

# Molecular Dynamics Simulation of Single Ions in Aqueous Solutions: Effects of the Flexibility of the Water Molecules

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We performed molecular dynamics simulations of single  $\text{Na}^+$  and  $\text{F}^-$  ions in aqueous solutions. Two single point charge water models with and without internal degrees of freedom were considered. Structural (radial distribution functions, orientation angles), dynamical (translational, vibrational, and reorientational motions), and other microscopic properties (hydration numbers, residence times) of ions and water molecules of their hydration shell were calculated. Our results are compared both with experimental data and with other simulation results using different interaction models. The influence of the flexibility of water molecules on the different properties is carefully discussed.

## 1. Introduction

Over the past few years many works have been devoted to connecting realistic microscopic models with measurable properties in liquids and liquid solutions. To achieve this the assumption of suitable solute–solute, solute–solvent, and solvent–solvent interaction potentials is required. In the case of polyatomic systems the geometry and constraints of the molecules must also be modeled. Molecular dynamics (MD) simulation is one of the most useful tools for establishing this relationship, especially for the study of dynamical properties together with structural ones.<sup>1</sup>

In the majority of MD simulations with polyatomic molecules completely rigid molecular models were assumed. One of the reasons for the common use of such unrealistic models is the saving in computational time. The high frequencies corresponding to the vibrational motions of atoms oblige us to use smaller time steps than the ones required when only the atomic translations are considered. Moreover, the determination of reliable intramolecular potentials is not easy and, because of the quantum mechanical nature of the internal vibrations, one may call into question their inclusion in MD simulations which are based on the numerical solution of the classical equations of motion. Despite this, it seems logical that reasonable molecular models allowing internal motions may be closer to the real systems than completely rigid models.

On the other hand, the understanding of the properties of electrolyte solutions in terms of their characteristics at the molecular level requires as much information as possible concerning the structure and motions of ions and water molecules of the hydration shells. In the literature there are several works where this kind of information is extracted from MD simulations of aqueous electrolyte solutions<sup>2,3</sup> and single ions in water.<sup>4–10</sup> However, the results given in these works show clear disagreements as a consequence of the differences among the assumed interaction potential models which were built using various hypotheses and in accordance with different procedures. Furthermore, rigid or flexible water models with different charge distributions may be

considered. The knowledge of the influence of some of the characteristics of an assumed microscopic model on the resulting properties can be very useful for both understanding the relationship between molecular and macroscopic behavior and modeling the interaction potentials. (It should be pointed out that the disagreements between the simulation results and the more recent experimental data are still important<sup>11</sup> and there does not exist any potential model that is able to reproduce completely the properties of water and ionic aqueous solutions.) This kind of information may be easily obtained from computer simulations by comparing the results of two computer experiments under identical conditions but with models differing only in the characteristics whose effects we are interested in.

Several studies on the effects of internal motions on the structural and transport properties of pure water have been performed.<sup>12–16</sup> In this work, we analyze the influence of the flexibility of the water model on the behavior of both the ions and the water molecules of the hydration shell. For each ion we performed two MD simulations that differed only in the constraints of the water molecules. Very similar ions, differing only in the sign of the charge, were chosen to eliminate the influence of both the ionic size and the strength of the Coulomb forces whose effects will be analyzed in a subsequent work.

Details concerning the interaction potentials and computer simulations are given in section 2. Sections 3 and 4 are devoted to the equilibrium properties, i.e., the ion–water radial distribution functions and the orientation of the water molecules of the hydration shell, respectively. The translational motions of ions and hydration shell water molecules are analyzed in section 5. Vibrational modes of water are also studied in section 5. The reorientational motions of water hydration molecules are considered in section 6. The results for hydration numbers and residence times of water around ions are discussed in section 7. Finally, the main conclusions of this work are summarized in section 8.

## 2. Computational Details

Molecular dynamics simulations were carried out on a system of one ion ( $\text{Na}^+$  or  $\text{F}^-$ ) and 125 water molecules with periodic boundary conditions. The length of one side of the cube (15.5 Å) was evaluated in order to have a solvent density of 1 g/cm<sup>3</sup>. The temperature of the system was kept at 298 K.

