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Hydrations of Metal Ions in Aqueous Electrolyte Solutions: A Raman Study

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With a simple theoretical derivation, we present a new correlation equation between a Raman ν_1 band and r_{M-O} , where ν_1 is the frequency of the total symmetric stretching vibrations of aquated metal ions and r_{M-O} is the distance between a metal cation and its coordinated water molecule. It is shown that there is a linear relationship between ν_1 and $1/r_{M-O}^2$ for the cations of the same valence with the same hydration number. Although the electrostatic theory for ionic hydration can explain most of the hydrations of both divalent and trivalent metal ions in aqueous electrolyte solutions, it became clear that the discreteness of water molecules must be taken into account for a future successful theory of ionic hydration.

Introduction

The interpretation of cation hydration in aqueous electrolyte solutions has been the subject of many discussions.¹⁻³ One of the most difficult problems in the molecular-level interpretation is that there are still only insufficient data for structural and/or thermodynamic parameters such as the ion-solvent distance and the force constants for the hydration bonds.

Thanks to recent extensive X-ray diffraction and neutron scattering experiments,^{4,5} a fairly large number of the M-O distances (M, a metal ion) are now available for hydrated metal ions $[M(OH_2)_n]^{z+}$ (n , number of coordinated water molecules). When the interactions between a metal ion and its coordinated water molecules are strong enough, a highly polarized Raman band (a ν_1 band) due to the symmetric M-O stretching vibrations is observed in the frequency region of 300–550 cm⁻¹.

Although there have been a large number of Raman ν_1 data for aqueous electrolyte solutions,^{6,7} there have been only a few cases in which the Raman ν_1 data have been examined to get insight into cation hydration.⁷⁻⁹ As the involvement of ligands other than water molecules in the inner-sphere coordination induces some frequency change in the M-OH₂ stretching vibrations,¹⁰ care must be exercised to distinguish ν_1 values for all-aquated cations from the ones for partially aquated cations. Therefore, as a first step, it is important to consider the hydration of all-aquated metal ions since all-aquated cations constitute a fundamental base for every study on cation hydration.

In the previous paper,¹¹ I reported the ν_1 data for hydrated divalent metal ions together with the empirical linear correlation between the ν_1 frequency and the bond distance (r_{M-O}) between a cation and its coordinated water molecule. As the Raman ν_1 data for hydrated metal ions are mostly reported for different purposes other than cation hydration,^{12,13} we here summarized

all the ν_1 values so far reported and analyzed them from the point of cation hydration.

First we present a simple theoretical derivation of a correlation equation between ν_1 and r_{M-O} , and then we discuss the ν_1 data by means of the derived relation.

Theoretical Consideration

The Born equation, which is the simplest form among many theoretical equations, is still one of the most frequently used formulas in describing cation hydration.^{2,3} In the Born model, interactions between a cation and solvent are considered to be electrostatic in origin with the ion viewed as a charged sphere of a radius r_c and the solvent as a dielectric continuum of dielectric constant D . Here, we also assume that the interactions between a metal ion and its coordinated water molecules are electrostatic. So far as the total symmetric stretching vibration is considered, the cation does not move so that its mass does not affect the ν_1 frequency. Accordingly the potential between a cation and its hydrated water molecule is represented by

$$\Phi = Ar^n - Br^m \quad (1)$$

where A and B are positive constants, n and m are positive integers, and r is the distance between the cation and its coordinated water molecule. When the energy of the pair of the ion and its hydrated water molecule is at its minimum, the force exerted between them is zero; hence

$$\left(\frac{\partial \Phi}{\partial r} \right)_{r=r_e} = 0 \quad (2)$$

where r_e is the equilibrium separation. It follows that the energy Φ_e , corresponding to the equilibrium separation, is

$$\Phi_e = -Br_e^{-m}(1 - m/n) \quad (3)$$

Elimination of A and B enables us to rewrite (1) as

$$\Phi = \Phi_e \frac{1}{(m-n)} \left\{ m \left(\frac{r_e}{r} \right)^n - n \left(\frac{r_e}{r} \right)^m \right\} \quad (4)$$

