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# Quantized Hydration Energies of Ions and Structure of Hydration Shell from the Experimental Gas-Phase Data

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With previous data on alkali metal and halide ions included [Rais, J.; Okada, T. *Anal. Sci.* **2006**, 22, 533], we analyzed rather broad data on ionic hydration from the point of view of gaseous cluster energetics. We have now added alkaline earth cations,  $\text{Zn}^{2+}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Bi}^+$ ,  $\text{Pb}^+$ , and alkylammonium cations. The present analysis revealed the octa-coordinated nature of alkaline earth cations, which is not fully pronounced for  $\text{Be}^{2+}$  and  $\text{Zn}^{2+}$ , existence of Eigen protonium complex, which is trigonally hydrated, and particular property of the first  $\text{OH}^-$ ,  $\text{H}_2\text{O}$  cluster. Whereas these findings are generally in accordance with theoretical model calculation studies, we have foreseen in addition tetrahedral hydration for halide anions and  $\text{Rb}^+$  and  $\text{Cs}^+$ , as well as for alkylammonium ions. The obtained picture of the quantized solvation of ions is mirrored in the ionization potentials of outer electrons of pertinent atoms. This is a second independent phenomenon, and together, they invoked a common pattern formation (“Aufbau”) obeying tetra- and octa-coordinated principles.

## Introduction

In our recent series of articles, we at first attempted to provide a rationale to explain the experimental fact that for many cases the Gibbs energies of transfer of cations from one solvent to another are expressed well as straight lines if plotted vs their respective Gibbs energies of hydration,  $\Delta_r G^\circ(i) = a\Delta G^\circ_{\text{hydr}}(i) + b$ .<sup>1</sup> This finding was experimentally checked again in a more recent paper for some immiscible liquid/liquid systems.<sup>2</sup> Already in the paper,<sup>1</sup> we have hinted that such behavior must reflect the formation of exactly formed first clusters of an ion with solvent. This property was studied in more detail in a subsequent paper dealing with simple alkali metal and halide ions.<sup>3</sup> It was found there that the energies of formation of gaseous clusters are all quantized with the number four.<sup>3</sup>

The quantized property found here concerns a more general and different sense than that pertaining to classical quantum mechanics. A second definition from WordWeb is appropriate: “to quantize = to restrict the number of possible values of (a quantity) or states of (a physical entity or system) so that certain variables can assume only certain discrete magnitudes that are integral multiples of a common factor”. For alkali metal and halide ions, such defined quantum numbers are 4, 3, 2, (1), according to which the *energies* of formation of the gaseous clusters  $n = 1, 2, 3, (4)$ , are quantized.

Thus, the first shell of the solvent molecules around these ions would be conceptually composed of four molecules, a fact that might seem to contradict common knowledge on hydration or coordination numbers of them. We shall tackle this question here just from the beginning, but the main purpose of this paper is to provide a broader picture of quantized hydration for various types of ions and to attempt a more general explanation of it.

Hydration in water is one of the most widely studied areas of aqueous physical chemistry of ions. Hydration numbers can

be found in almost any textbook on physical chemistry of solutions, but generally, they substantially differ according to author and according to experimental method (principally whether first or both first and second hydration layers are involved). Marcus in his renowned book<sup>4</sup> gives in the table “General Properties” the following hydration numbers of ions (in parenthesis):  $\text{Li}^+$  (5.2),  $\text{Na}^+$  (3.5),  $\text{K}^+$  (2.6),  $\text{Rb}^+$  (2.4),  $\text{Cs}^+$  (2.1),  $\text{F}^-$  (2.7),  $\text{Cl}^-$  (2.0),  $\text{Br}^-$  (1.8), and  $\text{I}^-$  (1.6), thus generally decreasing with the atom number of element and with no sign of constancy throughout the series. The hydration numbers determined from physicochemical properties like electrostriction, conductivity, or compressibility are defined by Marcus as operational, i.e., in principle, method-dependent. In a recent paper,<sup>5</sup> Marcus gives the following hydration numbers derived from electrostriction:  $\text{Li}^+$  (2.3),  $\text{Na}^+$  (2.9),  $\text{K}^+$  (0.8),  $\text{Cl}^-$  (1.7),  $\text{Br}^-$  (1.2), and  $\text{I}^-$  (0.5),<sup>6</sup> and notes that in some other approaches, like neutron diffraction, the total number of solvent molecules geometrically adjacent to an ion in the solution and not necessarily associated with it might be counted. Still, very different hydration numbers are to be found, e.g., in paper<sup>7</sup> [ $\text{Li}^+$  (6.6),  $\text{Na}^+$  (3.9),  $\text{K}^+$  (1.7),  $\text{Cl}^-$  (0),  $\text{Br}^-$  (0), and  $\text{I}^-$  (0)]. Generally, the hydration numbers obtained from physicochemical measurements decrease with the atomic number of an ion of the same charge and are lower for halide anions than for alkali metal cations.

The modern measurements by neutron diffraction, performed mostly in 2006, gave integer numbers and of opposite trend than hydration numbers quoted above, namely,  $\text{Li}^+$  (4),  $\text{Na}^+$  (5),  $\text{K}^+$  (6).<sup>8,9</sup> Also, new computational protocols invariably lead to an increase of the hydration number with increasing atomic number of the ion. This discrepancy in two sets of “hydration” numbers is understood if we realize that small ions exert a strong electrical field reaching several solvation layers of the solvent

**TABLE 1: Cluster Energetic for Simple Alkali and Halide Ions, H<sup>+</sup>, OH<sup>-</sup>, and Some Other Ions with Water as Ligand and with Low  $\kappa$ ,  $\Delta G_n^f$  in kcal/mol, 298 K**

ion	$\Delta G_1^f$	$\Delta G_2^f$ ( $\Delta G_2^f/\Delta G_1^f$ )	$\Delta G_3^f$ ( $\Delta G_3^f/\Delta G_1^f$ )	$\Delta G_4^f$ ( $\Delta G_4^f/\Delta G_1^f$ )	lit, remark
Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> ,	25, 17.6, 11.4,	18.9, 13.2, 8.9, 8.2, 7, 5.9	13.3, 9.3, 6.3, 5.9, 5, 4.2	7.5, 6.3, 4.4, 4.10, 3.8, 3	data collected, <sup>a</sup>
NH <sub>4</sub> <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup>	11.4, 9.6, 7.9	( $\phi = 0.750$ )	( $\phi = 0.531$ )	( $\phi = 0.363$ )	$\phi$ is average of all data
F <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup>	18.1, 8.8, 7.3, 5.7	12.4, 6.6, 6.2, 4.2	8.4, 5.1, 4.6, 3.1	5.9, 3.8, 3.1, 2.1	Hiraoka set <sup>a</sup>
		( $\phi = 0.758$ )	( $\phi = 0.559$ )	( $\phi = 0.394$ )	
H <sup>+</sup>	~160 <sup>b</sup>	25 <sup>c</sup> (0.162)	13.6 <sup>c</sup> (0.088)	8.5 <sup>c</sup> (0.055)	(H <sub>3</sub> O <sup>+</sup> ) <sup>d</sup>
			$\Delta G_3^f/\Delta G_2^f = 0.544$	$\Delta G_4^f/\Delta G_2^f = 0.34$	
OD <sup>-</sup>	16.9	10.7 (0.633)	7.73 (0.457)	5.45 (0.322)	with D <sub>2</sub> O <sup>e</sup>
O <sub>2</sub> <sup>-</sup>	12.5	9.71 (0.777)	7.02 (0.562)	n/a	<sup>f</sup>
Bi <sup>+</sup>	14.7	10.0 (0.680)	6.6 (0.445)	5.0 (0.340)	<sup>g</sup>
Pb <sup>+</sup>	11.7	9.3 (0.795)	6.2 (0.523)	4.6 (0.393)	<sup>h</sup>
Zn <sup>2+</sup>	101.9	86.6 (0.85)	53.6 (0.53)	41.2 (0.40)	<sup>i</sup>
	96.3	78.1 (0.811)	48.3 (0.502)	34.3 (0.356)	<sup>j</sup>
Be <sup>2+</sup>	146.1	118.4 (0.810)	74.2 (0.508)	45.7 (0.313)	<sup>k</sup>
PO <sub>3</sub> <sup>-</sup>	26.7	20.4 (0.764)	22.9 (0.858)	18.1 (0.678)	<sup>l</sup>

<sup>a</sup> Ref 3. <sup>b</sup> Estimated value; see text. <sup>c</sup> At 300 K, data from ref 20. <sup>d</sup> H<sub>3</sub>O<sup>+</sup> behaves as independent particle due to its immense binding energy. <sup>e</sup> Ref 30. <sup>f</sup> Ref 34. <sup>g</sup> At 300 K, data from ref 35. <sup>h</sup> At 300 K, data from ref 36. <sup>i</sup> At 0 K, data from ref 37. <sup>j</sup> At 298 K, data from ref 38. <sup>k</sup> At 0 K, data from ref 37. <sup>l</sup> With D<sub>2</sub>O, from ref 39.

and that in classical physicochemical hydration numbers either some water molecules out of the first hydration layer are entrained by the ion (typically small alkali metal cations and  $n_H$  determined from conductivity) or all hydration in the first shell are not fully counted (typically electrostriction and halide anions). Both of these effects are reflected in the  $n_H$ . Thus, these numbers are of less use, unless it is specified how many hydration layers they count, but this is not generally the case. In this study, we make use of the numbers strictly defined concerning the separate layers, mainly the first hydration layer. The optimal maximum number of molecules of the solvent in the first solvation layer is denoted here as  $\kappa_1$ .

