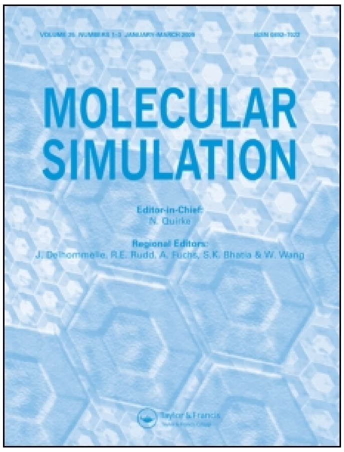

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On the Structure and Dynamic Properties of Aqueous Solutions: Molecular Dynamics Simulation of Cl^- and Cl^{2-} in Water

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ON THE STRUCTURE AND DYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS: MOLECULAR DYNAMICS SIMULATION OF CL^- AND CL^{2-} IN WATER

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Molecular dynamics simulations of Cl^- and Cl^{2-} in water with four slightly different versions of the simple point charge (SPC) potential have been carried out. Both structural and dynamic properties including reorientational and residence times, velocity autocorrelation functions, self diffusion coefficients and spectral densities have been analyzed. The influence of ionic charge as well as flexibility, molecular dipole moment, charge distribution and molecular geometry of water on the properties of ions and water molecules in the hydration shell is discussed.

KEY WORDS: Aqueous solutions, chlorine ions, Molecular Dynamics.

1 INTRODUCTION

Molecular dynamics (MD) simulation is a powerful tool for investigating the microscopic properties of liquids. Because of wide interest a large number of MD studies have been devoted to the study of water and ionic aqueous solutions. The reliability of the MD results depends upon the use of suitable potentials which in the case of molecular liquids like water requires a model of the interatomic interactions (or the interactions between molecular sites) as well as molecular geometry and charge distribution. However, despite the large number of potential models proposed none of them succeed in reproducing adequately all the properties of water and aqueous solutions. A detailed knowledge of the influence of the different characteristics of water molecules on the microscopic properties of aqueous solutions should be very helpful for 1) reliable modelling of water and 2) a deeper understanding of the behaviour of these systems at the molecular level.

It is well known that the molecular dipole moment (μ) is one of the most relevant parameters of water molecules and polarization plays a significant role in the intermolecular interactions. During the last years a considerable effort has been made for the development of polarizable potential models which consider fluctuating charges and/or geometry of water molecules [1 – 5]. However, effective pair potentials which include the averaged effects of the induced dipole moments (μ is greater than for isolated molecules) are frequently employed since the use of polarizable potentials increases substantially the computational costs but does not improve significantly the MD results. One of the more popular effective pair potentials for water is the simple point charge (SPC) model of Berendsen *et al.* [6]. Despite its simplicity this potential reproduces reasonably many of the characteristic properties of liquid water. Moreover, it has been later refined by including a polarization self-energy correction (SPC/E model) [7]. In the SPC/E model the effective electric charges are slightly larger than in the SPC model whereas the molecular geometry is the same ($\mu = 2.274$ D for SPC and 2.351 D for SPC/E).

A characteristic of water molecules that is often neglected is molecular flexibility. So, many MD studies of aqueous systems are carried out with rigid models such as SPC and SPC/E. However, several flexible potential models have been developed during the last years. Toukan and Rahman [8] proposed a SPC flexible model based on a simple grafting of intramolecular potentials onto the rigid SPC model without refitting the intermolecular potential parameters. The effects of the molecular flexibility on the microscopic properties of water [9–11] and ionic aqueous solutions [12, 13] were analyzed by performing MD simulations of SPC water with and without intramolecular degrees of freedom. However, flexibility increases the bond length and diminishes the bond angle so that the mean value of μ is larger than that for the original rigid model and the differences in the properties should be attributed to the influence of both flexibility and changes in μ. Teleman *et al.* [9] also compared the results for the flexible SPC model with those for a rigid model with a bond length and bond angle equal to the mean values obtained from the flexible MD simulations. Smith and Haymet [14] studied the effects of flexibility from MD simulations of Na^+—Cl^- solutions using the flexible central force potential [15] (the mean value of μ in this case is 1.984 D) and a rigid version of this model with a very close value of μ.