When the displacement of the hydrated water molecule from its equilibrium position is not large, the motion of the water molecule is described as a simple harmonic oscillation with frequency

$$\nu_1 = \frac{1}{2\pi r_e} \left(\frac{mn}{M} |\Phi_e| \right)^{1/2} \quad (5)$$

If the energy of attraction of an ion and its coordinated water molecule is mainly represented by the ion-dipole moment interaction, we get

$$\Phi_e = -\frac{ze\mu}{r_e^2} \left(1 - \frac{2}{n} \right) \quad (6)$$

where z is the charge of the cation, μ is the effective dipole moment

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TABLE I: Observed Raman Band Positions (in cm^{-1}) for M-OH₂ Stretching Vibrations of Hydrated Divalent Cations in Aqueous Electrolyte Solutions

solution	Raman ν_1 band/cm ⁻¹			
	glassy state	liquid state	lit.	$r_{\text{M}-\text{O}}/\text{\AA}$
BeCl_2 ($R = 10$) ^b	535 ± 3	529 ± 5	535^a	1.67^d
MgCl_2 ($R = 16$)	370 ± 3	357 ± 3	359^a	2.04^e
$\text{Ca}(\text{ClO}_4)_2$ ($R = 10$)		290 ± 10		2.43^e
MnCl_2 ($R = 18$)	366 ± 3	358 ± 5	352^b	2.20^e
FeCl_2 ($R = 20$)	388 ± 3	380 ± 5	370^b	2.12^e
$\text{Ni}(\text{NO}_3)_2$ ($R = 13$)	403 ± 3	390 ± 3	390^a	2.04^e
CuCl_2 ($R = 10$)	434 ± 3	390 ± 5	436^a	1.94^e
$\text{Cu}(\text{NO}_3)_2$ ($R = 12$)	437 ± 3	434 ± 3	436^a	1.94^e
$\text{Zn}(\text{NO}_3)_2$ ($R = 12$)	400 ± 3	390 ± 3	388^c	2.08^e
$\text{Cd}(\text{ClO}_4)_2$ ($R = 15$)	360 ± 3	356 ± 3	355^c	2.31^e
$\text{Hg}(\text{ClO}_4)_2$ ($R = 14$)	378 ± 3	372 ± 3	375^c	2.41^f
$\text{Pb}(\text{ClO}_4)_2$ ($R = 10$)		302 ± 5		2.60^g

^a From ref 6. ^b From ref 7. ^c From ref 16. ^d From ref 29. ^e From ref 4. ^f From ref 19. ^g Estimated from ionic radii of Pb^{2+} (1.20 Å) and O^{2-} (1.40 Å). ^h R is the ratio of moles of water to moles of salt in the solution.

of a hydrated water molecule, and M is the mass of a water molecule.¹⁴ Hence

$$\begin{aligned}\nu_1 &= \frac{1}{2\pi r_e} \left(\frac{mn}{M} |\Phi_e| \right)^{1/2} \\ &= \frac{z^{1/2}}{r_e^2} \left(\frac{n e \mu}{M \pi^2} \left(1 - \frac{2}{n} \right) \right)^{1/2}\end{aligned}\quad (7)$$

It is expected that the repulsion index n should be similar for the cations of the same chemical family, and the observed bond distance ($r_{\text{M}-\text{O}}$) is equal to the equilibrium separation (r_e). Thus we get

$$\nu_1 \approx \frac{C z^{1/2}}{r_{\text{M}-\text{O}}^2} \quad (8)$$

where C is a constant.

