E_{S-T} = -2.5$  kcal/mol; S = singlet, T = triplet). The calculation predicts for the bent (107°) Cl<sub>3</sub><sup>+</sup> cation two equal Cl-Cl distances of 1.998 Å [28]. Earlier reports on calculations of the singlet Cl<sub>3</sub><sup>+</sup> also predict a C<sub>2v</sub> geometry (2.010 Å, 105.6°) [29].

Both the Cl<sub>2</sub><sup>+</sup> and the Cl<sub>4</sub><sup>+</sup> cations are still to be prepared and are likely to be unstable (see the Thermodynamic Aspects section). However, they have been theoretically modeled with ab initio MO calculations [28]. The optimized geometry of Cl<sub>4</sub><sup>2+</sup> is nonplanar and has C<sub>2</sub> symmetry, with a ClClClCl torsional angle of 95°. The central Cl-Cl bond length is 2.013 Å and the terminal ones are 2.063 Å. The ClClCl bond angles are 108°. This dication is 135 kcal/mol less stable than the two Cl<sub>2</sub><sup>+</sup> radical cations ( $d$ , Cl-Cl = 1.874 Å). The structure of Cl<sub>4</sub><sup>2+</sup> resembles that of the HClClH<sup>2+</sup> dications [30]. Another recent calculation [31] for Cl<sub>4</sub><sup>2+</sup> also gave a bent geometry at full optimization.

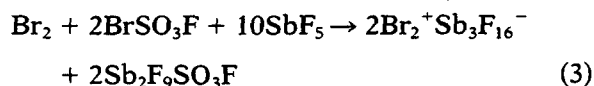
Although the fluorine cations F<sup>+</sup>, F<sub>2</sub><sup>+</sup>, F<sub>3</sub><sup>+</sup>, and

F<sub>4</sub><sup>2+</sup> are nonexistent in the solid state, the geometries and relative energies were studied with ab initio calculations [28]. A quantitative scale for the oxidizer strength of F<sup>+</sup> and F<sub>3</sub><sup>+</sup> has recently been developed by Christe and Dixon [32]. The formation of F<sup>+</sup> and its existence (or absence) as a reactive intermediate in the fluorination of highly electronegative compounds have been discussed [33,34]. Both experimental and computational studies have been reported for the energy levels in the gas phase [35–37]. For the F<sub>3</sub><sup>+</sup> cation, it is likely that it is also a bent singlet [28]. The optimization of F<sub>4</sub><sup>2+</sup> with 6-31G\* basis set showed that it has an open Z-like geometry. All F atoms are in the same plane with the FFF angles equal to 110°. The central FF bond is 1.368 Å, which is shorter than the terminal FF bond (1.57 Å). This dication was calculated to be 202 kcal/mol higher in energy than two isolated radical cation F<sub>2</sub><sup>+</sup> (1.232 Å) species [28].

### Bromine Cations

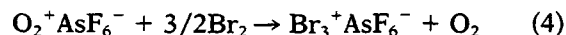
The homopolyatomic cations Br<sub>2</sub><sup>+</sup> [13,14,38–41], Br<sub>3</sub><sup>+</sup> [14,15,27,40–44], and Br<sub>5</sub><sup>+</sup> [14,15] have been well characterized. Whereas the Br<sub>2</sub><sup>+</sup> cation has been known for many years, both in form of its Sb<sub>3</sub>F<sub>16</sub><sup>-</sup> salt and in superacid solutions, it was not until 1991 that the structures of Br<sub>3</sub><sup>+</sup> (X-ray) and Br<sub>5</sub><sup>+</sup> (X-ray) were elucidated [14,16].

The principal synthetic route to Br<sub>2</sub><sup>+</sup> containing salts has been the coproportionation of a halogen fluoride like BrF<sub>5</sub> [38] or BrF<sub>3</sub> [13] and stoichiometric amounts of Br<sub>2</sub> in the presence of SbF<sub>5</sub> or the oxidation of Br<sub>2</sub> by SbF<sub>5</sub> either in SO<sub>2</sub> solution [17] or in a large excess of SbF<sub>5</sub> [45]. However, the oxidation of Br<sub>2</sub> by bis(fluorosulfonyl)peroxide, S<sub>2</sub>O<sub>6</sub>F<sub>2</sub>, followed by solvolysis in an excess of SbF<sub>5</sub> gives the purest material of Br<sub>2</sub><sup>+</sup>Sb<sub>3</sub>F<sub>16</sub><sup>-</sup> (Equations 2 and 3) [39].



The crystal structure of Br<sub>2</sub><sup>+</sup>Sb<sub>3</sub>F<sub>16</sub><sup>-</sup> [13,38] shows no significant interaction between the individual cations (with the closest intermolecular Br⋯Br distance 6.445 Å) and insulation by the intervening anions, consistent with the absence of significant magnetic concentration in this compound [39]. The Br<sub>2</sub><sup>+</sup> cation gives a resonance Raman spectrum and provides a suitable solute for solution studies in fluorosulfuric acid and in superacid media [39].

The first isolated Br<sub>3</sub><sup>+</sup> containing salt, Br<sub>3</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup>, was obtained from a reaction (according to Equation 4) discovered by Glemser and Smalc [42].



Quite recently, Christe et al. reported on the ac-

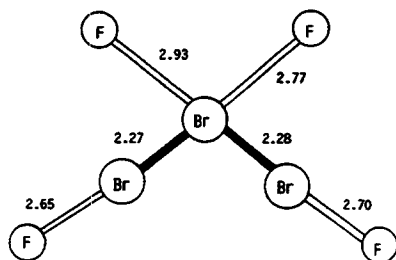


FIGURE 1  $\text{Br}_3^+$  cation with closest anion-cation contacts (Å) [14].

cidental isolation of crystalline  $\text{Br}_3^+\text{AsF}_6^-$  which was obtained from a sample of  $\text{BrF}_2^+\text{AsF}_6^-$  that had been stored for 20(!) years [14]. It was characterized by X-ray diffraction and Raman spectroscopy. It has been shown that  $\text{Br}_3^+\text{AsF}_6^-$  is isomorphous with  $\text{I}_3^+\text{AsF}_6^-$  (see below). The structure consists of discrete, predominantly ionic  $\text{AsF}_6^-$  ions with some cation-anion interaction causing distortion of the  $\text{AsF}_6^-$  octahedron [14]. The  $\text{Br}_3^+$  cation is symmetric with a bond distance of 2.270 Å (cf.  $\text{Br}_2$ , 2.281 Å) [14] and a bond angle of 102.5° (Figure 1).

