to write down the equations as soon as the structure is known.

The hydration numbers and the hydration shell structures of difference were found to increase in the order Na\(^+\) > Sr\(^{2+}\) > Ca\(^{2+}\). The site preferences for monovalent cations are I and I', and for divalent cations I > II > I' ≥ II.

Acknowledgment. The authors are indebted to the Belgisch National fonds voor Wetenschappelijk Onderzoek (N.F.W.O.) for research positions as Research Assistant (J.J.V.D.) and Research Director (W.J.M.). The authors thank the Fonds voor Kollektief en Fundamental Onderzoek (F.K.F.O.) for financial assistance.

Supplementary Material Available: Listings of positional parameters, population parameters, temperature factors, agreement factors, and bond distances and angles (2 pages). Ordering information is given on any current masthead page.

Molecular Dynamics Study of an Aqueous SrCl\(_2\) Solution

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A molecular dynamics simulation of a 1.1 m SrCl\(_2\) solution was performed with an improved central force model for water at the experimental density at room temperature. The ion-water and ion-ion potentials were derived from ab initio calculations. The simulation extended over 4 ps at an average temperature of 298 K. The structural properties of the solution are discussed on the basis of radial distribution functions and the orientation of the water molecules and their geometrical arrangement in the hydration shells of the ions. The dynamical properties are calculated from various autocorrelation functions. Results are presented for the influence of the ions on self-diffusion coefficients, hindered translations, librations, and internal vibrations of the water molecules.

1. Introduction

The structures of 1.1 m aqueous BeCl\(_2\), MgCl\(_2\), and CaCl\(_2\) solutions have been reported in a series of papers in recent years. The results have been derived from combined molecular dynamics (MD) simulations and X-ray diffraction studies. It has been found that the hydration numbers and the hydration shell structures of the alkaline-earth ions change with increasing ion size in a way which is quite different from that of the singly charged ions. The six water molecules in the first hydration shell of Li\(^+\) prefer an octahedral arrangement with some distortions about the octahedral positions. With increasing alkali-metal ion size the distributions around the octahedral positions broaden, resulting in a uniform distribution of the eight water molecules in the first hydration shells of the ions and Ca\(^{2+}\)—also well ordered—do not show any regular symmetry. The hydration numbers of all singly charged ions increase linearly with the ion-oxygen first-neighbor distance. The strong change from 6 to 9.2 which occurs in going from Mg\(^{2+}\) to Ca\(^{2+}\) seems to follow a different trend.

The recent investigation of a BeCl\(_2\) solution did not contribute to the clarification of this difference between the alkali-metal and alkaline-earth ions. The X-ray measurements of a 5.3 m solution indicate a hydration number for Be\(^{2+}\) of 4 in agreement with several NMR measurements, but at a concentration of 1.1 m they do not allow a definite conclusion because of the low scattering power of Be\(^{2+}\) for X-rays. The MD simulation of the 1.1 m solution leads to six octahedrally arranged water molecules in the first shell of Be\(^{2+}\). However, there also remains some doubt on the reliability of these results because pair potentials have been employed in the simulation which might not be sufficient for a correct description of the strong interactions between a water molecule and the small Be\(^{2+}\).

While work is in progress concerning the development of a three-body potential for the Be\(^{2+}\)–H\(_2\)O interactions, it seemed to be of interest to continue these investigations by the simulation of a 1.1 m aqueous SrCl\(_2\) solution. In the section 2 the ab initio calculations on which the various pair potentials are based are described and some details of the simulation are given. The structural properties of the solution are discussed in section 3 on the basis of radial distribution functions and the orientation of the water molecules in the first hydration shells of the ions and their geometrical arrangement. Also in section 3 the dynamical properties of the solution such as self-diffusion coefficients and the spectral densities of hindered translations, librations, and internal vibrations of the water molecules.