Results and Discussion

The summarized ν_1 data for all-aquated divalent metal ions are shown in Table I, and the plot of the ν_1 values against $1/r_{\text{M}-\text{O}}^2$ is shown in Figure 1. Here we used preferentially the ν_1 values for glassy aqueous solutions simply because a weak low-frequency Raman ν_1 band is observed more clearly in a glassy solution than in a liquid solution at room temperature¹² and because all-aquated metal ions tend to become more dominant in the glassy solution than in the liquid solution at room temperature when there are chemical equilibria among all-aquated metal ions and the aquated metal complex ions partially coordinated with anions such as chloride or nitrate ions.¹⁵ It can be seen that all the ν_1 data except the ν_1 value for Hg^{2+} ion correlate strongly with the reciprocal of $r_{\text{M}-\text{O}}^2$, indicating that hydration of divalent metal ions is mainly interpretable in terms of the ion-dipole moment interaction.

First we must give some interpretation of the fact that, as previously reported,¹¹ an approximately linear relation also holds between ν_1 and $1/r_{\text{M}-\text{O}}$. This can be explained as follows: When we express $r_{\text{M}-\text{O}}$ by the relation $r_{\text{M}-\text{O}} = r_0(1 + y)$, where r_0 is a reference bond distance and y is a variable less than 1, we obtain

$$1/r_{\text{M}-\text{O}} = 1/\{r_0(1 + y)\} \approx (1 - y)/r_0$$

$$1/r_{\text{M}-\text{O}}^2 = 1/\{r_0(1 + y)\}^2 \approx (1 - 2y)/r_0^2$$

Therefore, we easily understand that a linear relation holds be-

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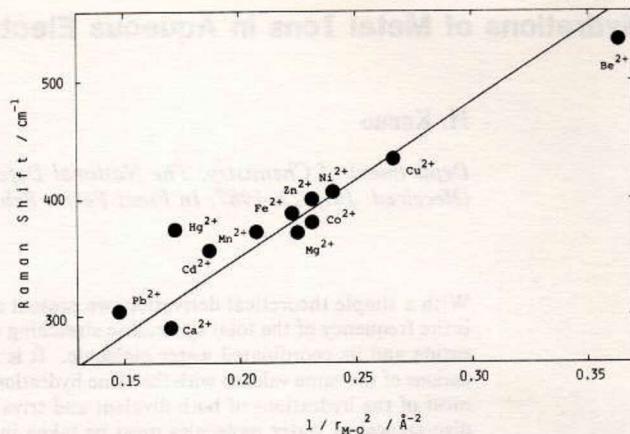


Figure 1. Correlation of the ν_1 bands for aquated divalent cations with the inverse square of the M-OH₂ distance ($1/r_{\text{M}-\text{O}}^2$). The ν_1 value for aquated Co²⁺ ions (380 cm⁻¹) was obtained from ref 6, and the $r_{\text{M}-\text{O}}$ value (2.08 Å) was from ref 4b. The equatorial $r_{\text{M}-\text{O}}$ value (1.94 Å) was used for the plotting of the ν_1 value of Cu²⁺ ions.

tween not only ν_1 and $1/r_{\text{M}-\text{O}}^2$ but also ν_1 and $1/r_{\text{M}-\text{O}}$ if only $y \ll 1$. The regression coefficients of the ν_1 vs $1/r_{\text{M}-\text{O}}$ and ν_1 vs $1/r_{\text{M}-\text{O}}^2$ relations are 0.93 and 0.94, respectively. Thus, from the regression coefficients it can be said that the correlations are very good.

At this point, it is fair to point out that Irish and Jarv¹⁶ found an almost linear relation between ν_1 and cation polarizing power $P = z/(r^+ S_{\text{eff}})$, where S_{eff} is the nuclear charge shielding factor as defined by Ahrens¹⁷. As the polarizing power of an ion can be roughly regarded as being equivalent to the ionic potential z/r^+ , we consider that the linear empirical relation between ν_1 and P is almost the same as the linear relation between ν_1 and $1/r_{\text{M}-\text{O}}$.