Reactions of excess of  $\text{Br}_2$  with either  $\text{BrF}_2^+\text{AsF}_6^-$  or  $\text{O}_2^+\text{AsF}_6^-$  produce mixtures of  $\text{Br}_3^+\text{AsF}_6^-$  and  $\text{Br}_5^+\text{AsF}_6^-$ . Based on its Raman spectra, the  $\text{Br}_5^+$  cation possesses a planar, centrosymmetric structure of  $C_{2h}$  symmetry with three semi-ionically bound, collinear, central Br atoms and two more covalently, perpendicularly bound, terminal Br atoms (X-ray, see later). The occurrence of a semi-ionic, three-center-four-electron bond in  $\text{Br}_5^+$  but not in  $\text{Br}_3^+$  is readily understood from a simple consideration of the number of valence electrons in each cation. In  $\text{Br}_3^+$ , all three Br atoms have an electron octet, whereas in  $\text{Br}_5^+$  the central Br atom is "hypervalent," possessing 10 valence electrons, which favors the formation of semi-ionic, three-center-four-electron bonds (Figure 2) [14,46].

The geometry of  $\text{Br}_5^+$  was calculated by use of the local density functional (LDF) method. The results show that for free  $\text{Br}_5^+$ , the lowest energy configuration is a skew structure (Figure 2) [47]. This structure is in contrast to the planar trans-configuration of  $C_{2h}$  symmetry found for  $\text{Br}_5^+$  in

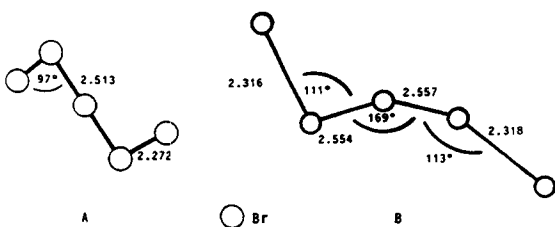
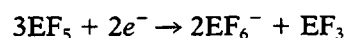


FIGURE 2 (A) Crystal structure [16] and (B) LDF structure [47] for  $\text{Br}_5^+$  (bond lengths in Å).

solid  $\text{Br}_5^+\text{EF}_6^-$  (E = As, Sb) [16]. The bonding in this cation is identical to that in the below described  $\text{I}_5^+$  salt (solid state) [23].

### Iodine Cations

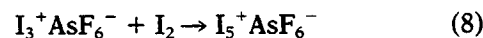
Numerous polyatomic iodine cations are known, and  $\text{I}_2^+$  [17,39],  $\text{I}_3^+$  [21],  $\text{I}_5^+$  [22],  $\text{I}_{15}^{3+}$  [23], and  $\text{I}_4^{2+}$  [20] salts have been characterized. All of the salts containing these cations can be prepared in  $\text{SO}_2$  solution by the oxidation of the element by  $\text{AsF}_5$  or  $\text{SbF}_5$ , respectively [4]. The strong oxidizers  $\text{AsF}_5$  and  $\text{SbF}_5$  act as two electron oxidants with the coincident formation of  $\text{AsF}_3$  and  $\text{SbF}_3$  and accompanying counteranions (Equation 5) (for thermodynamics, see the Thermodynamic Aspects section).



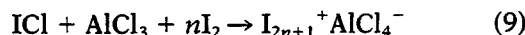
Examples of the formation of stable polyatomic, singly charged iodine cations are given in Equations 6 and 7.



$\text{I}_3^+\text{AsF}_6^-$  is observed to react with  $\text{I}_2$  to give  $\text{I}_5^+\text{AsF}_6^-$  (Equation 8) [4].



Reactions of  $\text{I}_2$  with  $\text{ICl}/\text{AlCl}_3$  mixtures have also been investigated by thermal, microscopic, and X-ray analysis [48]. The system contains only the phases  $\text{I}_3^+\text{AlCl}_4^-$  and  $\text{I}_5^+\text{AlCl}_4^-$  (and  $\text{ICl}_2^+\text{AlCl}_4^-$ ) and, by that, the cations  $\text{I}_3^+$  and  $\text{I}_5^+$  (Equation 9).



The oxidation of  $\text{I}_2$  by  $\text{S}_2\text{O}_6\text{F}_2$  at a 2:1 mole ratio followed by solvolysis in an excess of  $\text{SbF}_5$  also provides a simple, straightforward route to pure  $\text{I}_2^+\text{Sb}_2\text{F}_{11}^-$  [39].

Sodium fluoride and the Lewis acids  $\text{NbF}_5$ ,  $\text{TaF}_5$ , and  $\text{SbF}_5$  have been used to fix the levels of basicity and acidity in the solvent anhydrous HF in order to establish the acidity thresholds above which the cations  $\text{I}_5^+$ ,  $\text{I}_3^+$ , and  $\text{I}_2^+$  can be generated in solution [49]. Addition of an excess of the base  $\text{F}^-$  causes disproportionation of each of the cations to  $\text{I}_2$  and  $\text{IF}_5$ . When these disproportionation products are dissolved in HF and the acidity level is adjusted appropriately, the individual cations can be generated. It has been shown that the level of acidity is the principal determinant of the nature of the iodine cations generated in HF (Table 2) [49].

The existence of the  $\text{I}_7^+$  cation in the compound  $\text{I}_7^+\text{SO}_3\text{F}^-$  was reported by Chung and Cady [51].