Apparently, none of the above sets of values gives a constant value of  $\kappa_1 = 4$  at the first hydration layer for all alkali metal cations and NH<sub>4</sub><sup>+</sup> as proposed in our recent model.<sup>3</sup>

According to our opinion, Varma and Rempe at last solved the problem rather persuasively by model calculations.<sup>8</sup> The authors claim that (bold by authors of the present paper): “ab initio methods suggest that **all three ions (Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) prefer strong coordination with exactly 4 water molecules**, a result we find consistent with some older experimental measurements. Ab initio molecular dynamics (AIMD) simulations invariably identify additional “loosely” coordinated water molecules at the far slopes of the principle maxima of the radial distribution profiles for Na<sup>+</sup> and K<sup>+</sup> ions. We suggest that these **statistical admixtures of additional oxygen atoms have resulted in the most recent experimentally determined hydration numbers of Na<sup>+</sup> ions to be 5 and K<sup>+</sup> ions to be 6.**”

In fact, there is a rather broad confirmation of tetrahedral coordination for alkali metal and NH<sub>4</sub><sup>+</sup> ions in the recent experimental and mainly theoretical literature, given in the note below the main text.<sup>10</sup> Rather strong support for hydration number four was also gained recently from the side of gaseous clusters studies. Nakai et al. by ab initio theory confirmed the so-called “magic number” equal to four for the NH<sub>4</sub><sup>+</sup>(NH<sub>3</sub>)<sub>4</sub> cluster.<sup>11</sup> In two recent articles of Lisy et al., the hydration number four for Na<sup>+</sup> and K<sup>+</sup> in the gas phase was found.<sup>12,13</sup> However, the most prominent structure in gaseous clusters was found to be K<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> and not tetrahydrate according to an older paper.<sup>14</sup>

For halide ions F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> (as well as for Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>), a strong tendency toward  $\kappa_1 = 4$  was found in simulations performed by Topol et al.<sup>15</sup> Results of the latter paper are in full agreement with our empirical model described in ref 3.

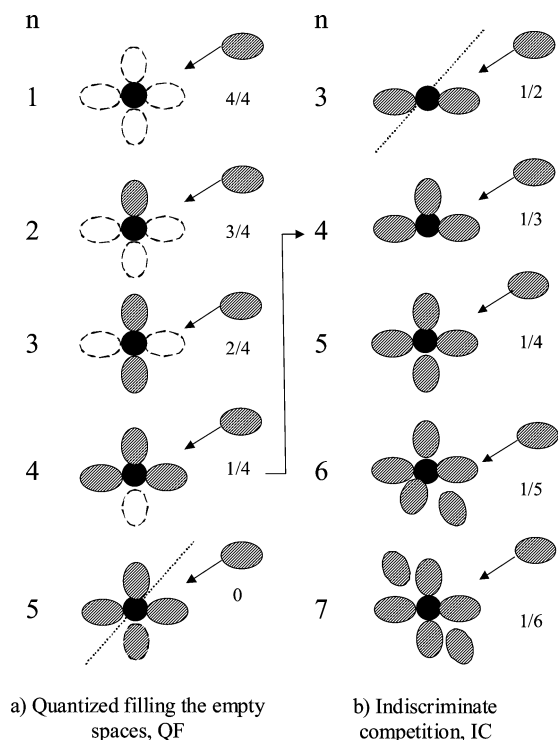
With the spur of the recent findings, we shall now broaden the empirical model, given in our previous paper<sup>3</sup> to other ions than alkali and halide, namely, to protons and OH<sup>-</sup>, some metallic cations, alkaline earth cations, and alkylammonium cations. Only aqueous solutions are considered here, and the properties referred to are therefore hydration-like. In addition, only gaseous clusters are considered here with the hope that the respective aqueous properties can be easily obtained as outlined in the paper.<sup>3</sup>

As already noted, the frequently used term “hydration number”  $n_H$  in connection with solvation of ions seem to be rather ill-defined. Analogically, “coordination number”  $n_{CN}$  is dependent on the outward sterical constraints, generally varying for crystals, enzymes, membrane channels, or other arrangements; thus, again any unequivocal and single value of  $n_{CN}$  for the ion cannot be arrived at. We use different approach here. Our quantum predetermined hydration number  $\kappa_1$  is equal to the highest number of solvent molecules in the first shell of ions derived from the gaseous cluster energetic, e.g., for alkali metal cations and halide anions  $\kappa_1 = 4$ , since  $\Delta G_2^f/\Delta G_1^f$  for them equals 0.750 and  $\Delta G_3^f/\Delta G_1^f = 0.531$ ; see Table 1, first row. The value  $\kappa_1 = 4$  corresponds perfectly to what Varma and Rempe found<sup>8</sup> for Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> cations, i.e.,  $n_H = 4$ . Thus, we can further suppose the following.

**Proposition I.** The gaseous cluster energetic ( $\Delta G_2^f/\Delta G_1^f$ ,  $\Delta G_3^f/\Delta G_1^f$ , etc.) gives real quantum numbers 4, 3, 2, and derived  $\kappa_1 = 4$  corresponds to the real predetermined structure in the first solvation shell of alkali metal and halide ions. This  $\kappa_1$  value is close to the hydration number in aqueous solution ( $\kappa_1 = 4 \sim n_H$ ). Thus, we propose that for other ions also it applies that  $\kappa_1 \sim n_H$ . If so, then well-known structures around heavier alkaline earth cations with  $n_H \sim 8$  would be mirrored in cluster energetic of these ions with quantum numbers 8, 7, 6, and so forth, and  $\kappa_1 = 8$ . Also, some more sophisticated structures like a trigonal solvation shell around the hydronium cation H<sub>3</sub>O<sup>+</sup> (Eigen cation) can be tested in this manner, hopefully to be reflected in relative energies of cluster formation described by numbers 3, 2 and  $\kappa_1 = 3$ .

The mechanism that corresponds to Proposition I we call “quantized filling”, QF, since free positions around an ion are by energetical jumps filled with water molecules. What is remarkable in the QF process is that the development of definite structures is governed rather by free energies and not possibly by conformation entropies as could be supposed at first sight.

Further, it can be easily conceived that the last cluster with  $n = \kappa_1$  will only rarely form. Its formation would demand an



**Figure 1.** 2D visualization of tetrahedral QF mechanism and its connection to IC mechanism; see text. The fifth cluster cannot form by the QF mechanism. If, e.g.,  $\kappa_1 = 4$ , for the IC mechanism it is supposed that just four water molecules are around the ion in the first solvation layer and other water molecules “compete” to be present there.

exact fit of  $\kappa_1$  molecules of solvent just into the first layer. This would be an ideal case occurring only for a quite specific geometry and size of solvent molecule exactly fitting into the last available position in the first solvation shell. On the other hand, the QF mechanism is fully developed for all clusters with  $n < \kappa_1$  for which any sterical constraints are absent. Hence, we formulate the following.

**Proposition II.** The cluster  $n = \kappa_1$  is a critical for a switchover from the process of QF into another mechanism of entrance of solvent molecules into the solvation layer of the ion valid for  $n = \kappa_1$  and  $n > \kappa_1$ .

From the results of the previous paper,<sup>3</sup> we know this mechanism and now we propose to broaden it to all studied ions. The process is identical to a formation of higher clusters referred to in the literature<sup>8</sup> as “statistical admixtures”. It follows that:

**Proposition III.** The entrance of solvent molecules starting from the cluster  $n = \kappa_1$  is determined by a completely different process than supposed for the first layer, namely, “indiscriminate competition”. In it, no quantized states exist, and probability plays a role in a natural sense that the probability and consequently the energy of entrance of any subsequent molecule of solvent into a cluster is reciprocally proportional to the number of molecules of solvent already present around the ion, i.e.,  $1/(n - 1)$ . We can call this mechanism “indiscriminate competition”, IC.

Again, somewhat against expectations, the IC process is reflected in the free energies of the process, but we did not test here the respective entropies of cluster formations.

The respective simple equations governing the proposed mechanisms are given in the Appendix.