A remarkable point in the plots shown in Figure 1 is that the first transition-metal ions together with Cd²⁺ and Pb²⁺ lie on the almost straight line although Co²⁺ ion deviates a little from the line. The deviation of the ν_1 value for [Co(OH₂)₆]²⁺ ions is attributed to the use of the ν_1 value for the liquid state.⁶ A shift of 10–20 cm⁻¹ is usually observed for a ν_1 band from a liquid state to a glassy state.¹¹ Accordingly, it is expected that $\nu_1(\text{Co}^{2+})$ will be on the line if the ν_1 value for the glassy solution is plotted.

It is a fairly general observation that the complex formation constants of the divalent metal ions (the first transition-metal ions from Mn²⁺ to Zn²⁺) fall in the order Mn²⁺ < Fe²⁺ < Co²⁺ < Ni²⁺ < Cu²⁺ > Zn²⁺, which is well-known as the Irving-Williams series.¹⁸ Taking into account the expectation that $\nu_1(\text{Co}^{2+})$ will be about 390 cm⁻¹ in a glassy Co(II)-salt solution, it is evident that the ν_1 values for the first transition-metal ions also follow the Irving-Williams series. As the distribution of d-electron density around a M²⁺ ion is not spherical for these divalent ions except Be²⁺, Ca²⁺, Mn²⁺, Hg²⁺, Cd²⁺, and Zn²⁺, a simple Born-type calculation should not give a correct hydration energy. However, the linear relation between ν_1 vs $1/r_{\text{M}-\text{O}}^2$ indicates that the electrostatic model can explain most of the hydration of a divalent transition-metal ion. We consider that the nonspherical nature of d-electron transition-metal ions must be taken into account for a successful interpretation of the hydrations of these metal ions.

A large deviation of $\nu_1(\text{Hg}^{2+})$ from the straight line, which is obtained from the least-squares curve fitting excluding the ν_1 values for Be²⁺ and Hg²⁺ ions, needs some explanation. From the straight line and the $r_{\text{M}-\text{O}}$ value (2.40 Å) for an aquated Hg²⁺ ion,¹⁹ the ν_1 frequency is expected to be around 310 cm⁻¹, but the observed ν_1 value is at 378 cm⁻¹ for the glassy Hg(ClO₄)₂ solution ($R =$

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TABLE II: Observed Raman Band Positions (in cm^{-1}) for M-OH₂ Stretching Vibrations of Hydrated Trivalent Cations in Aqueous Electrolyte Solutions

solution	Raman ν_1 band/ cm^{-1}			
	values obtained in our lab			
	glassy state	liquid state	lit.	$r_{\text{M}-\text{O}}/\text{\AA}$
AlCl ₃ ($R = 20$)	535 ± 3	525 ± 5	526 ^a	1.89 ^f
GaCl ₃ ($R = 20$)	530 ± 3	520 ± 5	(2.02) ^g	
In(NO ₃) ₃ ($R = 20$)	490 ± 3	475 ± 3	485 ^b	2.15 ^h
Fe(NO ₃) ₃ ($R = 20$)	506 ± 3		510 ^c	2.00 ^h
YCl ₃ ($R = 20$)	397 ± 3	380 ± 5		(2.33) ^g
ScCl ₃ ($R = 25$)	450 ± 3	440 ± 5		(2.18) ^g
Bi(NO ₃) ₃ ($R = 20$)	395 ± 3	390 ± 3	390 ^d	(2.57) ⁱ
TlCl ₃			450 ^e	2.23 ^j
LaCl ₃ ($R = 24$)	354 ± 3			2.58 ^k
CeCl ₃ ($R = 24$)	358 ± 3			(2.56) ^l
PrCl ₃ ($R = 24$)	361 ± 3			2.54 ^k
SmCl ₃ ($R = 24$)	367 ± 3			2.47 ^k
EuCl ₃ ($R = 24$)	369 ± 3, 394 ± 3			2.45 ^k
GdCl ₃ ($R = 20$)	371 ± 3, 396 ± 3			(2.43) ^l
TbCl ₃ ($R = 24$)	398 ± 3			2.41 ^k
DyCl ₃ ($R = 24$)	400 ± 3			2.40 ^k
TmCl ₃ ($R = 24$)	404.5 ± 3			2.36 ^k
YbCl ₃ ($R = 24$)	406 ± 3			2.35 ^k
LuCl ₃ ($R = 24$)	406.5 ± 3			2.34 ^k