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TABLE I: Optimized Sr²⁺-0 Distances and Sr²⁺-H₂O Binding Energies for Different Basis Sets

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>r_{SO2} Å</th>
<th>ΔE, kJ/mol</th>
<th>t°</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIDI**</td>
<td>2.527</td>
<td>188.0</td>
<td>38</td>
<td>12</td>
</tr>
<tr>
<td>MINI</td>
<td>2.530</td>
<td>175.4</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>HW10</td>
<td>2.505</td>
<td>215.6</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>HW2</td>
<td>2.518</td>
<td>213.5</td>
<td>2</td>
<td>13</td>
</tr>
<tr>
<td>HW2**</td>
<td>2.504</td>
<td>189.7</td>
<td>5</td>
<td>13</td>
</tr>
</tbody>
</table>

*Relative time needed for one SCF calculation. +The double asterisk indicates that 3p-type polarization functions for Sr²⁺ were augmented. |

2. Interaction Potentials and Details of the Simulation

All intermolecular potentials in the simulation presented here were of the pair potential type and consisted of a Coulomb part for which the Ewald summation was applied and of short-range parts for which the shifted force method was used. Water is described by a model which treats the intermolecular O-O, O-H, and H-H interactions by means of the latest version of the central force (CF) model (with the exception of a minor technical modification) but uses a three-body potential for a more correct description of the intramolecular interactions. This modification has led to a marked improvement with respect to the results of simulations of BeCl₂, MgCl₂, and CaCl₂ solutions. As the intermolecular part of the potential is very similar to the one employed in previous work, no model dependence is expected for the data obtained with this improved model, and a direct comparison is thus possible with the results of simulations of BeCl₂, MgCl₂, and CaCl₂ solutions.

For the Sr²⁺-O, Sr²⁺-H, Sr²⁺-Sr²⁺, and Sr²⁺-Cl⁻ interactions new Hartree-Fock calculations have been performed since ab initio calculations on the strontium-water system could not be found in the literature. Sr²⁺ with its 36 electrons is a rather large ion from the viewpoint of quantum mechanical calculations, and not many calculations have been reported. Therefore, a number of test calculations were performed in order to find a basis that allows a sufficiently accurate evaluation of the potential hypersurface with a still reasonable amount of computer time. In particular, the results of standard Hartree–Fock calculations have been compared with effective core potential (ECP) SCF calculations in which some of the inner electronic shells are decoupled from the valence electrons, resulting in faster calculations and reduced superposition errors. Regarding computer time, it was also important to answer the question whether the eight N-shell electrons can be attributed to the core or if they must be treated as Hartree–Fock valence electrons.

The optimized Sr²⁺-O distances and Sr²⁺-H₂O binding energies are given in Table I for different basis sets. MIDI and MINI denote Huzinaga's all-electron basis sets in double-ζ and single-ζ formulation, respectively. HW10 and HW2 are ECP basis sets from Hay and Wadt. In HW2 the N shell of strontium is attributed to the core while in HW10 it is left in the valence space. The DZP basis set of Dunning was used for the water molecule when the all-electron basis sets were employed for Sr²⁺. In all other calculations Dunning's oxygen basis set was replaced by an ECP one from Stevens et al.

It is assumed that the calculations with the MIDI** basis set lead to the most accurate results, and that all other distances and energies presented in Table I are within the limits of uncertainty expected at the Hartree–Fock level. The results achieved with the MIDI basis set, which has only single-ζ quality, do not deviate too much from the ones with MIDI**, thus indicating a rather small basis set superposition error for this system. It is even more important to note that only a small difference exists between HW2 and HW10. A breakdown of the ECP approximation would have led to much too short Sr²⁺-O distances in the HW2 case.

Finally, it was decided to use the HW2** basis set for the calculation of the whole potential surface as the polarization functions might somewhat improve the accuracy of the energy points for orientations outside the C₃v symmetry. Altogether about 250 points were calculated by moving the Sr²⁺ around a water molecule. The energy curve for the C₃v symmetry contains the global minimum and is shown in Figure 1. Similar calculations were performed for the one-dimensional Sr²⁺-O, Sr²⁺-Cl⁻, and Sr²⁺-Sr²⁺ pair potentials. For both ions MIDI** basis sets were used. In the case of Sr²⁺-Sr²⁺ no significant deviation from a purely electrostatic potential could be seen.

In previous work, a single analytical function with three adjustable parameters was fitted to the energy points after the Coulombic contributions—determined by the water model and the ionic charges—had been subtracted from the interaction energies. The Cl⁻–O, Cl⁻–H, and Cl⁻–Cl⁻ interactions were taken from the MgCl₂ simulation. They have been derived in the same way as described for Sr²⁺. The final pair potentials are listed in Table II.

