Paradigms and paradoxes: the ionization potential of atomic astatine \((Z=85)\), polonium \((Z=84)\), and some other elements—what does this value tell us about the energetics of atomic and diatomic halogens

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Abstract

The newly measured ionization potential of atomic astatine is discussed and compared with that of the recently determined value for polonium and for the other atomic halogens. Regularities in these atomic values are discussed and applied to the understanding of the energetics of diatomic halogens. Some surprises remain.

Keywords Astatine · Polonium · Fluorine · Halogens · Ionization potentials · Diatomic halogens

Introduction

Let us talk of species with chemical simplicity. Atoms are simpler than molecules. The simplest of elements are those for which \(s\) and \(p\) orbitals are “adequate” for their description of their atoms and for the formation of diatomic and larger molecules therefrom. We recognize these simplest elements as “main group,” “non-transition,” or “\(s\)-” and “\(p\)-block,” as opposed to the more complicated “transition metals” or “\(d\)-block” elements, never mind the “lanthanides (rare earth) and actinides” or “\(f\)-block.” In the current study, we limited our discussion mostly to the halogens, \(F\), \(Cl\), \(Br\), \(I\), and \(At\).

Among the uniquely defined and conceptually simplest properties of any element is its ionization potential (IP), the least amount of energy to remove one electron from the gaseous atomic species. This quantity is formally a simple chemical property and thus is definitionally not affected by compound formation, solution, salt, and any other intra- or intermolecular environment. Homonuclear diatomics (\(F_2, Cl_2, Br_2, I_2, At_2\)) and the related ions formed by the loss of an electron to form the related radical cation are among the simplest molecules to understand. Recently, HOMO-LUMO energy difference was related to between the IP and electron affinity (EA) difference to assist in deducing the colors and chromophores in elemental nonmetals focusing on compounds with lone pair bonds and \(\sigma\) electrons (\(X = F_2, Cl_2, Br_2, I_2, S_8, P_4\)) [1]. The EAs of the halogens were discussed as part of the understanding of the oxidizing powers of these elements [2].

In this study, we seek regularities in the molecular ionization potentials, in particular for the understanding of the chemistry of high \(Z\) elements. All energy quantities are given in electron volts, where we remind the reader that \(1 \text{ eV} \approx 23.06 \text{ kcal mol}^{-1} \approx 96.5 \text{ kJ mol}^{-1}\).

Atomic ionization potentials: measurements and regularities

The measurements of the ionization potential of the majority of the main group elements have been made and then have been collected and presented in a single, quite brief, now 50-year-old database [3]. In this now classic compendium, there are but two non-transition elements...
that are lacking their measured ionization potentials. These are the heavy halogen, astatine (At) with atomic number \(Z = 85\), and the even heavier alkali metal (Fr) with \(Z = 87\). Quite recently, this long-term missing value for astatine has been experimentally determined to high precision as \(9.31751 \pm 0.00008\) eV [4]. The literature value of the ionization potential of astatine’s neighboring elements, polonium (Po) with \(Z = 84\), is even more recent and even more precise presented as \(8.418072 \pm 0.000015\) eV [5], while that of francium (Fr) with \(Z = 87\) the likewise highly precise as \(4.0712 \pm 0.00004\) eV [6].

Soon after the publication of the aforementioned database ago [3], one of the current paper’s authors (JFL) published a brief note presenting simple numerical regularities for the values of the ionization potentials of the main group elements [7]. One such pattern asserts that for a given row in the periodic table, the sum of the ionization potential for the relevant alkali metal (group 1) and of the corresponding halogen (group 17) is nearly equal to those for the alkaline earth (group 2) and that of the chalcogen (group 16) elements. The rule can be written as

\[
\text{IP}(\text{group 1}) + \text{IP}(\text{group 17}) \approx \text{IP}(\text{group 2}) + \text{IP}(\text{group 16})
\]

(1)

For example, IP(Li) + IP(F) \(\approx\) IP(Be) + IP(O). Numerically, the two sums equal 22.81 and 22.91 eV, respectively. From the use of this approximation, we therefore suggest that

\[
\text{IP}(\text{Cs}, Z = 55) + \text{IP}(\text{At}, Z = 85) \approx \text{IP}(\text{Ba}, Z = 56) + \text{IP}(\text{Po}, Z = 84)
\]

