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The first and second ionization energies of the element 119: absolute hardness and Mulliken electronegativity for the cation 119^+ based on an empirical equation involving absolute hardness

Robson F. de Farias

Universidade Federal do Rio Grande do Norte, Cx. Postal 1664, 59078-970, Natal-RN, Brasil.
E-mail: robdefarias@yahoo.com.br

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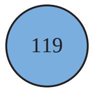
The following empirical equation was derived: U_{POT} = = $(-0.494r^+ + 122.392)(\eta^+ + \eta^-) - 109.514\eta^+ + 1191.694$ kJ mol^{-1}, where r^+ is the cation radius (pm), η^+ is the absolute hardness of the cation, and η^- is the absolute hardness of the anion. This equation in conjunction with Kapustinskii lattice energy values for element 119 halides was employed to calculate the first and second ionization energies of 4.04 and 20.72 eV, respectively; for the monocation 119^+, r^+ = 202.2 pm, η^+ = 8.34 and η^+ = 12.38. Furthermore, the second ionization energy for francium was calculated as 23.80 eV.



$119 \longrightarrow 119^+ + e^-$; 4.04 eV
$119^+ \longrightarrow 119^{2+} + e^-$; 20.72 eV

The search for new chemical elements resulted in the discovery of the elements 111–118 with some works dedicated to investigate/estimate/predict the properties of such elements.[1–5]

Despite the theoretical/computational efforts/improvements, depending on the chosen theoretical approach, the estimated values for a series of parameters (atomic radius, polarizability, *etc.*) can vary in a wide range. Because of the absence of experimental data for the majority of so-called superheavy elements, extrapolations and empirical equations can be a successful approach.[1]

Hence, and ironically, a primitive approach used since the times of Mendeleev can be employed to decide what theoretical approach is or is not reliable.

As recently shown,[6] straightforward relationships between the chemical hardness and the thermochemistry of cations make it possible to establish empirical equations relating chemical hardness[7] and a series of structural and atomic parameters.

In this work, an empirical equation based on the absolute hardness of Group I halides was employed in order to calculate some physical properties for the element 119 and its monocation, 119^+.

By means of the proposed empirical equation, trustable values of the physical properties of superheavy elements can be calculated, with the results consistent with related values obtained by quantum chemical relativistic calculations.

Using the values of absolute hardness (eV) for Li^+ (35.12), Na^+ (21.08), K^+ (13.64), Rb^+ (11.56) and Cs^+ (9.61); F^- (7.01), Cl^- (4.70), Br^- (4.24) and I^- (3.70), and reference values for the lattice energies of halides, the following empirical equation was derived:

$$U_{POT} = (-0.494r^+ + 122.392)(\eta^+ + \eta^-) - 109.514\eta^+ + 1191.694 \text{ kJ mol}^{-1}, \quad (1)$$

where r^+ is the cation radius (pm); η^+ is the cation absolute hardness (eV) and η^- is the anion absolute hardness (eV). Equation (1) shows that the lattice energy depends on only the anion absolute hardness.

The absolute hardness is η = (IE – EA)/2, where IE is the ionization energy, and EA is the electron affinity.

For each group of halides, a specific empirical equation with very high accuracy can be derived. For lithium halides, for example, $U_{POT} = 89.232(\eta^+ + \eta^-) - 2726.668$ (r = 0.999).

However, despite some lack of accuracy, the derived general equation can be applied for any Group I metal halide.

Using the cation radii (coordination number, 6) (pm)[8] of K^+ (138), Rb^+ (152), Cs^+ (167) and Fr^+ (180) and by extrapolation (plotting the M^+ radius as a Z function), the 119^+ radius was estimated at 202.20 pm. The obtained curve of r_{M^+} as a Z function is shown in Figure 1. From it, the following equation was derived: $r^+ = 0.618Z + 128.653$ (r^2 = 0.9844; sd = 3.9244). In the curve, the lighter elements of the group (Li and Na) were excluded in order to obtain a more realistic estimation to the heavier elements. For comparison, the curve of r_{M^+} as a Z function from Li to Fr is shown in Figure 2.

This value is in good agreement with a value of 215.9 pm calculated for the neutral atom[5] (in the sense that the cation radius should be, of course, shorter than the radius of the neutral atom).

As a self consistency test, the lattice energies for Li^+ to Cs^+ halides were calculated using equation (1) (Table 1).

As a first test, equation (1) was applied to Fr^+. Using the Kapustinskii equation[9] and a Fr^+ radius of 180 pm,[8] the lattice energies for francium halides can be calculated as 687.94, 606.30, 584.56 and 552.82 kJ mol^{-1} for FrF, FrCl, FrBr and FrI, respectively.

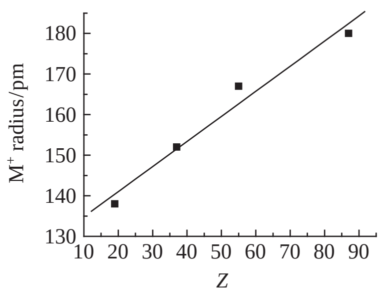


Figure 1 Cation radius as a Z function for K^+, Rb^+, Cs^+ and Fr^+.

Table 1 Lattice energy values for Li to Cs halides.