In this paper the effects of molecular flexibility are analysed by comparing the results from MD simulations of flexible or rigid SPC potentials with the same μ. The influence of μ is investigated from MD simulations using rigid SPC water molecules with the same electric charges or geometry (bond length and bond angles) but different μ. The properties for molecules with the same μ but different electric charges and geometry are also compared. The systems considered are made of single ions in water and the properties of ions and water in their hydration shells are calculated. Special attention is paid to the dynamic properties which are in principle more sensitive to the rather small differences among the potential models employed in this work. Cl^- and Cl^{2-} ions are considered. Although Cl^{2-} is unrealistic, the comparison of results for systems only differing in the ionic charge can provide interesting information on the microscopic behaviour of high charged electrolytes. In the last years, several studies of the effects of ionic charges on the properties of water have been published for cations [13, 16], but a similar analysis for negative charged ions is still lacking.

2 COMPUTER SIMULATIONS

MD simulations of systems made by one ion (Cl^- or Cl^{2-}) and 215 water molecules with periodic boundary conditions were carried out. The size of the cubic box was chosen to give a solvent density of 1 g/cm^3 and the temperature was kept at 298 K. A leapfrog Verlet algorithm with coupling to a thermal bath was used [17]. Time steps of 0.5 fs and 1.5 fs were employed for simulations with flexible and rigid water, respectively. Properties were calculated during MD runs of 75 ps after an equilibration period of 25 ps. Long-ranged Coulomb forces were computed using the Ewald summation method [18]. Although the treatment of long-range interactions in computer simulations is still a problem under discussion, a recent study on the dynamics of single ions in solution [19] has shown that Ewald summation and reaction field methods produce very similar results and represent a significant improvement compared to truncation or switching techniques.

Four potentials based on the SPC water model were used. The parameters of these potentials are given in Table 1. Model F is the flexible SPC potential of Toukan and Rahman [8]. The original rigid SPC potential of Berendsen *et al.* [6] is denoted by R1. Models R2 and R3 are rigid models with the same μ as F. The former has the electric charges of F and R1 and the bond length and bond angle equal to the average values obtained from the MD simulations with F. In the case of R3 the geometry of R1 is kept and the electric charges are changed. The ion-water interactions were those given by Pettitt and Rossky [20] in all the MD simulations.

3 STRUCTURE

The ion-water radial distribution functions ($g_{I-W}(r)$) obtained with the R1 model are shown in Figure 1. Functions corresponding to the other water models have not been plotted since they do not differ significantly from those for R1. So, flexibility of water has no noticeable effects on $g_{I-W}(r)$. This result is consistent with earlier findings for pure water [10, 11, 14]. According to Appendix C or Reference 11, the

Table 1 Water Models Used in Simulations.

Models	$q_H(e)$	$q_O(e)$	d_{OH}(Å)	$H\hat{O}H(deg)$	$\mu(D)$
F	0.41	−0.82	1.022*	105.6*	2.43
R1	0.41	−0.82	1.000	109.5	2.27
R2	0.41	−0.82	1.022	105.6	2.43
R3	0.4388	−0.8776	1.000	109.5	2.43

*Bond length and bond angles for the flexible model are the mean values during the MD simulation. Their statistical uncertainties are 0.026 Å and 4.0 deg, respectively.

differences in the radial distribution functions for rigid and flexible water reported in References 9, 12 and 13 should be attributed to a non complete equilibration of the different degrees of freedom during the MD simulations with the flexible model. We have effectively checked that in the flexible water simulations of References 12 and 13 the translational temperature was too high.

We calculated the running integration numbers ($n(r)$) as the integrals of the $g_{I-W}(r)$'s. The coordination number (cn) is defined as the value of $n(r)$ at the minimum of $g_{I-W}(r)$ (see Figure 1). The small disagreements between the findings from g_{I-O} and g_{I-H} (Table 2) provide a measure of the uncertainties of the cn values. According to the $g_{I-W}(r)$ results, cn for the different water models do not show important differences. cn is not affected by flexibility of water molecules and