The pertinent processes are depicted in Figure 1 for the example of univalent ions, where the left column corresponds to QF and the right one to IC. The least probable case, which

practically seems not to be occurring, is in the QF mechanism filling all four positions around the univalent ion in an ideal manner, so that no further molecule of solvent is involved (hence stricken in Figure 1). In the IC mechanism, the case in which the second molecule would compete with one already present is not logical simply because there is nothing to compete if three vacant positions around the ion still exist. The same would seem to apply for the  $n = 3$  cluster (stricken), but practically, the IC mechanism often still applies to the  $n = 3$  cluster from a cause up to now not fully clear. The measured  $\Delta G_4^f$  of the fourth cluster might be either  $\Delta G_4^f = 1/4 \Delta G_1^f$  (if only QF applies) or  $\Delta G_4^f = 1/3 \Delta G_1^f$  (if only IC applies); the two cases are connected by an arrow in the figure, and in practice, the real cases lie between these two extremes.<sup>3</sup>

For the sake of comparison with classical physicochemical studies, we also bring in the following text hydration numbers  $n_H$  from a renowned source of Marcus.<sup>4</sup>

The purpose of this paper is primarily to show on relatively large and diversified sets of data that the energetics of the water molecules in the first hydration layer of cations is of a quantized nature with quantum numbers  $\kappa_1 = 4$  up to 8. The mechanism of indiscriminate competition introduced<sup>3</sup> for univalent ions is verified for other ions in the present paper.

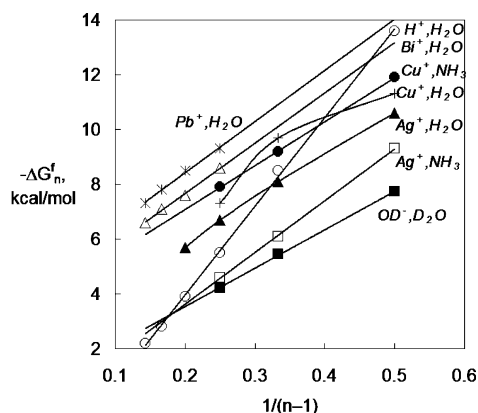
Throughout the paper, a simplified notation of the energetics of the clusters is used, e.g., the third cluster formed from the second one, sometimes denoted as (2,3), is in shorthand written as 3, e.g., the consecutive Gibbs energy of formation of the cluster with three water molecules from a cluster with two water molecules is denoted as  $\Delta G_3^f$ . Ionization potentials, IP's, are numerated according to a standard convenience; e.g., IP<sub>3</sub> is an ionization potential of the third electron of the atom when electrons 1 and 2 have already been removed.

**Model, First Solvation Shell with  $\kappa_1 = 4$  for Alkali Metal and Halide Ions.** The data for univalent alkali metal and halide ions concerning the QF mechanism, collected in our previous paper,<sup>3</sup> are given in the two first rows of Table 1. Data for the IC mechanism are not reproduced here; see the original paper.

**Proton, Hydroxide, and Some Metal Cations, Irregular First Solvation Shells. Proton.** The structure of the simplest complexes of protons with water is peculiar and up to now has not been definitely elucidated. Two basic structures are in play: the “Eigen cation”, in which the central hydronium cation  $H_3O^+$  is strongly hydrogen-bonded to three  $H_2O$  molecules forming  $H_3O^+(H_2O)_3$  or  $H_9O_4^+$ , and the “Zundel ion”, in which a proton lies midway between two water molecules  $H_2O-H^+-H_2O$ . The bare proton is so strongly bound to water that “the species could not exist in isolation”.<sup>16,17</sup> The existence of both  $H_3O^+$  and  $H_3O^+(H_2O)_3$  seems to be well-documented. According to a recent neutron diffraction study with hydrogen isotope substitution combined with Monte Carlo simulation, the  $H_3O^+(H_2O)_3$  structure was again found, but hydronium ions participated also in a construction of a distorted tetrahedral coordination.<sup>18</sup> The authors in ref 17 suppose a second hydration shell around  $H_3O^+(H_2O)_3$  composed of six water molecules with only small differences in hydrogen bond energies as compared to the bulk water. Studies of larger clusters of hydrated hydronium show that the hydronium ion may sit in the tetrahedral cavity of a collapsed water dodecahedron, thus forming the magic number cluster  $H_3O^+(H_2O)_{20}$ .<sup>19</sup>

The  $\Delta G_n^f$ 's ( $n = 2-8$ ) for protons were measured at 300 K by Kebablar et al.<sup>20</sup>  $\Delta G_1^f$  because of its high value could not be measured.<sup>20</sup> An estimate of  $\Delta G_1^f$  can be made from recently published Gibbs energies of hydration of the  $H_3O^+$  cation,  $\Delta G_{hydr}^0(H_3O^+)$ <sup>21,22</sup> in conjunction with known overall hydration





**Figure 2.**  $-\Delta G_n^f$  plotted against  $n/(n-1)$  for various ions and clusters; for better visibility, the data for  $\text{Ag}^+$ ,  $n\text{H}_2\text{O}$ ,  $\text{Ag}^+$ ,  $n\text{NH}_3$ , and  $\text{Cu}^+$ ,  $n\text{H}_2\text{O}$  clusters are plotted as  $(-\Delta G_n^f - 2)$ ; data for  $\text{Cu}^+$ ,  $n\text{NH}_3$ ,  $\text{Bi}^+$ ,  $n\text{H}_2\text{O}$  are plotted as  $(-\Delta G_n^f - 5)$ ; and data for  $\text{Pb}^+$ ,  $n\text{H}_2\text{O}$  plotted as  $(-\Delta G_n^f - 6)$ ; see text for the original data.

energy of  $\text{H}^+$ ,  $\Delta G_{\text{hydr}}^0(\text{H}^+)$ . It follows that  $\Delta G_1^f = \Delta G_{\text{hydr}}^0(\text{H}^+) - \Delta G_{\text{hydr}}^0(\text{H}_3\text{O}^+)$ , and in such a way, estimated  $\Delta G_1^f$  are  $-153.6^{21}$  or  $-160.6^{22}$  kcal/mol.<sup>23</sup> These figures compare well with previously estimated  $\Delta H_1^f = -165$  kcal/mol by Munson.<sup>24</sup> In any case,  $\Delta G_1^f \gg \Delta G_2^f$  for protons, and mutual comparison of these two values is of no avail. The stability of  $\text{H}_3\text{O}^+$  is exceptional.

This is reflected in the very small ratios of energies of the first four clusters, which are for the ratios  $\Delta G_2^f/\Delta G_1^f$ ,  $\Delta G_3^f/\Delta G_1^f$ , and  $\Delta G_4^f/\Delta G_1^f$  only 0.162, 0.088, and 0.055, respectively. If, however, we take the particle  $\text{H}_3\text{O}^+$  as a starting point in the enumeration, the energetic ratios for two consecutive clusters become equal to 0.544 and 0.34, respectively. The numbers do not correspond to tetrahedral quantization, for which the figures ought to be ideally 0.75 and 0.5, but are nearer to trigonal inner layers (ideally 0.666 and 0.333). This is in agreement with a postulated trigonal layer around the  $\text{H}_3\text{O}^+$  cation, because the Eigen cation should be seen from a thermodynamical point of view as an equilibrium property rather than the Zundel ion that reflects more the properties akin to abnormal ionic conductivity, therefore dynamic behavior.

The behavior of larger clusters obeys a linear dependence of  $-\Delta G_n^f$  on  $1/(n-1)$ , characteristic of the IC mechanism; see Figure 2.

