Theoretical Modeling of Magnesium Ion Imprints in the Raman Scattering of Water

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Hydration envelopes of metallic ions significantly influence their chemical properties and biological functioning. Previous computational studies, nuclear magnetic resonance (NMR), and vibrational spectra indicated a strong affinity of the Mg²⁺ cation to water. We find it interesting that, although monatomic ions do not vibrate themselves, they cause notable changes in the water Raman signal. Therefore, in this study, we used a combination of Raman spectroscopy and computer modeling to analyze the magnesium hydration shell and origin of the signal. In the measured spectra of several salts (LiCl, NaCl, KCl, MgCl₂, CaCl₂, MgBr₂, and MgI_2 water solutions), only the spectroscopic imprint of the hydrated Mg^{2+} cation could clearly be identified as an exceptionally distinct peak at \sim 355 cm⁻¹. The assignment of this band to the Mg–O stretching motion could be confirmed on the basis of several models involving quantum chemical computations on metal/water clusters. Minor Raman spectral features could also be explained. Ab initio and Fourier transform (FT) techniques coupled with the Car-Parrinello molecular dynamics were adapted to provide the spectra from dynamical trajectories. The results suggest that even in concentrated solutions magnesium preferentially forms a $[Mg(H_2O)_6]^{2+}$ complex of a nearly octahedral symmetry; nevertheless, the Raman signal is primarily associated with the relatively strong metal-H₂O bond. Partially covalent character of the Mg-O bond was confirmed by a natural bond orbital analysis. Computations on hydrated chlorine anion did not provide a specific signal. The FT techniques gave good spectral profiles in the high-frequency region, whereas the lowest-wavenumber vibrations were better reproduced by the cluster models. Both dynamical and cluster computational models provided a useful link between spectral shapes and specific ion-water interactions.

Introduction

Simple monatomic ions in aqueous environment are essential for many important biological processes in living organisms, such as osmotic regulation, neural impulses, muscle contraction, and protein conformational changes.¹⁻³ The metal ions often react quite specifically, exhibiting strong affinity to particular binding sites.⁴ Anions, such as halogens, appear more important for water bulk properties.⁵ It is clear that ionic physical properties are modulated by the hydration shell and interactions with the water molecules, but determination of the exact mechanisms is often hindered by the lack of experimental data. Some biological systems that could enlighten the role of the ions are difficult to crystallize. Nevertheless, many techniques, such as X-ray crystallography or NMR spectroscopy, did provide valuable insights into the origin of specific ionic interactions.^{1,6} Vibrational spectra allow one to estimate the metal-water bond strength.⁷ To contribute to this process, we explore the ability of the Raman scattering to detect specific ion-water interactions, particularly those of the magnesium ion providing the most distinct signal in the spectrum.

Vibrational properties probed by the Raman techniques and infrared absorption (IR) proved previously as sensitive indicators of the water structure. For example, the IR and Raman signal of the OH stretching seems to indicate clustering in liquid water as dependent on the temperature.^{8–10} Librational motions (within 700–900 cm⁻¹) are sensitive to the ice structure and isotopomer

composition.¹¹ Vibrational investigations of more complex ionic solutions are rarer.^{7,12}

The information about structure encoded into the spectral band frequencies and intensities can be to a great extent decoded by computer simulations. Unlike for isolated molecules, however, bulk water and aqueous ionic solutions provide a limited amount of spectral features. A large part of the structural information is reflected in an inhomogeneous broadening of spectral shapes and requires special interpretation procedures.^{13–15} Molecular dynamics (MD) with empirical $^{9,16-18}$ and ab initio 19,20 force fields provide the most flexible means for modeling of the structure and its development in time. Most often, the computationally efficient Car-Parrinello formulation of the ab initio molecular dynamics (CPMD) is preferred.²¹ The CPMD and other ab initio MD techniques particularly enhanced structural studies of ionic solutions that, being complicated electronic systems, cannot be described by empirical force fields.2,22,23

IR and Raman spectral profiles can be simulated by various Fourier transform techniques from the time dependence of the dipole and polarizability functions, respectively.^{18,20,24,25} The Fourier simulations can partially account for anharmonic effects and inhomogeneous broadening of spectral lines; in principle, however, they are constrained to the harmonic approximation. Alternatively, the instantaneous mode approximation and cluster approaches reproduce most of the spectral features.^{26,27} The static models do not include the motion explicitly but typically allow one to calculate spectroscopic properties at a higher approximation level, and provide more flexibility, potentially including also the anharmonic effects. In the present study, both ap-

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proaches are used, as they reveal different aspects of the origin of the Raman signal.

The metal ions obviously have no vibrational spectra themselves. The specific spectroscopic signal comes from the perturbed liquid water structure in the vicinity of the ion. Potentially, the weak water—water, metal—water, and other noncovalent interactions are involved, which makes the Raman technique very attractive, as it enables measurement to very low vibrational frequencies comprising fundamental vibrational modes that correspond to these weak interactions.^{7,28,29}

In this work, we have measured Raman spectra of several salts dissolved in water in order to map their influence on the water light scattering and, in final effect, on the water and hydration shell structure. As only the magnesium ion among the light metals exhibited an exceptionally specific band at ~355 cm⁻¹, we concentrated MD and ab initio modeling to this ion in aqueous solutions. Classical and Car-Parrinello MD were used to estimate the dynamical behavior of the hydration shell. Cluster and Fourier transform techniques were tested for generation of the Raman spectra. The computations confirm that the signal stems from the tight magnesium-oxygen binding and relatively rigid structure of the magnesium first hydration shell. The experimental results and CPMD computations indicate that the signal is not exclusively associated with an ideal octahedral structure but rather with individual Mg-O bond stretchings. A natural bond orbital analysis suggests that the Mg-O bond adopts a partially covalent character.

