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Structures, Vibrational Frequencies, and Stabilities of Halogen Cluster Anions and Cations, $X_n^{+/-}$, n = 3, 4, and 5

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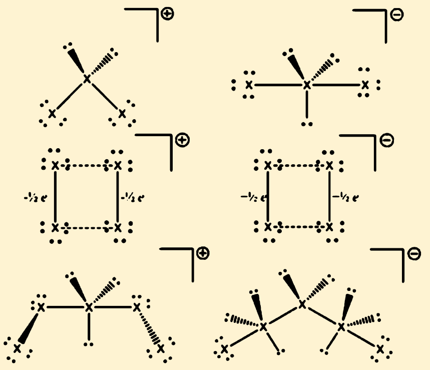
Supporting Information

ABSTRACT: The structures, vibrational frequencies, and thermodynamic stabilities of the homonuclear polyhalogen ions, X_3^+, X_3^-, X_4^+, X_4^-, X_5^+, and X_5^- (X = Cl, Br, I), have been calculated at the CCSD(T) level. The energetics were calculated using the Feller−Peterson−Dixon approach for the prediction of reliable enthalpies of formation. The calculations allow the following predictions where stabilities are defined in terms of thermodynamic quantities. (1) The X_3^+ cations are stable toward loss of X_2; (2) the X_3^- anions are marginally stable toward loss of X_2 with Cl_3^- being the least stable; (3) the X_4^+ cations and X_4^- anions are only weakly bound dimers of $X_2^{+1/2}$ and $X_2^{-1/2}$ units, respectively, but the cations are marginally stable toward decomposition to X_3^+ and X, with I_4^+ having the lowest dissociation energy, whereas the X_4^- anions decompose spontaneously to X_3^- and X; (4) the X_5^+ cations are only marginally stable at low temperatures toward loss of X_2, with Cl_5^+ being the least stable; and (5) the X_5^- anions are also only stable at low temperatures toward loss of X_2, with Cl_5^- being the least stable.



INTRODUCTION

Polyhalogen clusters have been extensively investigated both experimentally and theoretically because of their rich and interesting chemistry.[1−18] A wide range of properties including Lewis acidity, charge distributions, polarizability, and hypervalency of the halogens govern their structure, reactivity, and stability.[18−21] Such properties play an important role in high-conductivity halogen-doped organic systems[22−26] as well as high temperature superconducting transistors.[27,28]

The tri-atomic halogen cations, Cl_3^+, Br_3^+, and I_3^+, have molecular and electronic structures similar to and are electronically similar to SCl_2, OF_2, and Te_3^{2-}.[1] Cl_3^+ and Br_3^+ are less stable than I_3^+ and exist only in superacids or at low temperature or both.[6] The existence of Cl_3^+ was detected by Gillespie and Morton in 1979,[12] but it took until 1999 before Seppelt and coworkers[29] were able to determine the crystal structure of $[Cl_3^+][AsF_6^-]$. Cl_3^+ has been synthesized and characterized by both spectroscopic and crystallographic techniques.[29−33] The observed fundamental vibrational frequencies in Cl_3^+ are very close to those of those in isoelectronic SCl_2.[12] The Br_3^+ cation was characterized by UV−vis, IR, mass spectrometry, and X-ray crystallography.[9,17,33−35] The I_3^+ was synthesized and characterized by both spectroscopic and crystallographic techniques.[13,17,19,36,37] The Cl_3^-, Br_3^-, and I_3^- anions have been observed in the gas phase,[38,39] in solution,[40−42] and in the solid state[43−45] and characterized by spectroscopic techniques.[46−58] These trihalide anions (X_3^-) are linear and symmetric in solution, while in the solid phase both symmetric and asymmetric structures are found with the small deviations from linearity being caused by crystal packing forces.[23,49,51,59]

Tetra-atomic polyhalide cluster ions have attracted much less attention in experimental and theoretical studies than have the corresponding three- and five-atomic ones because of their lower stability. The only experimentally observed species are Cl_4^+ and Br_4^+. The X-ray crystal structure of the rectangular Cl_4^+ was reported for $[Cl_4^+][IrF_6]$.[60] Br_4^+ has been detected in gas phase electron deflection studies, but no structural data are available.[61]

Four penta-atomic polyhalide ions are known. Br_5^+ and Br_5^- have been synthesized and studied by spectroscopic techniques, and by X-ray crystallography.[17,23,35,62] Whereas Br_5^- is stable in

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water and nonpolar organic solvents, Br$_5^+$ exists only in strongly acidic media. I$_5^+$ and I$_5^-$ also have been studied using spectroscopic and X-ray techniques.[63−66]

A number of theoretical studies[29,32,38,60,63−80] of polyhalogon cluster ions are available in the recent literature. The levels of theory used for these studies have included density functional theory (DFT),[81] second-order Møller−Plesset perturbation theory (MP2),[82,83] and coupled-cluster single and double substitution with perturbatively connected triples (CCSD(T))[84−87] along with different basis sets. The structure and vibrational frequencies of Cl$_3^+$ have been predicted with molecular structure optimizations at the DFT,[32,74] MP2,[71,74] and CCSD(T)[32,76] levels employing various basis sets. Calculations at the MP2 and CCSD(T) levels of the molecular structures, frequencies, and thermochemistry of the Cl$_3^-$, Br$_3^-$, I$_3^-$, Cl$_5^-$, Br$_5^-$, and I$_5^-$ anions have been correlated with the experimental data.[67,68,70,77,80] A DFT level study of the molecular structure and vibrational frequencies of the Cl$_4^+$ cation have been compared with experiment,[60] and SCF and DFT computations have been reported for the Br$_4^+$ cation.[77,78] The electronic structures and energies of various rotamers of Cl$_5^+$ were predicted at the SCF level with a minimal basis set.[63] The structure, frequencies, and the charge distribution have been studied at the DFT level for Cl$_5^+$ and Br$_5^+$[72] and for Cl$_5^-$, Br$_5^+$, I$_3^+$, I$_3^-$, I$_5^+$, and I$_5^-$ at the MP2/3-21G level.[73] Thermochemical predictions, including bond dissociation energies, reaction energies, and enthalpies of formations, also have been studied at the DFT, MP2, and CCSD(T) levels.[32,67,70,75,77,79]

Our goal here is to provide reliable energetics for these species using the Feller−Peterson−Dixon approach[88−91] for the prediction of reliable enthalpies of formation based on CCSD(T) calculations. We have used such an approach recently to predict the properties of a range of polyhalogen species including iodine fluorides.[92,93] We have used the above approach to calculate the atomization energies at 0 K and enthalpies of formation at 0 and 298 K for the closed shell ions X$_3^+$, X$_3^-$, X$_5^+$, and X$_5^-$ (X = Cl, Br, and I) and the open shell ions X$_4^+$ and X$_4^-$.