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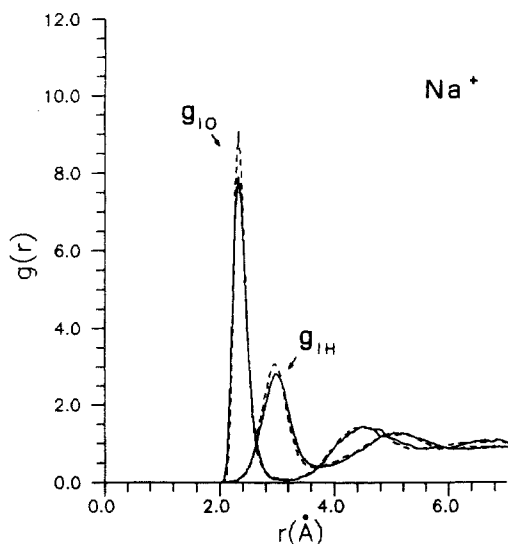


Figure 1. Ion-oxygen and ion-hydrogen radial distribution functions for  $\text{Na}^+$  ion. —, flexible water; ---, rigid water.

For each ion, we performed two simulations differing only in whether or not water internal degrees of freedom were included. In the rigid water (R) simulations we used the single point charge (SPC) model of Berendsen et al.<sup>17</sup> This is a pairwise additive site-site potential with the interaction sites positioned at the oxygen and hydrogen nuclear coordinates. For the flexible water (F) simulations we assumed the model proposed by Toukan and Rahman,<sup>18</sup> which is called the flexible SPC model because it adopts the same form as SPC for the intermolecular interactions but it allows the flexibility of molecules. Our choice of these two models was dictated in part by their wide use but, more importantly, with regard to this work, also by the fact that they are identical apart from the inclusion of internal motions.

The ion-water potentials we used consist of a Coulomb term and a short-range term. For the Coulombic interaction we took  $q_{\text{ion}} = +1e$  ( $\text{Na}^+$ ) and  $-1e$  ( $\text{F}^-$ ) and the oxygen and hydrogen charges corresponding to the SPC model. The requirement that the ion perceives the same charge distribution on a water molecule that the other molecules see on each other is necessary so as to obtain an asymptotically correct behavior of the correlation functions.<sup>19</sup> The short-range terms we used were Lennard-Jones (12-6) potentials with the parameters derived by Pettitt and Rossky<sup>9</sup> from ab initio calculations with the assumption of a charge distribution that was quite similar to the SPC model.

To carry out the simulations, we used a leapfrog Verlet integration algorithm.<sup>20</sup> A spherical molecular based cutoff with a radius equal to 7.5 Å was used for evaluating all interactions. R simulations were performed with a time step of 2 fs, and the SHAKE procedure<sup>21</sup> was employed to keep the interatomic distances fixed. In the F simulations we used a time step of 0.5 fs and the multiple time step technique proposed by Teleman and Jönsson<sup>22</sup> with  $n_{\text{slow}} = 4$ . Each run consisted of an initial equilibration period of 15 ps and a production period of 60 ps. Auxiliary simulations of pure water (R and F) under identical conditions were also carried out in order to analyze the influence of the ions on the water molecules of their hydration shells.

### 3. Ion-Water Structure

The results for the ion-oxygen and ion-hydrogen radial distribution functions ( $g_{\text{IW}}(r) = g_{\text{IO}}(r), g_{\text{IH}}(r)$ ) are shown in Figures 1 and 2. The placement of the peaks is not affected by the water

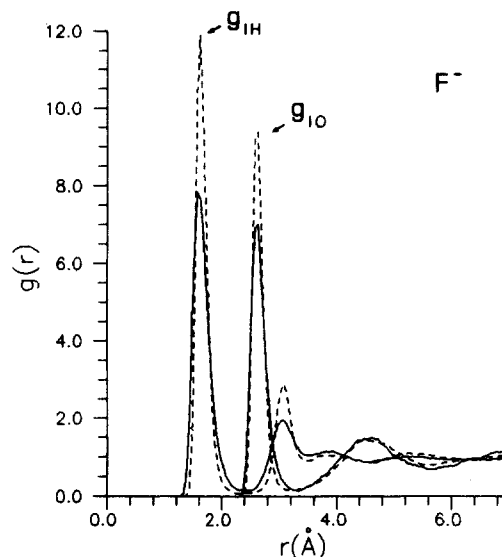


Figure 2. Same as Figure 1, except for  $\text{F}^-$  ion.

