Absolute Correlation Between Ionization and Hydration Energies for Cations

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Abstract

Calculations of hydration energies are extremely important in physical, chemical and life sciences, and therefore their values need to be accurately determined if these energies were to be used to derive the proper and correct physico-chemical mechanisms. Here, we prove the existence of absolute correlation between ionization and hydration energies for transition-metal cations. The said absolute correlation can be exploited in an unambiguous manner to verify the calculated hydration energies for divalent and trivalent transition metal cations.

Keywords: Hydration energy; Ionization energy; Transition metal cations; Renormalized interaction theory; Atomic polarizability.

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§1. Introduction

The primary aim of this report is to prove the existence of a proper (absolute) correlation between ionization energy and hydration energy for transition-metal divalent and trivalent cations. This is our novel result that has important application to predict the distribution of hydration energies for different cations and valence states. Here, absolute or one-to-one correlation means the following average ionization energy (ξ) inequality, $\xi_{\mathrm{A}^{x+}} > \xi_{\mathrm{B}^{x+}} > \cdots$ always imply the following hydration energy ($\mathit{\Delta} H_{\mathrm{hyd}}$) inequality, $\mathit{\Delta} H_{\mathrm{hyd}}(\mathrm{A}^{x+}) > \mathit{\Delta} H_{\mathrm{hyd}}(\mathrm{B}^{x+}) \cdots$ for the listed cations (A^{x+}, B^{x+}, $\cdots$) and for a given valence state, $x+$. In addition, proving the said correlation means that we shall provide the microscopic physics to validate the above implication between ionization and hydration energies. In particular, we shall expose the said correlation as absolute or one-to-one such that higher ionization energy of a given cation (of valence state $v+$) implies its hydration energy has also got to be higher, compared to a cation (of valence state $v+$) with lower ionization energy. Note this, if the valence state for cation A^{2+} is $x+ = 2+$, then $\xi_{\mathrm{A}^{2+}}$ refers to the summed first and second ionization energies of atomic A and divided by 2.

It turns out that the correlation between ionization and hydration energies has been observed much earlier in 1983 by House, Reif and Daniel House.[1] They were the first to calculate the general correlation (between hydration and ionization energies) for different cations with different valence states (1+, 2+ and 3+). The motivation behind their correlation is that if hydration enthalpy could be related to the effective radii of ions (from the relation, $\mathit{\Delta} H_{\mathrm{Hyd}} = -166Z^2/r_{\mathrm{eff}}$ kcal·mole^{-1}), then so does ionization energy, for a given charge (or valence state).[1] Here, the effective radius, r_{eff} denotes the apparent radius of an ion in the presence of solvent (in Å) and Z is the charge of the ion. Second, a linear relation is assumed[1] between hydration and ionization energies, which is defined by, $\mathit{\Delta} H_{\mathrm{Hyd}}(\mathrm{kcal{\cdot}mole^{-1}}) = M(IE) + B$, where IE is the total ionization energy needed to produce the cation,[2] while M and B are constants to be determined by fitting the values for $\mathit{\Delta} H_{\mathrm{Hyd}}$ (from Ref.[3]) and IE (from Refs.[2],[4]). They[1] had used the total ionization energies for 30 metal ions with valence states, 1+, 2+ and 3+ to find an empirical linear formula. The linear relationship is remarkable given its simplicity, which can indeed be used as guidelines to estimate the hydration energies or the total ionization energies for these metal ions. Thus, there is no doubt that House, Reif and Daniel House[1] have established the correlation between hydration and ionization energies, prior to our work presented here.

Given this background, what we shall bring to the table is the fact that there is a proper microscopic theory that proves the existence of an absolute (or one-to-one) correlation between hydration and ionization energies. We shall expose that the electronic polarization of an atom, which is microscopically related to ionization energy, can be exploited to show (with unambiguous physics) that ionization energy is proportional to the so-called renormalized attraction, which then can be proportionally associated to hydration energy. This proportionality for different cations, which is one-to-one, can be compared for a given solvent and for a given concentration of cations and solvent. The renormalized attraction[5] here refers to the notion of stronger non-chemical bond (no shared orbital between attracting chemical species) that can be stronger than that of van der Waals and hydrogen bonds between neutral atoms. This attraction also plays the crucial part when compared among different cations (for a given valence state) in cation–water systems. This attraction is maximized between two atoms (that can be attached to different molecules) with one of the atoms has high electronic polarization (namely, an atomic oxygen from a water molecule), while the other atom has smaller electronic polarization, which can be a cation.

Thus, the above one-to-one proportionality (between renormalized attraction and ξ) that gives rise to the one-to-one correlation is the one that is clearly missing from the analysis reported in Ref.[1] due to the approximated overall linear relationship among the scattered data for metal ions or cations. The reason for this missing microscopic details or relation hinges on the assumption that the calculated and/or experimentally determined hydration energies are accurate and they do not need corrections. This is in contrast with the experimental ionization energies, which are far more accurate and can be readily obtained from Ref.[6] One such correction mentioned above is carried out by including the ligand-field contribution into the hydration energy calculations as was done in Ref.[7]

If the hydration energies can be measured as accurate as the ionization energies, then the House-Reif-House plot between these energies would have also been approximately linear (as concluded in Ref.[1]), but the data would be strictly proportional ($\mathit{\Delta} H_{\mathrm{Hyd}} \propto IE$) without any exception. In other words, the data would not have been scattered as plotted in Ref.[1] The data would still be approximately linear because of the changing slope when one moves from cations with one valence state ($x+$) to another ($y+$). In other words, the slope for cations with $x+ = 2+$ (see Fig. 1(a)) differs from that of $y+ = 3+$ (see Fig. 1(b)). In Fig. 1(a) for the 2+ transition metal cations, the calculated data[8] indicate absolute correlation between averaged ionization energy (ξ) and hydration energy ($\mathit{\Delta} H_{\mathrm{hyd}}$). For the same cations with valence state 3+, the calculated data for Fe and Co (including all the experimental data) do not follow the prediction of ionization energy theory (IET). We shall discuss and explain why this is so in Analysis I and II.