The basic cubic container consisted of 200 water molecules, 4 cations, and 8 anions representing a 1.1 m SrCl₂ solution. The side length of the cube of 18.32 Å corresponds to the experimental density at room temperature of 1.145 g/cm³. A suitably scaled configuration from the simulation of a 1.1 m MgCl₂ solution served as starting configuration. After several thousand steps of equilibration the collection of data was started; the simulation was performed for about 16,000 time steps of 2.5 × 10⁻¹⁵ s each, leading to a total elapsed time of about 4 ps. The average temperature of the system

![Figure 1](https://example.com/figure1.png)

**Energies are given in 10⁻¹⁷ erg and distances are in Å. For intra-molecular potentials see ref 9.
TABLE III: Characteristic Values for the Radial Distribution Functions $g_{sr}(r)\)²

<table>
<thead>
<tr>
<th>α</th>
<th>β</th>
<th>$R_1$</th>
<th>$r_{m1}$</th>
<th>$g_{sa}(r_{m1})$</th>
<th>$R_2$</th>
<th>$r_{m2}$</th>
<th>$g_{sa}(r_{m2})$</th>
<th>$n_{sa}(r_{m1})$</th>
<th>$r_{m1}$</th>
<th>$g_{sa}(r_{m1})$</th>
<th>$r_{m2}$</th>
<th>$g_{sa}(r_{m2})$</th>
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<tr>
<td>Sr</td>
<td>O</td>
<td>2.44</td>
<td>2.63</td>
<td>10.6</td>
<td>2.99</td>
<td>3.18</td>
<td>0.10</td>
<td>9.8</td>
<td>5.0</td>
<td>1.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>H</td>
<td>3.04</td>
<td>3.35</td>
<td>4.90</td>
<td>3.68</td>
<td>4.00</td>
<td>0.13</td>
<td>20.1</td>
<td>5.35</td>
<td>1.69</td>
<td></td>
<td></td>
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<tr>
<td>Cl</td>
<td>O</td>
<td>2.94</td>
<td>3.18</td>
<td>3.49</td>
<td>3.57</td>
<td>3.95</td>
<td>0.64</td>
<td>7.8</td>
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<td>3.48</td>
<td>1.44</td>
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<tr>
<td>Cl</td>
<td>H</td>
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<td>2.98</td>
<td>2.58</td>
<td>2.86</td>
<td>0.46</td>
<td>6.5</td>
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<tr>
<td>O</td>
<td>O</td>
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<td>3.00</td>
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<tr>
<td>O</td>
<td>H</td>
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<td>1.93</td>
<td>1.23</td>
<td>2.17</td>
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<tr>
<td>H</td>
<td>H</td>
<td>2.17</td>
<td>2.30</td>
<td>1.55</td>
<td>2.73</td>
<td>3.05</td>
<td>0.78</td>
<td>6.7</td>
<td>3.74</td>
<td>1.15</td>
<td></td>
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</tr>
</tbody>
</table>

*R, $r_{m1}$, and $r_{m2}$ are the distances in Å where for the ith time $g_{sa}(r)$ is unity, a maximum, and a minimum, respectively. For O–H and H–H only intermolecular data are given.

Figure 2. Ion-oxygen and ion-hydrogen radial distribution functions and running integration numbers.

was 298 K, and no rescaling of the velocities was performed during the run in order to be able to obtain reliable velocity autocorrelation functions. The total energy was stable to better than 0.1% during the whole run.

3. Results and Discussion

(a) Radial Pair Distribution Functions (RDF). Figure 2 shows the RDFs $g_{sa}(r)$ for ion-oxygen and ion-hydrogen and the corresponding running integration numbers $n_{sa}(r)$, defined by

$$n_{sa}(r) = 4\pi\rho_0 \int_0^r g_{sa}(r')r'^2 dr'$$

where $\rho_0$ is the number density of the atoms of kind $\beta$. In Table III some of the characteristic values for the various RDFs are listed.

The first peak in the Sr$^{2+}$–O RDF is centered at 2.63 Å, which is by about 0.1 Å larger than the distance at which the minimum of the Sr$^{2+}$–water pair potential for the Cs$_2$H$_2$O$_5$ geometry has been found. About the same difference between the position of the first ion–oxygen peak and the minimum of the pair potential has been observed for the other alkaline-earth ions investigated so far, while in the case of the alkali-metal and halide ions both distances almost coincide. The stronger ion–water interactions in the case of doubly charged ions lead to repulsive forces between the water molecules in the first hydration shells and thus may prevent an approach to the distances of the potential minima.