^a From ref 28. ^b From ref 16. ^c From ref 13. ^d From ref 33. ^e From ref 31. ^f From: Caminiti, R.; Licheri, G.; Piccudaga, G.; Pinna, G.; Radnai, T. *J. Chem. Phys.* **1979**, *77*, 2473. ^g These are estimated by using Pauling's ionic radii (Ga³⁺, 0.62; Y³⁺, 0.93; Sc³⁺, 0.81; and O²⁻, 1.40 Å). ^h From ref 4. ⁱ Estimated by using Shannon's ionic radius of Bi³⁺ (1.17 Å). ^j From: Glaser, J. Doctoral Thesis, Royal Institute of Technology, Stockholm, 1981. ^k From ref 34. ^l Estimated from the $r_{\text{M}-\text{O}}$ values of adjacent hydrated rare-earth ions.

14). There are two possible causes for this large deviation: a small hydration number and a high covalency of the Hg(II)-OH₂ interactions. The former one is well exemplified by the observation that the conversion from an octahedral to a tetrahedral configuration of a metal halide usually results in an increase in the frequency of the symmetric stretching vibrations.²⁰ A similar frequency increase is seen in the hydration number change in rare-earth ions (Eu³⁺ and Gd³⁺ ions) from 9 to 8,²¹ which will be discussed in more detail later. Thus, if Hg²⁺ is tetrahedrally hydrated, i.e., [Hg(OH₂)₄]²⁺, it is only reasonable that the observed ν_1 is considerably higher than the one expected from the straight line, which is for octahedrally hydrated divalent metal ions. However, an X-ray diffraction study on an Hg(ClO₄)₂ solution reported that Hg²⁺ ions are octahedrally hydrated.¹⁹ On the other hand, it is important to note that Hg²⁺ ion has a strong tendency to complex formation and that the characteristic coordination numbers are two and four (Hg complexes with octahedral coordination are rather rare).²² The other possibility, which seems more plausible with the present available experimental data, is the high covalency of the Hg²⁺-OH₂ bond. In the Raman study by Irish and Jarv,¹⁶ it is reported that the molar intensities of the ν_1 bands increase in the order Mg²⁺ < Zn²⁺ < Cd²⁺ < Hg²⁺. The high intensity of the ν_1 band for aquated Hg²⁺ ions is a clear reflection that the Hg²⁺-OH₂ bond has high covalency.

Among hydrated divalent metal ions, Be²⁺ ion is the only one which has a hydration number different from 6, i.e., 4. Although most investigators using various spectroscopic methods²³⁻²⁷ have

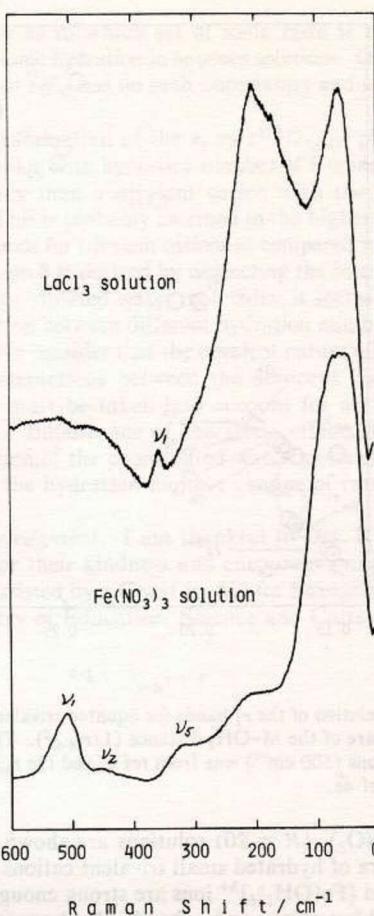


Figure 2. Raman spectra of the LaCl₃ ($R = 25$) and Fe(NO₃)₃ ($R = 20$) solutions in the glassy state at liquid nitrogen temperature. The ~200- and ~60-cm⁻¹ bands in the Raman spectrum for the glassy LaCl₃ solution are the restricted translational vibrations of water molecules. The intense ~60-cm⁻¹ band in the Fe(NO₃)₃ solution is due to the restricted rotational vibrations of nitrate ions which are superimposed on the restricted translational vibrations of water molecules.