(2)

Using the suggested ionization potentials of all four elements from the above sources [3–5], we derive the desired sums \(\text{IP}(\text{Cs}) + \text{IP}(\text{At})\) and \(\text{IP}(\text{Ba}) + \text{IP}(\text{Po})\) as \(13.21\) and \(13.63\) eV, respectively. The difference of the two sums is \(0.42\) eV and exceeds the combined uncertainties from experiment. Nonetheless, it is but a 3\% difference, encouragingly small give how little effort was needed to derive the sums of interest.

This encourages us now to consider the sum corresponding to that of the neighboring (inter-row) and even higher atomic number elements of the periodic table. In the particular, let us consider IP(\(\text{Fr}, Z = 87\)), IP(\(\text{Ts}, Z = 117\)), IP(\(\text{Ra}, Z = 88\)), and IP(\(\text{Lv}, Z = 116\)). More explicitly, we would expect IP(\(\text{Fr}) + \text{IP}(\text{Ts}) \approx \text{IP}(\text{Ra}) + \text{IP}(\text{Lv})\). Neither surprisingly nor disappointingy, the input values for the ionization potentials of the high Z elements (\(Z = 116\) and \(Z = 117\)) remain unmeasured, and thus we accept the high-level calculated values of 6.855 and 7.654 eV, respectively [8]. The experimental values of 5.279 eV [3] and 4.0712 ± 0.00004 eV [6] were taken for IP(Ra) and IP(Fr). The two sums are 11.73 and 12.13 eV, respectively. The difference of the two sums is \(0.40\) eV which exceeds the uncertainties from experiment but less than 4\%, again encouragingly small.

The aforementioned rule (Eq. 1) can be extended [7] to isoelectronic and thus even more cationic species. For example, using this rule and recognizing Be\(^+\) is isoelectronic with Li and Ne\(^+\) with F, B\(^+\) with Be, and F\(^+\) with O, we can correctly suggest IP(\(\text{Be}) + \text{IP}(\text{Ne}) \approx \text{IP}(\text{B}) + \text{IP}(\text{F})\). The two sums are \(59.17\) and \(60.13\) eV, respectively. The sum regularity so continues through at least the 17th ionization potentials of elements with appropriate atomic numbers.

What about anions where the relevant energy quantity is the electron affinity (EA, binding energy of an added electron, IP(\(X^–\) = EA(\(X\)))? What about the corresponding sums (IP(\(\text{He}^–\) + IP(\(\text{O}\)) and (IP(\(\text{Li}^–\) + IP(\(\text{N}\))), quantities more often written as (EA(\(\text{He}^–\) + EA(\(\text{O}\)) and (EA(\(\text{Li}^–\) + EA(\(\text{N}\))), respectively? Both \(\text{He}^–\) and \(\text{N}^–\) are unbound relative to the loss of an electron to form the neutrals \(\text{He}\) and \(\text{N}\): the electron affinities (EA) of these atoms are negative [9], and so we are thwarted in the application of our regularity.

**Atomic halogens: ionization potentials and electron affinities**

Atomic ionization potentials [3] increase in the order At (9.31751 ± 0.00008 eV) [4] < I (10.45 eV) < Br (11.81 eV) < Cl (12.91 eV) < F(17.42 eV). We expect metallic behavior, as defined by ionization potentials and the ease of forming cations, to decrease as we proceed up a column in the periodic table. Surprising perhaps, however, is that the electron affinities vary in the order: At \((2.41578 ± 0.00007\text{eV})\) [10] < I \((3.059038 ± 0.000010\text{eV})\) [11] < Br \((3.363590 ± 0.000003\text{eV})\) [12] < Cl \((3.612642 ± 0.000027\text{eV})\) [13] > F \((3.401190 ± 0.000004\text{eV})\) [12]. Albeit using much less precise values of the relevant electron affinities available, the comparatively low electron affinity of fluorine, when compared to the values of other halogens, has long been noted [14, 15]. More recently, this value has been interrelated with those from additional anomalies for nearby elements [2, 16, 17]. Based on these studies [2, 15–17], we accept the conclusion that having a completed octet for fluorine is accompanied by destabilization of ca. 1.2 eV [14].