TABLE I: Ionic Solvation Structure<sup>a</sup>

	$\text{Na}^+$			$\text{F}^-$		
	this work			this work		
	F	R	ref 9	F	R	ref 9
$R_{\text{IO}}$	2.325	2.325	2.30	2.62	2.62	2.75
$g(R_{\text{IO}})$	7.9	9.1	6.1	7.0	9.4	
$R_{\text{IH}}$	2.975	2.975	3.05	1.58	1.62	1.35
$g(R_{\text{IH}})$	2.8	3.1	1.8	7.9	11.9	
$\text{cn}_{\text{IO}}$	5.8	5.8	4.28	6.7	6.6	7.00
$\text{cn}_{\text{IH}}$	13.6	13.4	13.9	6.6	6.5	

<sup>a</sup>  $R_{\text{IO}}$  and  $R_{\text{IH}}$  are the positions of the  $g(r)$  first maxima in Å.

internal atomic motions, but the spread of atoms around their average positions leads to  $g_{\text{IW}}^{\text{F}}(r)$  values which are less structured than  $g_{\text{IW}}^{\text{R}}(r)$  values. This result is in agreement with the ones obtained from MD simulations of pure water comparing rigid and flexible models<sup>15,16</sup> (the anomalous increase of the water structure with the introduction of internal vibrations observed by Reimers and Watts<sup>12</sup> is probably due to defects in the potential<sup>16</sup>). The changes induced in the height of the  $g_{\text{IW}}(r)$  maxima by the flexibility of water are so important they they could hardly be reproduced by use of perturbation approaches.<sup>13,16</sup> The biggest differences between  $g_{\text{IW}}^{\text{F}}(r)$  and  $g_{\text{IW}}^{\text{R}}(r)$  for  $\text{F}^-$  show that the H-bridge bond of the anions with the water molecules of their hydration shell is less rigid than the bond of cations through heavier oxygen atoms.

We also calculated the running coordination numbers

$$n_{\text{IW}}(r) = 4\pi\rho_{\text{W}} \int_0^r g_{\text{IW}}(r') r'^2 dr' \quad (1)$$

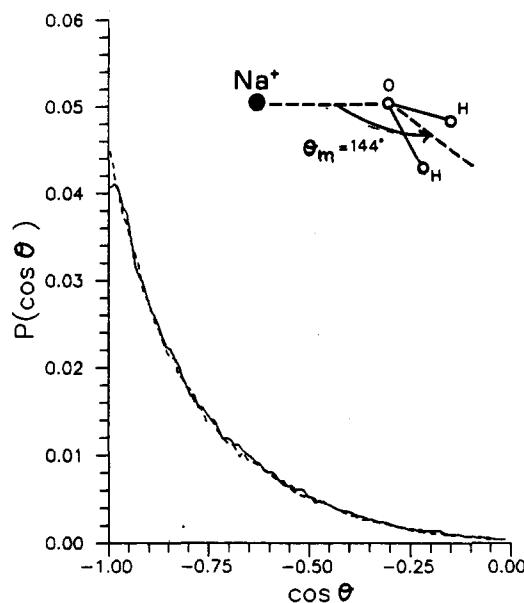
where  $\rho_{\text{W}}$  is the number density of W (oxygen or hydrogen) atoms. The coordination number ( $\text{cn}_{\text{IW}}$ ) is defined as the plateau value of  $n_{\text{IW}}(r)$  at distances close to the first  $g_{\text{IW}}(r)$  minimum. It should be noted that despite the discrepancies between  $g_{\text{IW}}^{\text{F}}(r)$  and  $g_{\text{IW}}^{\text{R}}(r)$  we did not find any significant difference between the  $n_{\text{IW}}$  values for R and F models (see Table I). Therefore, the changes in the height of the first  $g_{\text{IW}}(r)$  peaks due to the flexibility of water may be simply attributed to vibrational smearing.

For  $\text{F}^-$  the number of hydrogens contributing to the first  $g_{\text{FH}}(r)$  peaks is the same as the number of oxygens ( $\text{cn}_{\text{FH}} \approx \text{cn}_{\text{FO}}$ ) because, as will be shown in the next section, the H bond for  $\text{F}^-$  is linear<sup>7</sup> and only one of the hydrogens of the water molecules in the first hydration shell contributes to  $\text{cn}_{\text{FH}}$  (the other one corresponds to the second  $g_{\text{FH}}(r)$  maxima). For  $\text{Na}^+$  both hydrogens are at similar distances from the ion and we do not observe two  $g_{\text{NaH}}$  peaks in the first hydration shell. So, it should be expected that  $\text{cn}_{\text{NaH}} = 2\text{cn}_{\text{NaO}}$ . The bigger  $\text{cn}_{\text{NaH}}$  values calculated in this work show that hydrogens of the water molecules of the second

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TABLE II: Geometry of Water Molecules<sup>a</sup>

	bond length, Å	bond angle, deg
pure water	1.018 (1.016)	105.7 (104.9)
Na <sup>+</sup> shell	1.018	105.7
F <sup>-</sup> shell	1.019	105.6
R model	1	109.5

<sup>a</sup>Quantities in parentheses were obtained by Teleman et al.<sup>16</sup>Figure 3. Probability distribution of  $\cos \theta$  for water molecules in the first hydration shell of Na<sup>+</sup> ion. —, flexible water; ---, rigid water.