reported that the inner-sphere hydration number is 4, a few assert that it is 6.^{28,29} Marques et al.²⁸ assigned the Raman bands at 528 and 348 cm⁻¹ of a 2.6 mol dm⁻³ Be(NO₃)₂ solution to the ν_1 and ν_3' modes of an octahedral [Be(OH₂)₆]²⁺ ion. A recent molecular dynamics calculation by Yamaguchi et al.²⁹ also gives a hydration number of 6 for Be²⁺ ions in an aqueous BeCl₂ solution. However, with present available experimental data,^{23-26,30} we believe that the tetrahedral hydration is rather conclusive for aquated Be²⁺ ions. The tetrahedral [Be(OH₂)₄]²⁺ structure is well established in a hydrated BeSO₄·4H₂O crystal and Raman spectra of the salt give most definitive support for the tetrahedral structure of aquated Be²⁺ ions.³⁰ A recent X-ray diffraction study also reached the same conclusion.²⁹ As the $\nu_1(\text{Be}^{2+})$ value is a little below the line for octahedrally hydrated divalent metal ions, it is clear that the interactions between a Be²⁺ ion and its coordinated water molecules are weaker than the ones expected for tetrahedral hydration. This point was already discussed in the previous paper.¹¹

The summarized ν_1 values for hydrated M³⁺ ions are shown in Table II together with some literature values.^{16,27,31-33} As already reported,²¹ the ν_1 bands for hydrated rare-earth ions are very weak and are only observable in the glassy states of the solutions. Raman spectra of the ν_1 bands of glassy LaCl₃ ($R =$

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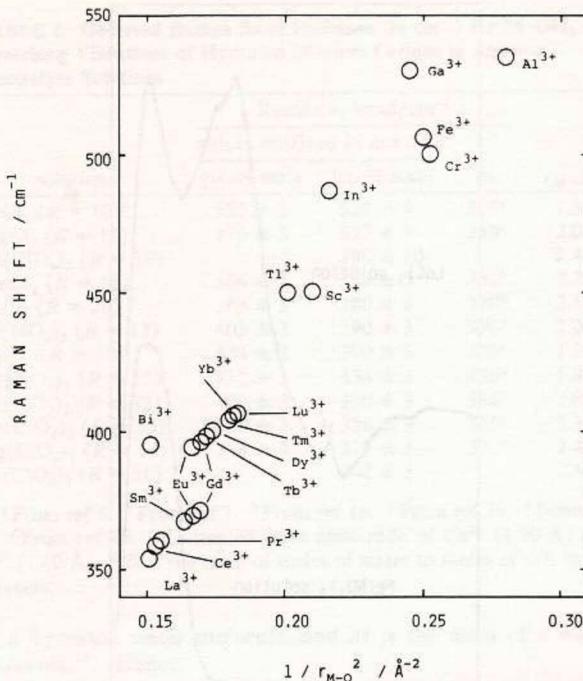


Figure 3. Correlation of the ν_1 bands for aquated trivalent cations with the inverse square of the $M-OH_2$ distance ($1/r_{M-O}^2$). The ν_1 value for aquated Cr^{3+} ions (500 cm^{-1}) was from ref 6, and the r_{M-O} value (1.99 \AA) was from ref 4a.