Methods

Experimental Section. Samples of the salts (LiCl, NaCl, KCl, MgCl₂, CaCl₂, MgBr₂, and MgI₂) were supplied by Sigma-Aldrich and used without further purification. Raman spectra were measured in a backscattering mode using the previously described ChiralRAMAN instrument (BioTools, Inc.).³⁰ The laser wavelength was 532 nm, laser power at the sample ~ 0.3 W, spectral resolution 10 cm⁻¹, and acquisition times 10–30 min. All spectral intensities were divided by accumulation time so that they are normalized to the same intensity scale. The Raman spectrum of an empty quartz cell was subtracted from all spectra. Note that the normalization is very approximate, as the collection angle of Raman scattering depends, among other factors, on the concentration and hence on the refractive index of the solution. For the HOH bending signals, Lorentzian bands were fitted to the experimental spectra with a correction to linear baseline using the SpectraCalc (Galactic Industries) software to get central peak positions and full widths at half-height.

Ab Initio Cluster Calculations. Geometries of metal (Na⁺, Ca²⁺, Mg²⁺) and water clusters were optimized by energy minimization at the HF, MP2, MP4, and B3LYP³¹ approximation levels and standard 6-311++G^{**} and aug-cc-pVTZ basis sets, using the Gaussian software.³² At the same level as for the optimization, harmonic frequencies and backscattered Raman transition intensities were calculated as³³

$$I_{180} = 7S_1 + S_0 \tag{1}$$

where $S_1 = \sum_{i=1...3,j=1...3} \alpha_{ij} \alpha_{ij}$ and $S_0 = \sum_{i=1...3,j=1...3} \alpha_{ii} \alpha_{jj}$ are the isotropic invariants of the transition polarizability. The spectra were generated using a temperature correction factor³³ and Lorentzian bands of full width at half-maximum $\Delta = 5 \text{ cm}^{-1}$ as

$$S(\omega) = I_{180} \left[1 - \exp\left(-\frac{\omega_i}{kT}\right) \right]^{-1} \frac{1}{\omega_i} \left[4 \left(\frac{\omega - \omega_i}{\Delta}\right)^2 + 1 \right]^{-1}$$
(2)

where *k* is the Boltzmann constant, *T* temperature, ω_i transition frequency, and ω the light frequency. The Gaussian program was also used for the natural bond orbital (NBO) analysis³⁴ of the wave function.

CPMD Simulations. Periodic boxes containing 33 water molecules and salt ions were created by the HyperChem program.³⁵ The sizes of the boxes approximately corresponded to the experimental densities of salt solutions at 300 K. The systems included pure water, hydrated Mg²⁺, Ca²⁺, Na⁺, and Cl⁻ ions, and a box containing three Mg and six Cl atoms corresponding to the experimentally investigated 5 mol/kg MgCl₂ solution. Within HyperChem and the Amber99 force field,^{36,37} classical molecular dynamics (MD) was run for 1 ns with 1 fs integration time steps and a temperature of 400 K to equilibrate the systems. The TIP3P³⁸ model as a part of Amber99 was used for water. Because this approach did not provide symmetric Mg²⁺ hydration, alternatively, the starting geometry with ideal octahedral [Mg(H2O)6]2+ geometry was created manually. Both approaches, however, gave very similar spectra and energies. The box geometry was optimized (Amber99) and input into the Car-Parrinello CPMD software package.³⁹ The same periodic boundary conditions, 4 au = 0.09676 fs time step, and energy cutoff of 85 Ry were used for all CPMD calculations performed with the BLYP³¹ functional and Troulier-Martins⁴⁰ norm-conserving pseudopotentials. The initial configuration was relaxed by six short CPMD runs comprising 200 steps. After each run, the system was quenched to the Born-Oppenheimer surface by reoptimizing the wave function. Subsequently, longer 2.5-10 ps production runs were performed. A temperature of 300 K was maintained with the Nosé-Hoover algorithm,⁴¹ which also kept the system in the canonical (NVT) ensemble. During the long simulations, the trajectory was saved at every step for the FT spectra generation and geometry analyses.

Spectral Simulations from Dynamical Trajectories. The spectral response was derived for an ensemble of *N* molecules with dipoles μ_i . A local field \mathbf{E}_i sensed by molecule *i* is the external electric field \mathbf{E}_0 plus the field from other dipoles^{42,43}

$$\mathbf{E}_{i} = \mathbf{E}_{0} + \frac{1}{4\pi\varepsilon_{0}} \sum_{j\neq i} \frac{3\boldsymbol{\mu}_{j} \cdot \mathbf{R}_{ij} \mathbf{R}_{ij} - \boldsymbol{\mu}_{j} R_{ij}^{2}}{R_{ij}^{5}} \qquad (3)$$

where $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ is the distance vector. The total dipole moment is

$$\boldsymbol{\mu}_{\text{total}} = \sum_{i} (\boldsymbol{\mu}_{i0} + \boldsymbol{\alpha}_{i} \cdot \mathbf{E}_{i}) \qquad (4)$$

$$\approx \sum_{i} (\boldsymbol{\mu}_{i0} + \boldsymbol{\alpha}_{i} \cdot \mathbf{E}_{0}) +$$

$$\frac{1}{4\pi\varepsilon_{0}} \sum_{i} \sum_{j \neq i} \boldsymbol{\alpha}_{i} \cdot \left(\frac{3\boldsymbol{\mu}_{0j} \cdot \mathbf{R}_{ij}\mathbf{R}_{ij} - \boldsymbol{\mu}_{0j}{R_{ij}}^{2}}{R_{ij}^{5}} + \frac{3\boldsymbol{\alpha}_{j} \cdot \mathbf{E}_{0} \cdot \mathbf{R}_{ij}\mathbf{R}_{ij} - \boldsymbol{\alpha}_{j} \cdot \mathbf{E}_{0}{R_{ij}}^{2}}{R_{ij}^{5}} \right)$$

and the total polarizability

$$\boldsymbol{\alpha} = \frac{\partial \boldsymbol{\mu}_{\text{total}}}{\partial \mathbf{E}_0}$$
$$= \sum_{i} \boldsymbol{\alpha}_i + \frac{1}{4\pi\varepsilon_0} \sum_{i} \sum_{i \neq j} \frac{3\boldsymbol{\alpha}_j \cdot \mathbf{R}_{ij} \boldsymbol{\alpha}_i \cdot \mathbf{R}_{ij} - \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j {R_{ij}}^2}{R_{ij}^5}$$
(5)