**Hydroxide.** The behavior of the  $\text{OH}^-$  anion is more regular than that of  $\text{H}^+$ , but still not devoid of certain subtleties. Marcus quoted a general hydration number of  $n_{\text{H}} = 2.7$ , but the datum from compressibility measurements was much larger, namely,  $n_{\text{H}} = 7.6$ .<sup>4</sup> Detailed calculations of hydration of  $\text{OH}^-$  were done by Pliego and Riveros<sup>25</sup> and by Astaghiri et al.<sup>26,27</sup> Pliego and Riveros considered and modeled the clusters  $\text{OH}^-(\text{H}_2\text{O})_3$  and  $\text{OH}^-(\text{H}_2\text{O})_4$ , which were deemed by the authors to be the most important species. Astaghiri et al. argued that a cluster  $\text{OH}^-(\text{H}_2\text{O})_3$  is the main hydrated particle in the paper,<sup>26</sup> but in subsequent study, they discussed another variant issuing from ab initio molecular dynamics calculations, namely, that  $\text{OH}^-(\text{H}_2\text{O})_4$  is the most stable one.<sup>28</sup> According to Astaghiri et al., it appears that  $\text{OH}^-(\text{H}_2\text{O})_3$  is still a prominent, and likely even dominating, coordination structure for  $\text{HO}^-$  (aq). However, in addition, the coordination number distribution is labile and includes less specifically structured  $n = 4$  possibilities, and  $\text{HO}\cdot(\text{H}_2\text{O})^-$  is a prominent subgrouping within larger inner-shell structures.<sup>27</sup> According to a recent neutron diffraction study with hydrogen isotope substitution combined with Monte Carlo simulation, the

$\text{OH}^-$  ion forms nonplanar hydrogen bonds with four water molecules, giving the  $(\text{H}_9\text{O}_5)^-$  complex.<sup>29</sup>

These findings correspond rather well with cluster energetics. We used here gaseous cluster data determined by Arshadi and Kebarle for the  $\text{OD}^-$  anion in  $\text{D}_2\text{O}$  supposing nearly the same values for  $\text{OH}^-$  and  $\text{H}_2\text{O}$ .<sup>30</sup> At first, it may be deduced that the energy of formation of the  $n = 1$  cluster does not differ from the trend of other halide anions; thus, the exceptional energetically loaded cluster  $\text{H}_3\text{O}^+$  is not applied in the  $\text{OH}^-$  case. The Gibbs energy of hydration of  $\text{OH}^-$  falls between those of  $\text{F}^-$  and  $\text{Cl}^-$ . The straight line is constructed analogically as in our previous paper,<sup>3</sup> namely, the dependence of the formation energy of the first clusters  $\Delta G_1^f$  of halide anions on their Gibbs energy of hydration  $\Delta G_{\text{hydr}}^0$  is<sup>31</sup>  $\Delta G_1^f = 0.0739\Delta G_{\text{hydr}}^0 + 16.293$ ; and the interpolated value for  $\text{OH}^-$  reads as  $-16.15$  kcal/mol. This is in reasonable agreement with the measured value  $-16.9$  kcal/mol.<sup>30</sup>

The energetics of the first four clusters substantially differs from that of halide anions. Namely, the ratio of  $\Delta G_2^f/\Delta G_1^f$  is only 0.633, considerably smaller than the value corresponding to tetrahedral geometry (0.75) and mimicking possibly the trigonal coordination (0.66). In our opinion, this finding only reflects the exceptional behavior of the  $\text{OH}^-$  anion, for which the first hydration water is bound at a defined geometry, in contrast to halide anions. Thus, the first cluster consumes relatively more available energy. Two other clusters are of "normal" QF tetrahedral behavior ( $\Delta G_3^f/\Delta G_1^f = 0.457$  and  $\Delta G_4^f/\Delta G_1^f = 0.322$ ), testifying overall tetrahedral coordination as found in ref 29. The data for higher clusters 3, 4, and 5 fall on a perfect straight line if plotted against  $1/(n-1)$  (IC mechanism, Figure 2).

**Some Other Ions.** Clusters with water and different other ions were studied; some of them of particular interest are gathered in Table 1.

$\text{Ag}^+$  and  $\text{Cu}^+$  clusters with water, but also with other solvents, were to a larger extent studied by Holland and Castleman.<sup>32</sup> The data for the first gaseous clusters were reported only for  $\text{Ag}^+$ . Marcus quotes for this ion a hydration number  $n_{\text{H}} = 3.1$  (from compressibility,  $n_{\text{H}} = 2.3$ , and from Stokes radii  $n_{\text{H}} = 5.9$ ).

The spectrum of the relative  $\Delta G^f$  values is similar to that of the  $\text{OH}^-$  ion, but now it appears that the  $\text{Ag}(\text{H}_2\text{O})_2^+$  particle is the energetically preferred one. Pertinent values are  $\Delta G_2^f/\Delta G_1^f = 0.75$  (exact tetrahedral),  $\Delta G_3^f/\Delta G_1^f = 0.347$  (abnormally small), and  $\Delta G_4^f/\Delta G_1^f = 0.246$  (again nearly ideal tetrahedral). This seems to be in good agreement with current chemical knowledge about 1:2 linear  $\text{Ag}^+$  complexes in water media (before the 1:2 solvate is formed, the central ion "supposes" that coordination number four will be obeyed, but after its formation and due to its stability, the energy of the 1:3 solvate is relatively small). Probably, the still more pronounced preference of the second cluster is with ammonia as a ligand ( $\Delta G_3^f/\Delta G_2^f = 0.268$ ;  $\Delta G_1^f$  not available). The theoretical QM/MM calculations of  $\text{Ag}^+$  hydration were done by Armunanto, Schwenk, and Rode.<sup>33</sup> Their results showed that the first hydration shell is of rather irregular shape and extreme lability, with an average coordination number of 5.5. Fast water-exchange processes between the first and second hydration shell were observed, leading to a preference of five- and sixfold coordinated species. Nevertheless, they observed in their visualization of 2 + 3 and 2 + 4 configurations the first hydration shell with two closer and three or four more distant water molecules. The behavior of second-shell clusters obeys

the IC mechanism well, with the exception of  $\text{Cu}^+$ ,  $\text{H}_2\text{O}$  clusters, as shown in Figure 2.

Arshadi and Kebarle determined  $\Delta G_f^1 - \Delta G_f^5$  for the anion  $\text{O}_2^-$ .<sup>34</sup> Three first molecules of water are in ideal tetrahedral coordination around this ion (Table 1). The  $\text{Bi}^+$  cation according to our analysis would assume at the first cluster a trigonal geometry, whereas second and third clusters behave as tetrahedral.<sup>35</sup> The  $\text{Pb}^+$  ion according to Table 1 is, however, tetrahedral for all four clusters.<sup>36</sup>

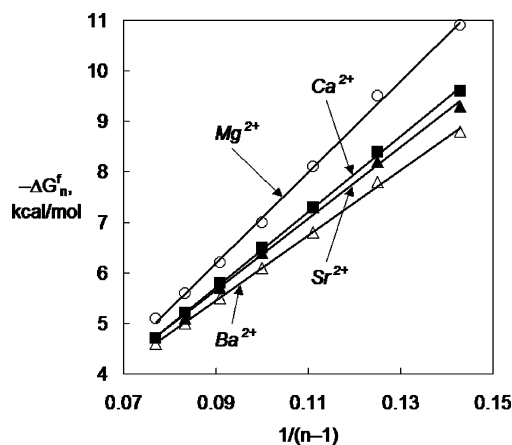
According to Tang and Castleman analysis, based on trends in  $\Delta H_f^n$  plotted vs  $n$ , both  $\text{Bi}^+$  and  $\text{Pb}^+$  ions are trigonal concerning the third cluster and tetrahedral for fourth cluster;<sup>35</sup> hence, their and our analyses do not necessarily coincide.

Further, we included in the table  $\text{Be}^{2+}$  and  $\text{Zn}^{2+}$ .  $\text{Be}^{2+}$  as a first member of the family of alkaline earth cations still behaves quite differently from them but, as will be seen, very closely to  $\text{Zn}^{2+}$ . In both cases, the  $\Delta G_f^n$  values were theoretically calculated. Data for  $\text{Zn}^{2+}$  and  $\text{Be}^{2+}$  at 0 K were taken from ref 37, whereas those values calculated for Zn at 298 °C are from ref 38. As it follows from the table, the first clusters of  $\text{Be}^{2+}$  and  $\text{Zn}^{2+}$  correspond to  $\kappa_1 = 5$  (0.810 measured, 0.800 from eq 4) and  $\kappa_1 = 7$  (0.85 measured, 0.857 from eq 4), respectively. However, for both ions the second cluster with water is already of the common tetrahedral structure. Due to the small size of the central ion and due to sterical hindrance of ligands in their immediate vicinity, these ions cannot continue to "Aufbau" fully developed structure of other alkaline earth cations, which is just only cursorily reflected in the behavior of the first cluster.

The last ion of some interest here is a metaphosphate anion  $\text{PO}_3^-$  as studied with the  $\text{D}_2\text{O}$  ligand by Keesee and Castleman.<sup>39</sup> This ion is surprisingly unreactive, and a small decrease of  $\Delta G_f^n$  values with increasing  $n$  is allegedly caused by the proceeding chemical reaction.<sup>39</sup>

The IC mechanism according to Figure 2 applies well for all ions from this category with the exception of  $\text{Cu}^+$  and water clusters. The correlation coefficients of straight lines in Figure 2 ranged from  $R^2 > 0.995$  for  $\text{Pb}^+$  and  $\text{Bi}^+$  to  $> 0.999$  for other ions. A characteristics of all the straight lines  $\Delta G_f^n$  vs  $1/(n-1)$  is a low value of the constant  $b$  in eq 2 ( $-2.5$  to  $0.75$ ) near the ideal competition with  $b = 0$ .<sup>3</sup> Consequently, in addition the values of slopes of the lines,  $a\Delta G_f^1$  lie near the values of  $\Delta G_f^1$ , i.e., if  $a \sim 1$ , then  $[\text{OD}^-, \text{Bi}^+, \text{Pb}^+ - \Delta G_f^1(\text{experimental})] = \sim 17, 15, 12$  kcal/mol, and  $\Delta G_f^1$  from IC competition mechanism  $\sim 14, 18, 11$  kcal/mol, respectively].