■ COMPUTATIONAL PROCEDURE

Equilibrium molecular structures for all polyhalogen cluster ions were optimized at the CCSD(T) level with the augmented correlation-consistent double-ζ and triple-ζ basis sets as described below.[94,95] Single point energies were calculated with the quadruple-ζ and quintuple-ζ basis sets at the triple-ζ geometries. The augmented correlation-consistent basis sets with tight-d functions (aug-cc-pV(n+d)Z) were used for Cl.[96,97] The augmented correlation-consistent polarized valence basis sets with effective core potential (aug-cc-pVnZ-PP) and aug-cc-pwCVnZ-PP (core−valence, CV calculations) were used for Br.[98] The augmented correlation-consistent polarized weighted core−valence basis sets with Stuttgart small-core relativistic effective-core potentials (RECP) (aug-cc-pwCVnZ-PP) were used for I,[99] guided by our prior work on iodine complexes.[92] For Br, the RECP subsumes the (1s^2, 2s^2, 2p^6) orbital space into the 10-electron core set, leaving the (3s^2, 3p^6, 3d^{10}, 4s^2, 4p^5) space with 25 electrons to be handled explicitly, with the (4s^2, 4p^5) electrons active in the valence correlation space. The RECP for I subsumes the (1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}) orbital space into the 28-electron core set, leaving the (4s^2, 4p^6, 5s^2, 4d^{10}, and 5p^5) space with 25 electrons to be handled explicitly. All CCSD(T) computations were performed with the core electrons frozen (FC) except for the bromine (when indicated) and iodine compounds. Henceforth these basis sets are collectively designated as ATZ. The atomic energies were calculated at the R/UCCSD(T) level starting with a restricted open shell Hartree−Fock and an unrestricted CCSD(T).[100−102]

The converged energies were extrapolated to the CBS limit using two schemes which have been evaluated by Feller et al.[103] along with other ones. The aug-cc-pVnZ energies were extrapolated using a mixed exponential/Gaussian function of the form given in eq 1

$$E(n) = E_{\text{CBS}} + A\exp[-(n-1)] + B\exp[-(n-1)^2] \qquad (1)$$

as first proposed by Peterson et al.[104] with $n = 2(D)$, $3(T)$, and $4(Q)$. In the second approach, the CBS limit was obtained by using a two-point extrapolation scheme with $l_{\max} = Q$, and 5 as in eq 2.[105]

$$E(l_{\max}) = E_{\text{CBS}} + B/l_{\max}{}^3 \qquad (2)$$

The following additional additive corrections to the total atomization energy (TAE) were used: zero-point vibrational energies (ΔE_{ZPE}), core−valence effects (ΔE_{CV}) for the Cl and Br compounds for the valence only calculations, a correction for scalar relativistic effects (ΔE_{SR}), and spin−orbit corrections (ΔE_{SO}). Zero-point vibrational energies were computed at the CCSD(T)/aug-cc-pVTZ level with the appropriate ECPs for Br and I. Core−valence (CV) computations were performed for all compounds containing Cl at the CCSD(T)/aug-cc-pwCVTZ[106,107] and at the CCSD(T)/aug-cc-pwCVTZ-PP[108] level for compounds containing Br. Scalar relativistic effects for Cl compounds were evaluated by using expectation values for the two dominant terms in the Breit−Pauli Hamiltonian, the so-called mass-velocity and one-electron Darwin (MVD)[109] corrections from configuration interaction singles and doubles (CISD)[110] calculations. Molecular spin−orbit corrections (2nd order for I$_3^{+/-}$ and I$_5^{+/-}$ as they are closed shell singlets for the ground state, see below) for the iodine compounds were obtained[111] at the DFT level with the B3LYP exchange-correlation functional[112−114] and the aug-cc-pVTZ-PP-SO basis set for I.[115] This level provides a computationally tractable level with reasonable accuracy.[92,111,116,117] The atomic spin−orbit corrections are $\Delta E_{\text{SO}}(\text{Cl}) = -0.84$ kcal/mol, $\Delta E_{\text{SO}}(\text{Br}) = -3.50$ kcal/mol, and $\Delta E_{\text{SO}}(\text{I}) = -7.24$ kcal/mol from the Table of Moore.[118]

The calculated total atomization energies, $\sum D_0$, are obtained from eq 3 for the Cl compounds and for the Br compounds with the valence only complete basis set (CBS) extrapolation.

$$\sum D_0 = \Delta E_{\text{elec}}(\text{CBS}) + \Delta E_{\text{ZPE}} + \Delta E_{\text{CV}} + \Delta E_{\text{SR}} + \Delta E_{\text{SO}} \qquad (3)$$

Equation 4 was used to calculate $\sum D_0$ for the compounds containing Br and I when the core−valence corrections are included in the CBS extrapolation.

$$\sum D_0 = \Delta E_{\text{elec}}(\text{CBS}) + \Delta E_{\text{ZPE}} + \Delta E_{\text{SR}} + \Delta E_{\text{SO}} \qquad (4)$$

By combining the $\sum D_0$ with the known enthalpies of formation $\Delta H^\circ_{\text{f}}$ at 0 K for the elements, $\Delta H^\circ_{\text{f}}(\text{Cl,g}) = 28.59 \pm 0.01$ kcal/mol, $\Delta H^\circ_{\text{f}}(\text{Br,g}) = 28.18 \pm 0.01$ kcal/mol, $\Delta H^\circ_{\text{f}}$ $(\text{I,g}) = 25.61 \pm 0.01$ kcal/mol, the gas phase $\Delta H^\circ_{\text{f}}$ values can be derived for the compounds of the current study.[119] We obtain enthalpies of formation at 298 K by following the procedures outlined by Curtiss et al.[120] Standard enthalpies of formation at 298 K were obtained by combining the atomic thermal corrections 1.10 kcal/mol (Cl), 2.93 kcal/mol (Br), and 1.58 kcal/mol (I)), with the molecular thermal corrections in the appropriate statistical mechanical expressions.[121]

All CCSD(T) calculations were performed with the MOLPRO2010[122] package of ab initio programs. Molecular spin−orbit correction computations were carried out with the NWCHEM[123] program. DFT calculations were done with the program Gaussian09[124] including tests of previous results and Natural Bond Orbitals (NBOs).[125,126] The NBOs were calculated at the DFT level with the B3LYP exchange-correlation functional with the augmented correlation-consistent basis sets described above at the triple-ζ level.

■ RESULTS AND DISCUSSION

Molecular Structures. The calculated geometries and NBO charges are summarized in Figures 1 and 2, respectively. The tri-atomic cations and anions are closed shell singlets. The cations can be derived from pseudotetrahedral structures with the central halogen possessing two covalently bound halogen ligands and two sterically active free valence electron pairs. The positive charge is mainly located on the central halogen atom.