The lower height of the first peak $g_{sa}(r)$ compared with the ones for Be$^{2+}$, Mg$^{2+}$, and Ca$^{2+}$ is in keeping with the larger size of Sr$^{2+}$. As in the case of the other alkaline-earth ions, a pronounced second peak in $g_{sa}(r)$ exists which is well separated from the first peak. A hydration number of 9.8 is found for Sr$^{2+}$ which is only by 0.6 larger than the one for Ca$^{2+}$ while the increase from Mg$^{2+}$ to Ca$^{2+}$ was 3.2.

Figure 3. Distributions of $\cos \theta$ for the water molecules in the first hydration shells of Sr$^{2+}$ and Cl$^-$.

X-ray measurements by Albright and by Caminiti et al. on SrCl$_2$ solutions have led to Sr$^{2+}$–O first-neighbor distances of 2.6 and 2.64 Å, respectively, in agreement with the results from the simulation. The hydration number of 7.9 for Sr$^{2+}$ deduced from the experiment by Albright is significantly lower than the one found here. This discrepancy might result from the difficulty of determining a reliable hydration number from X-ray experiments. The value of 8 reported by Caminiti et al. was determined by a model fit.

The positions and heights of the first and second peak in the Sr$^{2+}$–H RDF change relative to the other alkaline-earth ions as expected from the size of Sr$^{2+}$. The running integration number of $g_{sa}(r)$ at the first minimum gives about 20 in agreement with the hydration number of 9.8.

The positions of the peaks in the Cl$^-$–O and Cl$^-$–H RDFs are the same, in the limits of statistical uncertainty, for all alkaline-earth chloride solutions investigated. The heights of the first peaks in both RDFs increase with increasing counterion size, which in turn leads to a slight increase in the hydration number of Cl$^-$. This means that already in the 1.1 m solutions the structure of the hydration shell of the anions is influenced by the size of the doubly charged cations.

The O–O, O–H, and H–H RDFs in the 1.1 m SrCl$_2$ solutions are in the limits of statistical uncertainty the same as for the CaCl$_2$ solution. Therefore, they are not shown here.

(b) Orientation of the Water Molecules. The distributions of $\cos \theta$ for the water molecules in the first hydration shells of Sr$^{2+}$ and Cl$^-$ are shown in Figure 3. $\theta$ is defined as the angle between the dipole moment direction of the water molecule and the vector pointing from the oxygen atom toward the center of the ion. Figure 3 shows for Sr$^{2+}$ a strong preference for a trigonal orientation. The distribution is slightly broader than that for Ca$^{2+}$. The water molecules in the first hydration shell of Cl$^-$ form preferentially linear hydrogen bonds, with a distribution which is very similar to the one found for the 1.1 m CaCl$_2$ solution.

(c) Hydration Shell Structures. From the knowledge of the position of all particles as a function of time provided by the MD simulation, the geometrical arrangement of the water molecules

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Molecular Dynamics Study of an Aqueous SrCl$_2$ Solution

**Figure 4.** Densities of the projections of the oxygen atom positions of the 10 nearest-neighbor water molecules around Sr$^{2+}$ and Ca$^{2+}$ onto the xy plane of a coordinate system as defined in the text.

**Figure 5.** Average potential energy of a water molecule with respect to Sr$^{2+}$ and Cl$^{-}$ as a function of the ion-oxygen distance. The positions of the first maxima in the RDFs are marked by arrows.

in the first hydration shells of the ions has been deduced. In order to achieve this a coordinate system has been introduced where the ion defines the origin, one oxygen atom of the hydration shell water molecules the z axis, and a second one the $xz$ plane. The densities of the projections of the oxygen atom positions of the 10 nearest-neighbor water molecules around Sr$^{2+}$—collected at several hundred time steps spread over the whole simulation—onto the $xy$ plane of this coordinate system are shown in Figure 4 in the form of an axonometric drawing and compared with that for Ca$^{2+}$. The distribution of the eight water molecules in the first hydration shell of Cl$^{-}$ is found to be uniform just as in all other chloride solutions investigated so far and is, therefore, not shown here.

Figure 4 shows clearly that with increasing ion size (the ion-oxygen first-neighbor distances are 2.39 and 2.63 for Ca$^{2+}$ and Sr$^{2+}$, respectively) there is a tendency for a more uniform distribution of the water molecules in the first hydration shells. This result is not unexpected but quite different from the strong change from an octahedral symmetry found for Mg$^{2+}$ to the well-ordered hydration shell of Ca$^{2+}$ which has no regular symmetry.