A derivative of (5) with respect to the ε -coordinate of an atom λ present in molecule *m* is

$$\frac{\partial \boldsymbol{\alpha}}{\partial r_{\varepsilon}^{\lambda}} = \boldsymbol{\alpha}_{m}^{(\lambda\varepsilon)} + \frac{1}{2\pi\varepsilon_{0}} \sum_{j\neq m} \boldsymbol{\alpha}_{m}^{(\lambda\varepsilon)} \cdot \frac{3\boldsymbol{\alpha}_{j} \cdot \boldsymbol{R}_{mj}\boldsymbol{R}_{mj} - \boldsymbol{\alpha}_{j}\boldsymbol{R}_{mj}^{2}}{\boldsymbol{R}_{mj}^{5}} + \frac{3}{2M\pi\varepsilon_{0}} \sum_{j\neq m} \left[\frac{\boldsymbol{\alpha}_{j\varepsilon}\boldsymbol{\alpha}_{m} \cdot \boldsymbol{R}_{mj} + \boldsymbol{\alpha}_{j} \cdot \boldsymbol{R}_{mj}\boldsymbol{\alpha}_{m\varepsilon} + \boldsymbol{\alpha}_{m} \cdot \boldsymbol{\alpha}_{j}\boldsymbol{R}_{mj\varepsilon}}{\boldsymbol{R}_{mj}^{5}} - 5\frac{\boldsymbol{\alpha}_{j} \cdot \boldsymbol{R}_{mj}\boldsymbol{\alpha}_{m} \cdot \boldsymbol{R}_{mj}\boldsymbol{R}_{mj\varepsilon}}{\boldsymbol{R}_{mj}^{7}} \right] \quad (6)$$

In the derivation of the previous formula, we used the definition of molecular position as a geometrical center of M atoms with position vectors \mathbf{r}^i , $\mathbf{R}_m = M^{-1} \sum_{i=1}^M \mathbf{r}^i$, so that $M(\partial \mathbf{R}_m / \partial \mathbf{r}^{\lambda}) = 1$ is the identity matrix. We can thus formally carry out the computations with polarizability derivatives obtained for one molecule $(\mathbf{\alpha}_{m}^{(\lambda \varepsilon)})$ corrected by the interactions with the rest of the system. A similar approach using the "dressed" tensors was proposed for mixed molecular and colloidal systems.⁴⁴ The approximate expansions of the induced dipole in colloidal systems could be avoided using a matrix formulation;⁴⁵ for molecules of relatively weak polarizability, however, the perturbational approach presented above is sufficient. In eq 6, we originally adopted the atomic polarizability model⁴³ where all atoms were treated as polarizable spheres of isotropic polarizabilities α_i , i = 1...NAT. While this approach was useful for program tests and relating our method to previous works, we show more advanced results only, with the polarizability derivatives calculated ab initio by Gaussian.

From the coordinate derivatives of the polarizability (eq 6), the time derivatives were calculated by the chain rule, $\partial \alpha_{\alpha\beta}/\partial t$ = $\sum_{k\epsilon} (\partial \alpha_{\alpha\beta}/\partial r_{\epsilon}^{\ell}) (\partial r_{\epsilon}^{\ell}/\partial t)$, where $\partial r_{\epsilon}^{\ell}/\partial t = v_{\epsilon}^{\ell}$ are the MD (CPMD) velocities. The Fourier transforms of the polarizability derivatives

$$F_{\alpha\beta}(\dot{\alpha}_{\alpha\beta})(\omega) = \int_0^t \alpha_{\alpha\beta}(\tau) e^{-i\omega\tau} d\tau = \int_0^t \frac{i}{\omega} \dot{\alpha}_{\alpha\beta}(\tau) e^{-i\omega\tau} d\tau$$
(7)

provided the Raman intensity of the backscattered (180°) signal as

$$I_{180} = \frac{\omega K(7S_1' + S_0')}{t[1 - \exp(-\hbar\omega/(kT))]}$$
(8)

where $S_0 = \sum_{\alpha\beta} [(\text{Im } F_{\alpha\alpha})(\text{Im } F_{\beta\beta}) + (\text{Re } F_{\alpha\alpha})(\text{Re } F_{\beta\beta})], S_1 = \sum_{\alpha\beta} [(\text{Im } F_{\alpha\beta})(\text{Im } F_{\alpha\beta}) + (\text{Re } F_{\alpha\beta})(\text{Re } F_{\alpha\beta})], k \text{ is the Boltzmann constant, } T \text{ is the temperature, } K \text{ is an arbitrary intensity multiplier, and } \hbar \text{ is the Planck constant. For all of the simulated spectra, the y-scale is arbitrary, since the absolute intensities are not measured.}$

Spectral Simulations from CPMD Clusters. In a static model, 20 $[Mg(H_2O)_6]^{2+}$ and $[Cl(H_2O)_N]^-$ (N = 4-6) complex geometries were selected from randomly chosen CPMD snap-



Figure 1. Experimental Raman spectra of water and MgCl₂, MgBr₂, CaCl₂, and NaCl solutions at 20 °C.

shots and subjected to restricted normal mode optimization^{46,47} performed at the B3LYP/6-311++G**/PCM(H₂O) level. The program Qgrad⁴⁸ interfaced to Gaussian was used for the optimization; normal modes within i300(imaginary)...200 cm⁻¹ were kept fixed. Thus, the water molecules could approximately be maintained at instantaneous CPMD positions, while higher-frequency modes could be relaxed. Note that the relaxation is required to get the true harmonic vibrational frequencies. For the optimized geometries, Raman spectra were calculated by Gaussian at the B3LYP/6-311++G**/CPCM(H₂O) approximation level and averaged. A Lorentzian bandwidth of 15 cm⁻¹ was used for the spectra plotting.