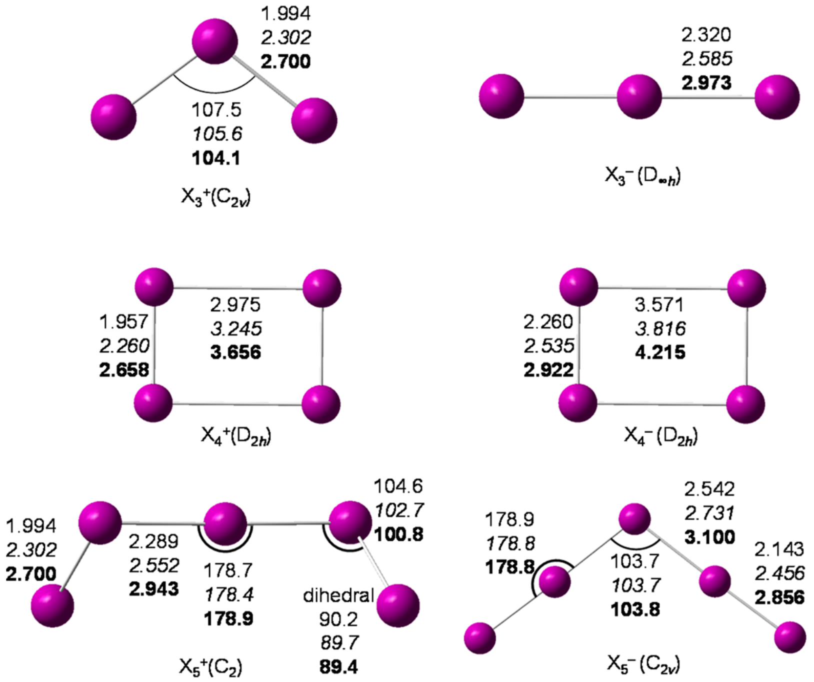

Figure 1. Calculated geometries at the CCSD(T)/aVTZ level (bond lengths in Å and bond angles in degrees). (Typeface: normal for Cl, italic for Br, and bold for I ions.)

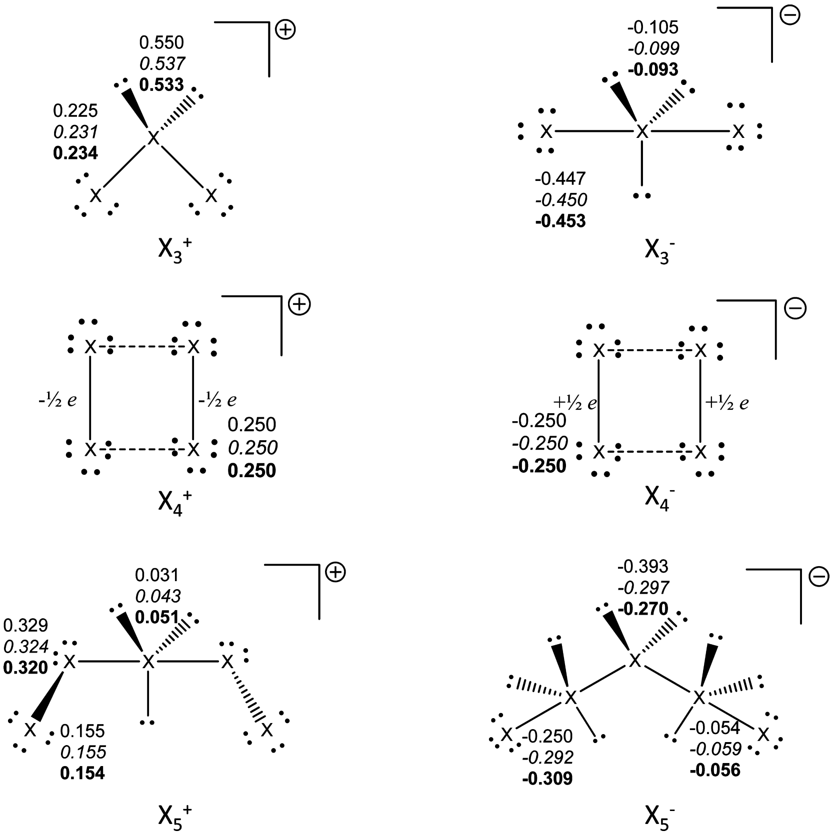

Figure 2. NBO Charges at the B3LYP/ATZ/ATZ-PP level. (Typeface: normal for Cl, italic for Br, and bold for I ions.)

The anions can be described as pseudotrigonal bipyramids with the central atom possessing three equatorial sterically active sp^2 hybridized valence electron pairs and using the third p-orbital for the formation of one linear semi-ionic 3c−4e bond for the two axial halogen ligands. As a consequence, the negative charges are located almost exclusively on the two terminal halogen atoms.

The tetra-atomic cations and anions are composed of two weakly van der Waals bound dimers with the positive and negative charges, respectively, being equally distributed over all four halogen atoms.

The structure of the penta-atomic cations might be derived from a linear central X_3^- unit with two long 3c−4e X−X bonds and two positively charged γ-halogen atoms attached to the two axial β-X atoms resulting in little charge on the central α-atom, large positive charges on the two β-X atoms, and moderate positive charges on the two terminal γ-X atoms. In contrast, the penta-atomic anions might be considered as two linear 3c−4e X_3 units sharing a common axial ligand and having large negative charges on the α- and γ-X atoms. The ground states of the penta-atomic cations could be singlets or triplets as the ground states of the halogen atomic cations are triplets with triplet−singlet splittings of 33.3, 32.6, and 39.2 kcal/mol for Cl^+, Br^+, and I^+ respectively.[118] The singlets are predicted to be 19.2 (20.3), 18.4 (20.0), and 17.8 (19.1) kcal/mol more stable than the triplets at the CCSD(T)(B3LYP)/aug-cc-pVTZ or aug-cc-PVTZ-PP basis sets for Cl_5^+, Br_5^+, and I_5^+, respectively, at the optimized B3LYP geometries. The discussion below is thus based on singlets for the tri-atomic and penta-atomic ions and doublets for the tetra-atomic ones.

A comparison of the calculated geometries with those experimentally observed is given in Table 1. The X_3^+ cations are bent with C_{2v} symmetry, and the X−X−X angle decreases slightly from 108° to 104° with increasing atomic number of the halogen. The calculated bond distance of Br_3^+ is 0.3 Å greater than that of Cl_3^+, and the bond distance of I_3^+ is 0.4 Å greater than that of Br_3^+. Previous computations on halogen diatomic compounds (Cl_2, Br_2, and I_2) at the CCSD(T) level with an aug-cc-PV*X*Z (*X* = 5, 6) basis set show similar trends with the bond lengths increasing by 0.3 Å from Cl_2 (1.991 Å) to Br_2 (2.294 Å) and by 0.4 Å for Br_2 to I_2 (2.673 Å).[116] The calculated CCSD(T)/aTZ Cl−Cl−Cl angle differs from the experimental values in the $[Cl_3^+][SbF_6^-]$ and $[Cl_3^+][AsF_6^-]$ X-ray crystal structures by only 2 to 3°, and the Cl−Cl bond lengths are in good agreement with experiment.[29] The experimental solid state angles[17,29,37] of Cl_3^+, Br_3^+, and I_3^+ are about 3° less than those predicted at the CCSDT(T)/ATZ level.

For X_3^- (X = Cl, Br, and I), several geometrical configurations with $D_{\infty h}$, C_{2v}, and C_s symmetries have been observed in the solid state X-ray structures due to crystal field and solvent effects. The isolated ions optimized to linear structures having $D_{\infty h}$ symmetry. The X−X bond distances increase by 0.27 Å from Cl to Br and by 0.39 Å from Br to I, in accord with the changes in the tri-atomic cations and the diatomics. The calculated bond lengths of Cl_3^-, Br_3^-, and I_3^- agree within 0.1 Å with the experimental X-ray structure values[51,52,68] as well as those from previous computational studies.[67,70,75,77] The current calculated values are the most reliable complete set available for these compounds in the gas phase. Riedel and co-workers[67] reported a bond distance for Cl_3^- at the CCSD(T)/aug-cc-pVDZ level, and our value at the aug-cc-pV(T+d)Z level is within 0.001 Å, showing the importance of the tight d functions. Sharp and Gellene[75] reported the bond distance for I_3^- at the CCSD(T)/TZ(2df)-ECP level, and their value with a smaller basis set is 0.01 Å longer than our value. The bond distances in X_3^- are about 0.3 Å longer than in X_3^+, consistent with the simple bonding picture proposed above.