The structures of salts containing the cations  $\text{I}_3^+$  [21],  $\text{I}_5^+$  [22], and  $\text{I}_{15}^{3+}$  [23] have been deter-

**TABLE 2** Important Iodine Cations Formed at Different Levels of Acidity of HF<sup>a</sup>

$-H_0^b$	
$\leq 10.80$	$I_2^+$
10.95–11.80	$I_3^+$ , $I_5^+$
15.65	$I_3^+$ , $I_2^+$ (trace)
15.90–16.05	$I_3^+$ , $I_2^+$
$\geq 16.20$	$I_2^+$

<sup>a</sup>Excess elemental iodine is present in all solutions.  $SbF_5$  was always used as the oxidizer; However,  $AsF_5$  should also be possible [49].

<sup>b</sup>For a definition of  $H_0$  cf. Ref. 50.

mined by X-ray crystallography (Table 3). All three structures can be understood in terms of simple VSEPR theory (Figure 3). The structure of solid  $I_{15}^{3+}$  is essentially that of three weakly bonded  $I_5^+$  molecules (Figure 3) (cf.  $d, I_5^+ \cdots I_5^+ = 3.42 \text{ \AA}$ ; I-I: sum of van der Waals radii =  $4.2 \text{ \AA}$ , sum of covalent radii =  $2.66 \text{ \AA}$ ). Therefore, although it contains  $I_5^+$  units, it can be regarded as a species consisting of trimeric  $I_{15}^{3+}$  chains.

While  $I_2^+Sb_2F_{11}^-$  in the crystalline state contains an isolated paramagnetic  $I_2^+$  unit [17,18] in common with  $Br_2^+$  [13] (see above), the  $AsF_6^-$  salt is diamagnetic and made up of  $I_4^{2+}$  units [19,20]. The structure of the  $I_4^{2+}$  cation is represented by a planar rectangle with a short I-I bond, almost identical in length to that in  $I_2^+Sb_2F_{11}^-$  (Table 3), and a long bond of  $3.26 \text{ \AA}$  (Figure 4).

Therefore,  $I_4^{2+}$  can be viewed as two  $I_2^+$  cations bound by a very weak four-center two-electron  $\pi^*-\pi^*$  bond. The unpaired electron in the  $I_2^+$  radical is in a  $\pi^*$  singly occupied MO (SOMO) (Figure 5) [52] and dimerization of the radicals is expected to involve primarily positive overlap of the two equivalent  $\pi^*$  SOMOs (Figure 6).

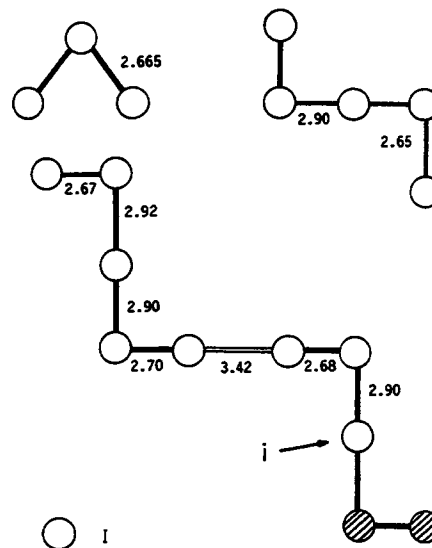
A weak, but definite S-S interaction in  $S_8^{2+}$  was originally recognized by Banister et al. [53] and later interpreted by Gleiter et al. [54] and Gillespie

**TABLE 3** Features of the Bond in Homopolyatomic Br and I Cations<sup>a</sup>

Cation	Symmetry	$d_{x-x}$ (Å)	Angle (°)	Reference
$Br_5^+$	$C_{2h}$	2.272/2.513	97.3	[16]
$Br_2^+$	$D_{\infty h}$	2.15		[4,13]
$Br_3^+$	$C_{2v}$	2.27	102.5	[14]
$Br_2$	$D_{\infty h}$	2.281		[14]
$I_2^+$	$D_{\infty h}$	2.557		[17]
$I_4^{2+}$	$C_{2h}$	2.58, 3.26	87–92	[20]
$I_3^+$	$C_{2v}$	2.665	101.75	[4]
$I_5^+$	$C_{2h}$	2.645/2.895	97.0, 180.0	[4]
$I_{15}^{3+}$		2.67/2.68–3.40 <sup>b</sup>	93–95, 162–179	[4]
$I_2$	$D_{\infty h}$	2.281		[14]

<sup>a</sup>This is slightly dependent on the anion (see the Reference section).

<sup>b</sup>Cf. Figure 3.

**FIGURE 3** A valence bond representation of the cations  $I_3^+$ ,  $I_5^+$ , and  $I_{15}^{3+}$  [4] (bond lengths in Å).

et al. [55] as the first example of a  $\pi^*-\pi^*$  bond. More examples of these types of bonds are given in the recent literature [4,56].

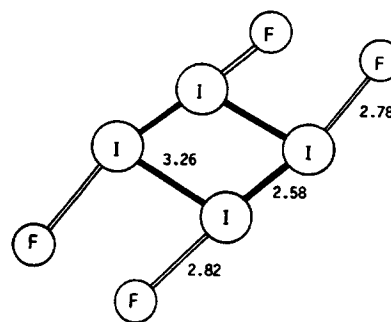
In contrast, a high bond energy is associated with the  $\pi^*$  monomer ( $I_2^+$ ) and the bonding therein. Thus, the  $\pi^*-\pi^*$  bonds follow the formation of the bonded fragments formed. In this regard, these cations are behaving as though they contain second row elements and are clear exceptions to the "double bond rule" [57,58] ( $I_2^+$  bond order 1.5) [56].