Results and Discussion

Experimental Spectra. In Figure 1, we display typical examples of the spectra for MgCl₂, MgBr₂, CaCl₂, and NaCl solutions. The signal from a quartz cell was subtracted, and spectra were normalized to the same accumulation time; nevertheless, the intensity scale should be considered rather informative. All salt solutions notably modify the Raman signal. However, such a significant increase in intensity of the HOH bending mode (\sim 1640 cm⁻¹) in the salt solutions was recorded that it cannot be explained solely by variations in the collection angle of Raman scattering caused by changes of the solution refractive indices. This result is surprising, since there are fewer water molecules per volume in the salt solutions than in pure water. Moreover, in the set of MgCl₂ solutions in D₂O, an increase of DOD bending and decrease of OD stretching mode intensity with increasing concentration were recorded (see later, Figure 7), which also suggests that the changes in aqueous Raman scattering caused by the salts reflect the solution structure.

The changes in relative intensities (spectral shapes) are more specific and occur mostly within the $200-1000 \text{ cm}^{-1}$ range. This region comprises the librational and rotational motion of water molecules, probably inseparable form the hydrogen bond stretching.^{16,18,27,49} Most probably, the observed line shapes reflect the structure of the metal cation hydration spheres, while the anions give less specific signals. For example, the divalent Mg and Ca metals perturb the spectra more than the monovalent sodium. Potassium and lithium chlorides behaved similarly to the sodium chloride and are not shown. The specific "355 cm⁻¹" magnesium band is present in Raman spectra of both in MgCl₂ and MgBr₂ salt solutions. There are no indications that the

 TABLE 1: Experimental Raman Peak Frequencies (cm⁻¹)

 of Various Aqueous Salt Solutions

| | <i>ν</i> (Μ••••OH ₂) | $\delta(\text{HOH})^a$ | $\delta(\text{HOH})^b$ | $\nu(H \cdots O) + \delta(HOH)$ |
|---|----------------------------------|------------------------|------------------------|---------------------------------|
| | Water Sol | utions | | |
| pure water 20 °C | | 1636 | 1638(115) | 2090 |
| MgBr ₂ 5 mol/kg 20 °C | 355 | 1642 | 1639(70) | 2011 |
| MgI ₂ 5 mol/kg 20 °C | 325 | 1625 | 1628(62) | |
| CaCl ₂ 5 mol/kg 20 °C | | 1647 | 1644(72) | 2060 |
| NaCl 5 mol/kg 20 °C | | 1649 | 1645(89) | 2063 |
| LiCl 5 mol/kg 20 °C | | 1648 | 1645(95) | 2063 |
| MgCl ₂ 5 mol/kg 20 °C | 355 | 1651 | 1647(83) | 2052 |
| MgCl ₂ 2.5 mol/kg 20 °C | 357 | 1648 | 1646(101) | 2068 |
| MgCl ₂ 1.3 mol/kg 20 °C | 361 | 1644 | 1644(111) | 2076 |
| MgCl ₂ 5 mol/kg 0 °C | 355 | 1651 | 1647(80) | 2048 |
| MgCl ₂ 5 mol/kg 48 °C | 352 | 1651 | 1646(83) | 2018 |
| | D ₂ O Solu | itions | | |
| pure D ₂ O 20 °C | | 1205 | 1204(72) | 1554 |
| MgCl ₂ in D ₂ O 5 mol/kg 20 °C | 337 | 1216 | 1210(57) | 1516 |
| $MgCl_2$ in D_2O 2.5 mol/kg 20 $^{\circ}C$ | 337 | 1210 | 1208(70) | 1522 |
| $MgCl_2$ in D ₂ O 1.3 mol/kg 20 $^{\circ}C$ | 332 | 1206 | 1206(73) | 1552 |

 a Peak maximum. b Peak center and width (in parentheses) from a Lorentzian band fit.

halogen anions would form a stable complex with Mg²⁺. Nevertheless, from the comparison of the bromide and chloride spectra, it is clear that also the anions cause minor spectral changes. However, their interpretation goes beyond the scope of this study. Supposedly, the role of the metal cation is dominant and the interaction of simple halogenide ions with water is weaker.^{1,5,12} For example, the computations indicate that the shortest Mg–O distance (~1.95 Å) is much smaller than a Cl–H hydrogen bond (~2.2 Å).

Individual peak positions are summarized in Table 1 for a wider variety of salts and experimental conditions. For example, the Mg–O stretching band moves to 352 cm⁻¹ at 48 °C; in MgI₂ solution, its line shape (not shown) is significantly distorted and it is centered even lower, at 325 cm⁻¹. In fact, a new band appears also at 225 cm⁻¹ for MgI₂. A similar shoulder at 202 cm⁻¹ is apparent also for MgBr₂.

The HOH bending vibration (at 1636 cm⁻¹ in pure water) moves up for most salts (except for MgI₂, where it goes down by ~10 cm⁻¹), up to 1651 cm⁻¹ for concentrated MgCl₂ solutions. This band also becomes significantly narrower for the salt solutions. The fitted Lorenzian bandwidth (cf. Table 1) changes from 115 cm⁻¹ in pure water to 62 cm⁻¹ for MgI₂. The combination band (HOH bending and hydrogen bond stretching) centered at 2090 cm⁻¹ in pure water moves down, up to 2011 cm⁻¹, and disappears completely for MgI₂. However, it should be noted that the MgI₂ solution is a brown absorbing liquid and its baseline may be significantly distorted. Especially the combination signal (>2000 cm⁻¹) may be hidden in the background radiation. The temperature of the sample around the laser beam may be elevated, unlike for the other salts.

The MgCl₂ spectral trends in D₂O mostly follow those for H₂O. All vibrational frequencies are shifted down due to the larger mass of deuterium. Also, the bandwidth of the DOD bending band in pure D₂O (72 cm⁻¹) is significantly smaller than that for the HOH (115 cm⁻¹) in H₂O, even more than it would correspond to the central frequency ratio (1204/1638).