25) and $Fe(NO_3)_3$ ($R = 20$) solutions are shown in Figure 2. Raman spectra of hydrated small trivalent cations such as $[Al(OH_2)_6]^{3+}$ and $[Fe(OH_2)_6]^{3+}$ ions are strong enough to give not only a ν_1 band but also ν_2 and ν_5 bands. In the cases of divalent cations, Be^{2+} ion is the only one that gives observable Raman bands (ν_2 and ν_4) other than a ν_1 band.

The plot of the ν_1 bands of all-aquated trivalent cations vs $1/r_{M-O}^2$ is shown in Figure 3. Although these ν_1 data scatter more than those of the divalent cations, an approximately linear relation is again obtained. Hydrated trivalent metal cations can be divided into three groups according to their inner-sphere hydration numbers: the six-water group (Al^{3+} , Ga^{3+} , Fe^{3+} , Cr^{3+} , In^{3+} , and Tl^{3+}),⁴ the eight-water group (heavy rare-earth ions) and the nine-water group (light rare-earth ions).³⁴ It is evident that a linear relationship holds better within each group than for the cations overall. Some hydrated cations (aquated Sc^{3+} and Bi^{3+} ions) have uncertain inner-sphere hydration numbers.³⁵

An inner-sphere hydration number change in the rare-earth-ion series is now well established.^{21,34} From the ν_1 frequency shift due to the hydration number change, we know that hydration enthalpy is greatly dependent on the inner-sphere hydration number. Bertha and Choppin³⁶ evaluated the hydration enthalpies for all the rare-earth members and found that the hydration enthalpy rapidly increases from Nd^{3+} to Tb^{3+} at which inner-sphere hydration number changes. Spedding and his co-workers³⁷⁻³⁹ gave ample experimental data demonstrating that transport and thermodynamic properties of aqueous rare-earth electrolyte solutions are greatly dependent on the inner-sphere hydration number of rare-earth ions. Glass transition temperatures of aqueous rare-earth chloride and perchlorate solutions show the S-shaped behavior across the series, reflecting the hydration number change

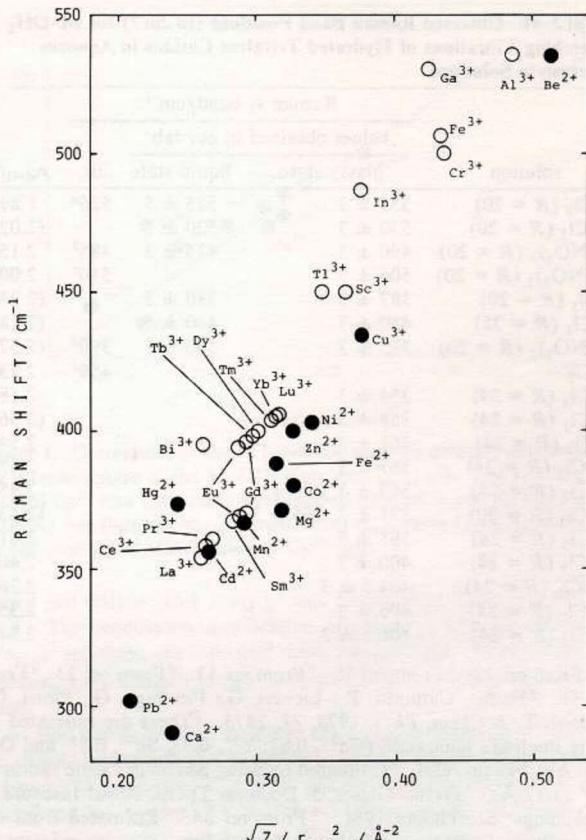


Figure 4. Correlation of the Raman ν_1 bands with $z^{1/2}/r_{M-O}^2$. ●, aquated divalent metal ion; ○, aquated trivalent metal ion.