Compound	U_{POT}/ kJ mol^{-1} (ref.)	U_{POT}/ kJ mol^{-1} (calc.)	Δ (%)	Compound	U_{POT}/ kJ mol^{-1} (ref.)	U_{POT}/ kJ mol^{-1} (calc.)	Δ (%)
LiF	1030	920	–10.7	KBr	671	667	–0.6
LiCl	834	724	–13.2	KI	632	638	+0.9
LiBr	788	685	–13.1	RbF	774	804	+3.9
LiI	730	639	–12.5	RbCl	680	695	+2.2
NaF	910	906	–0.4	RbBr	632	673	+6.5
NaCl	769	739	–3.9	RbI	617	648	+5.0
NaBr	732	706	–3.6	CsF	759	802	+5.7
NaI	682	667	–2.2	CsCl	670	710	+6.0
KF	808	818	+1.2	CsBr	647	692	+7.0
KCl	701	692	–1.3	CsI	613	670	+9.3

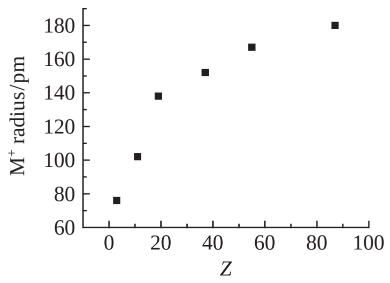


Figure 2 Cation radius as a *Z* function from Li$^+$ to Fr$^+$.

Applying these values in equation (1), the absolute hardness of Fr$^+$ can be calculated as 9.71, 9.77, 9.85 or 10.03 eV, respectively, with a mean value of 9.84 eV.

Using the χ^+ and η^+ values for Li$^+$ to Cs$^+$ is was verified that $\chi^+ = 1.057\eta^+ + 3.564$. Therefore, using $\eta^+ = 9.84$ eV calculated for Fr$^+$, the Mulliken electronegativity for such a cation can be calculated as 13.96 eV.

By the use of definitions of η and χ and substitution of the respective values in both equations, the IE and EA values can be calculated as 23.80 and 4.12 eV, respectively.

Note that the IE for the monocation corresponds to the second ionization energy for the neutral atom and that the EA for the monocation corresponds to the first IE for the neutral atom. Hence, the value of 4.12 eV calculated for the EA of Fr$^+$ is consistent with an experimental value[10] of 4.07 eV for the first IE for francium.

Hence, the reliability of the proposed equation and procedures was established. Of course, 23.80 eV is the value for the second ionization energy of francium.

Based on the Kapustinskii equation,[9] the lattice energies for 119$^+$ halides can be calculated as 651.44, 574.67, 555.10 and 526.35 kJ mol^{-1} for 119F, 119Cl, 119Br and 119I, respectively. Applying these values in equation (1), the absolute hardness for 119$^+$ can be calculated as 8.02, 8.31, 8.41 or 8.60 eV, respectively, with a mean value of 8.34 eV.

The Mulliken (or absolute) electronegativity is $\chi = (\mathrm{IE} + \mathrm{EA})/2$. Using the values of χ^+ and η^+ for Li$^+$ to Cs$^+$, the curve shown in Figure 3 was obtained, from which the following equation ($r^2 = 0.9998$; sd = 0.2528) was derived:

$$\chi^+ = 1.057\eta^+ + 3.564 \text{ eV}. \qquad (2)$$

Therefore, using the η^+ value of 8.34 eV calculated for 119$^+$, the Mulliken electronegativity of 12.28 eV can be calculated for this cation.

Using the definitions of η and χ and substituting the respective values in both equations, the IE and EA values can be calculated as 20.72 and 4.04 eV, respectively (Table 2).

As previously highlighted, the IE for the monocation corresponds to the second IE for the neutral atom, and the EA for the monocation corresponds to the first IE for the neutral atom. Therefore, first and second IEs for the element 119 are 4.04 and 20.72 eV, respectively.

Table 2 Calculated properties for the element 119 and cation 119$^+$.

Chemical species	Absolute hardness η^+/eV	Mulliken electronegativity χ^+/eV	1st IE/ eV	2nd IE/ eV
Element 119			4.04	20.72
Cation 119$^+$	8.34	12.38		

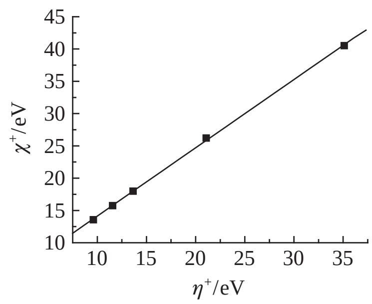


Figure 3 Absolute electronegativity as a function of absolute hardness, from Li$^+$ to Cs$^+$.

The first IEs (eV) for the other Group I elements are as follows: Li (5.39), Na (5.14), K (4.34), Rb (4.18), Cs (3.94) and Fr (4.07). The value of 4.04 eV calculated for the element 119 is in agreement with the increase observed from Cs to Fr as a consequence of relativistic contributions.[11,12] This value is also in very good agreement with the previous calculated values of 4.78[12] and 3.69–3.80 eV,[13] that is, the published (relativistic quantum chemical calculations) values from 3.69 to 4.78 eV with the value estimated in this work (4.04 eV) are very close to the mean calculated value of 4.24 eV.

Furthermore, the calculated second ionization energy (20.72 eV) is in very good agreement with the previously calculated value of 20.3–21.4 eV.[13]

Regarding the first IEs for Fr (4.07 eV) and element 119 (4.04 eV), based on a relativistic contraction,[11] one can expect an increase from Fr to element 119, which is not the case. This fact is in agreement with the hypothesis (based on the estimation and comparison with published quantum chemical data for the element 119 polarizability) that, for element 119 (the first one of the 8th row of the periodic table), the relativistic contributions have been overestimated and that an 'attenuation' of the relativistic effects could be expected for elements 119, 120 and beyond.

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