The said violation in the absolute correlation for the experimental data is the one captured in Ref.,[1] which gives the overall (not absolute) correlation between ξ and $\mathit{\Delta} H_{\mathrm{hyd}}$. However, this overall correlation is not an absolute correlation because all the available

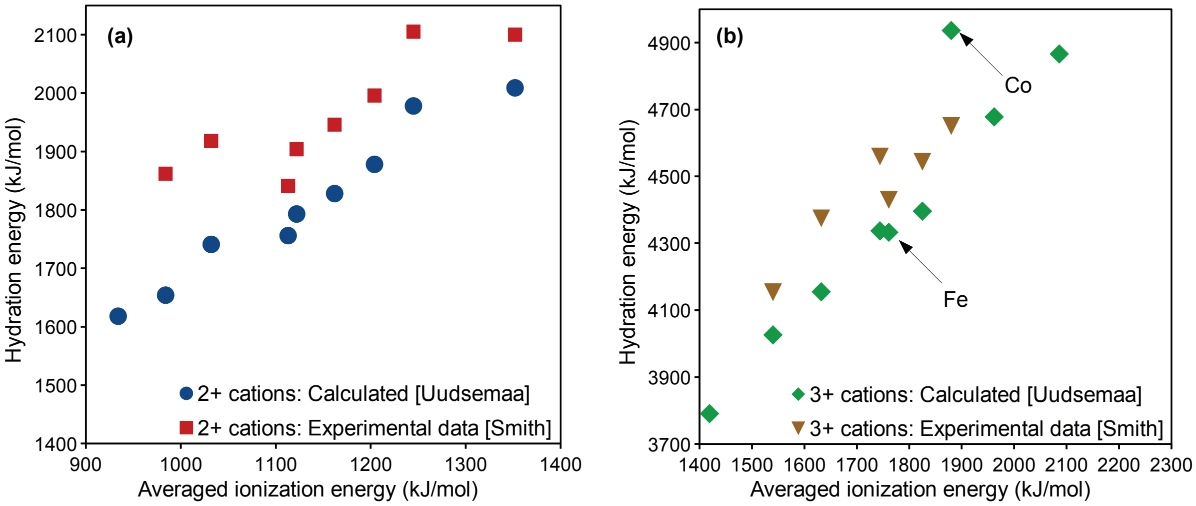

Fig. 1. The averaged ionization energy, ξ versus hydration energy ΔH_{hyd} plots for (a) 2+ (Calculated: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu; Experiment: Ti, V, Cr, Mn, Fe, Co, Ni, Cu) and (b) 3+ (Calculated: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu; Experiment: Ti, V, Cr, Mn, Fe, Co) cations. The calculated data (from the thermochemical method with 6 water molecules) were obtained from Uudsemaa,[8] while the experimental data were taken from Smith.[9] For 3+ cations, the calculated data for Fe and Co clearly do not follow the absolute proportionality between ξ and ΔH_{hyd}, and we shall evaluate this violation in Analysis II. The violation in the experimental data is expected due to many factors, which shall also be discussed in the texts in the subsequent sections.

cations hydration energies (or free energies or enthalpies) need corrections in one form or another. Absolute correlation is only possible if one can determine accurate values for the cations hydration energies. Our theory exposed here proves the existence of an absolute or one-to-one correlation between ξ and ΔH_{hyd}, which is stronger than the correlation proposed in Ref.[1] It is remarkable that the calculated data for 2+ cations (determined much earlier) by Uudsemaa[8] follow our proposed absolute correlation that shall be worked out in the subsequent section.

Here in this work, we shall first provide the theoretical justification for the existence of one-to-one correlation (not an overall linear relationship obtained from the scattered data as was done empirically in Ref.[1]). Hence, our strategy here is to demonstrate that such a correlation does exist by providing the technical details and theoretical arguments to support the said one-to-one correlation. This microscopic correlation shall also expose the fact that hydration energies for cations that interact with a particular solvent (as reported in Ref.[7]) need proper correction beyond ligand-field contribution, and this additional correction(s) should be further examined in the future by exploiting the cations ionization energies trend as a reference. Obviously, plotting another graph (as we did in Fig. 1(a) and (b)) for the hydration versus ionization energies (without proper corrections to the hydration energies) would lead us back to square one—to the same conclusion obtained in Ref.[1] (without absolute correlation). Apart from the highlighted novelty based on the one-to-one correlation, the reason to re-evaluate hydration energy is two-fold. First, its importance in bio-chemical systems and chemical thermodynamics to determine hydration enthalpy, solvation energy and hydration free energy.[7], [8], [10]–[15] Second, this correlation can also be used as an additional criterion to verify the hydration energy obtained from quantum chemical calculations,[7] thermochemical analysis[8] and fitting-parameter approaches such as the volume-based thermodynamics (VBT)[15] and the thermodynamic difference rule (TDR).[16]

§2. Technical details

We shall focus on cations because cations are the ones that attract the electrons from the anions (and not the other way round). The theory presented here also applicable for any cations and anions, provided that certain parameters such as the number of anions surrounding a cation, cations valence states and experimental conditions are fixed for proper comparison for different cations and anions. The mentioned proper comparison (with fixed parameters) shall lead us to the correct intermolecular and/or interatomic attraction that is neither *ad hoc* nor system-dependent. This intermolecular attraction can be applied to deduce the relative cation hydration energies, which is the primary theoretical result derived below. For example, one can apply the said attraction for different cations (or different ξ) to crosscheck the consistency of the calculated and/or the experimentally determined relative hydration energies for those same cations. This would be our novel application that can be deduced from the theoretical one-to-one proof exposed below.

The above novel application refers to the verification of the hydration energy versus cations trend (with an identical valence state) by exploiting the so-called averaged atomic ionization energies as the reference (see Fig. 2). The full theory of ionization energy is given elsewhere[17] and therefore, we only provide a brief theoretical derivation of the atomic polarizability based on this theory and its effect on renormalized attraction[5] between a cation and a water molecule. This attraction, which is a function of ionization energy, turned out to be proportional to the hydration energy of that cation. For example, smaller first ionization energy of Na^+ means its hydration energy is also smaller when compared to Li^+ with large first ionization energy. This means that there is a large renormalized attraction between Li^+ and a water molecule, provided that all other conditions are fixed.