in the middle of the series.⁴⁰ These are strong experimental evidence for the contention that the discrete nature of water molecules will have to be incorporated into a successful solution theory, instead of the continuous dielectric theory for aqueous electrolyte solutions. Importance of the discreteness of water molecules in the cation hydration is also shown by the ν_1 frequency of hydrated Al^{3+} ions. From the approximate linear relation between the ν_1 frequency and $1/r_{M-O}^2$ for hydrated Ga^{3+} , In^{3+} , and Tl^{3+} ions, it is expected that the ν_1 band of $[Al(OH_2)_6]^{3+}$ ions should be at about 580 cm^{-1} . On the other hand, the observed ν_1 frequency is at 535 cm^{-1} , which is about 50 cm^{-1} lower than the expected ν_1 value. We consider that this also arises from the mismatching between an Al^{3+} ion and the cavity, in which the Al^{3+} ion resides, created by the six-coordinated water molecules. The radius ratio (r^+/r^-) of an Al^{3+} ion and an H_2O (an O^{2-} ion) is 0.357 (Al^{3+} , $r^+ = 0.50\text{ \AA}$; O^{2-} , $r^- = 1.40\text{ \AA}$), which is out of the stable range for octahedral ionic structure ($0.41 < r^+/r^- < 0.73$).⁴¹ Thus we have three clear experimental data illustrating the importance of the relative sizes of cations and water molecules in the consideration of cation hydrations.

A brief comment on numerous ν_1 values of hydrated M^{3+} ions in cesium alums is in order. Best et al.⁴² observed Raman spectra for many cesium M(III)—alums [$M^{3+} = Ti^{3+}$, V^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , Rh^{3+} , and Ir^{3+}]. An interesting point of their ν_1 results is that the ν_1 frequency for a hydrated M^{3+} ion in a solid alum is always higher than that in a M(III)-electrolyte solution by $10-20\text{ cm}^{-1}$. This difference can be ascribed to the bond length (r_{M-O}) difference between the crystal and the solution.⁴³ The r_{M-O} value of $[M(OH_2)_6]^{3+}$ ions in an alum crystal is shorter than

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that in solution, indicating that the M-O bond strength should be stronger in the alum than in the solution.

Now we test the applicability of (8) to cation hydration. Figure 4 displays the ν_1 results for both divalent and trivalent cations as a function of $z^{1/2}/r_{M-O}^2$. All the ν_1 data approximately constitute a linear relationship, demonstrating that (8) is applicable to the hydration of most divalent and trivalent cations. It is inferred from the linear relation that the repulsion index n is rather invariant for both divalent and trivalent cations. It is reasonable that, different from ion packing in an ionic crystal, the repulsion term in (6) does not play an important role in the ion-coordinated water molecule interactions. In other words, the potential-well profile between a cation and a coordinated water molecule should be similar for most of the divalent and trivalent metal ions at their equilibrium positions.

An important consequence from Figure 4 is that instead of ionic radius the ion-coordinated water distance (r_{M-O}) is the parameter that should be employed for describing the hydration enthalpy and other thermodynamic properties relating to ionic hydration. The use of an observed r_{M-O} value can eliminate the uncertainty in using the ionic radius. Real ions are not hard spheres, and each useful set of ionic radii is obtained through procedures with some ambiguities and approximations. Thus there is bound to be some

uncertainty as to which set of ionic radii is to be chosen for describing ionic hydration in aqueous solutions. On the other hand, the observed r_{M-O} has no such uncertainty and no approximation is involved.

Close examination of the ν_1 vs $z^{1/2}/r_{M-O}^2$ plot shows that a trivalent cation with hydration number of 6 tends to give a higher ν_1 frequency than a divalent cation with the same hydration number. This is probably ascribed to the higher covalency of the M-OH₂ bonds for trivalent cations as compared with divalent ones.

As relation 8 is derived by neglecting the interactions between adjacent coordinated water molecules, it seems reasonable that the distinction between different hydration numbers now becomes obscure. We consider that the covalent nature of hydration bonds and the interactions between the adjacent coordinated water molecules must be taken into account for an improvement of relation 8. Importance of the steric effects arising from the configuration of the coordinated water molecules is best exemplified by the hydration number change of rare-earth ions.

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