**Homonuclear diatomics of the halogens: ionization potentials and electron affinities**

The ionization potentials of the homonuclear diatomics formed by the halogens (\(\text{F}_2, \text{Cl}_2, \text{Br}_2, \text{I}_2, \text{At}_2\)) increase as we proceed up the periodic table in the order: \(\text{At}_2\) (8.3 eV, an early estimate) [18] < \(\text{I}_2\) (9.30 eV) [19] < \(\text{Br}_2\) (10.52 eV) [20] < \(\text{Cl}_2\) (11.48 eV) [20] < \(\text{F}_2\) (15.70 eV) [21].
Using Hess’ law, we derive the difference of the dissociation energy of a species \([X_2]^+\) and \(X_2\) as the difference of the ionization potentials of \(X\) and \(X_2\). Accordingly, from the numbers given earlier in this study, we find that the dissociation energy of \([F_2]^+\) is 1.72 eV higher than that of \(F_2\). For the corresponding species with \(Cl\), \(Br\), and \(I\), the differences of the cation and neutral are 1.42, 1.29, and 1.15 eV, respectively. The diatomic cation has a dissociation energy higher than that of the corresponding neutral is sensible. The ionization process corresponds to the “removal” of an antibonding \(\pi^*\) electron from the neutral. It may be said that the diatomic \([X_2]^+\) species have one fewer atom with 8 electrons than the diatomic neutral \(X_2\) species and so, \([F_2]^+\) gains stabilization relative to \(F_2\) consistent with the logic of Politzer [14].

In relation to ionization potentials of the dihalogens, we now consider the electron affinities and the corresponding anions \([X_2]^−\). The electron affinity equals 3.01 eV for \(F_2\) [22], 2.50 eV for \(Cl_2\) [23], 2.62 eV for \(Br_2\) [24, 25], and 2.52 eV for \(I_2\) [26]. In other words, the electron affinity of the dihalogens decreases in the order \(F_2 > Cl_2 \approx Br_2 \approx I_2\). This seems reasonable until it is remembered that the electron affinities of the atomic halogens follow the order \(F (3.40 \text{ eV}) < Cl (3.61 \text{ eV}) < Br (3.36 \text{ eV}) < I (3.06 \text{ eV})\). In all cases, the electron affinity of the diatomic halogen is smaller than that of the atomic constituent. Thus, the bond energy for \([X_2]^−\) is smaller than that of neutral \(X_2\). This is a logical consequence of a half-occupied antibonding \(\sigma^*\) molecular orbital in the anion that was hitherto unoccupied in the neutral diatomic.

Said differently, the formal reaction

\[
X + [X_2]^− \rightarrow X^- + X_2
\]

is exothermic by 0.39, 0.99, 0.84, and 0.54 eV for \(F, Cl, Br,\) and \(I\), respectively. This reaction has the least exothermicity for \(X = F\). From these values, we deduce that completing an octet for atomic fluorine, cf. \(F^–\), provides less stabilization than the other atomic halogens, cf. \(Cl^−, Br^−, I^−\). This finding is consistent with Politzer [14] and also our earlier analysis made during discussion of the energetics of atomic and diatomic halogen cations.

**Conclusion**

We conclude our paper on the energetics of high \(Z\) atoms (\(Z = 84\) and \(Z = 85\) and their even higher \(Z\) congeners) and of small and simple halogen-containing ions (in the particular, monoatomic, and diatomic species). Simple additivity regularities for ionization potentials have been shown in this study. Fluorine paradoxes were discussed, e.g., lower EA of \(F(3.401190 \pm 0.000004 \text{ eV})\) in comparison to that of \(Cl(3.612642 \pm 0.000027 \text{ eV})\) and less stabilization on completing an octet for atomic fluorine, cf. \(F^−\), than the other atomic halogens, cf. \(Cl^−, Br^−, I^−\). Thus, the study of small and simple species is rightfully recognized as wonderfully rich and complicated.

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**Conflict of interest** All authors declare no conflicts of interest.

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