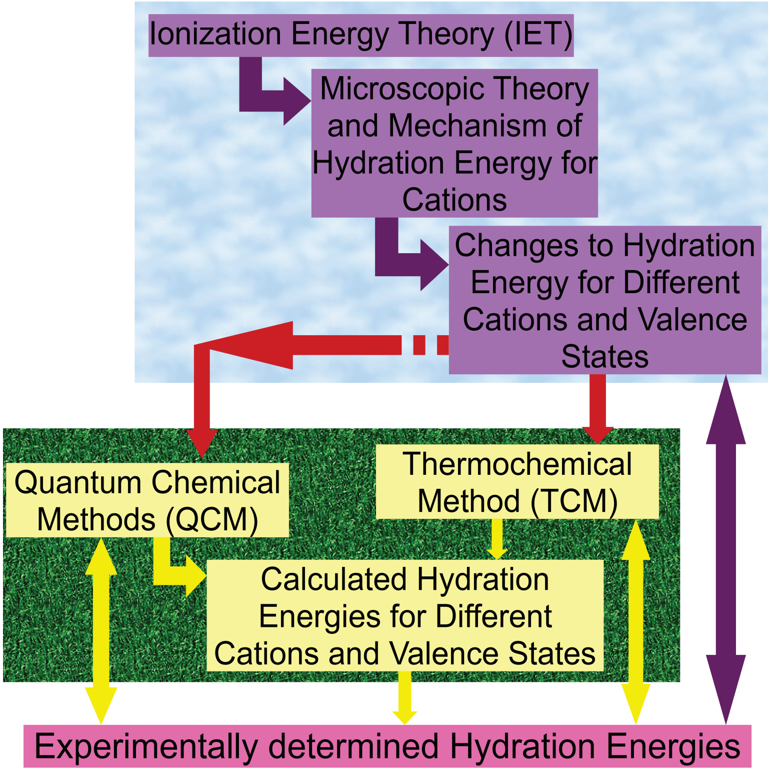

Fig. 2. A diagram that sketches three different approaches to evaluate the hydration energies for different cations and valence states. The approach presented here is based on IET, while the other two are labeled QCM and TCM where each of their results can be compared with experimental data. However, due to corrections needed in experimental data, QCM and TCM, one can readily exploit the one-to-one proof obtained from IET to crosscheck and to make further corrections to the distribution of hydration energy data obtained from experiments, QCM and TCM. Follow the red arrows that indicate the IET results can be used as an unambiguous reference for the other two methods, QCM and TCM, including the experimental data.

Thus, our proposition here reads—hydration energy is proportional to atomic ionization energy of a given cation, and for a given number of surrounding water molecules. It should be noted that hydration energy is not necessarily proportional or inversely proportional to solubility because solubility can be high for system with high or low hydration energy.[18] Here, hydration energy can be defined as the energy change if certain amount of gaseous ions are dissolved completely in water.[8] In other words, the hydration energy is defined as the energy released during the process, $\mathrm{A}^{2+}(\mathrm{gas}) + n\mathrm{H}_2\mathrm{O}$ (liquid) $\to \mathrm{A}^{2+}(\mathrm{aq})$ where $n \to \infty$ in experiments. To compare the calculated hydration energies from different methods and among different cations, we have to make sure the cations carry an identical valence state, and we need to fix n.

If the water molecules are electrostatically attracted to two different cations (A^{2+} and B^{2+}) of the same charge or valence state, say 2+, and if the strength of electrostatic attraction for A^{2+}—H_2O differs from that of B^{2+}—H_2O, then the physical reason for this is due to different ionization energies. This difference then leads us to different hydration energies for A^{2+} and B^{2+}. This attraction is of course depends on atomic polarizability of each cation, which is secondary, compared to the constant charge of 2+. In other words, for a given valence state, this different atomic polarizability is the one that is primarily responsible for different hydration energies among the cations. Since we are directly estimating the variation of hydration energy from the attraction between a cation and a water molecule, we do not need to consider all the chemical processes that occur in a thermochemical cycle or Born-Haber cycle or Born-Haber-Fajans cycle, which is usually needed to calculate hydration energy indirectly from chemical thermodynamics. We shall make obvious that our method and proposition presented above and derived below are independent of chemical thermodynamics approach.

Table I. Electron configuration of valence electrons in $4s$ and $3d$ orbitals for the transition metal atoms in the first transition series.

Orbital	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s$	2	2	2	2	1	2	2	2	2	1	2
$3d$	0	1	2	3	5	5	6	7	8	10	10

Note this, we actually need the atomic polarizability, and not the polarizability of the cations, A^{2+} or B^{2+} because the valence electrons (from water molecules) are the ones that are polarized toward the cations, and this water-molecule polarization depends on the averaged unoccupied energy levels of the cations (or the first two occupied energy levels of atomic A or B). This polarizability determines which atoms (or cations with the same valence state) could attract the electrons from the water molecules. For an anion however, the above logic of exploiting the atomic polarizability is trivial,[19] which explains why Table I lists the electron configuration for atoms, and not divalent cations. In Table I, the averaged ionization energies (the first and the second ionization energies) for Cu → Cu^{2+} and Cr → Cr^{2+} correspond to the electron configuration for Cu and Cr with $4s = 1$ and $3d = 10$ and $3d = 5$, respectively.

In other words, the averaged ionization energies to obtain Cr^{2+} and Cu^{2+} nicely match their respective significantly larger than expected ionization energies (see Fig. 4(a)). Anyway, if the charge differs for the above cations, A^{+} and B^{2+}, then the strength of electrostatic attraction is also dominantly contributed by these different charges such that the effect of atomic polarizability is again secondary.[20] Here, the concentration and molecular polarizability of these water molecules are constants. Therefore, hydration energy is directly proportional to ionization energies, which is then inversely proportional to atomic polarizability of the cations. This least polarizable electrons of an atom can be readily estimated from the ionization energy approximation such that smaller ionization energy of an atom implies easily polarizable outer or valence electrons on the basis of ionization energy theory.[17]

Here, the ionization energies for monovalent cations (namely, K^{+}, Na^{+}, Li^{+}, Rb^{+} and Cs^{+}) refer to their respective atomic (namely, K, Na, Li, Rb and Cs) first ionization energies. On the other hand, for divalent or larger valence-state cations, we have a straightforward averaging formula, which reads,

$$\xi_{\mathrm{atoms}} = \sum_{j} \sum_{i}^{z} \frac{1}{z} \xi_{j,i}(\mathtt{X}_j^{i+}), \tag{2·1}$$

the subscript j denotes the type of chemical element ($\mathtt{X}_j$) in a particular molecule or solid, while the other subscript, $i = 1, 2, \cdots, z$, counts the valence electrons originating from a particular atom. For example, if we have Cd^{2+}, then $j = 1$ in $\mathtt{X}_j^{i+}$, which denotes the chemical element, Cd^{2+}, while $i = 2$ denotes the two valence electrons that have been removed from Cd. In this case, the average ionization energy for Cd^{2+} is simply given by

$$\xi_{\mathrm{Cd}^{2+}} = \frac{1}{2} \sum_{i}^{2} \xi_{\mathrm{Cd}^{i+}} = 1250 \ \mathrm{kJmol}^{-1}, \tag{2·2}$$

because $j = 1$ comes only from one cation, Cd^{2+}. In other words, j counts the number of cations or atoms that needed to be included in averaging. This means that we require an energy proportional to 1250 kJmol^{-1} to excite or polarize any one of the two valence electrons from an atomic Cd. The first and second ionization energies for Cd are 867.8 kJmol^{-1} and 1631.4 kJmol^{-1}, respectively. The formal physical theory that validates the above averaging (see Eq. (2·1) or Eq. (2·2)) even for complex processes have been established in our previous work.[17], [20]