The Cl_4^+ ion is bound by weak interactions and has a rectangular D_{2h} symmetry with two short Cl−Cl bonds and two long Cl···Cl bonds. The shorter Cl−Cl length of 1.96 Å is similar to that found in neutral Cl_2 (1.99 Å) and longer than in the Cl_2^+ ion (1.89 Å),[127] consistent with a bond order of 1.0 in Cl_2, 1.5 in Cl_2^+, and 1.25 for each "Cl_2" in Cl_4^+. The predicted long Cl···Cl bond is in agreement with experiment[60] as well as with previous predictions to within 0.04 Å. Although there is no experimental evidence for the Br_4^+ ion, two theoretical studies have been reported.[77,78] A DFT study at the B3LYP level predicted that the Br_4^+ ion has C_2 symmetry with an H_2O_2-like torsion angle[77] whereas an SCF study predicted a linear $D_{\infty h}$ structure.[78] Optimization from the C_2 structure at the CCSD(T) level led to the rectangular D_{2h} structure, which is analogous to the experimental structure of the Cl_4^+ cation.[77] This difference is due to the failure of most common density functionals to properly describe the long-range electron correlation involved in weak interactions.[128−132] To further test this, we confirmed that the B3LYP structure with the aug-cc-pVTZ-PP basis set has C_2 symmetry but that the dispersion corrected ωB97X-D[133,134] functional with same basis set yielded the D_{2h} structure.

The tetra-atomic anions have longer X−X bonds than the cations by about 0.25 to 0.3 Å, similar to what is predicted for the tri-atomic ions. The weak interactions between the two $Cl_2^{-0.5}$ moieties are now almost 0.6 Å longer than in the cations, consistent with the additional charge repulsion arising from the added negative charge.

In the gas phase, we and others[67] predict that Cl_5^- has a V-shaped structure. In the solid state, the crystal structure[135] of $[PPh_2Cl_2]^+[Cl_5^-]$ shows that the Cl_5^- is best described as a Cl_2 weakly complexed to a Cl_3^- with a distorted L-type structure. Riedel and co-workers[67] used Raman spectroscopy in combination with computational chemistry results to study $[NR_4]^+Cl^-$ salts with excess chlorine for R = Me, Et, *n*-Pr, and *n*-Bu. They assigned $[NMe_4]^+Cl_5^-$ to the V-shaped structure and $[NMe_4]^+Cl_5^-$ to the distorted L-shaped structure. Thus, the Cl_5^- anion is readily distorted in the solid state. The CCSD(T)/auc-cc-pVTZ structure[67] of Cl_5^- is in good agreement with our CCSD(T)/auc-cc-p(V+d)TZ structure.

The structure of Br_5^+ has been determined in the solid state for $[Br_5^+][AsF_6^-]$ and $[Br_5^+][SbF_6^-]$.[35] The cation has a planar C_{2h} symmetry with a central Br_3-entity that is linear. The terminal Br−Br bond distances of 2.27 Å are very similar to the Br−Br bond distance of 2.28 Å in Br_2, consistent with considering this ion as having two $Br_2^{+1/2}$ molecules bonded to a Br atom. The two central Br−Br distances of 2.51 Å are significantly longer, and the linear Br_3 central unit is somewhat reminiscent of the linear arrangement in the Br_3^- anion. In contrast to the observed planarity, the calculated structure has C_2 symmetry with a torsion angle of 90°, but the predicted central and terminal Br−Br bond lengths are within 0.05 Å of both experiment and previous DFT studies.[72,77] Our terminal Br−Br−Br angle calculated at the CCSD(T)/ATZ-PP level is about 5° larger than experiment and 6 to 10° smaller than previous theoretical studies.[72,77] The calculated central Br−Br−Br angle is closer to linear and 2 to 10° larger than found in previous theoretical studies.[72,77] For the I_5^+ ion in $[I_5^+][AsF_6^-]$, the X-ray structure[63] showed that the terminal I−I bond distance is also very similar to that in I_2.

For I_5^-, our predicted structure is very similar to the one found for solid $[N(CH_3)_4^+][I_5^-]$, however the optimized gas phase terminal I−I−I angle is bent by 1.5° from linear toward the outside of the ion whereas the experimental solid state value is bent by 5.5° toward the inside.[64] In addition, I_5^- can be readily distorted in the crystal field, and a linear structure is known from the crystal structure[136] of (trimesic acid·H_2O)$_{10}$$H^+I_5^-$, while that[137] of (phenacetin)$_2$$H^+I_5^-$ has I_3^- and I_2 units. The predicted I_5^- structure at CCSD(T)/ATZ approximates the

Table 1. Calculated Structural Parameters for Selected Ions at the CCSD(T)/aVTZ Level Compared to Experiment