**Figure 6.** Normalized velocity autocorrelation functions for oxygen atoms, hydrogen atoms, Sr$^{2+}$, and Cl$^{-}$, their running integrations according to eq 2, and spectral densities in arbitrary units in the frequency range 0 < $\omega$ < 1000 cm$^{-1}$.

which are marked in Figure 5 by arrows, appear at a slightly larger distance than the minima in $\langle V(r) \rangle$. This difference shows that there is not enough space available in the hydration shells for all water molecules to settle at the distance of the potential energy minimum (see above).

(e) Self-Diffusion Coefficients. Figure 6 shows the normalized velocity autocorrelation functions $C_{\alpha\beta}(t)/C_{\alpha\beta}(0)$ for the oxygen atoms, the hydrogen atoms, and for Sr$^{2+}$ and Cl$^{-}$. Also given are the integrals

$$D_i(t) = \frac{1}{\hbar} \int_0^t C_{\alpha\beta}(t') \, dt'$$

which in the limit $t \to \infty$ converge toward the self-diffusion coefficients of species $i$. The autocorrelation function (acf) of a quantity $a_i$—with $a_i$ either a scalar or a vector—is calculated from the simulation by

$$C_{\alpha\beta}(t) = \frac{1}{N_iN \sum_{\alpha=1}^N \sum_{\beta=1}^N a_{\alpha}(t) a_{\beta}(t+i)}$$

where $N$ denotes the number of particles and $N_i$ the number of time averages. The various acfs are shown in Figure 6 only up to a lengths of 4.75 $\times$ 10$^{-13}$ s in all four cases to ease the comparison, in spite of the fact that the motional regimes are obviously very different. It is also clear that this length is not sufficient to converge eq 2 to the self-diffusion coefficients.

The self-diffusion coefficient of Cl$^{-}$ is found to be $(1.2 \pm 0.3) \times 10^{-5}$ cm$^2$ s$^{-1}$. In the limits of the relatively large statistical uncertainty this value is the same as found from simulations of 2.2 m NaCl, KCl, and NH$_4$Cl solutions. The result indicates that at moderate concentrations $D_{Cl^{-}}$ does not depend strongly on the cation. The value for Sr$^{2+}$ of $(0.6 \pm 0.1) \times 10^{-5}$ cm$^2$ s$^{-1}$ is lower than that for Na$^+$, K$^+$, and NH$_4^+$ but is the same in the

limits of error as for Li⁺ when calculated from a simulation of a 2.2 m LiI solution. The self-diffusion coefficients of the cations in electrolyte solutions depend not only upon their masses but also on their charges and sizes as the latter two properties are responsible for the strength of the interactions between the ion and its hydration shell water molecules. In order to investigate this complicated interdependence by MD simulations, a much higher accuracy would be needed than the one possible for the time being.

An important advantage of the MD simulations is the possibility of calculating the single ion effects on the motions of the water molecules. This is achieved by subdividing the 200 water molecules into three subsystems: hydration water of the cation (cw), hydration water of the anion (aw), and bulk water (bw). The first hydration shells are defined in terms of cation-oxygen and anion-hydrogen distance (here \( r(Sr^{2+}-O) \leq 2.8 \text{ Å} \) and \( r(Cl^{-}-H) \leq 2.75 \text{ Å} \)), leading to an average of 39.7 molecules contributing to the cw functions and 48.7 molecules contributing to the aw functions. The subdivision into the three classes is only carried out at correlation origin (\( t_i \) in eq 3). The exchange of water molecules between the three classes is assumed to be negligible during the typical lengths of the correlations.

The self-diffusion coefficients for bulk water and hydration water of CI⁻ are the same in the limits of statistical uncertainty \((1.4 \pm 0.2) \times 10^{-5} \text{ cm}^2\text{s}^{-1}\), while the one for the hydration water of Sr²⁺ is smaller by about 35% than that of bulk water. The difference in the self-diffusion coefficients between the hydration water of anion and cation results from the difference in strength of the ion-water interactions (see, e.g., Figure 2). Even stronger reductions than for Sr²⁺ have been reported earlier for the hydration water of the Li⁺. For the hydration water of CI⁻, both slight reductions (in NaClI and KClO₃ solutions) and slight increases (in NH₄ClO₃ solutions) of the self-diffusion coefficients have been reported, indicating a slight counterion dependence. The self-diffusion coefficients for both ions are significantly smaller than the ones of their hydration water.