The fundamental physics that captures the technical reason why one can exploit the ionization energy value to determine many other different physical parameters, including the hydration energy, is contained within the *i*onization energy based *F*ermi-*D*irac *S*tatistics (or distribution *f*unction),

$$f_{i\mathrm{FDS}} = \frac{1}{\exp\left[\lambda(E_0 \pm \xi - E_{\mathrm{F}}^0)\right] + 1}. \tag{2·3}$$

Here, $\lambda = 1/k_{\mathrm{B}}T$ where k_{B} is Boltzmann constant and T is the temperature, while E_0 denotes the ground state energy at zero temperature, is independent of the type of chemical composition and any other external disturbances. The changes due to chemical elements and compositions, as well as other external disturbances are captured by ξ. The Fermi level, E_{F}^0 is also for zero Kelvin, and again independent of the type of chemical composition and any other external disturbances, which can be taken to be zero. For zero Kelvin, one should replace[21] λ with that of the Arulsamy constant, $\lambda_{\mathrm{Arulsamy}} = [3\hbar^2(4\pi\epsilon_0)^2]/[m_{\mathrm{el}}e^4]$ where $\hbar$ is Planck constant divided by 2π, ϵ_0 denotes the permittivity of free space, while m_{el} and e are the electron mass and charge, respectively. Equation (2·3) tells us that for smaller ionization energy (ξ) value (averaged for a system) due to changing chemical composition, then the electron excitation probability is larger, and *vice versa.* Note this, the positive sign in '±' is for electrons, while the negative sign is for holes. The general renormalized Hamiltonian that captures this effect is given by,

$$H_{\mathrm{IET}}\Psi(\mathbf{r},t) = (E_0 \pm \xi_{\mathrm{matter}}^{\mathrm{quantum}})\Psi(\mathbf{r},t) \propto (E_0 \pm \xi_{\mathrm{atom}}^{\mathrm{constituent}})\Psi(\mathbf{r},t), \tag{2·4}$$

where IET stands for ionization energy theory, $\Psi(\mathbf{r},t)$ is the many body wavefunction for a given chemical composition and the Arulsamy proportionality originates from the fact that $\xi_{\mathrm{matter}}^{\mathrm{quantum}} \propto \xi_{\mathrm{atom}}^{\mathrm{constituent}}$. The details and the proofs for these equations and the stated proportionality known as the Arulsamy approximation can be found in Ref.,[17] and for a brief introduction, see Ref.[22] Apparently, in all our averaging and analysis, we make use of ξ as a shorthand notation for $\xi_{\mathrm{atom}}^{\mathrm{constituent}}$.

Next, the important parameter that controls the hydration energy is the atomic polarizability. Atomic polarizability can be related to ξ in a straightforward manner from the following derivation. In particular, we can start from the frequency-dependent effective electric field acting on an ion. In this case, the valence electrons shall respond to the frequency-dependent local electric field, $\mathbf{E}(\omega,t)$ that can be written as a function of ξ,

$$\mathbf{E}(\xi,t) = \mathbf{E}_0(\xi)\exp\left[-\mathrm{i}\omega(\xi)t\right], \tag{2·5}$$

where $\mathbf{E}(\xi,t)$ is the time- or frequency-dependent non-equilibrium electric field that varies for different ions (even for a given ion), while $\mathbf{E}_0(\xi)$ is the equilibrium electric field that is a constant for a given ion. Moreover, $\omega(\xi) = \omega_0\exp\left[(\lambda/2)(\xi - E_{\mathrm{F}}^0)\right]$ for mathematical convenience. The electrons with total charge, $-Z_je$ and mass, Z_jm_{el} are bounded to their nucleus where j counts the number of electrons. From now on, we no longer need to differentiate the notations between m^* and $m_{\rm el}$, and therefore, we shall simply label $m^* = m_{\rm el} = m$, whereas M refers to ion's mass. Anyway, the said bound electrons can be represented by the harmonic oscillator, which are composed of mass $Z_j m$, that are attached to the nucleus via an imaginary spring (see Fig. 3). On the basis of Hooke's law, the force,

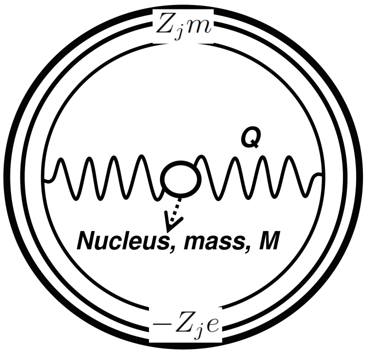

Fig. 3. A semiclassical atom with discrete energy levels and energy-level spacing (the gaps between circles). This atom has a total charge of $-Z_j e$ and total electron mass, $Z_j m$ where Q is the spring constant, or denotes the interaction potential constant, while j counts the number of electrons in this particular atom.

$$\mathbf{F}[\mathbf{r}(t)] = -Q\mathbf{r} = Z_j m \frac{{\rm d}^2\mathbf{r}}{{\rm d}t^2}, \tag{2·6}$$

and the displacement of this mass from its equilibrium position ($\mathbf{r}_0$) is given by,

$$\mathbf{r}(\xi, t) = \mathbf{r}_0(\xi)\exp\left[-{\rm i}\omega(\xi)t\right], \tag{2·7}$$

which can be used together with Eq. (2·6) to obtain the spring constant,

$$Q = Z_j m\omega_0(\xi)^2 = Z_j m\omega_0^2 \exp\left[\lambda(\xi - E_{\rm F}^0)\right], \tag{2·8}$$

where $\omega_0(\xi)$ denotes the angular frequency of oscillation about the equilibrium. To derive the potential energy, $\phi_{\rm P}(\mathbf{r})$, we recall the Taylor series by assuming that the oscillation is small enough so that we could parabolize (not linearize) the oscillation in the vicinity of $\mathbf{r}_0$. Therefore, the electrostatic potential,

$$\phi'_{\rm P}(\mathbf{r}) = \phi_{\rm P}(\mathbf{r}_0) + \phi_{\rm P}^{(1)}(\mathbf{r}_0)(\mathbf{r} - \mathbf{r}_0) + \frac{1}{2}\phi_{\rm P}^{(2)}(\mathbf{r}_0)(\mathbf{r} - \mathbf{r}_0)^2 + \mathtt{O}[(\mathbf{r} - \mathbf{r}_0)^{\mathtt{m}}]. \tag{2·9}$$