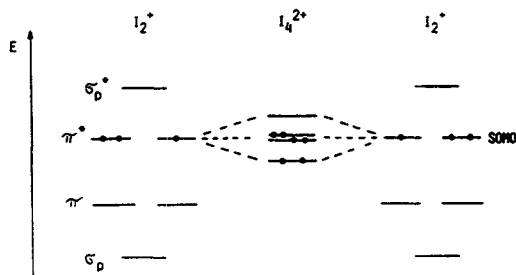
Recently, for homopolyatomic (and binary) I-I bound species, a simple correlation between the I-I bond distance and the wavenumber of the stretching mode has been established [59] using the relationship (Table 4, Figure 7)

$$\tilde{\nu} (\text{cm}^{-1}) = -1170.8 + 1356.0d (\text{\AA}) - 314.9d^2 (\text{\AA}^2).$$

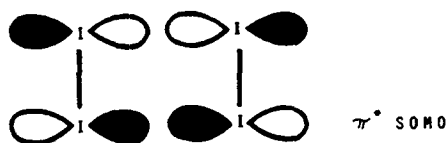
## HETEROPOLYATOMIC CATIONS

Numerous heteropolyatomic halonium cations have been characterized [2,12]. They are usually pre-

**FIGURE 4** Structure of the  $I_4^{2+}$  cation in  $I_4^{2+}$  ( $SbF_6^-$ ) ( $Sb_2F_{14}^-$ ) with cation-anion interactions [20] (bond lengths in Å).

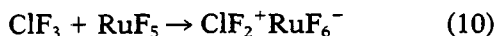


**FIGURE 5** Qualitative MO diagram of two  $I_2^+$   $\pi^*$  radicals interacting to give a positive overlap of two equivalent  $\pi^*$  SOMOs.



**FIGURE 6** Dimerization of two  $I_2^+$   $\pi^*$  radicals with positive overlap of two equivalent  $\pi^*$  SOMOs.

pared from the appropriate interhalogen and a halide-ion acceptor. A recent example for the straightforward reaction of an interhalogen and a halide-ion acceptor is given in Equation 10 [60].

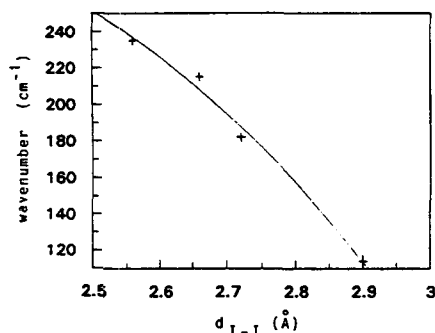


A nice example of a reaction in which the inter-

**TABLE 4** Experimental and Calculated Bond Lengths and Stretching Frequencies for I-I Bound Species [59]

	$\nu_{exp} (cm^{-1})$	$\nu_{calcd} (cm^{-1})^a$	$d_{exp} (\text{\AA})$	$d_{calcd} (\text{\AA})^b$
$I_2^+$	235	237	2.56	2.65
$I_3^+$	220	214	2.67	
$I_2^-$	215	208	2.66	2.73
$I_3^-$	114	113	2.90	2.99

<sup>a</sup>Estimated,  $\nu (cm^{-1}) = -1170.8 + 1356.0d (\text{\AA}) - 314.9d^2 (\text{\AA}^2)$ .  
<sup>b</sup>Calculated: MP2 [59].



**FIGURE 7** Correlation for the bond lengths and stretching frequencies in I-I bound species [59].

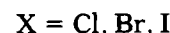
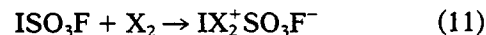
**TABLE 5** Features of the Bond in Heteropolyatomic Halogen Cations<sup>a</sup>

Cation	Symmetry	$d (\text{\AA})$	Angle ( $^\circ$ )	Reference
$ClF_2^+$	$C_{2v}$	1.57	96.4	[60,65]
$Cl_2F^{+b}$	$C_5$	1.579 (Cl-F) 1.953 (Cl-Cl)	103.9	[66]
$BrF_2^+$	$C_{2v}$	1.69	93.5	[2]
$IF_2^+$	$C_{2v}$			[2]
$ICl_2^{+c}$	$C_{2v}$	2.268	97.2	[67]
$I_2Cl^+$	$C_5$			[63]
$IBr_2^{+c}$	$C_{2v}$	2.42	100.0	[68]
$I_2Br^+$	$C_5$			[63]
$IBr_{0.75}Cl_{1.25}$	$C_5$	2.43, 2.37	97.7	[68]
$ClF_4^+$ (ax/eq)	$C_{2v}$	1.63, 1.57	110, 170	[12]
$rF_4^+$ (ax/eq)	$C_{2v}$	1.86, 1.77	96, 173	[2]
$IF_4^+$ (ax/eq)	$C_{2v}$	1.83, 1.79	92, 160	[12]
$ClF_6^{+c}$	$O_h$			[69]
$BrF_6^{+c}$	$O_h$			[70]
$IF_6^{+c}$	$O_h$			[71]

<sup>a</sup>This is slightly dependent on the anion (see the Reference section).

<sup>b</sup>Calculated MP3/6-311G (2df) [66]; <sup>c</sup>Raman [63]; and <sup>d</sup>IR, Raman [12].

halogen is also used as an oxidant is the behavior of Au which dissolves in  $BrF_2$  to give  $BrF_2^+AuF_4^-$  [12,61,62]. The synthesis of interhalogen fluoro-sulfates is accomplished by the oxidative addition of the corresponding halogen or interhalogen molecules to iodine(I)fluorosulfate (Equation 11) [63].



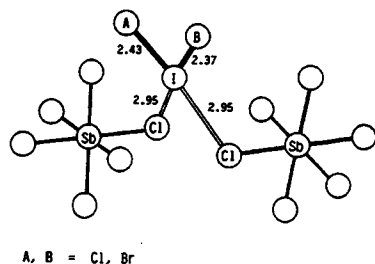
Gillespie, however, has shown by X-ray crystallography that the species of the empirical formula  $ISO_3F$  (cf. Equation 11) have a  $FO_2SO-I(I)-OSO_2F$  structure, which can be regarded as containing  $I^{3+}$  and  $I^-$  [64].

Since most of the known polyatomic cations had been prepared up to the middle of the seventies, they have been reviewed extensively by Shamir [12]. The known species and the features of their bonds are summarized in Table 5.