Although it is well-known that the central force model leads to too low absolute values for the self-diffusion coefficient in pure water reasonably well. Therefore, the results presented here seem to be reliable at least in their relation to each other.

(j) Hindered Translations. The Fourier transforms of the velocity autocorrelation functions for the various atoms in the aqueous SrCl₂ solution—as shown in the left side of Figure 6—are presented in the right column for frequencies up to 1000 cm⁻¹. The Fourier transforms for Sr²⁺, Cl⁻, and O represent the spectral densities of the hindered translational motions for the ions and all water molecules in the solution, where in the O case the librations of the water molecules also contribute slightly. In the case of the H atoms it mainly reflects the librational motions of the water molecules and will be discussed in more detail in the next section. As in the case of the self-diffusion coefficients, the hindered translations, librations, and internal vibrations of the water molecules have been calculated separately for the three water subsystems and for the motions perpendicular and parallel to the plane of the water molecule, calculated from the center-of-mass velocities. Figure 7 shows that in all three subsystems the motions parallel to the plane of the molecule contribute more to the high-frequency region than the ones perpendicular to the plane. Keeping in mind the three-dimensional structure of water, it appears—in accordance with the assignment of the two frequencies—that almost any motion parallel to the molecular plane involves the stretch of a hydrogen bond while motions perpendicular to the plane of the molecule involve mostly the bending of bonds.

The spectral densities for the hydration water of Cl⁻ are similar to the ones for bulk water, except that the motions of the molecules seem to be more isotropic here. There are no significant differences between these spectra and the ones for pure water. The same conclusion has been drawn from other simulations of electrolyte solutions with Cl⁻ as anion. The hydration water of the Cl⁻ is thus dynamically still quite similar to bulk water which is in keeping with the structure of the hydration shell discussed above.

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The spectral densities of the perpendicular and parallel motions of the hydration water molecules of the Sr$^{2+}$ are completely different from the ones for bulk water. They are strongly anisotropic. The spectral density of the parallel motions has a maximum at about 250 cm$^{-1}$ while the one for the perpendicular motions shows two maxima. The peak at about 50 cm$^{-1}$ can be considered a remnant of the bulk water one and appears on top of a broad and somewhat asymmetric band with a maximum at about 180 cm$^{-1}$ and extending to about 350 cm$^{-1}$. The dynamical behavior of these molecules is clearly dominated by forces different from the ones prevailing in the bulk. With the structure of the hydration shell in mind one may conclude that the motions parallel to the plane are mostly controlled by the strong ion–water interactions while the ones perpendicular to the plane result from repulsions between neighboring water molecules in the hydration shell. The small peak visible at the position of the O–O bending peak in pure water may be taken as an indication of to what extent the hydrated water molecules participate in hydrogen bonds with their neighbors in the bulk. Experimental values for the ion–water vibrational frequencies are not available for the Sr$^{2+}$ ion. For comparison, values of 359 and 290 cm$^{-1}$ have been reported for this vibration of water molecules hydrated to Mg$^{2+}$ and Ca$^{2+}$, respectively. It is reasonable to expect that the corresponding value for Sr$^{2+}$ should be lower.

(g) Librational Motions. In order to calculate the various librational and vibrational modes from the velocity acfs of the hydrogen atoms, a scheme has been developed which is described in the Appendix. The application of this scheme leads to the spectral densities of the librations around the three main axes of the hydration water as defined in the insert, calculated separately for the hydration water of Sr$^{2+}$, Cl$^{-}$, and bulk water (—) and given in arbitrary units.

The strong Sr$^{2+}$–water interactions lead to a well-defined first hydration shell where the oxygen atom density goes up to about 10 times the average one (Figure 2) and results in a strong preference for an orientation where the dipole moment of the water molecule points away from the center of the ion (Figure 3). Consequently, these water–water interactions cause an additional hindrance for the rotations around the x and y axes which explains the blue shift for the hydration shell molecules while the rotation around the z axis remains rather unaffected. This explanation is in accordance with the results of simulations of 2.2 m KCl, NH$_4$Cl, and LiI solutions with the ST2 model for water. It has been found that K$^+$ and NH$_4^+$ do not significantly influence the librational motions of their hydration shell water molecules because of the weaker ion–water interactions compared with Sr$^{2+}$.

In contrast, Li$^+$ causes a blue shift of about 200 cm$^{-1}$ for the librational motions around all three principal axes of the six water molecules in its first hydration shell. The difference between Li$^+$ and Sr$^{2+}$ as far as the z axis is concerned results from the orientation of this hydration shell molecule. While in the simulations with the ST2 model for water a lone pair orbital is directed toward the cation, a trigonal orientation is found in the case of the CF model.