After absorbing the constant, $\phi_{\rm P}(\mathbf{r}_0)$, after enforcing,

$$\phi_{\rm P}^{(1)}(\mathbf{r})\big|_{\mathbf{r}=\mathbf{r}_0} = \frac{\partial\phi_{\rm P}(\mathbf{r}_0)}{\partial\mathbf{r}} = 0, \tag{2·10}$$

and after dropping the other higher order terms, $\mathtt{O}[(\mathbf{r}-\mathbf{r}_0)^{\mathtt{m}}] = 0$ for $\mathtt{m} > 2$ (because $\mathbf{r} - \mathbf{r}_0 \in [0,1)$), we can obtain the harmonic oscillator potential energy or interaction potential constant,

$$\phi_{\rm P}(\mathbf{r}) = \phi'_{\rm P}(\mathbf{r}) - \phi_{\rm P}(\mathbf{r}_0) = \frac{1}{2}\frac{\partial^2\phi_{\rm P}(\mathbf{r})}{\partial\mathbf{r}^2}(\mathbf{r}-\mathbf{r}_0)^2, \tag{2·11}$$

$$= \frac{1}{2}Q\mathbf{r}^2, \tag{2·12}$$

$$= \frac{1}{2}Z_j m\omega_0(\xi)^2\mathbf{r}^2, \tag{2·13}$$

that exclusively defines the parabolic oscillation. Note this, Eq. (2·12) also satisfies (as it should be) the condition stated in Eq. (2·10),

$$\left.\frac{\partial\phi_{\rm P}(\mathbf{r})}{\partial\mathbf{r}}\right|_{\mathbf{r}=\mathbf{r}_0} = \frac{\partial\phi_{\rm P}(\mathbf{r}_0)}{\partial\mathbf{r}} = \frac{\partial}{\partial\mathbf{r}}\left(\frac{1}{2}Q\mathbf{r}_0^2\right) = 0. \tag{2·14}$$

Having found the potential energy, we can now write down the proper equation of motion on the basis Eq. (2·6) in the presence of $\mathbf{E}(\xi,t)$,

$$Z_j m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = -Q\mathbf{r} - Z_j e\mathbf{E}(\xi,t), \tag{2·15}$$

which implies that,

$$\mathbf{r}_0(\xi) = -\frac{Z_j e\mathbf{E}_0}{Q - Z_j m\omega(\xi)^2}, \tag{2·16}$$

$$= -\frac{e\mathbf{E}_0}{m\big[\omega_0(\xi)^2 - \omega(\xi)^2\big]}, \tag{2·17}$$

$$= -\frac{e\mathbf{E}_0}{m\big[\omega_0^2 - \omega^2\big]}\exp\big[\lambda(E_{\rm F}^0 - \xi)\big]. \tag{2·18}$$

From the electronic polarization,

$$\mathbf{p}(\xi,t) = \mathbf{p}_0(\xi)\exp[-\mathrm{i}\omega(\xi)t] = -Z_j e\mathbf{r}, \tag{2·19}$$

we can derive the equation that defines the frequency-dependent atomic polarizability ($\alpha_{\rm at}(\omega,\xi)$),

$$\mathbf{p}_0(\xi) = \left[\frac{Z_j e^2}{m\big[\omega_0^2 - \omega^2\big]}\exp\big[\lambda(E_{\rm F}^0 - \xi)\big]\right]\mathbf{E}_0, \tag{2·20}$$

$$= \alpha_{\rm at}(\omega,\xi)\mathbf{E}_0. \tag{2·21}$$

The static renormalized atomic polarizability is straightforward (from Eq. (2·21)),

$$\lim_{\omega\to 0}\alpha_{\rm at}(\omega,\xi) = \alpha_{\rm at}(\xi) = \frac{Z_j e^2}{m\omega_0^2}\exp\big[\lambda(E_{\rm F}^0 - \xi)\big]. \tag{2·22}$$

Obviously, we did not employ any linear approximation, and therefore, non-linear effects are automatically captured due to the facts that the harmonic oscillation is parabolic (see how we applied the Taylor series), and the change to the interaction strength is exponentially driven (see the renormalization factor). We have made use of this semiclassical version of atomic polarizability to expose the correct and consistent physics as to why atoms or cations with large ξ attracts the electrons from the atoms or molecules with small ξ. This unequivocal exposition cannot be made with any quantum chemical methods, which is a fact. The quantum mechanical version of $\alpha_{\rm at}(\omega, \xi)$ can be constructed from Eq. (2·21), and the quantum mechanical definition of polarization,

$$\mathbf{p} = -Z_j e\langle\psi_v|\mathbf{r}_0|\psi_j\rangle \exp\left[-{\rm i}\omega(\xi)t\right], \tag{2·23}$$

where ψ_v and ψ_j are the time-independent wavefunctions, and the polarization is also a function of ξ (see the parameter $\omega(\xi)$ in the exponential factor in Eq. (2·23)). This factor with ξ permits us to determine the interatomic and intermolecular attraction strength, which in turn leads us to deduce the changes to the hydration energy for different cations in the presence of different anions. In particular (from Eqs. (2·20), (2·21) and (2·23)),

$$\begin{aligned}
\alpha_{\rm at}(\omega, \xi) &= \sum_w\sum_v \left\langle \psi_v \left| \frac{Z_{w;v}e^2}{m\big[\omega^2_{0;w;jv} - \omega^2\big]} \exp\big[\lambda(E^0_{{\rm F};w} - \xi_{w;jv})\big] \right| \psi_j \right\rangle, && (2·24)\\
&= \sum_w\sum_v \frac{Z_{w;v}e^2}{m} \exp\big[\lambda E^0_{{\rm F};w}\big] \left\langle \psi_v \left| \frac{\exp\big[-\lambda\xi_{w;jv}\big]}{\big[\omega^2_{0;w;jv} - \omega^2\big]} \right| \psi_j \right\rangle, && (2·25)\\
&= \sum_w\sum_v \frac{Z_{w;v}e^2}{m} \exp\big[\lambda(E^0_{{\rm F};w} - \xi_{w;jv})\big] \frac{F_{w;jv}}{\big[\omega^2_{0;w;jv} - \omega^2\big]}, && (2·26)
\end{aligned}$$

where $F_{w;jv}$ is the oscillator strength of the electric dipole transition from the initial atomic state, j, to another state, v, for $w^{\rm th}$ atom. Whereas, $\xi_{w;jv}$ and $Z_{w;v}$ are the respective energy-level spacing and atomic number for $w^{\rm th}$ atom that has Z_v polarized electrons in the excited (or polarized) atomic state. Fortunately, we do not need to use Eq. (2·24) for we already know why and how $\alpha_{\rm at}(\omega, \xi)$ can change for different atoms and for different solids with different atomic (or chemical) compositions.