Hydrated Metal-Ion Geometries. Although the dynamical coordination number of the Mg²⁺ is known to be lower than six even in ideal conditions ($N \sim 5.85$),¹ the ideal octahedral geometry with N = 6 well represents the predominant structure of the first hydration shell of the magnesium ion.⁶ In Table 2,

the metal-water oxygen and OH bond distances calculated for the [Mg(H₂O)₆]²⁺ complex at different levels are compared to the $Mg^{2+} \cdot H_2O$ system, and to the $[Ca(H_2O)_6]^{2+}$ and $[Na(H_2O)_6]^+$ complexes. More ab initio results are compiled in Table 1s of the Supporting Information. The calculated vacuum Mg-O distances are similar to those reported previously;⁶ however, embedding the system into the polarizable dielectrics (CPCM) shortens the distance in $[Mg(H_2O)_6]^{2+}$ by ~0.016 Å and improves thus the agreement of the calculations with experimental X-ray studies, where an average Mg-O distance of 2.063–2.068 Å is encountered.⁶ On the other hand, the distances in the Mg²⁺·H₂O bimolecular system are too short, even with the CPCM model, which reflects known deficiencies of the continuum approach in representations of strong polar interactions.^{50,51} The Amber MD geometry parameters are reasonable; nevertheless, the quantum CPMD clearly provides more reliable data.

The calcium and sodium ions also form computationally stable octahedral complexes, but the distances between the metal and the water oxygen are significantly larger than those for Mg. For Ca^{2+} , this can be partially attributed to its larger covalent radius than Mg²⁺. The calculated metal-water oxygen distances agree with the previously reported theoretical results⁵² as well as with the known ionic radii.¹ Interestingly, the calculated Na-O and Ca-O distances are quite similar and, depending on the approximation used, one can be smaller or longer than the other. The OH distance does not seem to be significantly perturbed by the water coordination to the metals. The HF and higher-correlated MP2/MP4/CCSD(T) and B3LYP method give very similar results; the larger aug-cc-pVTZ basis brings only minor shortening of the Mg-O distance. On the basis of the comparison with the presumably most reliable MP4 and CCSD(T) computations, we can conclude that the computationally faster B3LYP method is adequate for a reliable description of the metal-water cluster geometries. The results thus suggest that the Mg-O link behaves to some extent like a stable single covalent bond. An analogous strong Mg-O interaction was also observed for Mg2+ methanol solutions.22

The geometry parameters obtained from the static CPMD computations (Table 2) were quite similar to those observed for the ab initio optimized clusters. Next, we look at the average geometries during the dynamics. The simulations with the HyperChem starting geometries and those starting with the arbitrarily T_h symmetrized Mg(H₂O)₆ initial structure provided very similar results. In accord with previous studies,^{2,4} the radial distribution function of water oxygens around the magnesium ion (Figure 2) exhibits an exceptionally sharp and narrow peak at ~ 2.1 Å. A similar peak can also be observed for concentrated MgCl₂ solution (dashed line in Figure 2), where the number of water molecules coordinated around Mg²⁺ was limited to $N \sim 3$. Nevertheless, the CPMD approach reveals more differences between the calcium and sodium ions than the static computations summarized in Table 2; the Ca²⁺ binds the water molecules much more efficiently and perturbs the water ordering to a larger distance than Na⁺, although less than Mg²⁺ exhibiting a secondary peak at \sim 4.2 Å. Test MD computations reproduced this peak also with the Amber99 force field, and excluded an artifact influence of the limited box size (Figure 1s in the Supporting Information). The CPMD distribution gives more realistic Mg····O distances than MD; both dynamical models predicted a much broader chlorine ··· hydrogen distance distribution than for the Mg (cf. Figure 2s in the Supporting Information).

TABLE 2: Calculated Geometry Parameters (Å) for Some Model Metal-H₂O Clusters

| | [MgH | $_{2}O]^{2+}$ | [Mg(H | $_{2}O)]_{6}^{2+}$ | [Ca(H | $[20]_{6}^{2+}$ | [Na(H | $_{2}O)_{6}]^{+}$ |
|------------------------------|----------------------------|---------------|---------------|--------------------|-----------------|-----------------|---------------|-------------------|
| level | $\overline{d_{ m Mg-O}}^a$ | $d_{ m H-O}$ | $d_{ m Mg-O}$ | $d_{ m H-O}$ | $d_{ m Ca-O}$ | $d_{ m H-O}$ | $d_{ m Na-O}$ | $d_{ m H-O}$ |
| Amber99 | 1.878 | 0.996 | 2.000 | 0.981 | 2.643 | 0.975 | 2.421 | 0.964 |
| BLYP/CPMD | | | 2.120 | 0.979 | 2.427 | 0.979 | | |
| CCSD(T)/6-311++G** | 1.956 | 0.975 | 2.100 | 0.965 | 2.399 | 0.965 | 2.355 | 0.961 |
| B3LYP/6-311++G** | 1.942^{a} | 0.980^{a} | 2.111^{a} | 0.948^{a} | 2.414^{b} | 0.974^{b} | 2.386 | 0.963 |
| B3LYP/aug-cc-pVTZ | 1.916 | 0.979 | 2.100 | 0.966 | | | 2.393 | 0.963 |
| $B3LYP_{CPCM}/6-311++G^{**}$ | 2.039 | 0.978 | 2.084 | 0.965 | 2.368 | 0.977 | 2.397 | 0.972 |
| Exp. | | | 2.063^{a} | | 2.397° | | | |

^a Reference 6. ^b Reference 58. ^c Reference 59.



Figure 2. Calculated (CPMD) radial distribution functions for the Mg^{2+} , Ca^{2+} , and Na^+ hydrated metal ions. For the $Mg^{2+}\cdots O$ distance, the calculated RDF in a 5 mol/kg $MgCl_2$ solution is also plotted as the dashed line.



Figure 3. Calculated (CPMD) distributions of the aqueous oxygen (red) and hydrogen (green) atoms around the central Mg^{2+} ion.

From the calculated water 3D probability distribution in the octahedral magnesium complex in Figure 3, we see that the oxygen atoms indeed oscillate only moderately around the equilibrium positions. On the other hand, the hydrogen positions are dispersed more as the water molecules bound in the complex are perturbed by hydrogen bonds to molecules from the second hydration sphere.