### Triatomic Species

All of the triatomic interhalogen species are bent (cf. Table 5). For the cations  $I_2Cl^+$  and  $I_2Br^+$ , an unsymmetrical constitution (I-I-X<sup>+</sup>), with X = Cl or Br, is preferred over a symmetrical one (I-X-I<sup>+</sup>) [63]. That for triatomic ions the heavier halogen occupies the central position appears to be a structural principle for both interhalogen cations and anions [63].

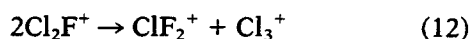
The crystal structures of the strange and untypical  $IBr_2^+Sb_2F_{11}^-$  and  $IBr_{0.75}Cl_{1.25}^+SbCl_6^-$  have been determined recently [68]. The distorted cation  $IBr_{0.75}Cl_{1.25}^+$  has one terminal interaction at 2.427  $\text{\AA}$ , very close to the I-Br distance in  $IBr_2^+$ , while the other terminal distance is 2.373  $\text{\AA}$ , much



**FIGURE 8** Structure of  $\text{IBr}_{0.75}\text{Cl}_{1.25}^+\text{SbCl}_6^-$  showing the coordination about iodine and antimony (distances in Å) [68].

longer than the I-Cl distance in the  $\text{ICl}_2^+$  cation (2.268 Å) [68] (Figure 8).

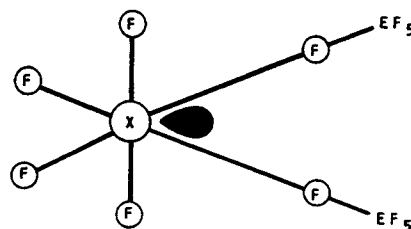
The preparation of the  $\text{Cl}_2\text{F}^+$  cation in the form of its  $\text{AsF}_6^-$  and  $\text{BF}_4^-$  salts was first reported by Christie and Sawodny in 1969 [72]. The ion is rather unstable in solution and disproportionates completely in  $\text{SbF}_5/\text{HF}$ , even at  $-76^\circ\text{C}$  [2] (Equation 12).



Although the question whether the  $\text{ClF}_2^+$  ion has a symmetric or an asymmetric structure could not be answered for a long time [25,72–77], recently it has been shown that the comparison of the theoretically predicted vibrational frequencies and IR and Raman intensities with the reported experimental values provides clear evidence that  $\text{Cl}_2\text{F}^+$  has an asymmetric bent ( $C_s$ ) Cl-Cl-F<sup>+</sup> structure [66]. The total energies calculated at the MP4(SDTQ)/6-311G(2df) level by using geometries obtained at MP3/6-311G(2df) and corrected by zero-point vibrational energies show that asymmetric Cl-Cl-F<sup>+</sup> is 43.0 kcal/mol more stable than the symmetric form Cl-F-Cl<sup>+</sup>. The theoretically predicted vibrational frequencies and Raman intensities agree well with the experimentally obtained data and assignments for Cl-Cl-F<sup>+</sup> reported by Gillespie and Morton [25]. The Cl-F bond strength in Cl-Cl-F<sup>+</sup> is predicted as 41.6 kcal/mol, significantly higher than in Cl-F-Cl<sup>+</sup> (21.2 kcal/mol) but lower than in diatomic ClF (59.4 kcal/mol) and ClF<sup>+</sup> (68.4 kcal/mol) [66]. The Cl-Cl bond in Cl-Cl-F<sup>+</sup> is quite strong (63.3 kcal/mol), even stronger than in  $\text{Cl}_2$  (58.0 kcal/mol) but weaker than in  $\text{Cl}_2^+$  (90.1 kcal/mol) [66].

### Pentaatomic Species

The pentaatomic cations  $\text{ClF}_4^+$ ,  $\text{BrF}_4^+$ , and  $\text{IF}_4^+$  as  $\text{AsF}_6^-$  or  $\text{SbF}_6^-$  salts all have been structurally characterized by X-ray crystallography (Table 5) and are isoelectronic with  $\text{SF}_4$ ,  $\text{SeF}_4$ , and  $\text{TeF}_4$  and adopt the same disphenoidal ( $C_{2v}$ ) configuration [2]. This is illustrated in Figure 9. In the  $\text{XF}_4^+$  cations, two different X-F bond lengths as well as two different F-X-F bond angles were observed. The repulsion between the nonbonding electron pair and



**FIGURE 9** Structure of  $\text{XF}_4^+$  cations ( $X = \text{Cl}, \text{Br}, \text{I}$ ) with strong interactions with the  $\text{EF}_6^-$  anions ( $E = \text{As}, \text{Sb}$ ).

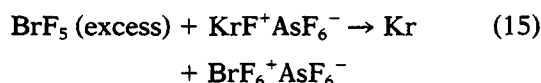
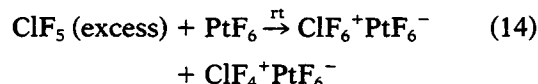
bond pairs decreases the angles between axial and equatorial bonds. Moreover, there are strong subsidiary interactions with the anions, the coordination about the central atom X being pseudooctahedral, with four short X-F distances and two longer X...F distances.

### Heptaatomic Species

Of the heptaatomic cations,  $\text{IF}_6^+$  has been known for some time since it can be made by fluoride-ion transfer from  $\text{IF}_7$  (Equation 13) [12].



Because  $\text{ClF}_7$  and  $\text{BrF}_7$  do not exist [2], alternative preparative procedures must be devised. The cations have been made by oxidation of the pentafluorides with extremely strong oxidizers, such as  $\text{PtF}_6$ ,  $\text{KrF}^+$ , or  $\text{KrF}_3^+$  (Equations 14 and 15) [2,12].