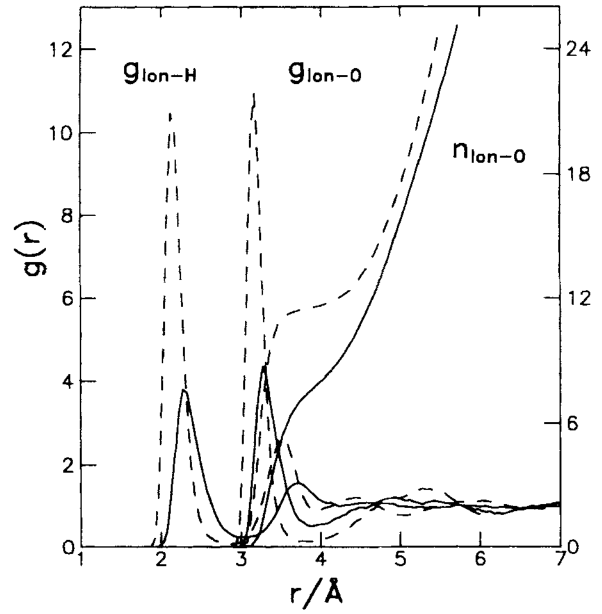

Figure 1 Ion–oxygen and ion–hydrogen radial distribution functions and running integration numbers——— Cl^- ; ----- Cl^{2-}.

Table 2 Coordination Numbers (cn).

	ion-O		*ion-H*	
Model	*Cl^-*	*Cl^{2-}*	*Cl^-*	*Cl^{2-}*
F	7.5	11.5	7.2	11.4
R1	8.0	11.8	7.5	11.7
R2	7.5	11.4	7.3	11.4
R3	7.0	11.0	6.7	10.8

slightly diminishes when μ increases. The same tendency has been observed using a polarizable water model [5]. The smallest cn corresponds to the R3 model. However, this value is still bigger than that obtained from recent neutron diffraction experiments (cn $= 6.2 \pm 0.3$) [21].

As expected, the hydration shell of Cl^{2-} displays more structure than the Cl^- shell. The first $g_{I-W}(r)$ maxima are markedly higher and slightly shifted towards smaller r-values (about 0.1 Å). Moreover the first $g_{I-W}(r)$ minima for Cl^{2-} are very close to zero and the corresponding cn values are much bigger. These results indicate that the hydration shell of the Cl^{2-} ion is constituted by 11–12 molecules. It should be noted that these results are completely different from those for cations in water [12, 13, 16] which show that cn does not depend significantly on the ionic charge of cations. We have also analyzed the orientation of water molecules by calculating the angle θ between the dipole vector and the ion-water position vector (more details are given in reference 12). We have obtained $\theta = 55$ deg with a fluctuation of 16 deg for Cl^- and $\theta = 49$ deg with a fluctuation of 9 deg for Cl^{2-}. These results suggest that linear O—H···Cl bonds are formed in both cases.

4 DYNAMIC PROPERTIES

The velocity autocorrelation functions ($C(t)$) of Cl^- and Cl^{2-} ions are represented in Figure 2. $C(t)$ functions for different water models show the same qualitative behaviour. The marked oscillations of the $C(t)$'s for the divalent ion should be attributed to the solid-like oscillatory motions of Cl^{2-} in the cage formed by molecules of its hydration shell.

Because of the relatively long tails of the $C(t)$'s, self-diffusion coefficients (D) cannot be easily obtained by integration of these functions and were calculated from the slope of the mean square displacements (Table 3). Results for Cl^- using the F and R1 models are in reasonable agreement with the experimental datum ($D = 2.03\ 10^{-5}$ cm^2/s [22]) whereas for the other models the values of D are too low. D coefficients for Cl^{2-} are markedly smaller, which is consistent with the formation of relatively more stable hydration shells constituted by 11–12 water molecules. The results for F and R2 indicate that ionic mobility slightly increases with flexibility. This was also observed by Smith and Haymet [14]. The greater D for R1 can be attributed to a decrease of cohesive forces between the ions and water when μ diminishes. However, a comparison of the results for R2 and R3

Table 3 Diffusion Coefficients and Residence Times.