ion	param[a]	calcd	expt[b]
Cl_3^+ (C_{2v})	r(Cl–Cl)	1.994	1.980(1) $[Cl_3^+][AsF_6^-]$[29]
			1.972(1) $[Cl_3^+][SbF_6^-]$[29]
			1.994(1) $[Cl_3^+][SbF_{11}^-]$[29]
			1.983(2) $[Cl_3^+][SbF_{16}^-]$[29]
	∠(Cl–Cl–Cl)	107.5	105.1(4) $[Cl_3^+][AsF_6^-]$[29]
			104.5(1) $[Cl_3^+][SbF_6^-]$[29]
			105.6(7) $[Cl_3^+][SbF_{11}^-]$[29]
			105.1(4) $[Cl_3^+][SbF_{16}^-]$[29]
Cl_3^- ($D_{\infty h}$)	r(Cl–Cl)	2.314	2.227(4), 2.305(3) $[As(C_6H_5)_4]^+Cl_3^-$[52]
		2.313[67]	
	∠(Cl–Cl–Cl)	180.0	177.45 (15) $[As(C_6H_5)_4]^+Cl_3^-$[52]
Cl_5^- (C_{2v})	r_{cen}(Cl–Cl)	2.542	
		2.543[67]	
	r_{ter}(Cl–Cl)	2.143	
		2.155[67]	
	$∠_{center}$(Cl–Cl–Cl)	103.7	
		103.9[67]	
	$∠_{ter}$(Cl–Cl–Cl)	179.3	
Br_3^+ (C_{2v})	r(Br–Br)	2.302	2.270(5) $[Br_3^+][AsF_6^-]$[17]
	∠(Br–Br–Br)	105.6	102.5(2) $[Br_3^+][AsF_6^-]$[17]
Br_3^- ($D_{\infty h}$)	r(Br–Br)	2.585	2.548(1) $[VBr_2(CH_3CN)_4]^+Br_3^-$[51]
I_3^+ (C_{2v})	r(I–I)	2.700	2.660(2), 2.669(2) $[I_3^+][AsF_6^-]$[37]
	∠(I–I–I)	104.1	101.7(6) $[I_3^+][AsF_6^-]$[37]
I_3^- ($D_{\infty h}$)	r(I–I)	2.972	2.9037 (7), 2.9150 (7) $[C_{15}H_{13}N_4O_2S^+][I_3^-]$[68]
		2.982[75]	
	∠(I–I–I)	180.0	176.57 (2) $[C_{15}H_{13}N_4O_2S^+][I_3^-]$[68]
Cl_4^+ (D_{2h})	r(Cl–Cl)	1.957	1.941(3) $[Cl_4^+][IrF_6^-]$[60]
	r(Cl···Cl)	2.975	2.937(3) $[Cl_4^+][IrF_6^-]$[60]
Br_5^+ (C_2)	r_{cen}(Br–Br)	2.552	2.512(1) $[Br_5^+][AsF_6^-]$[35]
		2.554/2.557[72]	
		2.572[72]	2.514(1) $[Br_5^+][AsF_6^-]$[35]
		2.593[77]	
	r_{ter}(Br–Br)	2.302	2.268(2) $[Br_5^+][AsF_6^-]$[35]
		2.316/2.318[72]	2.275(1) $[Br_5^+][AsF_6^-]$[35]
		2.310[72]	
		2.302[77]	
	$∠_{ter}$(Br–Br–Br)	102.7	96.91(4) $[Br_5^+][AsF_6^-]$[35]
		110.9/112.4[72]	97.69(5) $[Br_5^+][AsF_6^-]$[35]
		108.9[72]	
		107.6[77]	
	$∠_{ter}$(Br–Br–Br)	178.7	180.0 $[Br_5^+][AsF_6^-]$[35]
		168.6[72]	
		180.0[72]	
		175.8[77]	
	dihedral	89.7	180.0 $[Br_5^+][AsF_6^-]$[35]
		82[72]	
		91.0[77]	
I_5^+ (C_2)	r_{cen}(I–I)	2.943	2.895(1) $[I_5^+][AsF_6^-]$[63]
	r_{ter}(I–I)	2.700	2.645(1) $[I_5^+][AsF_6^-]$[63]
	$∠_{ter}$(I–I–I)	100.8	97.0 (1) $[I_5^+][AsF_6^-]$[63]
I_5^- (C_{2v})	r_{cen}(I–I)	3.101	3.17 $[N(CH3)_4^+][I_5^-]$[64]
		3.114[73]	
		3.065[75]	
	r_{ter}(I–I)	2.856	2.81 $[N(CH3)_4^+][I_5^-]$[64]
		2.866[73]	
		2.857[75]	
	$∠_{center}$(I–I–I)	103.8	95 $[N(CH3)_4^+][I_5^-]$[64]
		106.0[73]	
		120.8[75]	
	$∠_{ter}$(I–I–I)	178.8	174.5 $[N(CH3)_4^+][I_5^-]$[64]
		178.2[73]	
		176.7[75]	

[a] Bond distances in Å and bond angles in degrees; ter = terminal. [b] All experimental structures are from X-ray crystal structures.

Table 2. Observed and Calculated Frequencies (cm^{-1}) at the CCSD(T)/aVTZ Level

ion	point group	symmetry	frequency calcd	frequency exptl
Cl_3^+	C_{2v}	a_1	503.5	489 $[Cl_3^+][AsF_6^-]^{12}$ $462^{a,33}$
			200.5	225 $[Cl_3^+][AsF_6^-]^{12}$ $236^{a,33}$
		b_2	523.8	508 $[Cl_3^+][AsF_6^-]^{12}$ $515^{a,33}$
Cl_3^-	$D_{\infty h}$	σ_g	261.2	268 $[Pr_4N^+][Cl_3^-]^{55}$ 375 $[NaCl_3]^{b,46}$ 345 $[KCl_3]^{b,46}$ 340 $[RbCl_3]^{b,46}$ 327 $[CsCl_3]^{b,46}$
		σ_u	254.0	268 $[Pr_4N^+][Cl_3^-]^{55}$ 276 $[NaCl_3]^{b,46}$ 258 $[KCl_3]^{b,46}$ 253 $[RbCl_3]^{b,46}$ 225 $[CsCl_3]^{b,46}$
		π_u	158.8	
Br_3^+	C_{2v}	a_1	302.5	293 $[Br_3^+][AsF_6^-]^{17}$ $281^{a,33}$
			102.8	124 $[Br_3^+][AsF_6^-]^{17}$
		b_2	289.6	297 $[Br_3^+][AsF_6^-]^{17}$
Br_3^-	$D_{\infty h}$	σ_g	160.6	168 $[Bu_4N^+][Br_3^-]^{c,56,57}$ 172 $[Me_4N^+][Br_3^-]^{c,45}$ 170 $[Et_4N^+][Br_3^-]^{c,45}$ 177 $[Bu_4N^+][Br_3^-]^{c,45}$ 168 $[PhEt_3N^+][Br_3^-]^{c,45}$ 170 $[PPh_3^+][Br_3^-]^{c,45}$ 156 $[Oct_4N^+][Br_3^-]^{c,45}$ 154 $[CetylMe_3N^+][Br_3^-]^{c,45}$ 162 $[Thiuram][Br_3^-]^{c,d,45}$ 162 $[Bu_4N^+][Br_3^-]^{e,41}$ 163 $[Bu_4N^+][Br_3^-]^{f,41}$ 154 $[K^+][Br_3^-]^{b,46}$
		σ_u	186.0	187 $[Bu_4N^+][Br_3^-]^{c,56,57}$ 191 $[Me_4N^+][Br_3^-]^{c,45}$ 203 $[Et_4N^+][Br_3^-]^{c,45}$ 193 $[Bu_4N^+][Br_3^-]^{c,45}$ 200 $[PhEt_3N^+][Br_3^-]^{c,45}$ 187 $[Oct_4N^+][Br_3^-]^{c,45}$ 206 $[CetylMe_3N^+][Br_3^-]^{c,45}$ 193 $[Thiuram^+][Br_3^-]^{c,d,45}$ 189 $[Bu_4N^+][Br_3^-]^{e,41}$ 192 $[Bu_4N^+][Br_3^-]^{f,41}$ 214 $[K^+][Br_3^-]^{b,46}$
		π_u	87.5	80 $[Et_4N^+][Br_3^-]^{c,45}$ 98 $[Bu_4N^+][Br_3^-]^{c,41}$ 102 $[PhEt_3N^+][Br_3^-]^{c,45}$ 96 $[PPh_3^+][Br_3^-]^{c,45}$ 102 $[CetylMe_3N^+][Br_3^-]^{c,45}$ 104 $[Thiuram^+][Br_3^-]^{c,d,45}$
Br_5^+	C_2	a	308.4 303^{72}	309, 304, 295 $[Br_5^+][AsF_6^-]^{35}$
			165.4 161^{72}	174, 220 $[Br_5^+][AsF_6^-]^{35}$
			104.5 94^{72}	84, 170 $[Br_5^+][AsF_6^-]^{35}$
			36.8 45^{72}	
			17.1 26^{72}	
		b	308.3 300^{72}	305, 295, 290, 275 $[Br_5^+][AsF_6^-]^{35}$
			153.9 180^{72}	260,185 $[Br_5^+][AsF_6^-]^{35}$
			113.1 105^{72}	
			30.0 33^{72}	
I_3^+	C_{2v}	a_1	197.1	207^{13}
			57.6	114^{13}
		b_2	205.0	233^{13}
I_3^-	$D_{\infty h}$	σ_g	112.2	113 $[Bu_4N^+][I_3^-]^{56,57}$
			107.8^{75}	107 $[Me_4N^+][I_3^-]^{58}$
		σ_u	138.7	135 $[Bu_4N^+][I_3^-]^{56,57}$
			129.3^{75}	138 $[Me_4N^+][I_3^-]^{58}$
		π_u	56.8	74 $[Me_4N^+][I_3^-]^{58}$
			58.2^{75}	
I_5^-	C_{2v}	a_1	160.6	155 $[Me_4N^+][I_5^-]^{66}$
			95.1	113 $[Me_4N^+][I_5^-]^{66}$
			57.1	
		a_2	50.4	
		b_1	57.2	
			16.8	
		b_2	142.3	145 $[Me_4N^+][I_5^-]^{66}$
			98.8	83, 76, 74 $[Me_4N^+][I_5^-]^{66}$
			49.4	