Bond Strengths and Vibrational Frequencies. The relatively strong Mg^{2+} –O binding is reflected in the vibrational properties of the $[Mg(H_2O)_6]^{2+}$ complex. Harmonic frequencies calculated for optimized structures at seven approximation levels

are summarized in Table 3. The mode assignment is based on potential energy distributions of internal vibrational coordinates as well as on a visual inspection of the normal mode displacement. The six Mg^{2+} –O bonds generate three normal modes of A_g , T_u (triple degenerate), and E_g (double degenerate) symmetries. Note that, for the T_h point group only, the gerade symmetry modes (A_g , E_g , T_g) are Raman active (cf. Table 4).⁵³ Ungerade modes are active in IR and can be assigned to previous observations (Table 3, ref 7). Although due to dynamical symmetry distortions the T_h symmetry rules may not hold in solution, from the calculated intensities (Table 4), the totally symmetric "breathing" mode clearly dominates in the Raman spectrum within the Mg–O stretching region. Unlike Mg²⁺, the Ca^{2+} and Na²⁺ octahedral aqueous clusters exhibit metal–O stretching frequencies (Table 5) too low to be detectable.

As discussed before, although lacking the d-orbitals, magnesium binds to water as strongly as much heavier elements.⁷ Our NBO analysis indicates that the relative strength of the Mg-O bond is also reflected in its partially covalent character. A "non-bonding" natural lowest unoccupied molecular orbital (LUMO)³⁴ centered on the metal ion (Figure 4) was identified that could clearly be associated with the magnesium binding to the water molecules in the complex. Its partial occupations and the metal natural charges are summarized in Table 6, also for other metals and clusters with chlorine. The nonzero occupancy of the natural LUMO indicates that it can be associated with the metal binding to the water molecules for all of the Na⁺, Ca²⁺, and Mg²⁺ metal ions. The highest value of the occupancy for Mg thus correlates with the strongest metal-water bond. Moreover, the calculated natural charge of the metal ion is lower than an ideal ionic charge (+1 for Na, +2 for Mg and Ca) by approximately the amount of the natural LUMO occupancy. Perhaps surprisingly, for the $[Mg(H_2O)_6]^{2+}$ cluster, there are negligible differences in the occupancy and the charge for the vacuum and solvent environments (Table 6).

The water lone-pair orbital aligned along the metal–O bond slightly differs for the three ions (Figure 4) as well. It is most extended in the $[Mg(H_2O)_6]^{2+}$ complex, where it is even partially localized on the metal. This simplified picture suggests that, although the metal–O bond strengths are different, the nature of the metal–water interaction is similar for all of the ions. Interestingly, the shape (not shown) and occupation (last two lines in Table 6) of the "unoccupied" central orbital remain similar in complexes where some water atoms are replaced by Cl^- .

All quantum methods in Table 3 provide reasonable estimates of the complex vibrations. For HF, the HOH bending frequencies $(1792-1799 \text{ cm}^{-1})$ are somewhat higher, and the Mg–O breathing frequency (320 cm⁻¹) is lower than the experimental ones (1653 and 355 cm⁻¹, respectively). The larger aug-cc-pVTZ basis set brings only a minor improvement over the 6-311++G** basis set. Embedding the [metal•(H₂O)₆] clusters in implicit

TABLE 3: Fundamental Vibrational Frequencies of the [Mg(H₂O)₆]²⁺ Complex^a

| | | | | | B3LYP | | | | |
|-------------------|------|------|------|------|-------|------|---------------------|-------------------------|--------------------------------|
| | HF | MP2 | | b | С | d | <i>b</i> , <i>c</i> | exp. | (gas phase) |
| 16 Ag | 1799 | 1678 | 1670 | 1664 | 1575 | 1644 | 1574 | 1653 | δ (HOH) |
| 15 Eg | 1794 | 1674 | 1665 | 1660 | 1569 | 1635 | 1571 | | $\delta(\text{HOH})$ |
| 14 T _u | 1792 | 1673 | 1664 | 1659 | 1571 | 1634 | 1570 | | $\delta(\text{HOH})$ |
| 13 T _u | 607 | 579 | 566 | 416 | 503 | 540 | 486 | 627^{e} | H ₂ O wagging |
| 12 T _g | 589 | 549 | 543 | 516 | 481 | 528 | 459 | 591 | wag $+$ in plane rot. |
| 11 T _u | 487 | 417 | 439 | 415 | 407 | 419 | 405 | 421^{e} | in plane H_2O rot. |
| 10 A _u | 433 | 406 | 427 | 407 | 277 | 372 | 256 | | axial H_2O rot. |
| 9 A _g | 320 | 319 | 314 | 318 | 337 | 335 | 360 | 355 | $v_{breathing}(Mg-O)$ |
| 8 T _g | 453 | 380 | 410 | 392 | 203 | 309 | 185 | | in plane H ₂ O rot. |
| $7 T_u$ | 388 | 386 | 378 | 368 | 163 | 300 | 163 | 178^{e} | $\nu(Mg-O)$ |
| 6 T _g | 299 | 237 | 286 | 275 | 132 | 285 | 134 | | axial H ₂ O rot. |
| 5 E _g | 253 | 266 | 249 | 246 | 263 | 263 | 273 | 309 ^e | $\nu(Mg-O)$ |
| $4 E_u$ | 230 | 186 | 213 | 205 | 153 | 250 | 134 | | axial H ₂ O rot. |
| 3 T _u | 166 | 155 | 155 | 160 | 99 | 165 | 102 | 133 ^e | $\delta(OMgO)$ |
| 2 Tg | 136 | 92 | 122 | 129 | 59 | 135 | 46 | | $\delta(OMgO)$ |
| $1 T_u$ | 100 | 97 | 96 | 99 | 42 | 88 | | | $\delta(OMgO)$ |

^{*a*} By default, the 6-311++G** basis set was used. Raman-active modes are indicated in bold. ^{*b*} aug-cc-pVTZ basis set. ^{*c*} PCM solvent model (Gaussian). ^{*d*} COSMO solvent model (Turbomole). ^{*e*} IR spectra, ref 7, tentative assignment only.