	$D_{Cl}(\times 10^{-5} cm^2 s^{-1})$		$D_O(\times 10^{-5} cm^2 s^{-1})$		$\tau(ps)$	
Model	Cl^-	Cl^{2-}	Cl^-	Cl^{2-}	Cl^-	Cl^{2-}
F	1.8	0.6	2.1	1.4	10.0	78
R1	2.2	0.8	2.7	1.1	7.2	85
R2	1.2	0.4	1.6	0.9	11.3	80
R3	1.0	0.2	1.4	0.6	12.5	102

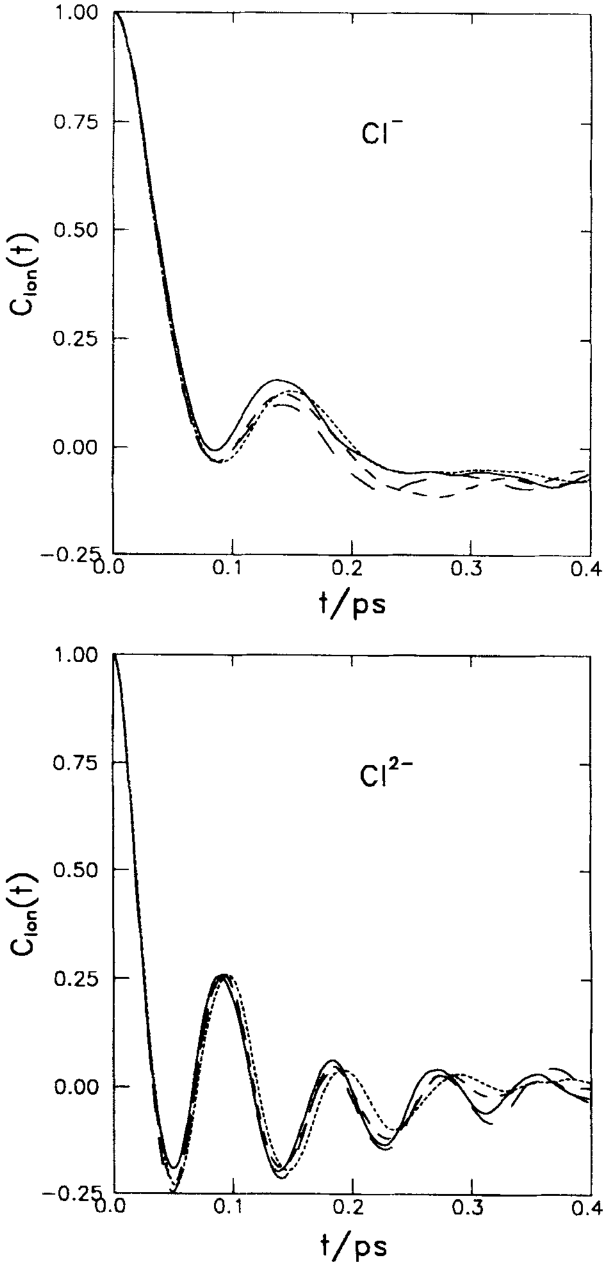

Figure 2 Ion velocity autocorrelation functions for different water models ——— F; ------ R1; ---- R2; — — — R3.

shows that the D coefficients are not only dependent on the value of μ but also on the distribution and values of the electric charges. As a general trend, we observe that D diminishes as the electric charges assumed in the water model increase. The D coefficients of the oxygens of water molecules in the ionic hydration shells were also determined and the results are reported in Table 3. In all cases the oxygen D coefficients are greater than those for the corresponding ions and show the same qualitative changes with the water model.

Times of residence (τ) of water molecules in the first coordination shell were calculated according to the procedure described in refs. 12 ad 23. The resulting τ values (Table 3) corroborate that hydration shells of divalent ions are much more stable than those of monovalent ions. Although in general τ increases when D decreases, some results for Cl^{2-} do not obey this rule. This may be due to the large values of τ for Cl^{2-} which cannot be accurately determined from MD simulations of less than one hundred picoseconds.