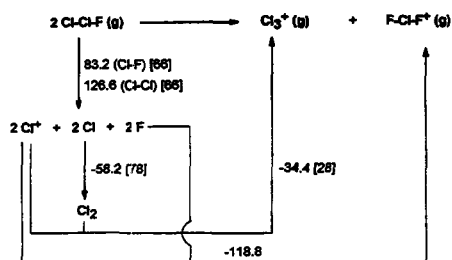


Vibrational spectra and  $^{19}\text{F}$  NMR studies on all three cations  $\text{XF}_6^+$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and the  $^{129}\text{I}$  Mössbauer spectrum of  $\text{IF}_6^+\text{AsF}_6^-$  establish octahedral ( $O_h$ ) symmetry as expected for species isoelectronic with  $\text{SF}_6$ ,  $\text{SeF}_6$  and  $\text{TeF}_6$ , respectively [2,12,69]. The X-ray powder photography shows that  $\text{BrF}_6^+\text{AsF}_6^-$  [70] and  $\text{IF}_6^+\text{AsF}_6^-$  [71] have structures of the NaCl type, containing octahedral cations and anions.

## ENERGETICS

### Thermodynamic Aspects

The thermodynamic criteria governing the existence of the known homopolyatomic cations of group 17 (the halogens) recently have been established by Burford et al. [4]. An excellent description on how to estimate the reaction enthalpies is given in this review [4] (for accuracy, cf. Ref. [4]). A similar procedure can be applied to predict the



**SCHEME 1** Energy cycle for the reaction according to Equation 12 (all values in kcal/mol).

existence (or nonexistence) of heteropolyatomic cations. This can be demonstrated by the following examples.

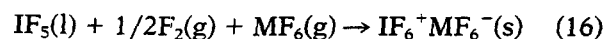
- A. Why does  $\text{Cl}_2\text{F}^+$  disproportionate according to Equation 12 although the number of Cl-Cl and Cl-F bonds remains unchanged?

To illustrate this, we have constructed a simple thermodynamic cycle which represents the reaction according to Equation 12 (Scheme 1). Since the anion ( $\text{AsF}_6^-$ ) remains unchanged, and the reaction proceeds in solution, the calculations were performed on a system containing all species in the gas phase, the entropy terms not being included. The enthalpy of the reaction has been estimated to be  $\Delta H(12) = -2$  kcal/mol, in agreement with the experimental result [2].

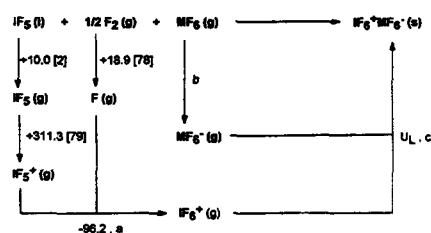
The driving force for this disproportionation seems to be the remarkably weak Cl-F bond in  $\text{Cl-Cl-F}^+$  (cf. Ref. [66]) which is still weaker than in the neutral ClF. This might be due to the fact that the positive charge in  $\text{Cl-Cl-F}^+$  is distributed over both Cl atoms (partial charge at atom, calculated: F,  $-0.12$ ;  $-\text{Cl}$ ,  $+0.83$ ;  $-\text{Cl}$ ,  $+0.29$  [66]), whereas in  $\text{ClF}_2^+$ , the central Cl atom carries all the positive charge. Moreover, the value of  $\Delta H(12) = -2$  kcal/mol is likely to be underestimated as the Cl-F bond energy in  $\text{ClF}_2^+$  was taken to be equal to that in the neutral ClF and the reaction according to Equation 12 should be even more thermodynamically favorable.

- B. What is the lowest limit for the electron affinity of  $\text{MF}_6$  which can stabilize the  $\text{IF}_6^+\text{MF}_6^-$  salt?

The thermodynamics of a reaction according to Equation 16 can be described using a simple energy cycle (Scheme 2) (N.B. the species  $\text{MF}_6$  are either volatile liquids ( $\text{PtF}_6$ ) or gases ( $\text{WF}_6$ ) at room temperature; therefore, the gaseous state has been taken for the calculations).



Although the lattice energies of the three salts are essentially identical, the electron affinity increases remarkably from  $\text{WF}_6$  to  $\text{PtF}_6$ . Therefore, the en-

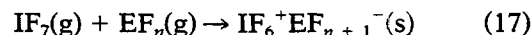


**SCHEME 2** Energy cycle for the reaction according to Equation 16 (all values in kcal/mol). (a)  $\Delta H(\text{IF}_5^+ + \text{F} \rightarrow \text{IF}_6^+)$  estimated to be equal to  $1.5 \times \text{BE}(\text{I-F}, \text{IF}_5) = -96.2$  kcal/mol; calibrated on  $\Delta H(\text{NF}_3^+ + \text{F} \rightarrow \text{NF}_4^+) = -100$  kcal/mol [80] and  $\text{BE}(\text{N-F}, \text{NF}_3) = -66.5$  kcal/mol [78]. (b)  $E_A$ :  $\text{WF}_6$ , 85.4 kcal/mol [52];  $\text{UF}_6$ , 119.6 [52];  $\text{PtF}_6$ , 184.5 [24,81]. (c)  $U_L$  calculated from the molecular volume  $V_M$  using the linear relationship for  $\text{A}^+\text{B}^-$  salts:  $U_L = 556.3 V_M (\text{\AA}^3)^{-0.33} + 26.3$  [82,83].  $V_M(\text{IF}_6^+)$  was taken to be equal to  $V_M(\text{IF}_5) = 115 \text{\AA}^3$  (from  $d_{293} = 3.207 \text{ g/cm}^3$  [2]);  $V_M(\text{MF}_6^-)$  was taken to be equal to  $V_M(\text{MF}_6)$ ;  $V_M(\text{PtF}_6) = 105 \text{\AA}^3$  [79],  $V_M(\text{WF}_6) = 109 \text{\AA}^3$  [79];  $V_M(\text{UF}_6)$  was taken to be equal to  $V_M(\text{WF}_6)$ . This gives  $U_L(\text{IF}_5^+\text{PtF}_6^-) = -118.5$  kcal/mol and  $U_L(\text{IF}_6^+\text{WF}_6^-) = U_L(\text{IF}_6^-\text{UF}_6^-) = -117.9$  kcal/mol.

thalpies of Reaction 16 have been estimated to be  $\Delta H(16, \text{M} = \text{W}) = +41$  kcal/mol,  $\Delta H(16, \text{M} = \text{U}) = +7$  kcal/mol, and  $\Delta H(16, \text{M} = \text{Pt}) = -59$  kcal/mol, and  $\text{PtF}_6^-$  is the only likely candidate that is able to oxidize  $\text{IF}_5$ . In fact,  $\text{PtF}_6^-$  salts of the heptaatomic  $\text{XF}_6^+$  cations ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) have been described [2], whereas no  $\text{UF}_6^-$  or  $\text{WF}_6^-$  containing compound has been reported. In close relationship with this problem is question C.