TABLE 4: $[Mg(H_2O)_6]^{2+}$ Complex, Raman Intensities of Fundamental Vibrations^{*a*}

| TABLE 5: | [Metal \cdot (H ₂ O) ₆] | Clusters, | Calcula | ted (B3LYP/ |
|------------|--|-----------|------------|-------------|
| 6-311++G* | **) Frequencies, | and Inter | nsities of | Fundamental |
| Vibrations | | | | |

Na⁺

1632

1630

1629

351

354

131

326

172

211

210

205

I (au)

Ca²⁺

0.09

4.13

0.08

0.25

1.22

0.76

Na⁺

4.35

0.04

0.01

1.67

0.09

Mg²⁺

0.00

3.88

0.00

1.13

1.88

0.34

 $\omega (\text{cm}^{-1})$

 Ca^{2+}

1673

1670

1669

506

503

444

325

262

415

311

220

Mg²⁺

1670

1665

1664

566

543

439

427

314

410

378

286

| | | B3I | v IDI at | | |
|-------------------|------|------|----------|------|-------------------|
| | MP2 | | b | С | |
| 16 Ag | 0.02 | 0.00 | 0.12 | 0.25 | M: |
| 15 E _g | 4.42 | 3.88 | 3.11 | 5.55 | 16 A _g |
| 14 T _u | 0 | 0 | 0 | 0 | 15 E _g |
| 13 T _u | 0 | 0 | 0 | 0 | 14 T _u |
| 12 T _g | 0.06 | 0.00 | 0.00 | 1.00 | 13 T _u |
| $11 T_{u}^{-}$ | 0 | 0 | 0 | 0 | 12 T _g |
| 10 A _u | 0 | 0 | 0 | 0 | 11 T _u |
| $9 A_g$ | 0.89 | 1.13 | 2.45 | 1.58 | 10 A _u |
| 8 T _g | 1.89 | 1.88 | 1.27 | 0.85 | $9 A_g$ |
| $7 T_u^{\circ}$ | 0 | 0 | 0 | 0 | 8 T _g |
| 6 T _g | 0.05 | 0.34 | 0.31 | 0.44 | $7 T_u$ |
| $5 E_g^-$ | 0.18 | 0.20 | 0.23 | 0.17 | 6 T _g |
| 4 E _u | 0 | 0 | 0 | 0 | $5 E_g$ |
| 3 T _u | 0 | 0 | 0 | 0 | 4 E _u |
| 2 T _g | 0.02 | 0.02 | 0.01 | 0.63 | 3 T _u |
| 1 T _u | 0 | 0 | 0 | 0 | 2 T _g |
| | | | | | |

^{*a*} By default, the 6-311++G^{**} basis set was used; Mg–O stretching vibrations are indicated in italics. ^{*b*} aug-cc-pVTZ basis set. ^{*c*} PCM solvent model (Gaussian).

(PCM, COSMO) solvent models improves the Mg–O stretching frequencies; however, the Gaussian implementation of PCM (and also that of COSMO, not shown) provides HOH bending frequencies that are too low. From Table 4, we see that the intensities are even more sensitive to the computational model than the frequencies. The PCM environment, for example, causes a modest (~40%) increase against vacuum; the intensity calculated with the larger aug-cc-pVTZ basis is more than doubled against that obtained with the smaller 6-311++G** set.

As the ideally symmetric clusters may be disturbed in real solutions, we also investigated spectra obtained with a varying number of water molecules around the Mg²⁺ ion (Figure 3s in the Supporting Information). The position of the strongest Mg–O stretching band was found to be relatively stable for the higher-coordinated (N > 2) clusters, drifting only within 330–375 cm⁻¹. The minor fluctuations of the frequency are consistent with the minor differences observed experimentally for different anions that presumably influence the number of water molecules present around Mg²⁺. For instance, MgBr₂ gives

249 237 0.20 138 0.02 0.02 213 157 163 155 88 54 122 77 i56 0.02 0.32 96 57 $1 T_u$ 33 a broader peak than MgCl₂, there is a shoulder around 410 cm⁻¹ and a broadband at 600 cm⁻¹ for chloride, and a maximum 550 cm⁻¹ for bromine. The computations indicate that even partially hydrated magnesium ions in concentrated solutions may be visible in the spectra due to the Mg-O vibration. The narrowness of the experimental peak and previous ab initio and CPMD computations^{1,2} nevertheless suggest a strong tendency toward the hexahydrated complexes. The higher-frequency wagging modes (~450-530 cm⁻¹) also significantly contribute to the Raman scattering. However, their resulting signal is much broader (cf. Figure 1), as they are mixed with the water hydrogen bond stretching and water librational motions.

Many features observed in the experimental Raman spectra could also be obtained from the CPMD trajectories by the modified Fourier transform method. For example, the simulated pure water spectrum in Figure 5 exhibits the main features observed experimentally, in particular the HOH bending band at 1608 cm⁻¹ (observed at ~1650 cm⁻¹) and the broad signal around 460 cm⁻¹. The simulated HOH bandwidth (~130 cm⁻¹) is somewhat larger than the experimental one (115 cm⁻¹, Table 1). The anharmonic combination signal above 2000 cm⁻¹ cannot be modeled using this approach, as the simulations based on classical trajectories are restricted to harmonic potentials.²⁵ For



Figure 4. Comparison of the $[M(H_2O)_6]$ NBO lone pair (LP) and NBO-LUMO (Mg only) orbitals (B3LYP/6-311++G**/PCM(H₂O) calculation).

TABLE 6: Occupancy of the Metal Nonbonded LUMO and the Natural Charge (q) in Model Complexes as Obtained by the NBO Analysis³⁴ of the B3LYP/6-311++G**/PCM Wave Function

| complex | occ. | q |
|--------------------------|-------|-------|
| $[Na(H_2O)_6]^+$ | 0.073 | 0.927 |
| $[Ca(H_2O)_6]^{2+}$ | 0.102 | 1.855 |
| $[Mg(H_2O)_6]^{2+}(vac)$ | 0.172 | 1.821 |
| $[Mg(H_2O)_6]^{2+}$ | 0.175 | 1.819 |
| $[Mg(H_2O)_5Cl]^+$ | 0.201 | 1.783 |
| $[Mg(H_2O)_4Cl_2]$ | 0.222 | 1.752 |

the MgCl₂ solution (red curve in Figure 5), the signal of the Mg-O stretching is clearly apparent; however, its Raman intensity is significantly underestimated and the width is too broad. Also, the narrowing of the HOH bending band observed for the salt solutions (Table 1) is not reproduced. Thus, we see



Figure 5. Raman spectra of pure water and 5 mol/kg MgCl₂ solution obtained from the CPMD trajectories (\sim 4 ps) by the Fourier transform method.