Reorientational times were calculated through a set of time correlation functions defined as

$$C_l(t) = \langle P_l(\vec{u}_i(t) \cdot \vec{u}_i(0)) \rangle \tag{1}$$

where P_l is the l th Legendre polynomial and $\vec{u}_i(t)$ is a unit vector that characterizes the orientation of the molecule. We considered four unit vectors, *i.e.*, $\vec{u}_1(t)$ in the direction of the dipole moment vector, $\vec{u}_2(t)$ in the intramolecular proton-proton direction, $\vec{u}_3(t) = \vec{u}_1(t) \times \vec{u}_2(t)$ orthogonal to the plane of the water molecule and $\vec{u}_4(t)$ along the ion-oxygen direction. The $C_l(t)$ functions corresponding to the $\vec{u}_1(t)$ vector for water molecuels in the first hydration shell of Cl^{2-} are shown in Figure 3. Reorientational times τ_l were calculated by assuming an exponential decay of $C_l(t)$ at long times [12, 13]

$$C_l(t) \cong \exp(-t/\tau_l) \tag{2}$$

Results summarized in Table 4 show that, in general, reorientational times are greater when the ion-water complexes are more stable. However, it should be noted that except for $\vec{u}_4(t)$ the values of τ_l for Cl^- and Cl^{2-} do not show important differences.

It should be noted that although R_2 and R_3 models have the same dipole moment their quadrupole moments show noticeable differences, *i.e.* the cartesian components of the molecular quadrupole tensor Q_{xx}, Q_{yy} and Q_{zz} [24] are 2.026, -1.887 and -0.138 respectively (in units of 10^{-26} esu cm^2) for R_2 and 2.226, -1.950 and -0.316 for R_3. It was suggested that quadrupole moments are important parameters for characterization of water models [24]. Our results for R_2 and R_3 (Tables 3 and 4) show that diffusion coefficients are higher for R_2 whereas residence times and reorientational times are higher for R_3. So, in general, mobility diminishes as the molecular quadrupole moment of water increases.

The spectral densities $\hat{S}(\omega)$ associated to the motions of ions and water molecules in the hydration shells were calculated by Fourier transforming the corresponding $C(t)$ functions. According to the $C(t)$ results, the $\hat{S}(\omega)$ spectra for different water models are very similar. In the case of the hydrogen atoms of the F model the high frequency bending and stretching intramolecular vibrational modes can also be

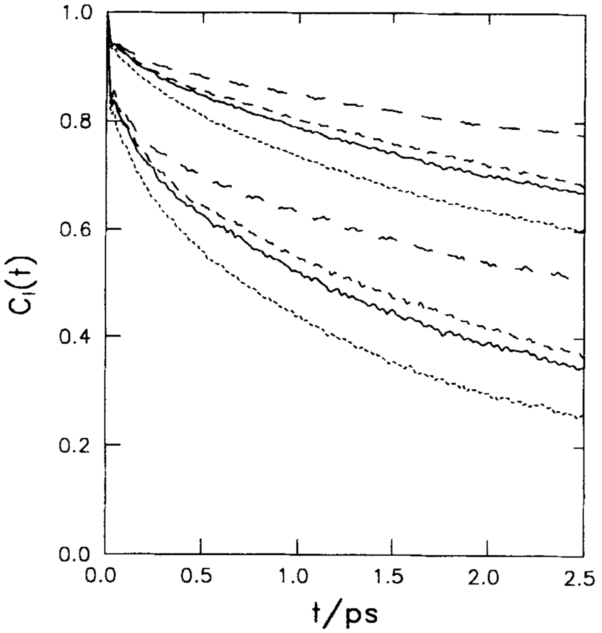

Figure 3 Reorientational time correlation functions ($C_1(t)$, upper; $C_2(t)$, lower) of the dipole moments ($\vec{u}_1$) of water molecules in the first hydration shell of Cl^{2-} for different water models ——— F; ------ R1; ----- R2; — — — R3.

analyzed. Figures 4, 5 and 6 display the results obtained from the flexible water simulations.

$\hat{S}(\omega)$ functions corresponding to the ionic motions (Figure 4) show two peaks indicating the existence of two predominant frequencies. The Cl^- and Cl^{2-} peaks at lower frequencies are, approximately, at the same positions as the maxima of $\hat{S}(\omega)$

Table 4 Reorientational Times (in ps).