- C. What is the limit of the fluoride ion affinities to abstract a  $\text{F}^-$  ion from  $\text{IF}_7$ ?

The enthalpies of Reaction 17 can be estimated from a simple thermodynamic energy cycle (Scheme 3).

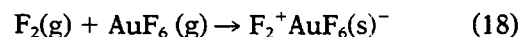


$$n = 3, \text{E} = \text{B}; n = 5, \text{E} = \text{As}, \text{Sb}$$

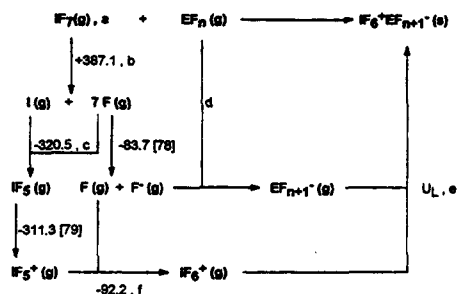
Reaction 17 is exothermic for all the  $\text{EF}_n$  species discussed:  $\Delta H(17, \text{E} = \text{B}) = -19$  kcal/mol,  $\Delta H(17, \text{E} = \text{As}) = -32$  kcal/mol, and  $\Delta H(17, \text{E} = \text{Sb}) = -30$  kcal/mol. This is reflected in the fluoride ion affinity of  $\text{EF}_n$  (see Scheme 3) and the lattice energy, which are both large enough to compensate for the high ionization potential of iodine (or  $\text{IF}_5$ ); therefore, cation formation is feasible. In fact, stable  $\text{IF}_6^+$  salts containing anions, such as the very weak bases  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ , and  $\text{BF}_4^-$ , have been prepared [12].

- D. Would " $\text{AuF}_6$ " be able to stabilize  $\text{F}_2^+$ ?

An energy cycle representing the thermodynamics of Reaction 18 is given in Scheme 4.



The heat of Reaction 18 was estimated to be  $\Delta H(18)$

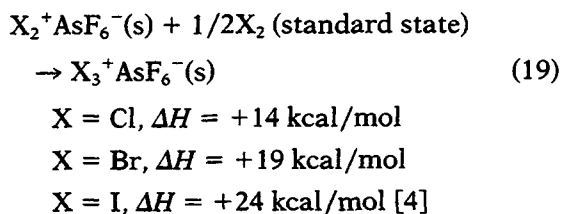


**SCHEME 3** Energy cycle for the reaction according to Equation 17 (all values in kcal/mol). (a) bp(IF<sub>7</sub>) = 4.8°C (subl.) [2]. (b) BE(I-F, IF<sub>7</sub>) = 55.3 kcal/mol [52]. (c) BE(I-F, IF<sub>5</sub>) = 64.1 kcal/mol [52]. (d) FIA: BF<sub>3</sub>, -92 [82]; AsF<sub>5</sub>, -111 [4]; SbF<sub>5</sub>, -111 [4] kcal/mol. (e) For U<sub>L</sub>, see Scheme 1; V<sub>M</sub>(IF<sub>6</sub><sup>+</sup>) = 115 Å<sup>3</sup> (see Scheme 2), V<sub>M</sub>(AsF<sub>6</sub><sup>-</sup>) = 105 Å<sup>3</sup> [4], V<sub>M</sub>(SbF<sub>6</sub><sup>-</sup>) = 119 Å<sup>3</sup> [84], V<sub>M</sub>(BF<sub>4</sub><sup>-</sup>) = 66 Å<sup>3</sup> [85] (estimated from V<sub>M</sub>(NF<sub>4</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup>) = 182 Å<sup>3</sup> [86] and V<sub>M</sub>(NF<sub>4</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>) = 129 Å<sup>3</sup> [87]). This gives U<sub>L</sub>(E = B) = -124.7, U<sub>L</sub>(E = As) = -118.5, and U<sub>L</sub>(E = Sb) = -116.6 kcal/mol. (f) See (a), Scheme 2.

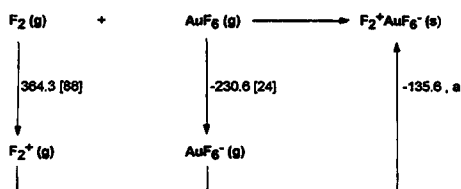
= -2 kcal/mol. The entropy, however, has not been included, and it is obvious that ΔS strongly favors the decomposition of F<sub>2</sub><sup>+</sup>AuF<sub>6</sub><sup>-</sup>. On the other hand, at very low temperatures, F<sub>2</sub><sup>+</sup>AuF<sub>6</sub><sup>-</sup> might very well exist, and the question whether an F<sub>2</sub><sup>+</sup> containing salt exists must be regarded as still open.

### The Hard-Soft Acid-Base Principle

Interestingly, the formation of X<sub>3</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> from X<sub>2</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> (X = Cl, Br, I) and X<sub>2</sub> was calculated to be unfavorable for all three halogens and the formation of X<sub>5</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> only slightly favorable [4] (Equation 19).



These trends do not reflect the experimental ob-



**SCHEME 4** Energy cycle for the reaction according to Equation 18 (all values in kcal/mol). (a) V<sub>M</sub>(AuF<sub>6</sub><sup>-</sup>) was taken to be equal to V<sub>M</sub>(PtF<sub>6</sub>) = 105 Å<sup>3</sup>, V<sub>M</sub>(F<sub>2</sub><sup>+</sup>) = 27 Å<sup>3</sup> [4]; for the calculation of U<sub>L</sub>, see Scheme 2.