[a] Matrix at 12 K. [b] Ar matrix. [c] Salts in the solid state. [d] Thiuram = tetramethylthiuram disulfide. [e] In nitrobenzene solution. [f] In *n*-propanol solution.

previous MP2 values,[73] but deviates from those of a previous DFT study[75] which underestimated the central I–I bond length by 0.04 Å and overestimated the central I–I–I bond angle by 17°.

In the X_5^+ cations, the bond distances of the terminal X_2 groups are very similar to those found in the tri-atomic cations and also in the neutral diatomics. The central X–X bond distances are 0.25 to 0.3 Å longer than the terminal ones. In the penta-atomic anions, the terminal X–X bond distances are 0.15 Å longer than those in the penta-atomic cations, and the central bond distances are 0.25, 0.18, and 0.16 Å longer than those found in the cations. The NBO charge distributions are quite similar for all ions when going from Cl to I, except for X_5^- where the negative charge on the terminal X atom increases significantly on going from Cl to I, while that on the central atom decreases.

Vibrational Frequencies. In Table 2, the harmonic vibrational frequencies, calculated at the CCSD(T)/aVTZ level, are compared with the experimental ones of the ions for which experimental values are known. The harmonic vibrational frequencies of the ions not reported in Table 2 are listed in the Supporting Information. The overall agreement between the computed and experimental frequencies is reasonable, especially considering that the calculated values are harmonic values

Table 3. Components for CCSD(T) Atomization Energies for $X_n^{+/-}$ (X = Cl and Br; n = 1−6) in kcal/mol[a]

reaction	CBS DTQ[b]	CBS Q5[c]	ΔE_{ZPE}[d]	ΔE_{CV}[e]	ΔE_{SR}[f]	ΔE_{SO}[g]	$\sum D_0$ (0 K)[h] DTQ	$\sum D_0$ (0 K)[h] Q5
$Cl_3^+ + e^- \to 3Cl$	−163.11	−161.27	−1.76	0.27	−0.07	−2.52	−167.19	−165.35
$Cl_3^- \to 3Cl + e^-$	167.92	168.55	−1.27	0.20	−0.24	−2.52	164.09	164.72
$Cl_4^+ + e^- \to 4Cl$	−129.33	−127.45	−2.26	0.48	−0.12	−3.36	−134.59	−132.71
$Cl_4^- \to 4Cl + e^-$	158.09	159.13	−2.12	0.29	−0.38	−3.36	152.52	153.57
$Cl_5^+ + e^- \to 5Cl$	−91.54	−88.89	−3.06	0.51	−0.06	−4.20	−98.35	−95.70
$Cl_5^- \to 5Cl + e^-$	236.63	238.07	−2.19	0.48	−0.35	−4.20	230.38	231.82
$Br_3^+ + e^- \to 3Br$	−152.90	−151.98	−0.99	0.27		−10.50	−163.99	−163.07
$Br_3^- \to 3Br + e^-$	162.73	163.15	−0.77	0.90		−10.50	152.27	152.69
$Br_4^+ + e^- \to 4Br$	−122.78	−121.81	−1.29	0.85		−14.00	−137.14	−136.17
$Br_4^- \to 4Br + e^-$	153.01	153.52	−1.21	1.08		−14.00	138.71	139.23
$Br_5^+ + e^- \to 5Br$	−82.74	−81.24	−1.75	1.12		−17.50	−100.86	−99.37
$Br_5^- \to 5Br + e^-$	228.54	229.50	−1.46	1.68		−17.50	211.05	212.01
$I_3^+ + e^- \to 3I$	−133.86	−132.66	−0.67			−15.42	−149.96	−148.76
$I_3^- \to 3I + e^-$	156.37	157.11	−0.55			−18.21	137.60	138.34
$I_4^+ + e^- \to 4I$	−106.93	−105.59	−1.01			−21.70	−129.63	−128.30
$I_4^- \to 4I + e^-$	148.96	149.66	−0.79			−23.47	124.70	125.40
$I_5^+ + e^- \to 5I$	−67.21		−1.15			−27.04	−95.40	
$I_5^- \to 5I + e^-$	220.06		−1.03			−29.62	189.40	

[a] The atomic asymptotes were calculated with R/UCCSD(T). [b] Values extrapolated by using eq 1. aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ with valence electrons only correlated for Cl. aug-cc-pVDZ-PP, aug-cc-pVTZ-PP, and aug-cc-pVQZ-PP valence electrons only correlated for Br. aug-cc-pwCVDZ-PP, aug-cc-pwCVTZ-PP, and aug-cc-pwCVQZ-PP with all electrons correlated for I. [c] Extrapolated by using eq 2. aug-cc-pVQZ, and aug-cc-pV5Z with valence electrons only correlated for Cl. aug-cc-pVQZ-PP and aug-cc-pV5Z-PP valence electrons only correlated for Br. aug-cc-pwCVQZ-PP and aug-cc-pwCV5Z-PP with all electrons correlated for I. [d] The zero point energies for the polyatomic ions were taken as 0.5 of the sum of the harmonic frequencies calculated at the CCSD(T) level with the appropriate triple-ζ basis set. [e] Core−valence correction calculated as the difference in energy between the valence electron correlation calculation and that with the appropriate core electrons included at the CCSD(T) level with the aug-cc-pwCVTZ basis set for Cl and the aug-cc-pwCVTZ-PP basis set for Br. There is no CV correction for I as these electrons are included in the CBS extrapolations. [f] The scalar relativistic correction for Cl is based on a CISD(FC)/VTZ MVD calculation and is expressed relative to the CISD result without the MVD correction, i.e., including the existing relativistic effects resulting from the use of a relativistic effective core potential. There is no additional scalar relativistic correction for Br and I due to the use of effective core potentials. [g] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's Tables. Our I_2 value is −11.7 kcal/mol. [h] The theoretical value of $\sum D_0$ (0 K) was computed with the CBS estimates.

and the experimental values include an anharmonic component. An additional issue is that the experimental data have a countercation or counteranion present and this can complicate the spectra, especially for the trihalides which are known to have asymmetric structures in the solid state.[56,57] Our results clearly show that the use of alkali countercations does not yield symmetric structures for the trianions.