It is fortunate because we do not need to exploit Eq. (2·24) by guessing the wavefunctions, ψ_j, ψ_v, $\cdots$, which do not correctly represent the physical properties of electrons in any quantum matter, except for some ground state energy related properties. The physically true wavefunctions are only available for atomic hydrogen; because there is only one electron with zero electron-electron interaction. Note the important relation, $\alpha_{\rm at}(\omega, \xi) \propto \exp\big[\lambda(E^0_{{\rm F};w} - \xi_{w;jv})\big]$ from the renormalized polarizability equation, Eq. (2·24), which is what we wanted. The renormalization procedure exploited above is based on the energy-level spacing renormalization group method presented in Ref.[23] The complete details on the said renormalization group method are given in Ref.[23]

The above atomic polarizability equation gives rise to the possibility of renormalized attraction between neutral (and polarizable) atoms and between a cation and a water molecule. This particular electrostatic attraction is different for different cations even for an identical valence state cations, surrounded by water molecules. This renormalized attraction is stronger for cations with least atomic polarizability, and the said attraction is proportional to the hydration energy. The responsible renormalized attraction is of the first type (or type I), and is given by,[5]

$$\tilde{V}^{\mathrm{I}}_{\mathrm{renormalized}}(\xi) = \hbar\omega'\bigg(\frac{1}{\sqrt{2}} - 1\bigg)\exp\bigg[\frac{1}{2}\lambda\xi\bigg], \tag{2·27}$$

where the parameter that wears a tilde ($\tilde{V}$) means a renormalized parameter, while $\hbar\omega'$ is the ground state energy in the absence of interaction and at zero Kelvin, which is nothing but E_0 that has appeared in Eqs. (2·3) and (2·4). This notation, $\hbar\omega'$ is the standard one used in the derivation of van der Waals attraction, which has also been adopted in the renormalized interaction theory to derive $\tilde{V}^{\mathrm{I}}_{\mathrm{renormalized}}(\xi)$. In general, the renormalized function contains an exponential term, which is a function of ξ, and in this particular case, the renormalization factor reads, $\exp\left[\frac{1}{2}\lambda\xi\right]$. Here, the renormalized attraction between a cation and a water molecule is large for cations with large atomic ionization energy or ξ. Therefore, the hydration energy is also expected to be large for cations with large ξ. The above comparison (and elsewhere) refer to the cations with a fixed valence state, + or 2+ or 3+ or, $\cdots$.

If one calculates the binding energies for Ca^{2+}—$\mathrm{H_2O}$ and Zn^{2+}—$\mathrm{H_2O}$ using the computational AMOEBA force-field model, then one could obtain three contributing components. These three components refer to the van der Waals interaction, multipole electrostatics and polarization of outer electrons. The said contributions do not imply that the binding energy between a particular cation and a water molecule is not entirely due to polarization but composed of van der Waals, multipole electrostatics and polarization effects. We should note here that the origin of van der Waals force and the multipole-electrostatic effect themselves are due to electronic polarization[5], [24], [25] of water molecules. In other words, the van der Waals force and multipole electrostatics have got to be zero in the absence of polarization, which stays true even for the electrostatic interaction between a permanent dipole and a cation.

Here, the electronic polarization of a cation, say A^{2+}, refers to atomic polarizability of the first two electrons (valence electrons) from atomic A because the cation, A^{2+} attract the electrons from the anions. This atomic-polarizability induced renormalized attraction is the one that is solely responsible for the different attraction strengths between different cations (for a given valence state) and water molecules. In the following analysis I and II, we shall apply the notion of ionization energy and its proportionality to hydration energy (as introduced above) to evaluate the changes to hydration energy with respect to different transition metal cations (M^{2+} or M^{3+}). Moreover, we should take note that the hydration energy values used here have been made to be absolute (or positive) values for convenience so as to make proper comparison between ionization and hydration energies. This sign conversion does not change the physics of hydration energy discussed here.

To make use of the above correlation, we can plot the different hydration energies against different cations (with an identical valence state), and this hydration energy trend is the one that should be compared with the ionization energy trend obtained from the ionization energies plotted against the same different cations (with an identical valence state). The increasing and decreasing ionization energy trend against cations is the one that should be satisfied by the hydration energy trend calculated from chemical thermodynamics plotted against the same different cations. Therefore, the correlation presented here is not suitable to compare the absolute hydration energy value for each cation.

Only in the second stage of the chemical thermodynamics calculations, one can compare the calculated hydration energy for each cation with the well-established hydration energy value, but then, this comparison should not violate the ionization energy trend stated above. Therefore, the ionization energy trend can be used as a reliable first-order reference to crosscheck the accuracy of different methods employed to calculate hydration energies for different cations (with an identical valence state).

§3. Results and Discussion

3.1. *Analysis I: Divalent cations*

In the following Analysis I and II, we prefer to use the unit, kcal·mole^{-1} originally used by earlier researchers that would permit the reader to crosscheck the data points. Secondly, the conversion is given by 1 kcal·mole^{-1} = 4.184 kJ·mol^{-1}, whose duty is to simply shift all the data points by a conversion constant, equally without any change to the distribution of the data points (before and after the shifting). This means that the cations hydration energy trend stays intact regardless of whether one uses kcal·mole^{-1} or kJ·mol^{-1}. The experimental hydration energies for the divalent cations in Ref.[26] (without correction) agree with the averaged ionization energies (see Fig. 4(a)) such that we do not need any correction from the ligand field stabilization energies for V^{2+}, Cr^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}. But any correction that is implemented for each cation should follow the ionization energy trend plotted in Fig. 4(a). In particular, the hydration energies reported in Ref.[26] for Mn and Zn are smaller than V and Ni, respectively, which should not be the case from the ionization energy trend depicted in Fig. 4(a). Therefore, the experimental hydration energies for the divalent transition cations need to be further corrected perhaps from other refinements coming mostly from the screening effect. Even after the correction, the magnitude of the correction(s) for each divalent transition metal ion should not violate the increasing or the decreasing ionization energy trend shown in Fig. 4(a).