**Alkaline Earth Cations, First Solvation Shell with  $\kappa_1 = 6-8$ .** The alkaline earth cations in water are rather commonly viewed as hexacoordinated (octahedral). Marcus assigns the following general hydration numbers to them:<sup>4</sup>  $\text{Mg}^{2+}$  (10.0),  $\text{Ca}^{2+}$  (7.2),  $\text{Sr}^{2+}$  (6.4), and  $\text{Ba}^{2+}$  (5.3). The opposite trend for the first-layer hydration numbers is postulated in a recent review<sup>40</sup> (in brackets are given  $\kappa_1; \kappa_2$ ):  $\text{Mg}^{2+}$  (6.0; 18.3),  $\text{Ca}^{2+}$  (7.6; 19.1),  $\text{Sr}^{2+}$  (9.0; 20.4),  $\text{Ba}^{2+}$  (9.3; 23.5). Hydration energies and structures were studied by the evaporation of water from hydrated alkaline earth metal ions produced by electrospray ionization, in a Fourier transform mass spectrometer by Rodriguez-Cruz et al.<sup>41</sup> The above authors claimed that  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  are hexahydrated with six molecules of water in the first hydration shell. Theoretical calculations<sup>42</sup> were limited up to  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  clusters with  $n = 6$ . As well, Asthagiri et al. suppose hexahydrates in the first hydration shell for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .<sup>43</sup> On the other hand, Schwenk et al. arrived at their calculations to the first hydration number  $\kappa_1$  of  $\text{Ca}^{2+}$  equal to 7.1, 7.6, and 8.1 according to protocol.<sup>44</sup> At the conclusion section of the above article, the authors claim that a preferred



**Figure 3.**  $-\Delta G_f^n$  plotted against  $n/(n-1)$  for alkaline earth cations and  $n > 7$ ; data from ref 45 and note 47. The straight lines are defined as  $y = 90.096x - 1.9117$ ,  $R^2 = 0.9982$  ( $\text{Mg}^{2+}$ );  $y = 74.723x - 1.0082$ ,  $R^2 = 0.9993$  ( $\text{Ca}^{2+}$ );  $y = 70.901x - 0.7189$ ,  $R^2 = 0.9964$  ( $\text{Sr}^{2+}$ ); and  $y = 64.572x - 0.3638$ ,  $R^2 = 0.9991$  ( $\text{Ba}^{2+}$ ).

coordination number  $\kappa_1 = 8$  with a square antiprismatic structure was found while referring to other studies. Pavlov et al. have found stable structures of hydrated  $\text{Mg}^{2+}$  up to  $n = 7$  and for  $\text{Ca}^{2+}$  up to  $n = 8$ .<sup>37</sup> Peschke et al. found that six or seven molecules can be filled in the inner shell of  $\text{Sr}^{2+}$ , while for  $\text{Ba}^{2+}$ , the inner shell number may be as high as 8 or 9.<sup>45</sup> New QM/MM simulations led finally to  $\kappa_1 = 6$  for  $\text{Mg}^{2+}$  (table in the pertinent paper) and  $\kappa_1 = 8$  for  $\text{Ca}^{2+}$  (text in the same paper; in the table, the value 7.6 appears).<sup>46</sup>

$\Delta G_f^n$  for  $n = 1-6$  could not be measured because of their large values.<sup>45</sup> Thus, in the above paper authors measured  $\Delta G_f^n$  of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  with water molecules starting from the cluster  $n = 6$ .<sup>45,47</sup> For smaller clusters, they adopted the values quantum theoretically calculated by Pavlov et al. by the B3LYP method with large 6-311+G(2d,2p) basis sets.<sup>37</sup> Peschke et al. claimed a good agreement between values measured by them and recalculated values of Pavlov et al., for the cases where measured and computed data exist, thus proving that the calculated values are correct. The correctness of values calculated in ref 37 is further supported here on the basis of measured values for  $\text{Sr}^+$  cation—two sets of calculated and one set of measured values display similar, at first sight almost identical, patterns. The values for the  $\text{Sr}^+$  cation reported here were measured by Tang et al.<sup>48</sup>

We supposed at first that the behavior of alkaline earth cations is just a duplicate of what we found for alkali metal cations, i.e.,  $\kappa_1 = 8$  for all. Indeed, satisfactory straight lines in supposed octacoordination were found with  $R^2 = 0.975$  ( $\text{Sr}^+$ ), 0.993 ( $\text{Ca}^{2+}$ ), and 0.988 ( $\text{Mg}^{2+}$ ) as also seen from Figure 3. Yet, analysis that is more precise was done as described in the Supporting Information and is reflected in Table 2.

The results in the form of experimental results ( $\text{Sr}^+$ ) or calculated by density functional method ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) on one hand and those calculated from eq 4 on the other hand are compiled in Table 2 together with the deviations of the two methods. If the values of the last ones for the highest clusters are omitted, since the mechanism of indiscriminate competition might break in them, the overall relative error is lower than 5%. In the last rows of the table, the best contemporary estimates of  $\kappa_1$  are given, and it is seen that they coincide with our values, thus proving the viability of the QF mechanism.

The situation for  $\text{Sr}^+$  is interesting, in which the first four water molecules around the ion assume  $\kappa_1 = 7$  and only for

**TABLE 2: Cluster Energetic for Alkaline Earth Cations,  $-\Delta G_n^f$  in kcal/mol,  $t$  Indicated in Table**

cluster no. $n$	Sr <sup>+</sup> exper. <sup>a</sup>	Sr <sup>+</sup> eq 4	$\delta^b$	Mg <sup>2+</sup> calcd B3LYP <sup>c</sup>	Mg <sup>2+</sup> eq 4 <sup>d</sup>	$\delta$	Ca <sup>2+</sup> calcd B3LYP <sup>c</sup>	Ca <sup>2+</sup> eq 4 <sup>e</sup>	$\delta$
1	25.2	—	—	81.5 (74.6) <sup>h</sup>	—	—	56.9 (49.5) <sup>h</sup>	—	—
2	22.1	21.6 <sup>f</sup>	−0.5	70.9 (63.4) <sup>h</sup>	67.9	−3.0	47.5 (42.3) <sup>h</sup>	49.8	2.3
3	17.1	18 <sup>f</sup>	0.9	55.1 (48.7) <sup>h</sup>	54.3	−0.8	42 (34.3) <sup>h</sup>	42.7	0.7
4	13.8	14.4 <sup>f</sup>	0.6	43.9	40.8	−3.2	35.6	35.6	0.0
5	11.5	12.6 <sup>g</sup>	1.1	28	27.2	−0.8	27.7	28.5	0.8
6	9.2	9.45 <sup>g</sup>	0.25	24.5 (16) <sup>i</sup>	13.6	−10.9	24.7 (16.1) <sup>i</sup>	21.3	−3.4
7	7	6.3 <sup>g</sup>	−0.7	3.9 (12.8) <sup>i</sup>	—	—	13.8 (10.9) <sup>i</sup>	14.2	0.4
8	5.1	3.15 <sup>g</sup>	−1.95	—	—	—	8.8 (9.6) <sup>i</sup>	7.1	−1.7
$\kappa_1$ literature	6–7 (for Sr <sup>2+</sup> ) <sup>i</sup>	—	—	up to 7 <sup>k</sup>	—	—	up to 8 <sup>k</sup>	—	—
$\kappa_1$ this work	—	7–8	—	6 <sup>j</sup>	6	—	8 <sup>j</sup>	8	—

<sup>a</sup> Ref 48, at 300 K. <sup>b</sup>  $\delta = \Delta G_n^f$  (eq 4) −  $\Delta G_n^f$  (experimental or modeled). <sup>c</sup> Ref 37, calculated by density functional method B3LYP, used with very large 6-311+G(2d,2p) basis sets for 0 K. <sup>d</sup> With  $\kappa = 6$ . <sup>e</sup> With  $\kappa = 8$ . <sup>f</sup> With  $\kappa = 7$ . <sup>g</sup> With  $\kappa = 8$ . <sup>h</sup> Ref 38 data recalculated to 298 K by a program given to the authors by authors of ref 37. <sup>i</sup> Ref 45, experimental data at 298 K. <sup>j</sup> Ref 45. <sup>k</sup> Ref 37. <sup>l</sup> Ref 46.

higher hydrates is the expected  $\kappa_1 = 8$  reached ( $\kappa_1 > 8$  cannot apply reasonably for alkaline earth cations; see Discussion section).