**TABLE 6** Experimental HSAB Parameters

	<i>I<sub>P</sub></i> (eV)	<i>E<sub>A</sub></i> (eV)	<i>χ</i> (eV)	<i>η</i> (eV)	Reference
F	17.42	3.40	10.41	7.01	[90]
Cl	13.01	3.62	7.31	4.70	[90]
Br	11.84	3.36	7.60	4.24	[90]
I	10.45	3.06	6.76	3.70	[90]
Cl <sub>2</sub>	11.40	2.40	6.90	4.50	[90]
Br <sub>2</sub>	10.65	2.60	6.62	4.03	[4,94]
I <sub>2</sub>	9.30	2.60	6.00	3.40	[90]
I <sub>2</sub> <sup>•</sup>	19.10	10.50	14.80	4.30	[90]
Br <sup>+</sup>	21.60	11.80	16.70	4.90	[90]
I <sub>2</sub> <sup>+</sup>	17.00 <sup>a</sup>	9.30 <sup>b</sup>	13.20	3.90	[4,90]

<sup>a</sup>*I<sub>P</sub>* (I<sub>2</sub><sup>+</sup>) estimated to be equal to 2 × *I<sub>P</sub>* (I) - BE (I - I<sub>2</sub><sup>+</sup>) [4].

<sup>b</sup>*I<sub>P</sub>* of the "anion" (I<sub>2</sub>) [90].

servations; this fact demonstrates the approximate nature of the calculations. Therefore, further refinement of the calculations is necessary to improve agreement with the experimental results.

Recently, two new chemical concepts have been derived from density functional theory [89–93]. These are the absolute electronegativity, *χ*, and the absolute hardness, *η*. The approximate definitions of these quantities are *χ* = 0.5 (*I<sub>P</sub>* + *E<sub>A</sub>*) and *η* = 0.5 (*I<sub>P</sub>* - *E<sub>A</sub>*) [89]. The relationships apply to any isolated chemical system, atom, ion, molecule, or radical. A number of values have been calculated for various systems [91], using experimental values of *I<sub>P</sub>* and *E<sub>A</sub>* (Table 6).

If two chemical systems, A and B (e.g., I<sub>2</sub><sup>+</sup> and I), are brought into contact, electrons will flow from the one of lower *χ* to that of higher *χ* until the electronegativities become equalized. An approximate value for Δ*N*, the number of electrons transferred, is given by

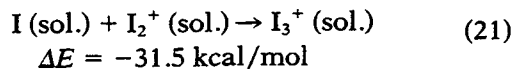
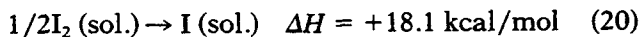
$$\Delta N = (\chi_A - \chi_B)/2(\eta_A + \eta_B) [89].$$

The energy change due to the charge transfer is given by

$$\Delta E = -(\chi_A - \chi_B)^2/4(\eta_A + \eta_B) [90].$$

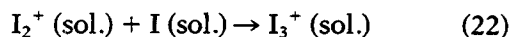
It appears that the quantities *χ* and *η* (and Δ*N* and Δ*E*) are very useful for estimating the reactivity of a molecule (atom, radical, ion) [92,95–98].

For the reaction of iodine (I) with I<sub>2</sub><sup>+</sup>, which is most unfavorable due to simple thermodynamic estimations (see above), the Δ*N* and Δ*E* values have been calculated to be Δ*N* = 0.43 and Δ*E* = -1.36 eV (-31.5 kcal/mol). The calculated gain in energy is substantially larger than the heat of formation of I from I<sub>2</sub> [78]. Therefore, a clear picture emerges if we combine the two models, assuming that the I–I bond energy for the gas phase can be taken for solution (Equations 20 and 21).





For Reaction 22, the gain in energy is therefore roughly  $-13.4$  kcal/mol and favors the reaction of  $I_2^+$  and  $1/2I_2$  to give the more stable  $I_3^+$ . This is in good agreement with the observation and does reflect the experimental results [4].



## CONCLUSIONS

Salts of homopolyatomic (except fluorine) and heteropolyatomic cations of the halogens (group 17) constitute a well-established class of compounds. In general, structures are as expected from simple valence theory (VSEPR) and the isoelectronic principle. However, some special structural principles should be mentioned:

1. In heteropolyatomic cations (e.g.,  $IBr_2^+$ ,  $IBrCl^+$ ,  $Cl_2F^+$ ), the heavier atoms occupy the central position.
2. Charge delocalization and bond alternation leads to the presence of particularly short I–I and Br–Br bonds in the homopolyatomic iodine and bromine cations (e.g.,  $I_2^+$ ). These cations can be regarded as containing examples of thermodynamically stable  $4p\pi-4p\pi$  bonds and  $5p\pi-5p\pi$  bonds and are clear exceptions to the double bond rule.
3. The dimerization of two  $I_2^+$  radicals to give the diamagnetic planar  $I_4^{2+}$  (rectangle) is best described in terms of a  $\pi^*-\pi^*$  bond involving positive overlap of two equivalent  $\pi^*$  SOMOs.

Criteria for the stability of the homo- and heteronuclear polyhalonium cations have been established on thermodynamic grounds. The extended hard-soft acid-base (HSAB) principle can help to determine the behavior of a polyhalonium species, because the properties of the absolute electronegativity and the hardness are intimately related to the gain and loss of electrons by the system.

Finally, high-level ab initio calculations often provide a definitive answer on the question about the structure for species which cannot be examined by single crystal X-ray diffraction studies (e.g.,  $Cl_2F^+$ ).

*Note added in proof:* Quite recently, the first book to comprehensively explore inorganic speciation in super acids covering the polyatomic cations of the nonmetallic elements has been published [99].

## ACKNOWLEDGMENTS

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