		$\vec{u}_1$		$\vec{u}_2$		$\vec{u}_3$		$\vec{u}_4$	
Model	*Ion*	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2
F	Cl^-	5.3	2.4	5.8	3.7	3.3	2.0	16.5	5.6
	Cl^{2-}	8.6	3.4	8.6	3.8	4.0	3.3	49.1	17.1
R1	Cl^-	4.8	2.1	5.4	3.1	3.1	1.9	15.3	5.1
	Cl^{2-}	6.8	2.6	7.2	3.2	3.0	2.8	34.7	11.9
R2	Cl^-	7.2	3.1	9.3	4.9	5.0	2.5	19.4	6.9
	Cl^-	9.2	3.6	9.7	4.4	4.7	3.6	49.9	17.3
R3	Cl^-	8.6	3.8	15.9	8.4	6.6	3.3	20.8	7.4
	Cl^{2-}	15.8	6.5	18.8	8.3	9.0	5.6	85.4	29.1

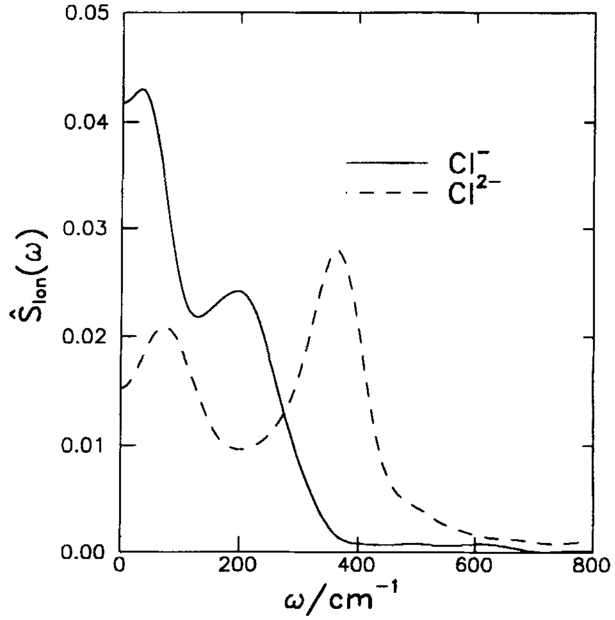

Figure 4 Power spectra of the ion velocity autocorrelation functions.

for the oxygens in the corresponding hydration shells (Figure 5). The existence of low frequency $\hat{S}(\omega)$ maxima is characteristic of dense liquids (around $\omega = 50\ \mathrm{cm}^{-1}$ for pure water) and in this case may be associated with the oscillatory motions of the ion-water complexes in the liquid. The second peak of $\hat{S}(\omega)$ for ions should be attributed to the oscillatory motions of ions inside the hydration shells. The higher peak obtained for Cl^{2-} reflects the prevalence of these oscillations for the double charged anion. Consistently with the greater strength of the Cl^{2-}- water interactions the frequencies of these motions are bigger for Cl^{2-} than for Cl^-.

One of the characteristic trends of $\hat{S}(\omega)$ of oxygen in pure water is the presence of a shoulder around $\omega = 200\ \mathrm{cm}^{-1}$ that is associated with the existence of hydrogen bonds [25]. Although somewhat narrower and shifted toward lower frequencies than for pure water, this shoulder is also shown by $\hat{S}(\omega)$ of oxygen in the Cl^- shell. However, in the case of Cl^{2-} the shoulder has practically disappeared (Figure 5). This suggests that the number of hydrogen bonds between water molecules in the Cl^{2-} hydration shell and neighbouring molecules outside the shell in rather small and the tetrahedral structure characteristic of liquid water is greatly reduced. A similar conclusion was obtained from the analysis of the spectral density for water molecules in the hydration shell of the Ca^{2+} cation [16].

Results in Figure 6 show that the influence of Cl^- and Cl^{2-} ions on the hydrogen $\hat{S}(\omega)$ bands is somewhat different. The librational ($\cong 500\ \mathrm{cm}^{-1}$) and bending ($\cong 1900\ \mathrm{cm}^{-1}$) bands of the Cl^- hydration shell are similar to those of pure water [26] but slightly shifted towards lower frequencies while for water molecules in the Cl^{2-} hydration shell we can observe a shift in the opposite direction. The stretching