The analysis of higher clusters of Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> for the correlation  $\Delta G_n^f$  vs  $1/(n-1)$  is shown in Figure 3. Again, good straight lines are obtained with  $R^2 > 0.99$ , and the characteristic property is seen in that the second term on the right-hand side of eq 2 is close to zero (see legend to Figure 3). This testifies that a nearly ideal IC mechanism applies; however, exact values of  $\Delta G_1^f$  cannot be arrived at ( $\Delta G_1^f \approx -90.1$  kcal/mol for Mg<sup>2+</sup> from Figure 3, literature value at 298 °C −74.6;  $\Delta G_1^f \approx -74.7$  kcal/mol for Ca<sup>2+</sup> from Figure 3, literature value at 298 °C −49.5). The value for the first cluster of Sr<sup>2+</sup> from our analysis is  $\Delta G_1^f \approx -70.9$  kcal/mol, which is much more negative than for Sr<sup>+</sup> (−25.2 kcal/mol), with all probability implying the importance of an electrostatic contribution when comparing these two ions.

**Protonated Alkylammonium Cations, First Solvation Shell with  $\kappa_1 = 4$  for Mono- and Disubstituted and  $\kappa_1 = 3$  for Trisubstituted Cations.** This is the last case to be treated in this paper. Tetraalkylammonium ions have  $n_H$  in water ranging from 1.3 (Me<sub>4</sub>N<sup>+</sup>) to 0.9 (Bu<sub>4</sub>N<sup>+</sup>).<sup>4</sup> More interesting for our paper are the values of  $n_H$  measured for differently substituted ions in nitrobenzene.<sup>49</sup> These read for primary alkylammonium ions as  $n_H \approx 1.7$ –1.5, for secondary as  $n_H \approx 1.07$ –1.01, and for tertiary as  $n_H \approx 0.7$ –0.5 (the authors studied Me, Et, and *n*-Bu substituted ions; the second entry is for *n*-Bu substituent). Osakai et al. based their work on these findings and with the results of calculations by the PM3 method with the CaChe MOPAC program claimed that the optimized structure of the hydrated ion MeNH<sub>3</sub><sup>+</sup> is that comprising oxygen atoms of three water molecules bound through the oxygen atoms to the ion hydrogens. Thus, the supposed structures would be AlkNH<sub>3</sub><sup>+</sup>·3H<sub>2</sub>O, Alk<sub>2</sub>NH<sub>2</sub><sup>+</sup>·2H<sub>2</sub>O, and Alk<sub>3</sub>NH<sup>+</sup>·H<sub>2</sub>O.<sup>49</sup> The water numbers in these structures are approximately twice the experimentally found  $n_H$  values. Incomplete development of the hydration structure in nitrobenzene is understandable from the fact that the measured  $n_H$  values of tetrasubstituted Alk<sub>4</sub>N<sup>+</sup> were also lower (0)<sup>49</sup> in nitrobenzene than tabulated values for water as a solvent. The analogical conclusion for MeNH<sub>3</sub><sup>+</sup> ion (waters bound through their oxygens to H atoms of the ion) was reached by ab initio calculations performed by Kim et al.<sup>50</sup> Theoretical work ((DFT and MM/MD) indicated a first solvation sphere of three waters for primary alkylammonium ions (one bonding to each H-center on −NH<sub>3</sub><sup>+</sup>), in agreement with the above findings.<sup>51</sup>

For the purpose of  $\Delta G^f$  analysis, we use a recent study of Gilligan et al. in which the data of interest for some protonized

**TABLE 3: Hydration of Alkylammonium Ions in the Gas Phase,  $\Delta G_1^f - \Delta G_3^f$  in kcal/mol at 298 K from ref 49**

ion	$\Delta G_1^f$	$\Delta G_2^f$	$\Delta G_3^f$	$\Delta G_2^f/\Delta G_1^f$	$\Delta G_3^f/\Delta G_1^f$
CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	9.0 ± 2	6.7 ± 1.2	4.9 ± 1.2	0.74	0.54
(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	7.8 ± 0.8	5.8 ± 1.4	3.8 ± 1.8	0.74	0.49
<i>n</i> -C <sub>2</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	8.3 ± 0.3	6.3 ± 0.5	4.5 ± 0.9	0.76	0.54
<i>n</i> -C <sub>3</sub> H <sub>7</sub> NH <sub>3</sub> <sup>+</sup>	8.2 ± 0.7	6.0 ± 1.1	4.3 ± 1.2	0.73	0.52
<i>n</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>3</sub> <sup>+</sup>	8.1 ± 0.9	5.8 ± 0.7	4.2 ± 0.9	0.72	0.52
<i>n</i> -C <sub>5</sub> H <sub>11</sub> NH <sub>3</sub> <sup>+</sup>	7.9 ± 0.4	5.8 ± 0.9	4.2 ± 2.2	0.73	0.53
<i>n</i> -C <sub>6</sub> H <sub>13</sub> NH <sub>3</sub> <sup>+</sup>	7.9 ± 0.7	5.8 ± 0.9	4.2 ± 1.6	0.73	0.53
<i>n</i> -C <sub>7</sub> H <sub>15</sub> NH <sub>3</sub> <sup>+</sup>	7.9 ± 0.5	5.7 ± 0.4	4.1 ± 1.4	0.72	0.52
<i>n</i> -C <sub>8</sub> H <sub>17</sub> NH <sub>3</sub> <sup>+</sup>	7.9 ± 0.7	5.8 ± 0.6	4.1 ± 1.3	0.73	0.52
(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup>	6.9 ± 2.9	4.0 ± 1.8	2.6 ± 0.7	0.58	0.38

alkylammonium cations were obtained by electrospray ionization—high—pressure mass spectrometry.<sup>52</sup> The respective data for  $\Delta G_n^f$  together with calculated ratios  $\Delta G_2^f/\Delta G_1^f$  and  $\Delta G_3^f/\Delta G_1^f$  are given in Table 3. The fulfillment of the quartet rule is striking and probably also suggests that the measured data are more precise than the estimate made by the authors.<sup>52</sup>

As it is seen, the tetrahedral coordination applies for all mono- and one disubstituted alkylammonium ions, but the presence of the third substituents hinders the development of the tetrahedron. For monosubstituted ions, the overall decrease of  $\Delta G_n^f$  values with the length of substituents is small, being mostly apparent for the first members of alkyl chain series.

Although the quartet rule is mentioned nowhere in the paper,<sup>52</sup> the authors concluded, similarly as we did, that the “water molecules preferentially cluster about the quaternary nitrogen; the charged side, and the alkyl chains lie away from the ion”.<sup>52</sup> Actually, if water molecules were bound through the hydrogen atoms, then the number of coordination sites would decrease with the number of alkyl substituents, and for AlkNH<sub>3</sub><sup>+</sup> cations, it would attain a value of 3 and not the observed value of 4. If water molecules were bound to H atoms and to H atoms of the nitrogen-adjacent CH<sub>2</sub> group with equal energies, the decrease of the  $\Delta G$  ratios would not fall rapidly between (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup> and (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>.

The analysis of the results of Table 3 thus shows that water molecules are probably bound directly to the charged central nitrogen atom. The lack of hindrance of one or two alkyl substituents on the  $\kappa_1 = 4$  value indicates that the alkyl chains are placed in favorable positions during hydration. Only the third alkyl substituent changes the situation dramatically. The ratios  $\Delta G_2^f/\Delta G_1^f$  and  $\Delta G_3^f/\Delta G_1^f$  (0.58 and 0.38, respectively) are closer to trigonal (0.66 and 0.33) than to tetragonal coordination (0.75 and 0.5) and indicate that only three molecules of water are accommodated at the (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup> ion.



## Discussion

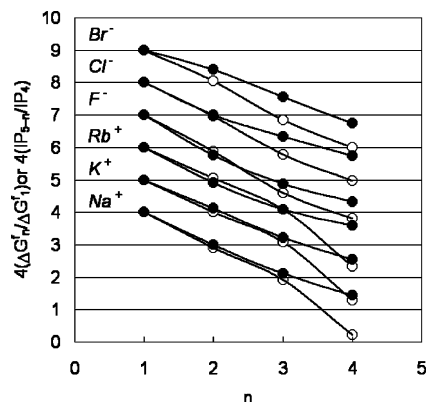
A cautionary remark must be made again first. The classical hydration numbers  $n_H$  of ions as found in various textbooks, and reviews are not consistent enough and vary from source to source. Several such  $n_H$  values were shown in the main text. During the preparation of the manuscript, we found still another review with again somewhat different results. Collins et al. argue that the dominant forces on ions in water are short-range forces of a chemical nature.<sup>53</sup> Mainly on the basis of gel sieving chromatography on Sephadex G-10, they found that  $\text{Li}^+$  has 0.6 tightly bound water molecules,  $\text{Na}^+$  has 0.25 tightly bound water molecules, and  $\text{K}^+$  has no tightly bound water. Their other values are  $n_H = 1.9$  for  $\text{H}^+$ , 2.8 for  $\text{OH}^-$ ,  $\text{Mg}^{2+}$  has 5.8 tightly bound waters in the first layer, while  $\text{Be}^{2+}$  has 4 water molecules in the first layer and 1.3 in the second layer. The results for univalent ions thus strongly differ from the results of this paper, whereas the data for  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$  (4 and 6, respectively) are in agreement with our results.