The calculated values for Cl_3^+ are in reasonable agreement with experiment for the two stretches being ~15 cm^{-1} above the stretches for the AsF_6^- salt.[12] The calculated bend is lower than experiment by about 25 cm^{-1}, which could be due to a solid state effect. The calculated results for the σ_g stretch in Cl_3^- are in good agreement with the experimental results for the $[Pr_4N]^+$ salt[55] but not with the results[46] for the alkali ion salts. This suggests that the alkali ion salts are distorted in the matrix, a well-known phenomenon for such anions.[56,57] What is surprising is that the calculated σ_u stretch is in good agreement with all of the salts within 20−30 cm^{-1}, even when the σ_g value is not.

The calculated frequencies for Br_3^+ are in good agreement with the experimental values[17] for the AsF_6^- salt within 20 cm^{-1} with the largest deviation again for the bend. We predict an inverse ordering of the a_1 and b_2 stretches as compared to experiment. For Br_3^-, the calculated values are in good agreement with the available experimental data[41,45,56,57] for all of the different countercations, again within 20 cm^{-1} except for the σ_u stretch for the K^+ salt,[46] which is likely to have a distorted structure in the experiment, just as for Cl_3^-. Note that the order of the σ_g and σ_u stretches switch for Br_3^- (and I_3^-) as compared to Cl_3^- with the $\sigma_g > \sigma_u$ in Cl_3^-. The Br_5^+ frequencies are in reasonable agreement considering the fact that the experimental solid state structure is planar with C_{2h} symmetry and the calculated structure is clearly not planar. This has been previously discussed.[72]

The calculated values for I_3^+ are in reasonable agreement with the experimental values[13] for the stretches, but the calculated bend is a factor of 2 lower than experiment due to solid state interactions or to an incorrect assignment (perhaps the observed band should be assigned as $2\nu_2$) due to the very small value which would be very difficult to observe. The calculated stretches for I_3^- are in good agreement with the experimental stretches for the $[Bu_4N]^+I_3^-$ and $[Me_4N]^+I_3^-$ salts.[56,58] The calculated values for the two stronger outer stretches for I_5^- are in very good agreement with the experimental values[66] for the $[Bu_4N]^+I_5^-$ salt where the I_5^- is bent. The calculations do not agree as well with the lower frequency transitions assigned for the inner I−I stretches, and the differences can be attributed to the role of the counterions in the solid state. The observed bend of 40 to 50 cm^{-1} is consistent with the predicted bends.

Thermochemistry. We first discuss the components to the total dissociation energies in Table 3. The differences between the two extrapolation approaches to the CBS limit are not large with the largest being 1.5 kcal/mol for Br_5^+. We were unable to do the calculations at the aug-cc-pV5Z-PP level for $I_5^{+/-}$ as we are correlating all of the outer core electrons and these calculations become computationally too expensive. The heats of formation with the Q5 extrapolation are more negative than the DTQ extrapolated values. The most likely value usually falls between the DTQ CBS and Q5 CBS extrapolated values[103] with the Q5 values usually closer to experiment.

The core−valence correction increases from Cl to Br to I reaching a maximum value for 1.7 kcal/mol for bromine, clearly showing that it should not be neglected. There are none for iodine since the outer core electrons are included in the CBS calculations.

There are two relativistic corrections that need to be considered. The scalar relativistic corrections for the chlorine compounds are small. There are none for the bromine and iodine compounds due to the use of an effective core potential. The atomic spin−orbit corrections for the halogen atoms are not small and are included for the chlorine and iodine compounds. Molecular second-order spin−orbit corrections also need to be included for the iodine compounds. The spin−orbit correction for I_2 is −12.4 kcal/mol (−14.4 kcal/mol for the atoms plus a 2.0 kcal/mol second-order correction for the diatomic from a second-order molecular spin−orbit effect calculation obtained with augmented triple-ζ basis set and a relativistic ECP[116]). Our simpler DFT approach gives a value of −11.7 kcal/mol for I_2, suggesting a possible error of ∼0.4 kcal/mol per I atom in the dissociation energies due to the spin−orbit effects. The spin−orbit corrections for the iodine ions exhibit some interesting properties. The molecular SO correction for I_3^+ (6.2 kcal/mol) is larger than that for I_3^- (3.4 kcal/mol) by almost a factor of 2. The molecular SO corrections are larger for I_4^+ (7.1 kcal/mol) than found for I_4^- (5.3 kcal/mol). Again, a larger SO molecular correction is predicted for I_5^+ (9.0 kcal/mol) than for I_5^- (6.4 kcal/mol). Thus, there seems to be a minimum of about 1 kcal/mol/I atom molecular SO correction in these systems.

The calculated enthalpies of formation are summarized in Table 4. Experimental heats of formation for X_3^- have been derived from X^-−X_2 bond dissociation energies for X = Cl, Br, and I, and those for X_5^- from X_3^-−X_2 bond dissociation energies for X = Br and I. The calculated value of −78.2 kcal/mol for Cl_3^- is in excellent agreement with the experimental one of −77.9 ± 1.2 kcal/mol,[38] as is the value of −73.2 kcal/mol for Br_3^- compared to the experimental one of −73.9 ± 1.7 kcal/mol.[38] The experimental value for I_3^- is −60.2 ± 1.4 kcal/mol,[39] and the computational results are in good agreement with the experimental value, being slightly more negative. There is a slightly larger difference between the computational and experimental results for Br_5^- with an experimental value of −75.5 ± 2.4 kcal/mol.[38] The calculated value shows a 6.5 kcal/mol difference from the experimental value of −56.6 ± 2.2 kcal/mol for I_5^-.[39] This difference is larger than would be expected from the current work on I_3^-, and prior work on IF_x and IF_xO_y.[92,93] This difference is discussed in more detail below in terms of the reaction energies.

Table 4. Calculated Enthalpies of Formation (kcal/mol) at 298 K

ion[a]	ΔH_f(DTQ)[a]	ΔH_f(Q5)[b]	$\Delta\Delta H_f$(DTQ−Q5)[c]
Cl_3^+	253.0	252.7	0.3
Cl_3^-	−78.3	−78.2	−0.1
Cl_4^+	248.9	248.4	0.5
Cl_4^-	−38.2	−39.0	0.8
Cl_5^+	241.3	240.7	0.6
Cl_5^-	−87.4	−87.6	0.2
Br_3^+	243.1	242.2	1.1
Br_3^-	−72.7	−73.2	0.5
Br_4^+	242.5	241.5	1.0
Br_4^-	−34.4	−34.9	0.5
Br_5^+	232.2	230.7	1.5
Br_5^-	−79.0	−79.9	0.9
I_3^+	225.6	224.4	1.2
I_3^-	−61.6	−62.3	0.7
I_4^+	230.2	228.9	1.3
I_4^-	−25.1	−25.7	0.7
I_5^+	220.5		
I_5^-	−63.1		

[a] From eq 1 CBS extrapolation + additional corrections. [b] From eq 2 CBS extrapolation + additional corrections. [c] $\Delta\Delta H_f$(DTQ−Q5) = ΔH_f(DTQ) − ΔH_f(Q5).