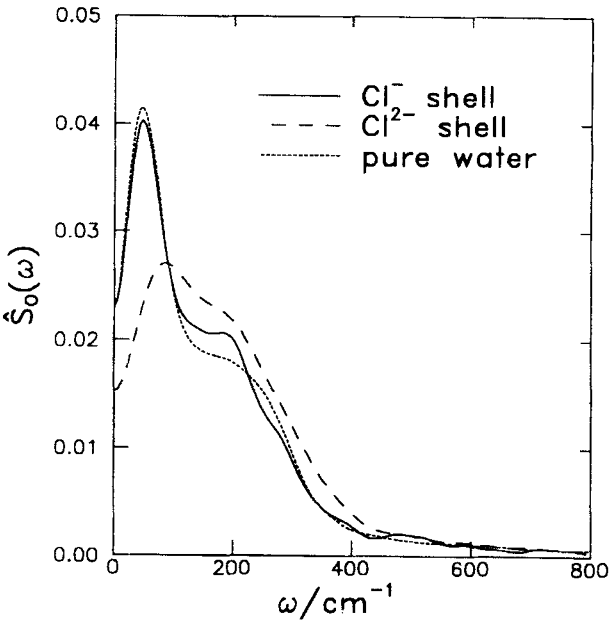

Figure 5 Power spectra of the oxygen velocity autocorrelation functions. Pure water results from Ref. 25.

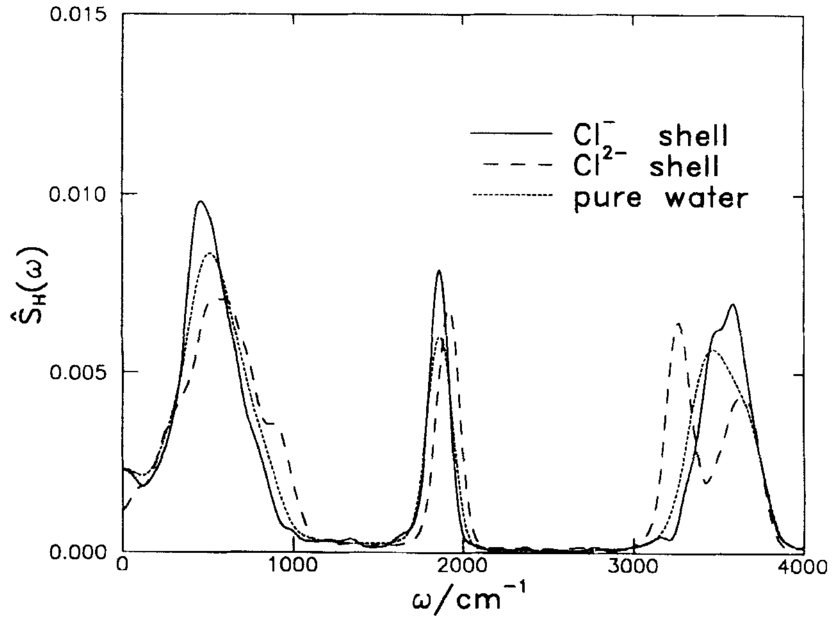

Figure 6 Power spectra of the hydrogen velocity autocorrelation functions from flexible water simulations. Pure water results from Ref. 26.

band ($\cong$ 3500 cm^{-1}) is the most influenced by ions. Two separated peaks which could be associated to the symmetric and asymmetric stretching modes appear in $\hat{S}(\omega)$ for the Cl^{2-} hydration shell. The separation is not so clear in the case of Cl^-. As compared with pure water, the stretching bands for water close to the two ions are shifted in opposite directions.

5 CONCLUSIONS

The results of this work show that the structure of ionic hydration shells is little influenced by flexibility of water molecules as well as by small changes in the molecular dipole moment and charge distribution. Dynamic properties are more sensitive to changes in water molecular models. D coefficients tend to increase with flexibility and when μ diminishes. In general, when the stability of the ion-water complexes (large τ) is greater, the diffusivity is smaller whereas reorientational times are bigger.

When Cl^- is replaced with Cl^{2-} both coordination number and stability of hydration shells increase significantly. As a consequence of the formation of larger and more stable ion-water complexes both diffusion of ions and water molecules in the hydration shell and reorientational motions of water molecules become slower. Oxygen spectral densities indicate that the hydrogen bonded network characteristic of pure water is largely destroyed around divalent anions. Moreover the intramolecular motions of water molecules are markedly influenced by neighboring double charged anions as is revealed by the existence of two separated peaks on the stretching band of the hydrogen power spectra of molecules in the Cl^{2-} hydration shell.

Acknowledgement

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