On the other hand, and this we see as particularly significant, is the good agreement of the values of  $\kappa_1$  derived here with the values calculated theoretically from modern calculation protocols as discussed in Introduction and in the last two rows of Table 2.

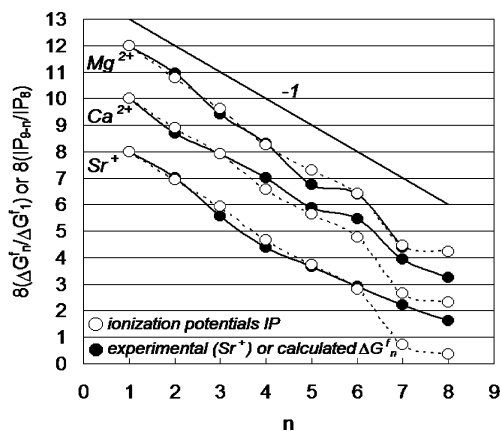
Another example converging with our values and permitting a closer look at our values of  $\kappa_1$  and their difference from coordination numbers  $n_{\text{CN}}$  issues from two recent articles.<sup>54,55</sup> Dudev et al.<sup>54</sup> critically evaluated the Cambridge Structural Database (CSD) currently containing 200 000 high-resolution X-ray structures of metal complexes for various hydrated metallic cations of periodic table. They reported 13 structures of hydrated  $\text{Li}^+$  with  $n_{\text{CN}} = 4$  and only one with  $n_{\text{CN}} = 5$ . Analogically for  $\text{Na}^+$ , there exist 3 structures with  $n_{\text{CN}} = 6$  and 2 structures with  $n_{\text{CN}} = 4$ . For  $\text{Be}^{2+}$ , 3 structures with  $n_{\text{CN}} = 4$  do exist, whereas as many as 65 structures do exist for  $\text{Mg}^{2+}$  and  $n_{\text{CN}} = 6$ . Few structures were found for  $\text{Ca}^{2+}$  ( $n_{\text{CN}} = 7, 6, 8$ ) and only one structure for both  $\text{Sr}^{2+}$  ( $n_{\text{CN}} = 8$ ) and  $\text{Ba}^{2+}$  ( $n_{\text{CN}} = 9$ ). As supposed,  $n_{\text{CN}}$  values differ according to crystal arrangement, but we notice that the agreement with our  $\kappa_1$  is better than for hydration numbers determined from other experimental methods; see, e.g., alkali metal cations and data reported in the first paragraph of the Discussion section.

Still more significant for our purpose is the second paper from the same laboratory.<sup>55</sup> In it, the  $n_{\text{CN}}$  values of hydration of alkali metal and alkaline earth cations in the gaseous phase and in water were calculated by density functional theory (DFT) and compared with some other results. DFT results read as (in bracket the values  $n_{\text{CN}}$  by DFT and for comparison our values  $\kappa_1$  in bold are given):  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Be}^{2+}$  (4; **4**),  $\text{Rb}^+$  (4 or **4**),  $\text{Mg}^{2+}$  (6; **6**),  $\text{Ca}^{2+}$  (6; **8**), and  $\text{Sr}^{2+}$  (7; **7–8**). The results compare well with the exception of  $\text{Ca}^{2+}$  (see below); hence, a way to converge the values seems to be apparent. The authors further discuss the  $n_{\text{CN}}$  values found for bare gaseous cations (these strictly speaking are those defined by us as  $\kappa_1$ ) and those  $n_{\text{CN, aq}}$  in an aqueous environment. The differences are rather subtle: for  $\text{Li}^+$ ,  $\text{Be}^{2+}$ , and  $\text{Mg}^{2+}$ , the values  $n_{\text{CN}}$  are identical to  $n_{\text{CN, aq}}$ . It is claimed that  $\text{Ca}^{2+}$  prefers gaseous  $n_{\text{CN}} = 6$  in full agreement with our  $\kappa_1 = 6$ , but in aqueous environment, all three hydrates with  $n_{\text{CN, aq}} = 6, 7$ , and  $8$  may be present.  $\text{Sr}^{2+}$  prefers in the gas phase  $n_{\text{CN}} = 7$  rather than  $n_{\text{CN}} = 8$ , but  $n_{\text{CN, aq}} = 8$  seems to prevail in aqueous solution.

Our hope is that our empirical method together with sophisticated calculations can make a valuable tandem, and we believe that for values not yet calculated, e.g.,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and alkylammonium cations, the future results will comply with our empirical model. The strength of the model calculations is



**Figure 4.** Quartet rule for  $-\Delta G_n^f$  of alkali metal cations and halide anions mirrored in consecutive ionization potentials of respective atoms. Experimental data as they were gathered in ref 3. For better visibility, each doublet of curves above  $\text{Na}^+$  is shifted vertically up by one unit.



**Figure 5.** Octet rule for  $-\Delta G_n^f$  of alkaline earth cations mirrored in consecutive ionization potentials of respective atoms. Experimental data for  $\text{Sr}^{2+}$  from ref 48 and for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  from ref 37; for better visibility, the  $(-\Delta G_n^f - 2)$  are plotted on the y-axis for  $\text{Ca}^{2+}$  and  $(-\Delta G_n^f - 4)$  for  $\text{Mg}^{2+}$ .

already now proven for the case of hydration of alkaline earth cations. The values arrived at theoretically by Pavlov et al.<sup>37</sup> are exact to such an extent of precision that they could be treated by Peschke et al.<sup>38</sup> as experimental values. We did the same and Figure 5 justifies that decision, because the three lines there have the same pattern.

The constant value of  $\kappa_1 = 4$  found for the series of all alkali metal and halide ions is striking and needed more support.

In finding it, we started for the case of alkali metal cations with a somewhat oversimplified model. The classical electrostatic picture would suggest that the solvation of, e.g.,  $\text{Cs}^+$  proceeds by adding the donor polar molecule acting as a dipole to the core of the ion. No quantization will occur in this case. Another possible mechanism suggested<sup>53</sup> is a chemical reaction in the first layer of ions. This is again not a good idea, since no chemical bonds are formed during solvation. The only plausible mechanism at this time is a reaction of the solvating molecule as an electron donor with the ion. In it, a part of the electron density of a (basic) solvent is transferred to an ion and an electron donor bond is formed.<sup>1</sup> This process can be viewed as a degenerate partial neutralization of the ion charge (only a small portion of energy is transferred in this process, e.g., the first ionization potential of  $\text{Cs}$  is  $\sim 90$  kcal/mol, whereas the  $\Delta G_1^f$  of  $\text{Cs}^+$  in water is only 7.9 kcal/mol). Now, the question is how the second and following molecules of the solvent will interact with the ion. This at first glance can be so that the second



molecule of solvent interacts with the second electron counted from the surface of the ion, since if we want to have an intimate describing picture, no other possibility appears to be possible. This seems to be true if looking at Figure 4 from which respective relative IP values have the same dependence as those of energies of cluster formations. However, the same is true for halide ions. Thus, if this interaction is to be valid, then:

**Proposition IV.** If a causal connection among the patterns of gaseous ion cluster formation, Aufbau, and ionic potentials of an atom exists, then this connection is independent of the charge of an ion in a cluster.

The above proposition is corroborated by the fact that the  $\Delta G_n^f$ 's of neutral alkali metal clusters with water again display the four-coordination property, e.g., Hertel et al. have found that for photoionization of Na clusters both with water and with ammonia a remarkable break in the properties occurs for  $n = 4$ .<sup>56</sup> This finding was later broadened for Li, Na, and K clusters with ammonia by Takasu et al.<sup>57</sup> Thus, Proposition IV, if valid, concerns all +1, 0, and -1 valence ions.

No anionic or neutral counterparts exist for bivalent cations. However,  $\kappa_1 = 8$  applies well both for univalent  $\text{Sr}^+$  as well as for double-charged alkaline earth cations as seen from Figure 5; this again is in agreement with Proposition IV (the IP values in Figures 4 and 5 are from ref 58). It must be, however, noted that, even if the pattern formation is independent of charge, the charge is decisive for the absolute value of  $\Delta G_n^f$ ; for  $\text{Sr}^+$  this is equal to -25.2 kcal/mol, but for  $\text{Sr}^{2+}$ , it might be as high as  $\sim -71$  kcal/mol according to Figure 3.

The existence of a kind of mutual causal interdependence of cluster energetics with ionization potentials is somewhat corroborated by few subtle effects.