Next, let us look at the correction made and justified in Ref.[7] for the hydration free energies plotted in Fig. 4(b). Even after the correction made in Ref.,[7] the overall trend does not follow the ionization energy trend plotted in Fig. 4(a). Hence, according to the ionization energy trend, further corrections to hydration free energies are needed for the calculated values reported in Ref.[7] The problem with modern electronic structure calculation is the use of fitting-parameter technique to evaluate *ad hoc* interaction terms with guessed wavefunctions. Therefore, a proper general rule cannot be deduced from such calculations, for example, we would always be guessing which interaction terms are dominant, and their relative strengths, and we always need experimental data for support despite the fact that the experimental data themselves may need corrections. As such, we provide here a first-order rule that is unambiguous to estimate the variation to the hydration energy for transition metal cations without any fitting parameter, guessed function nor *ad hoc* interaction terms. In addition, our predictions are much closer to experimental data trend as discussed above and in the section below.

There is no doubt that the hydration energy for each cation calculated from the quantum chemical method (see the solid squares plotted in Fig. 4(b)) needs to be crosschecked (before and after corrections). Such crosschecking can be readily done by comparing the hydration energy trend for different cations (from quantum calculations) with that of the ionization energy trend (see Fig. 4(a)). The said comparison is the primary application of our theory, which is useful to deduce the allowable corrections for the calculated hydration energies for the cations. In particular, the corrected data plotted in Fig. 4(b) is inadequate when one compares the data with that of Fig. 4(a). The obvious disadvantage of our approach is that we cannot calculate the hydration energy for each cation such that we can only deduce the relative cations hydration energies from the same cations ionization energies. Nevertheless, we have turned this disadvantage to something useful.

Finally, it is true that quantum chemical method has the advantage of calculating absolute hydration energy value for each cation, but this does not change the fact that the calculated values need correction even if the calculated data are close to the experimental data for two reasons. First, the experimental data themselves need corrections, and sec-

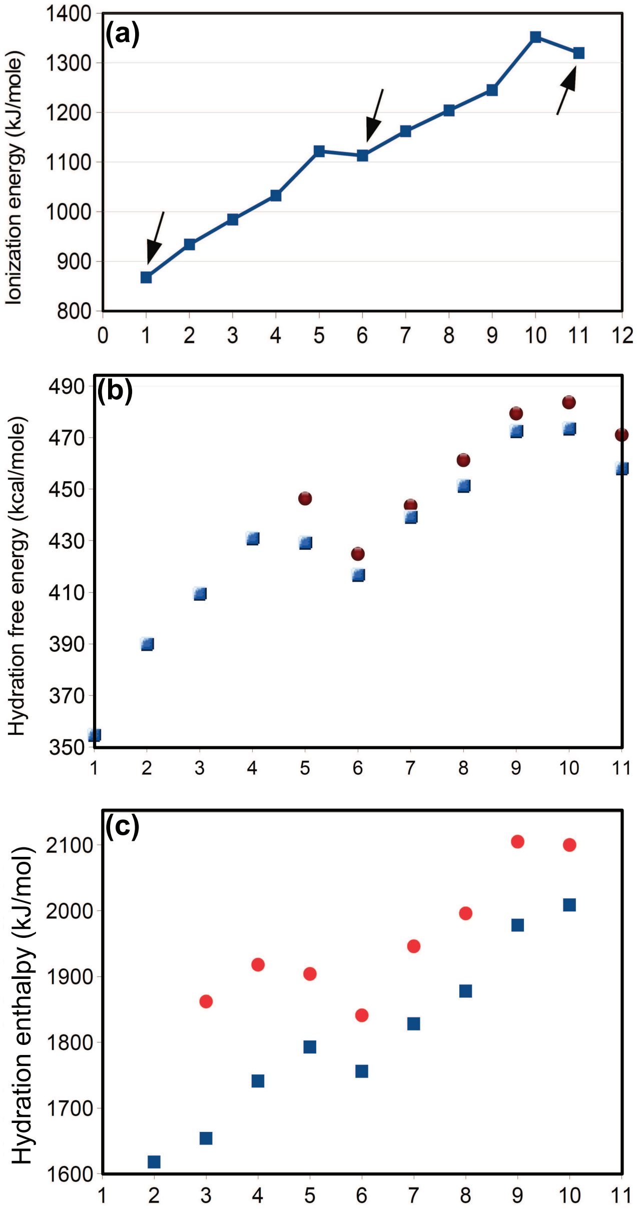

Fig. 4. Average ionization energies for divalent cations (listed in the x-axis), 1:Ca^{2+}, 2:Sc^{2+}, 3:Ti^{2+}, 4:V^{2+}, 5:Cr^{2+}, 6:Mn^{2+}, 7:Fe^{2+}, 8:Co^{2+}, 9:Ni^{2+}, 10:Cu^{2+} and 11:Zn^{2+}. (a) The solid line is a guide for the eyes. This trend (the change to ionization energy and with changing divalent cations) follow the experimentally determined hydration energies without any correction as reported in Ref.[26] (b) The solid circles are the uncorrected experimental data (not available for all cations listed here), while the corrected calculated data (from Ref.[7]) are plotted with solid squares. The calculated hydration free energies plotted in (b) do not follow the trend plotted in (a). (c) The solid circles are the uncorrected experimental hydration enthalpies, while the corrected data are plotted with solid squares (both experimental and theoretical data from Ref.[8]).

ond, the quantum chemical method needs to be consistent for all cations, not for selective cations. This consistency can now be checked by comparing the cations hydration energy trend with that of the ionization energy trend for the same cations (for a given number of anions, cations valence state and relevant experimental conditions). If each cation is subject to different environment (has different types of anion and/or different number of anions attached to a cation, including different temperatures and pressures), then there is no point of plotting Fig. 4(b) because the distribution of data in Fig. 4(b) is physically meaningless. Physically meaningless here means that one cannot exploit the data distribution to derive the correct correlation nor the microscopic physics of hydration energy. This is why the cations ionization energy trend can be exploited as the proper guide.

Note this, hydration energies are influenced by temperature, and so do the ionization energies, where obviously, the ionization energy of a system becomes smaller at higher temperatures and the ionization energy or the Arulsamy approximation reads—the ionization energy for a particular system for $T > 0$ K is proportional to $T = 0$ K. This means that, the ionization energy trend is strictly valid as a guide for a given temperature and for given concentrations of a particular cation type and water molecules, which is as it should. However, the requirement that the hydration energy trend should obey the ionization energy trend does not imply, in any way, that their respective slopes should be made comparable. We only require the increasing and the decreasing ionization energy trend to be strictly followed. This means that, the precise magnitudes of corrections needed for the hydration energies cannot be deduced from the ionization energy trend.