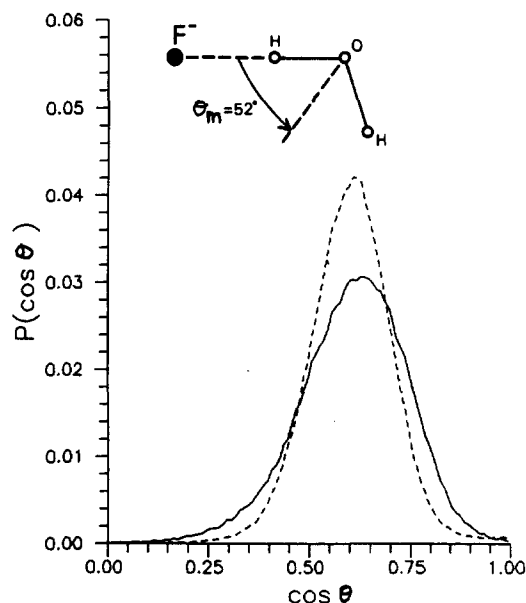
shell also contribute to the first  $g_{\text{NaH}}(r)$  maxima. Similar relations between  $cn_{\text{IO}}$  and  $cn_{\text{IH}}$  were obtained from theoretical<sup>9</sup> and Monte Carlo<sup>7</sup> methods.

Table I summarizes our coordination numbers and first  $g_{\text{IW}}(r)$  maxima (placement and height) together with the ones found by Pettitt and Rossky<sup>9</sup> for the same systems using the extended RISM integral equation formalism and a rigid model for water. For Na<sup>+</sup> the positions of the peaks are in agreement but our  $g_{\text{NaW}}$  maxima are bigger even for the F model. For F<sup>-</sup> there are also discrepancies in the placement of the peaks. Our coordination numbers are close to the expected value  $cn_{\text{IW}} = 6$  whereas Pettitt and Rossky found  $cn_{\text{IW}}$  values with larger differences with regard to the octahedral arrangement. In general, our results are more similar to the ones obtained from other computer simulations with different interaction models.<sup>2,4-7</sup> The ion-water potential used by Pettitt and Rossky is the same one that is employed in this work, but they used a rigid transferable intermolecular potentials (TIPS) model<sup>9,23</sup> including a short-range O-H repulsion for the water-water interactions. However, the TIPS potential does not differ significantly from that from the SPC model. So, we think that the disagreements cannot be justified by the differences in the water models, but they are probably due to the approximations involved in the RISM theory.

#### 4. Geometry and Orientation of the Water Molecules

As in the work of Teleman et al.<sup>16</sup> the average geometry of the water molecules for the F model show small differences in relation to the rigid model. The mean bond length increases and the mean bond angle decreases when the intramolecular motions are incorporated (Table II). However, unlike the results obtained by Heinzinger<sup>24</sup> for MgCl<sub>2</sub> aqueous solutions using the central force (CF) water model, we did not observe any significant influence of the ions on the geometry of the hydration water molecules.

For the study of the orientation of the water molecules in the ionic hydration shells, we considered the angle between the dipole

Figure 4. Same as Figure 3, except for F<sup>-</sup> ion.TABLE III: Orientation of Water Molecules<sup>a</sup>

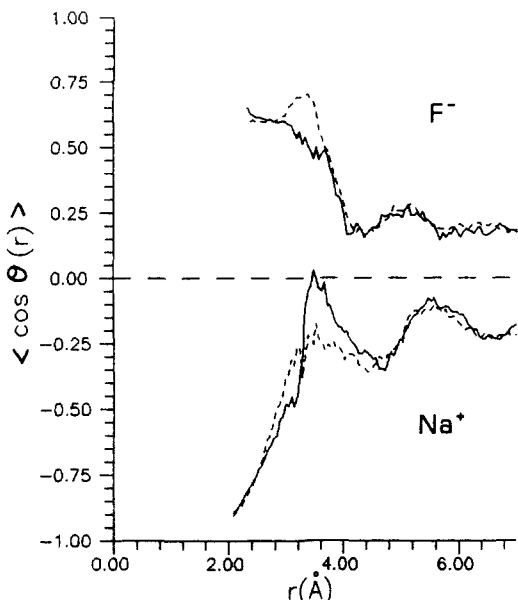
		$\theta$ mean values, deg	
		Na <sup>3</sup>	F <sup>-</sup>
this work	F	144	52.5
	R	145	51.5
this work (from $g(r)$ )	F	147	52.8
	R	156	54.8
other simulations	A	160	
	B	132	52.5
	C	139	