The enthalpies of formation can be used to calculate the energetics of various reactions as shown in Table 5. The experimental atomic energies at 298 K were used.[119] The experimental electron affinities[138−140] and ionization potentials[141] were used to obtain the heat of formation of the anions and cations respectively in the ion convention excluding the enthalpy of the electron. For the reaction enthalpy for $Cl_3^+ \rightarrow Cl^+ + Cl_2$, lower level calculations at the DFT (78.0 kcal/mol) and MP2 (70.1 kcal/mol) levels[32] are in good agreement with our higher level values, as is the previous CCSD(T)/cc-pVQZ value[32] of 73.2 kcal/mol. Our calculated values for the X^-−X_2 bond dissociation energies for X = Cl, Br and I are the best available. They are in good agreement with other CCSD(T) values for X = Cl and Br with smaller basis sets and without additional corrections, although the comparison is difficult as the exact definition of the thermodynamic quantity is not defined. For X = I, the difference is larger, due to the use of a smaller basis set in the prior work. The dissociation energies for $X_5^- \rightarrow X_3^- + X_2$ for X = Cl and Br with smaller basis sets are in good agreement with our values.

The X^-−X_2 bond dissociation energies from flowing afterglow experiments are 23.7 ± 1.2, 30.4 ± 1.7, and 30.1 ± 1.4 kcal/mol for X = Cl, Br, and I. These are in excellent agreement with the calculated values with the largest difference being 2 kcal/mol for X = I. The experimental bond dissociation energies for $X_5^- \rightarrow X_3^- + X_2$ for X = Br and I are 9.6 ± 1.7 and 11.2 ± 1.4 kcal/mol, respectively. These values are 4.1 kcal/mol for X = Br and 5.0 kcal/mol for X = I below the calculated values. The errors in the calculations are unlikely to be more than 1 kcal/mol for these reaction energies for three closed shell species. In addition, any second-order relativistic effects will approximately cancel for these reactions. As the experimental heats of formation[38,39] for Br_5^- and I_5^- are derived from these reaction energies, the results strongly suggest an issue with the experimental reaction clustering energies. At 298 K,

Table 5. Calculated Reaction Energies (kcal/mol) at 298 K[a]

reaction	ΔH_{rxn}(DTQ)[b]	ΔH_{rxn}(Q5)[c]
$Cl_3^+ \rightarrow Cl^+ + Cl_2$	75.4	77.2
$Cl_4^+ \rightarrow Cl_3^+ + Cl$	33.2	33.3
$Cl_5^+ \rightarrow Cl_4^+ + Cl$	36.7	37.5
$Cl_5^+ \rightarrow Cl_3^+ + Cl_2$	12.0	12.8
$Cl_5^+ \rightarrow 2Cl_2 + Cl^+$	87.3	90.0
$Cl_3^- \rightarrow Cl^- + Cl_2$	23.8 24.5[67]	24.4
$Cl_4^- \rightarrow Cl_3^- + Cl$	−10.2	−9.7
$Cl_5^- \rightarrow Cl_4^- + Cl$	77.6	78.0
$Cl_5^- \rightarrow Cl_3^- + Cl_2$	9.4 9.0[67]	10.2
$Cl_5^- \rightarrow 2Cl_2 + Cl^-$	33.2	34.7
$Br_3^+ \rightarrow Br^+ + Br_2$	62.8	63.7
$Br_4^+ \rightarrow Br_3^+ + Br$	29.4	29.5
$Br_5^+ \rightarrow Br_4^+ + Br$	38.9	39.5
$Br_5^+ \rightarrow Br_3^+ + Br_2$	19.4	20.0
$Br_5^+ \rightarrow 2Br_2 + Br^+$	82.2	83.7
$Br_3^- \rightarrow Br^- + Br_2$	30.2 30.4[80]	30.6
$Br_4^- \rightarrow Br_3^- + Br$	−11.5	−11.4
$Br_5^- \rightarrow Br_4^- + Br$	71.3	71.8
$Br_5^- \rightarrow Br_3^- + Br_2$	13.7 13.5[80]	14.2
$Br_5^- \rightarrow 2Br_2 + Br^-$	43.9	44.8
$I_3^+ \rightarrow I^+ + I_2$	55.6	56.8
$I_4^+ \rightarrow I_3^+ + I$	20.9	21.1
$I_5^+ \rightarrow I_4^+ + I$	35.3	
$I_5^+ \rightarrow I_3^+ + I_2$	19.8	
$I_5^+ \rightarrow 2I_2 + I^+$	75.5	
$I_3^- \rightarrow I^- + I_2$	31.2 27.2[75]	32.0
$I_4^- \rightarrow I_3^- + I$	−11.0	−10.9
$I_5^- \rightarrow I_4^- + I$	63.5	
$I_5^- \rightarrow I_3^- + I_2$	16.2	
$I_5^- \rightarrow 2I_2 + I^-$	47.4	

[a] Ionization potential (Cl) = 12.96764 eV, electron affinity (Cl) = 3.612709 ± 0.000087 eV, ionization potential (Br) = 11.81381 eV, electron affinity (Br) = 3.363583 ± 0.000044 eV, ionization potential (I) = 10.45126 eV, and electron affinity (I) = 3.05900 ± 0.00010 eV. [b] From ΔH_f(DTQ) values in Table 4 plus atomic or atomic ion heats of formation from experiment. [c] From ΔH_f(Q5) values in Table 4 plus atomic or atomic ion heats of formation from experiment.

Cl_5^- was not observed in the flowing afterglow. This is not surprising as the reaction enthalpy for $Cl_5^- \rightarrow Cl_3^- + Cl_2$ is predicted to be 9.4 kcal/mol at the DTQ level and 10.2 kcal/mol at the Q5 level. The entropies of the various species can be calculated from the structures and vibrational frequencies giving a $T\Delta S$ term of 8.6 kcal/mol at 298 K. Thus, the free energy will only be slightly negative making it very difficult to observe Cl_5^- under the experimental conditions of the flowing afterglow, consistent with our reaction energy prediction. In addition, the low dissociation energy for loss of Cl_2 from Cl_5^- is consistent with the ease of distorting the Cl_5^- from a V-shape to a distorted L-shape in the crystal.

The Cl^- affinity of Cl_2 is lower than that for Br^- with Br_2, and the I^- affinity of I_2 is comparable to the Br^- affinity of Br_2. We predict that X_4^- will dissociate to give a tri-atomic anion and a halogen atom. The tetra-atomic anion is therefore a metastable species with respect to dissociation but is bound in a well as shown by all positive second derivatives (all real frequencies). We note that Cl_5^+ will lose Cl_2 with a binding energy of less than 13 kcal/mol, so, on a free energy scale, it is likely to decompose close to 300 K depending on any additional barriers to Cl_2 loss. Br_5^+ and I_5^+ both have a larger X_2 binding energy, close to 20 kcal/mol, but are going to be sensitive to loss of X_2. Cl_5^- is also likely to lose Cl_2 and will do so at a lower temperature than the cation. Br_5^- and I_5^- are more stable with respect to loss of the corresponding X_2, but again can readily release X_2 at higher temperatures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete citations for references122 123, and 124. Calculated structural parameters for selected ions at the CCSD(T)/aVTZ level. Harmonic frequencies for all of the compounds. Optimized geometries using CCSD(T)/aug-cc-pVTZ. Electronic energies used in the calculation of the total atomization energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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