3.2. *Analysis II: Divalent and trivalent cations*

The above Analysis I may seem inadequate for the justification of using the ionization energy trend as one of the primary references to deduce the changes to the hydration energy for different transition metal cations (with an identical valence state). Therefore, we provide here further support as to why the said reference (with respect to ionization energy trend) is unequivocal. For example, to further justify why the above corrections are needed for the hydration energies reported in Fig. 4(b), we need to re-examine the correctness of the correlation between the ionization energy and hydration energy. To do that, we can compare the ionization energy trend with the corrected hydration enthalpies calculated by Uudsemaa[8] based on chemical thermodynamics, which are depicted in Fig. 4(c). This is to verify the correctness of ionization energy trend in an independent manner.

Obviously, the corrected hydration enthalpies for all the divalent cations plotted in Fig. 4(c) follow exactly as predicted by the ionization energy trend (see Fig. 4(a)), and not as predicted by Asthagiri et al.[7] (see Fig. 4(b)). Given this background, it is worth

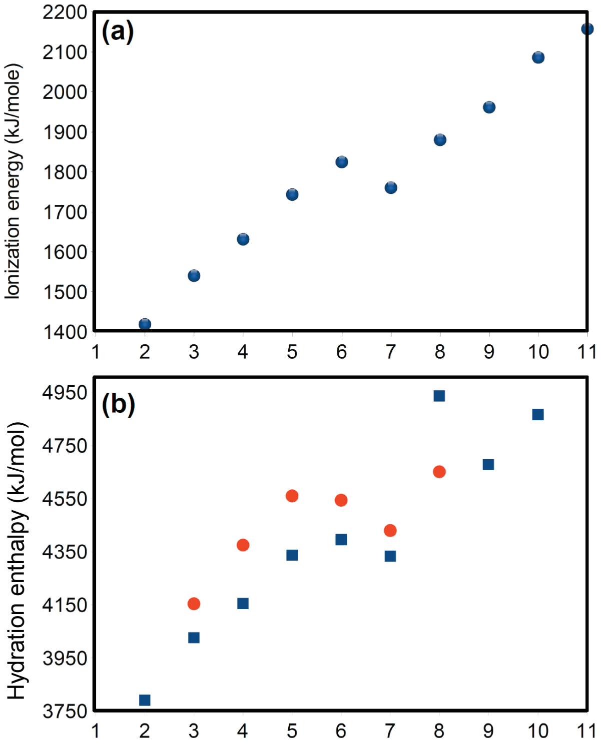

Fig. 5. (a) Average ionization energies (the averaging follows Eq. (2·1)) for the trivalent transition metal cations. The labels 2 to 11 in the x-axis refer to 2:Sc^{3+}, 3:Ti^{3+}, 4:V^{3+}, 5:Cr^{3+}, 6:Mn^{3+}, 7:Fe^{3+}, 8:Co^{3+}, 9:Ni^{3+}, 10:Cu^{3+} and 11:Zn^{3+} cations, respectively. The hydration enthalpies plotted in (b) should follow the trend indicated by (a). (b) Uncorrected (solid circles) and the corrected (solid squares) hydration enthalpies for the same trivalent cations (from Uudsemaa[8]). The hydration enthalpies for the cations, Cr^{3+}, Fe^{3+} and Co^{3+} do not satisfy the ionization energy trend plotted in (a), which implies further corrections are needed for Cr^{3+} or Fe^{3+}, and Co^{3+}.

considering the proposed correlation between ionization energy and hydration energy as a proper guidance or reference in the calculation of hydration energies from chemical thermodynamics. We now crosscheck whether the correction made by Uudsemaa[8] for divalent cations that happen to obey the ionization energy trend can also remain true for trivalent cations. We shall check whether the corrected hydration enthalpies for trivalent cations also follow the ionization energy trend depicted in Fig. 5(a) exactly. The corrected hydration enthalpies for the transition metal trivalent cations calculated by Uudsemaa[8] based on chemical thermodynamics do follow the ionization energy overall trend, but with only two exceptions (compare Fig. 5(a) with the corrected data listed in Fig. 5(b)), which can be further corrected.

In particular, the correction made to Co^{3+} is too large to the extent that its corrected value is much larger than the corresponding experimental datum. The other exception is that the hydration enthalpy for Fe^{3+} should be at least slightly larger than that of Cr^{3+} (see the positions of Fe^{3+} with respect to Cr^{3+} in Fig. 5(a)). In contrast, the hydration enthalpy (after the correction made by Uudsemaa,[8] see Fig. 5(b)) for Fe^{3+} is slightly smaller than that of Cr^{3+}, which should not be the case from the ionization energy trend (see Fig. 5(a)). As a consequence, the ionization energy trend can be regarded as a reliable first-order reference, and moreover, this reference is based on proper quantum and renormalization group theories, known as the ionization energy theory.

§4. Conclusion

In conclusion, we have established the existence of a proper correlation between ionization energy and hydration energy. This correlation can be readily exploited to crosscheck the corrections made to the experimental and calculated data of hydration energies for cations (with an identical valence state). In particular, we have made use of the atomic-polarization induced renormalized attraction, which is a function of ionization energy to justify the proportionality between the ionization energy and hydration energy for the transition-metal divalent and trivalent cations. In the first part of our analysis, we found that the hydration enthalpies of divalent cations reported by Uudsemaa[8] obey the ionization energy trend without any exception. In the second part, the hydration enthalpies for trivalent cations from Uudsemaa[8] also follow the ionization energy trend except for these two cations, Fe^{3+} and Co^{3+}. From the theoretical correlation proposed herewith, we can confidently claim that these two trivalent cations (Fe^{3+} and Co^{3+}) need further corrections such that the corrected values should follow the ionization energy trend. However, the experimenters and the researchers who employ QCM and TCM should identify the corrections, namely, the physical parameters and experimental conditions that needed to be adjusted or fixed in their calculations and experiments in order to maintain the agreement between hydration and ionization energy trends. In addition, we can also safely state that the hydration energies determined from the chemical thermodynamics approach are relatively more reliable than the hydration energies calculated using the quantum chemical methods, especially when the cations are compared with other cations of the same valence state.

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Availability of data and material: This work makes use of experimental data that have been published elsewhere by different authors as listed in the relevant references and are subject to copyright laws.

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