Both ions cause a significant blue shift of the librational frequencies around the x and y axes relative to bulk water while the maxima in the spectral densities for the rotations around the dipole moment axis show only small changes, hardly outside the limits of statistical uncertainty (Figure 8 and Table IV). The effect of anion and cation on the peak maximum of the librations around the y axis is quite similar while the shift caused by Sr$^{2+}$ in the case of the x axis is about twice as large as that of Cl$^-$.

|| total water | bulk water | hydration water |
|---|---|---|---|---|
| $R_1$ | $P_{\text{max}}$ | 445 ± 10 | 410 ± 10 | 500 ± 10 | 465 ± 10 |
| $R_2$ | $P_{\text{max}}$ | 620 ± 10 | 595 ± 10 | 640 ± 15 | 650 ± 15 |
| $R_3$ | $P_{\text{max}}$ | 405 ± 10 | 405 ± 10 | 390 ± 10 | 420 ± 20 |
| $Q_1$ | $P_{\text{max}}$ | 3450 ± 10 | 3475 ± 10 | 3335 ± 10 | 3420 ± 10 |
| $Q_2$ | $P_{\text{max}}$ | 1705 ± 5 | 1705 ± 5 | 1690 ± 10 | 1710 ± 10 |
| $Q_3$ | $P_{\text{max}}$ | 3580 ± 10 | 3595 ± 10 | 3460 ± 10 | 3540 ± 20 |

*In the case of the vibrations the widths at half-height, $\Delta P$, are given additionally.


Figure 8. Spectral densities of the librations around the three main axes of the water molecule as defined in the insert, calculated separately for the hydration water of Sr$^{2+}$, Cl$^-$, and bulk water (—) and given in arbitrary units.

differences emerge between pure water and the solution. This motions of the water molecules in the three water subsystems in arbitrary units.

hydration shells, resulting in average values of 0.9753, 0.9768, and 0.9815 with bulk water for which a value of 2.00 D has been calculated. The weaker interactions between Cl- and water are reflected in the smaller red shift of the O-H stretching frequencies of about 50 cm^-1 for the hydration shell molecules relative to bulk water. Again, this shift is in keeping with the increase of the average O-H distance. The bending frequency of the water molecules is not influenced by Cl-. The width at half-height of all three vibrational peaks is, relative to bulk water, much more strongly increased for the hydration water of Sr^2+ than for Sr^2+. The broader frequency distribution in the case of Cl- seems to be a consequence of a strong cation effect on the O-H stretching frequencies of the hydration shell water molecules from the simulations have recently been confirmed experimentally for several divalent cations. The bending vibration is only slightly affected by the presence of the ions and shifts to the red by about 15 cm^-1 hardly outside the limits of error. The peaks have approximately the same width as in bulk water.

The weaker interactions between Cl- and water are reflected in the smaller red shift of the O-H stretching frequencies of about 50 cm^-1 for the hydration shell molecules relative to bulk water. Again, this shift is in keeping with the increase of the average O-H distance. The bending frequency of the water molecules is not influenced by Cl-. The width at half-height of all three vibrational peaks is, relative to bulk water, much more strongly increased for the hydration water of Cl- than for Sr^2+. The broader frequency distribution in the case of Cl- seems to be a consequence of the less pronounced first hydration shell and especially of the broader distribution of cos \( \theta \) relative to the one for Sr^2+ (Figure 3).

(i) Collective Motions. The ion–water stretching vibrations of water molecules in the hydration shell of Sr^2+ have been studied from their center-of-mass velocities with a procedure similar to the one described in the Appendix for the intramolecular stretches of the water molecules. The ratio of the masses involved is less favorable here for such a simplified procedure than in the water molecule. It is nevertheless expected that qualitative features of the ion–water stretching vibrations can be detected with this method. Figure 10 shows the result. The spectral densities for the symmetric (full) and asymmetric (dashed) stretching vibrations of water molecules in the hydration shell of Sr^2+, given in arbitrary units.

percentage of bulk water molecules remains so high that only small differences emerge between pure water and the solution. This has also been demonstrated from simulations of the librational motions in a 2.2 m LiCl solution and the vibrations in a 1.1 m CaCl_2 solution.