First, for alkaline earth atoms, the IP ratios would suggest  $\kappa_1 = 8$  for all (see Supporting Information), whereas actual  $\kappa_1$  values are lower for lighter ions. This fact seems in accordance with the above proposition, because in IP no such effects connected with mounting the solvent molecules around an ion (sterical hindrance, etc.) are present, and indeed for all of them, octacoordinated conformation is the best fit.

Second, we are able on the basis of IP ratios to also evaluate the cluster energetics for alkylammonium. The following reasoning concerning the IP of N seems to apply. Pentavalent nitrogen upon formation of alkylammonium ions gets rid of one electron, giving a positively charged ion. Hence, the electrons 2, 3, 4, and 5 (calculated from the outermost electron) ought to be responsible for the tetrahedral solvation behavior. Indeed,  $\text{IP}_3/\text{IP}_5$  and  $\text{IP}_4/\text{IP}_5$  for nitrogen are 0.485 and 0.791,<sup>58</sup> respectively, thus reasonably close to the values 0.5 and 0.75 posited for tetrahedral coordination. No other combination of relative IP's, even if tried, worked well for nitrogen.<sup>59,60</sup>

Still, there may be no interdependence of ionization potentials with cluster energetics. Then, the observed analogies would concern two independent phenomena and the following can be said:

**Proposition V.** If a causal connection among the patterns of gaseous ion cluster formation, Aufbau, and ionic potentials of an atom does not exist, the two represent a more general principle applying to both.

This principle could be common with, e.g., tetrahedral coordination of ubiquitous carbon or tetrahedral coordination of oxygen atom in liquid water, hence the common overall tendency of nature to form tetrahedral coordination. Yet, we are prone to prefer Proposition IV, since the probability of the all characteristics of cluster formation and ionization potentials being the same as found here, without any causal connection,

is considered to be small. The final answer can be hopefully determined in the future by model calculations.

In any case, the rules found in our paper are in their simplicity similar to the well-known Langmuir's octet rule.<sup>61</sup> Together with him, we can say, "The results obtained by the use of the postulates [propositions here—J.R., T.O.] are so striking that one may safely reason that the results establish the fundamental correctness of the postulates [propositions]." The tendency of nature to be guided by magical numbers 4 and 8 is not limited only to the chemical bonds but also to hydration and solvation processes.<sup>62</sup>

The last point to be dealt with here is the proposed strength of binding of the solvent molecules to the central ion. We in fact did not bring anything new to the question in this paper, and such questions as whether the molecules are "irrotationally bound" (in dielectric relaxation terminology) or "bound sufficiently strongly to be removed from the solvent" (in terms of colligative properties) can be answered here no better than in the original papers devoted to the studies of gaseous clusters.

On the other hand, we should pinpoint the dual character of the hydration as exemplified here by two different mechanisms considered in this paper, i.e., QF and IC. Although in the former stable positions around an ion are proclaimed, in the IC mechanism *all* molecules, including those in the first quantized layer, are involved. The proposed picture is as follows. The quantum numbers in the QF mechanism correspond to a "scaffold" formed around the ion, and the hydrating molecules just fit into it. On the other hand, the relative ease of mutual exchange of water molecules into the "scaffold" and out of it explains the peculiar character of the IC mechanism.

## Conclusions

In this paper, it has been shown that the hydration process in the first hydration layer around an ion obeys defined quantum numbers concerning the energetics of formation of consecutive clusters, and according to our previous findings, we believe that the concept applies more generally also to solvation by other solvents than water. The results of simple analysis reveal in agreement with the best theoretical protocols that (i) the first hydration shell of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  contains four molecules of water ( $\kappa_1 = 4$ ) and that (ii) in the hydration shell of alkaline earth cations approximately eight molecules of water ( $\kappa_1 = 8$ ) participate. In addition, the structures of more irregular ions like  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{Be}^{2+}$ , and  $\text{Zn}^{2+}$  established here do correspond to modern views on their solvation, still bringing some new aspects, e.g.,  $\text{Be}^{2+}$  and  $\text{Zn}^{2+}$  mimic the higher  $\kappa$  only in the first cluster, and further clusters are already tetrahedral. We found here that for  $\text{Rb}^+$  and  $\text{Cs}^+$  ions also the  $\kappa_1 = 4$  applies, the same as for halide anions. Primary and secondary alkylammonium ions behave nearly ideally; they contain in the first shell four molecules of water.

The solvation process is mirrored in the respective ionization potentials of atoms, which obey sensitively quartet and octet rules for simple alkali metal and halide atoms and alkaline earth metal atoms, respectively. The properties of atoms are more important for solvation than simple charges in the sense of the mode by which energy is divided among the consecutive clusters.

The findings of this study are remarkably in agreement with the theoretical studies considered here as the best. It is so for  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  ( $\kappa = 4$ ),<sup>8</sup> for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ ,<sup>15</sup> and for alkaline earth cations  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .<sup>37</sup> Good

agreement with recent studies by Tunell et al.<sup>55</sup> is also observed. These facts are highly encouraging, and hopefully may signify a possible future convergence of experimental and simulated results.

## Appendix

In our previous paper, we argued that the formation energy of the  $n$ th gaseous cluster around alkali metal and halide ions with tetrahedral coordination is empirically given by two relations 1 and 2<sup>63</sup>

$$\Delta G_n^f = \left[ 1 - \frac{(n-1)}{4} \right] \Delta G_1^f \quad (1)$$

$$\Delta G_n^f = \left( \frac{a}{n-1} \right) \Delta G_1^f + b \Delta G_1^f \quad (2)$$

We have argued that eq 1 applies for  $n = 1-3$ , since in practice the case of ideal tetrahedral filling never occurs. Concerning eq 2, already the fourth cluster might behave as obeying the mechanism of IC, and as seen from Figure 1, just in this case the resulting  $\Delta G_n^f$  will differ for IC and QF mechanisms. For many ions, eq 2 applies for the third cluster; hence, we plotted the dependences of  $\Delta G_n^f$  on  $1/(n-1)$  in Figure 2.

$a$  and  $b$  are correction parameters expressing how well the fourth (or  $\kappa$  molecule) fits into cluster. In the ideal case of  $a = 1$  and  $b = 0$ , eq 2 becomes simply

$$\Delta G_n^f = \left( \frac{1}{n-1} \right) \Delta G_1^f \quad (3)$$

The relation held approximately for all cases treated here.

For the general case, when  $\kappa_1$  water molecules can enter into the first solvation layer, the eq 1 simply becomes

$$\Delta G_n^f = \left[ 1 - \frac{(n-1)}{\kappa_1} \right] \Delta G_1^f \quad (4)$$

An equivalent mirror relation for ionization potentials of studied ions was checked here

$$\text{IP}_n = \frac{n}{\kappa_i} \text{IP}_{\kappa_i} \quad (5)$$

where  $\kappa_i$  corresponds to the number of the  $\kappa_i$ th ionization potential. Equation 5 for  $n = \kappa_i + 1$  leads to

$$\frac{\text{IP}_{\kappa_i+1}}{\text{IP}_{\kappa_i}} = \frac{\kappa_i + 1}{\kappa_i} \quad (6)$$

Together with eq 5, this is rewritten as follows:

$$\frac{\kappa_i}{\text{IP}_{\kappa_i}} (\text{IP}_{\kappa_i+1} - \text{IP}_n) = \kappa_i + 1 - n \quad (7)$$

In Figures 4 and 5, eq 7 was plotted together with eq 4 for alkali metal ions and halide anions, and alkaline earth metal ions, respectively.

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**Supporting Information Available:** Analyses of  $\Delta G_n^f$  for alkaline earth cations and of consecutive ionization potentials of alkaline earth atoms are given to check eq 4 and eq 5 and to give the best fit of  $\kappa_1$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (60) In the literature, we can find several empirical rules allegedly suitable for a rough estimate of IP's of outer electrons. Benson (Benson, S. W. *J. Phys. Chem.* **1989**, *93*, 4457) argued that generally one can represent successive ratios by  $\text{IP}(J)/\text{IP}(J+1) \sim J/(J+1)$ , where  $\text{IP}(J)$  is the  $J$ th ionization potential of the species considered. Recently, rather arduous discussion on this rule lead by Lowe (e.g., Lowe, J. P. *Chem. Educ.* **2000**, *77*, 155; **2002**, *79*, 30, 429) and Rioux and DeKock (e.g., Rioux, F.; DeKock, R. L. *Chem. Educ.* **2002**, *79*, 29, 429) appeared. This was mainly oriented on the question of whether the energy of an electron is to be viewed as potential or kinetic, which is of less interest here. The above rule of Benson of course differs from the rules given in this article.
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- (63) In our previous article,<sup>3</sup> a typographical error occurred on the right side of eq 2; the formula is retyped correctly here.