<sup>a</sup> A, from  $g(r)$  with the MCY potential;<sup>6</sup> B,  $\theta_m = \cos^{-1}(\cos \theta)$  with the ST2 potential;<sup>2,26</sup> C, the same as B with the CF potential.<sup>2</sup>

vector of the water molecules and the ion-oxygen position vector (see Figures 3 and 4). Usually this kind of information is deduced from the positions of the maxima of  $g(r)$  functions arising from diffraction experiments or computer simulations. However, large uncertainties should be attributed to the results using this method<sup>25</sup> since the orientation angles are very sensitive to small changes of both the  $g(r)$  placements and the geometrical parameters of the water model. Computer simulations allowed us to obtain more reliable information from the atomic positions. The mean values of  $\theta$  ( $\theta_m$ ) obtained from both methods are summarized in Table III. The discordant value of  $\theta_m$  for Na<sup>+</sup> calculated from  $g(r)$  is just an example of the sensitivity of this procedure. In this case the discrepancy between the results for R and F models is only due to the small differences between the bond length and angles (Table II) since the placements of  $g(r)$  maxima are the same.

In accordance with other results for cations,<sup>2,5,6</sup> our  $\theta_m$  values show a trigonal orientation of water in the Na<sup>+</sup> hydration shell. Nevertheless, small discrepancies with numerical  $\theta_m$  values given in other papers may be observed in Table III. Although these disagreements may be attributed to differences in the interaction models, we do not think that this is the main reason. The  $\theta$  value of Impey et al.<sup>6</sup> has a wide range of uncertainty because it was calculated from  $g(r)$ . With regard to the result of Heinzinger,<sup>24</sup> despite using the data directly obtained during the simulations, they do not report the  $\theta_m$  value, and the data included in Table III were obtained from  $\langle \cos \theta \rangle$ . For the anions, linear hydrogen bonds were observed from neutron diffraction experiments<sup>27</sup> and computer simulations with different potential models.<sup>2,5,7,26</sup> We obtained for F<sup>-</sup>  $\theta_m$  values in very good agreement with these results

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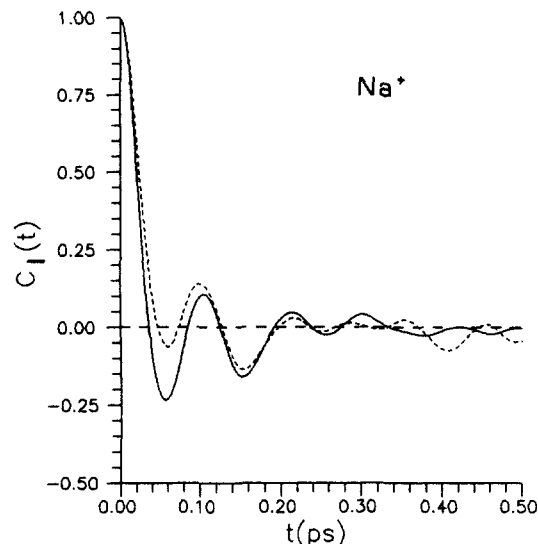
**Figure 5.** Mean value of  $\cos \theta$  as a function of the ion-oxygen distance. —, flexible water; ---, rigid water.

but in clear disagreement with the symmetrical arrangement predicted from NMR experimental data.<sup>28,29</sup>

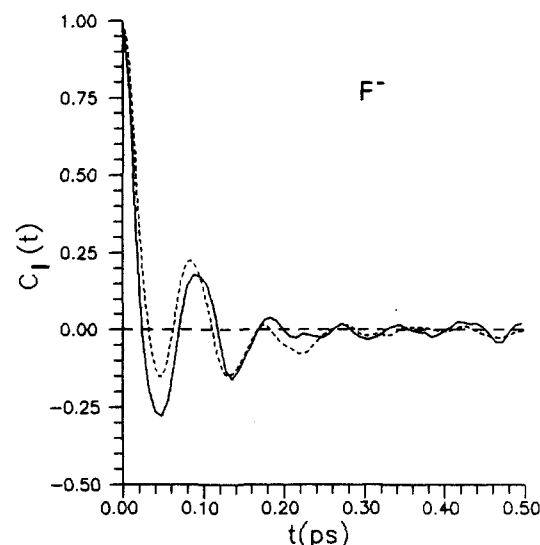
Heinzinger<sup>2,24</sup> observed that  $\cos \theta$  probability distributions ( $P(\cos \theta)$ ) depend on the assumed potential. This dependence was especially noticeable for  $\text{Na}^+$ . Our  $P(\cos \theta)$  distribution for  $\text{Na}^+$  (Figure 3) resembles the one reported by Heinzinger for the CF potential model while it disagrees with the one for the ST2 model. This is reasonable because the arrangement of the negative charges in the ST2 model is very different from the ones in the CF and SPC models. Nevertheless, our  $P(\cos \theta)$  distribution for  $\text{F}^-$  is in good agreement with the one resulting from the ST2 model. This is a consequence of the similarity between the distribution of positive charges in the ST2 and SPC molecules together with the prevailing influence of the positive charges in the formation of the anion-water complexes.