Figure 6. Calculated (MP2/cc-pVTZ) dependence of the relative energy of the $Mg^{2+} \cdot H_2O$ complex on the Mg-O distance, the adiabatic vibrational energy levels, and the corresponding wave functions.

that, although the CPMD-FT model has the potential to comprise both geometrical and dynamical factors of the metal-water interactions, its inherent approximations (Newtonian trajectories and harmonic potentials) may cause inaccuracies in the simulated spectra.

To investigate a larger part of the potential surface governing the Mg-H₂O interaction at least qualitatively, we calculated energies of a complex consisting of Mg²⁺ cation and one water molecule, as dependent on the metal-oxygen distance (Figure 6). The $C_{2\nu}$ symmetry was conserved, and all other coordinates were relaxed. Indeed, the symmetry of the potential is apparently distorted already for modest deviations from the minimum. Thus, the partial anharmonic character may account for some of the inconsistencies in the FT simulation above. When exact adiabatic one-dimensional wave functions are calculated numerically as dependent on the $r(Mg \cdots OH_2)$ coordinate,⁵⁴⁻⁵⁷ the anharmonicity transfers to the asymmetry of the wave functions (Figure 6). Nevertheless, the vibrational energy levels remain approximately equidistant, similarly as in the harmonic case, within $2-5 \text{ cm}^{-1}$.

Finally, the Raman spectra of the octahedral hydrated $[Mg(H_2O)_6]^{2+}$ complex were generated by the force field diagonalization directly from 20 randomly selected CPMD clusters (subjected to the constrained normal-mode optimization, see Methods) and averaged. Such an approach corresponds to the instantaneous mode approximation,^{26,27} as can be justified by the predominantly harmonic character of the vibrational motions (cf. Figure 6). The backscattered Raman spectra for the H₂O and D₂O complexes thus obtained are compared to the experimental spectra in Figure 7. The cluster approach provided similar spectral shapes as the FT method; however, the Mg-O signal (at ${\sim}318~\text{cm}^{-1}$ for $H_2O)$ is more distinct and more evidently corresponds to the experimental one (355 cm^{-1}) . Strictly speaking, the calculated water bands (shoulder at 559 cm⁻¹ and HOH bending peak at 1645 cm⁻¹) should not be directly compared to experiment which includes also free water molecules. Nevertheless, we see that also these frequencies and bandwidths reasonably correspond to the observed ones. The experimental frequency of the shoulder (605 cm⁻¹) is higher than the theoretical one, but this is not surprising, as the limited clusters lack the water hydrogen bond network. More importantly, the deuteration effects are well reproduced by the calculation, in particular the red shift of the Mg-O stretching signal (experimentally at 355 cm⁻¹ in H₂O and 338 in D₂O, i.e., a difference of 17 cm⁻¹), calculated as 318-307 = 11 cm⁻¹. Thus, the assignment of the band to the Mg-O bond stretching is ultimately confirmed.



Figure 7. Upper panel: Calculated (B3LYP/6-311++G**/PCM) Raman spectra of the $[Mg(H_2O)_6]^{2+}$ and $[Mg(D_2O)_6]^{2+}$ complexes, average from 20 instantaneous CPMD geometries. Bottom panel: Corresponding experimental spectra of the 5 mol/kg MgCl₂ H₂O and D₂O solutions measured at 20 °C.

The cluster models are thus superior to the CPMD-FT simulations for the lowest-frequency vibrations. The FT method, nevertheless, can well reproduce the inhomogeneous HOH bandwidth, or the HOH \rightarrow DOD bending frequency shift (1620 \rightarrow 1210 cm⁻¹, experimentally 1647 \rightarrow 1216 cm⁻¹), and the shift of the lowest-frequency signal (<1000 cm⁻¹, see Figure 4s in the Supporting Information). To obtain insight also into the Raman scattering of the hydrated chlorine anions, we simulated the spectra for 20 clusters of hydrated Cl⁻ obtained by CPMD, containing four to six water molecules from the first hydration sphere. The normal mode optimization was not used in this case, not to affect the CPMD geometry distribution; otherwise, the same approximation (B3LYP/6-311++G**/PCM) was used as for Mg^{2+} . In comparison with the magnesium, chlorine anion causes a high-frequency shift of the HOH bending band (cf. Figure 5s in the Supporting Information) and an overall Raman intensity increase but no specific signal in the lowest-frequency region. Finally, spectra of hexacoordinated Mg²⁺ clusters with a varying number of water molecules and chlorine ions (not shown) and spectra of the large CPMD cluster corresponding to the 5 mol/kg MgCl₂ solution (Figure 6s in the Supporting Information) were simulated, which are, however, consistent with the previous simulations. They suggest that the spectral signal around 355 cm⁻¹ originates in the Mg–O binding, and survives in distorted or incomplete hydration shells, in particular when some water molecules are replaced by chlorine.

Conclusions

Among the Raman spectra of concentrated salt solutions, we identified a strong signal for Mg^{2+} that could be, in accord with previous computational studies and experimental data, attributed to the strong magnesium—water binding. On the basis of the quantum-chemical computations, we could also determine that the specific 355 cm⁻¹ peak is not exclusively associated with a complete octahedral hydration of Mg^{2+} but stems mostly from the vibrations of the Mg–O linkage. Partially covalent character of the bond was confirmed by the natural bond orbital analysis.

Both the static cluster and dynamical models reproduced the most significant experimental spectral features. The isotopic shifts observed for the D_2O solutions were reproduced by the computations, and thus, the normal mode assignment could be verified. Hydrated chlorine anion clusters did not exhibit a Raman signal interfering with that of the metal. The data confirmed the large potential of the Raman spectroscopy for the studies of solution structure and dynamics. In particular, although the monatomic ions do not vibrate themselves, they moderate the solvent signal in a specific way that faithfully reflects their hydration patterns.

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Supporting Information Available: CPMD-FT Raman spectra simulation of Mg^{2+} in H_2O and D_2O , hydrated Cl^- spectral simulations, and CPMD and MD radial distribution function comparisons. This material is available free of charge via the Internet at http://pubs.acs.org.

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