(h) Intramolecular Geometry and Vibrations. The ion–water interactions lead to an increase of the intramolecular O–H distance and a decrease of the HOH angle for the water molecules in their hydration shells, resulting in average values of 0.9753, 0.9768, and 0.9815 Å as well as 100.7°, 100.3°, and 99.2° for bulk water, hydration water of Cl-, and hydration water of Sr^2+, respectively. These changes in geometry together with the partial charges on the O and H atoms lead to an increase of the dipole moment for the water molecules in their hydration shell water molecules of Sr^2+ by about 2% compared with bulk water for which a value of 2.00 D has been calculated.

From the well-known empirical relationship between the intramolecular O–H distances and the frequencies of the O–H stretching modes of about 20000 cm^-1 for the hydration shell molecules of Sr^2+ and Cl-, respectively. The spectral densities of the three normal mode vibrations calculated by Fourier transformation from the acfs of the H-atom velocities—after separation according to the method described in the Appendix—are presented in Figure 9 separately for bulk water and hydration water of Sr^2+ and Cl-. The figure shows that the symmetric and asymmetric O–H stretching vibrations are well separated, which justifies the approximation described in the Appendix. The frequencies of the peak maxima and the width at half-height have been collected in Table IV.

In the bulk water the positions of all peaks are identical, within the error margins, with the ones found in the bulk water of a CaCl_2 solution. The corresponding values for the stretching vibrations in pure water are 3460 ± 15 and 3560 ± 15 cm^-1 at 300 K and 3475 ± 10 and 3580 ± 10 cm^-1 at 335 K. With respect to the

![Figure 9](image9.jpg)  
**Figure 9.** Spectral densities of the three intramolecular vibrational motions of the water molecules in the three water subsystems in arbitrary units.

![Figure 10](image10.jpg)  
**Figure 10.** Spectral densities of the symmetric (solid) and asymmetric (dashed) ion–water stretching vibrations of adjacent water molecules in the hydration shell of Sr^2+, given in arbitrary units.

(29) Bopp, P., unpublished results.


(31) Bopp, P., unpublished results.
Electroneutrality Coupling of Electron Hopping between Localized Sites with Electroinactive Counterion Displacement. 1. Potential-Step Plateau Currents

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Electroneutrality coupling of electron hopping between localized redox sites and electroinactive counterion displacement induces a "migration" enhancement of the potential-step plateau current responses. This is investigated for systems containing fixed redox ions, mobile electroinactive counterions, and fixed "supporting" electroinactive counterions under semi-infinite diffusion-migration conditions. The current response is easily computed as a function of the ratio of the "mobility" of the electrons and the mobility of the electroinactive counterions and of the relative excess of supporting counterions. The effect of the latter is to suppress the contribution of migration. As the mobility of the electroinactive counterions decreases, the current response increases as a consequence of migration. The dependency of the apparent electron-hopping "diffusion" coefficient upon the concentration of electroactive material goes beyond the simple proportionality reaching eventually a cubic dependence when the mobility of the electroinactive counterions is much lower than the mobility of electrons. This behavior is illustrated with an experimental example taken from literature data. How the ratio between the reduction current of the fully oxidized film to the oxidation current of the same fully reduced film depends upon the various experimental parameters is also discussed.

Introduction

Electron hopping between localized sites, for example, in redox polymers, is necessarily accomplished by the displacement of electron transfer inactive ("electronic") counterions so as to maintain electroneutrality. The question thus arises of the effect of the electroinactive counterion displacement on the rate of charge transport in such systems. If electron hopping could be likened with an ordinary ion displacement, as is sometimes done, this would amount to investigating the diffusion and migration of electrons and counterions as coupled by electroneutrality, both obeying the classical Fick and Nernst–Planck laws. This picture is not in fact quite correct since the electron actually hops between two adjacent redox sites of different oxidation states. As shown earlier, as far as charge transport under a concentration gradient is concerned, this is formally equivalent to a "diffusion" (obeying Fick's law) of the two immobile redox sites with the same diffusion coefficient, $D_e = k_c \Delta x^2 C_e \epsilon$ ($k_c$, bimolecular electron-transfer rate constant at zero driving force; $C_e$, total redox site concentration; $\Delta x$, mean distance between two adjacent redox sites). The effect of an electric field is formally equivalent to "migration" of the immobile redox centers with the same mobility. It does not, however, obey the classical Nernst–Planck law but rather a second-order law deriving from the bimolecular character of electron hopping as opposed to the monomolecular character of...