The average value of  $\cos \theta$  as a function of the distance of the ion to the oxygen atom ( $\langle \cos \theta(r) \rangle$ ) was also determined. The resulting curves are represented in Figure 5, and they show that the influence of the ion on the orientation of water molecules is of little importance beyond the first shell. In the case of  $\text{Na}^+$  the orientation also changes with the distance over the range of the first  $g(r)$  peak. The dipole moments of water molecules that are closest to the  $\text{Na}^+$  ion are completely oriented ( $\theta = 180^\circ$ ), and when the distance increased the orientation diminishes. This is consistent with the wide range of values shown by  $P(\cos \theta)$ . On the other hand,  $\langle \cos \theta(r) \rangle$  is nearly constant in the  $\text{F}^-$  first shell. This means that all water molecules in the first shell have similar orientations and, consequently,  $P(\cos \theta)$  is less spread out. Our results for  $\langle \cos \theta(r) \rangle$  are in general agreement with the ones obtained from molecular dynamics simulation of electrolyte solutions.<sup>2,24,26</sup> However, we did not find any change of sign of  $\langle \cos \theta(r) \rangle$  for long distances as observed in these works. This change of sign may be due to the interactions with other neighboring ions<sup>26</sup> that do not exist in our dilute solutions.

The influence of the internal degrees of freedom on the orientation of water molecules is, in general, rather small (Figures 3–5). The probability distributions  $P(\cos \theta)$  with R and F models for  $\text{Na}^+$  are identical although little discrepancies may be observed for  $\text{F}^-$ . This is consistent with the smaller rigidity of the H-bridge bond for anions already noticed in the previous section. The small disagreements among F and R results for  $\langle \cos \theta(r) \rangle$  are of little significance, and they are not very reliable because they correspond to distances for which  $g(r)$  functions show their first minima.



**Figure 6.**  $\text{Na}^+$  velocity autocorrelation functions. —, flexible water; ---, rigid water.



**Figure 7.** Same as Figure 6, except for  $\text{F}^-$  ion.

Therefore, these  $\cos \theta$  values are less averaged than the remaining ones.

## 5. Translational Motions

The microscopic dynamical behavior of ions was investigated by means of their velocity autocorrelation functions  $C_1(t)$  and self-diffusion coefficients  $D_1$ . As we can see in Figures 6 and 7, the  $C_1(t)$  curves show the same oscillatory shape already observed in other simulations.<sup>6,8,10</sup> The placement of our  $C_1(t)$  minima for  $\text{Na}^+$  are very close to the ones obtained by Wilson et al.<sup>8</sup> and Berkowitz and Wan<sup>10</sup> with the MCY and TIP4P potentials, respectively. The  $C_1(t)$  functions reported by Impey et al.<sup>6</sup> corresponding to a simulation with the same interaction model as the one used by Wilson et al. show minima that are shifted toward higher values of time. This difference may be attributed to two factors, i.e., the lower temperature and (or) the use of the Ewald's method for the evaluation of the electrostatic interactions in the work of Impey et al. Similar displacements of the  $C_1(t)$  minima can be seen if the results of Impey et al. for  $\text{F}^-$  are compared with ours.

The biggest differences among the  $C_1(t)$  functions from different potential models and simulations are shown by the depth of their first minima. For example, we may observe a noticeable increase in these minima when the flexible model for water is considered. This enlargement of the cage effects on the ions suggests that the intramolecular atomic motions in water molecules allow the

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TABLE IV: Self-Diffusion Coefficients,  $D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$ 

		F model	R model	other <sup>6,16</sup>	exptl <sup>30</sup>
ions ( $D_i$ )	Na <sup>+</sup>	0.9	1.5	1.0 <sup>a</sup>	1.33
	F <sup>-</sup>	0.6	1.7	0.9 <sup>a</sup>	1.47
water ( $D_O$ )	Na <sup>+</sup> shell	1.5	2.7		
	F <sup>-</sup> shell	0.8	2.5		
	pure water	4.6	3.7	6.1 <sup>b</sup> /4.4 <sup>c</sup>	2.31

<sup>a</sup> Data of ref 6 correspond to other temperatures (282 K for Na<sup>+</sup> and 278 K for F<sup>-</sup>). <sup>b</sup> Corresponds to the F model. <sup>c</sup> Corresponds to the R model.<sup>16</sup>

formation of more stable hydrate complexes.

The self-diffusion  $D$  coefficients are ordinarily calculated by integration of the velocity autocorrelation functions or from the long-time slope of the mean square displacements ( $r^2(t)$ ). The oscillatory behavior of  $C_i(t)$  functions involves serious problems for the determination of the  $D_i$  coefficients, and we calculated them from  $r^2(t)$ . Our  $D_i$  values, which are listed in Table IV, showed uncertainties of  $\pm 0.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . As expected from the  $C_i(t)$  results, the  $D_i$  coefficients are smaller when internal degrees of freedom of water are included.

Wilson et al.<sup>8</sup> and Berkowitz and Wan<sup>10</sup> calculated  $D_i$  for Na<sup>+</sup> from the  $C_i(t)$  functions and obtained values that are too small, i.e.,  $0.4 \times 10^{-5}$  and  $0.67 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , respectively. Our results with the R model are close to the experimental data<sup>30</sup> whereas bigger discrepancies are shown by the  $D_i$  values obtained by using other potentials (Table IV). Nevertheless, we do not think that the comparison of  $D_i$  values resulting from simulations and experiments would be an advisable way for testing the reliability of the interaction potentials because a great part of the microscopic information is removed by the averaged procedure involved in the determination of macroscopic properties such as the  $D$  coefficients. Moreover, there are many difficulties for the determination of sufficiently accurate  $D_i$  data from both computer and laboratory experiments.

To obtain information on the water translational motions, we calculated the  $C_O(t)$  functions and the  $D_O$  coefficients (from  $r_O^2(t)$ ) for the oxygen atoms. For the water molecules close to the ions the first  $C_O(t)$  minima are deeper and the self-diffusion coefficients (Table IV) smaller than the ones corresponding to pure water. This behavior was also observed in other simulations,<sup>2</sup> and it is due to the formation of long-lived ion-water complexes. In such cases it is usually assumed<sup>29</sup> that  $D_i = D_O$ . This relationship is only qualitatively fulfilled by our  $D$  values despite the fact that the residence times of water in the hydration shells (defined in section 7) are notoriously larger than the  $C_O(t)$  and  $C_i(t)$  relaxation times, which are lower than 0.5 ps. On the other hand, the  $D_O$  coefficients for pure water are greater for the F model than for the R model. This result is in qualitative agreement (Table IV) with the one obtained by Teleman et al.,<sup>16</sup> and it indicates that, in general, the flexibility of molecular models speeds up the dynamics of molecules. Thus, the geometrical distortions of water molecules facilitate their hindered translational motions. Nevertheless, in the case of ions the higher stability of complexes involves slower diffusional motions for both the ions and water molecules in the hydration shells when the internal atomic motions are considered.

Figure 8 shows the  $C_H(t)$  function of hydrogen atoms for the water molecules of the F<sup>-</sup> hydration shell. As was expected, the intramolecular motions generate high-frequency oscillations in the  $C_H(t)$  curve. In order to improve the characterization of the atomic motions, the power spectra  $f(\omega)$  of the  $C(t)$  functions are usually calculated:<sup>18</sup>

$$f(\omega) = \int_0^\infty C(t) \cos \omega t \, dt \quad (2)$$

Figure 9 shows the  $f_H(\omega)$  results for pure water and water in the F<sup>-</sup> shell obtained with the F model. There are three bands

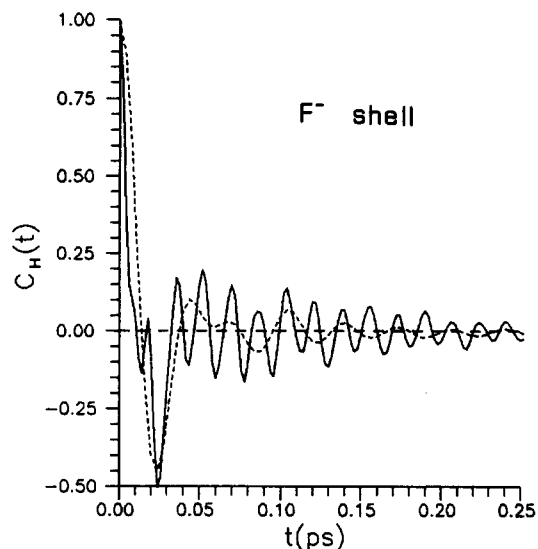


Figure 8. Hydrogen velocity autocorrelation functions for the hydration shell of F<sup>-</sup>. —, flexible water; ---, rigid water.

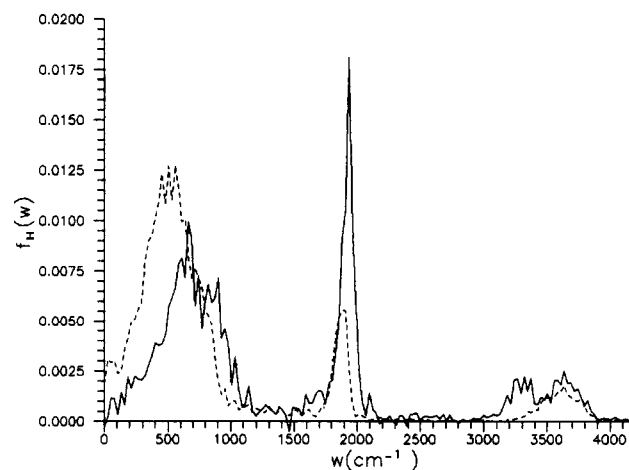


Figure 9. Power spectra of hydrogen velocity autocorrelation functions from flexible water simulations. —, hydration shell of F<sup>-</sup>; ---, pure water.

that correspond to the librational motions of water molecules ( $\approx 500 \text{ cm}^{-1}$ ), the HOH bending mode ( $\approx 1900 \text{ cm}^{-1}$ ), and the OH stretching modes ( $\approx 3500 \text{ cm}^{-1}$ ). The presence of F<sup>-</sup> ion shifts the librational and bending bands toward higher values of frequencies while the stretching band is shifted toward lower frequencies. The same qualitative effect was observed in other simulations<sup>2,3</sup> for Ca<sup>2+</sup> hydration water. We may also observe in Figure 9 that the bending vibrations are noticeably increased and the stretch band is broken up into symmetric and asymmetric modes due to the influence of the F<sup>-</sup> anion. On the other hand, the  $f_H(\omega)$  function for Na<sup>+</sup> hydration water is close to the one for pure water. When the R model is used, only frequencies corresponding to the librational motions are allowed and no significant differences between the  $f_H(\omega)$  librational bands for R and F models were observed.

The  $f_O(\omega)$  functions (Figure 10) show a peak that may be attributed to the O—O—O bending.<sup>3</sup> For the R model, no important changes induced by the ions have been detected in  $f_O(\omega)$  for F<sup>-</sup>, but a broader maximum slightly shifted toward the higher frequencies appears when the F model is used. Moreover, a peak around  $1900 \text{ cm}^{-1}$  may be observed in this case. The comparison between the  $f_O(\omega)$  functions for Na<sup>+</sup> hydration water and pure water shows the same qualitative features, although less marked, than the ones for F<sup>-</sup>.

## 6. Reorientational Motions

The complete description of the dynamical properties of molecular liquids requires the consideration of the reorientational

(30) Hertz, H. G. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 3, Chapter 7.

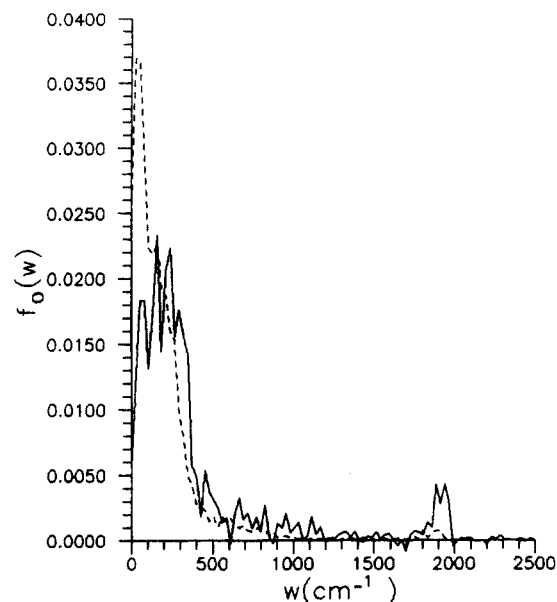


Figure 10. Same as Figure 9, except for oxygen velocity autocorrelation functions.

TABLE V: Water Reorientational Correlation Times (in ps)

unit vectors	<i>l</i>	pure water		Na <sup>+</sup> shell		F <sup>-</sup> shell	
		F	R	F	R	F	R
$\vec{u}_1$	1	2.2	3.2	12.1	8.9	6.0	4.8
	2	1.1	1.3	3.0	2.4	2.5	1.8
$\vec{u}_2$	1	1.8	3.0	2.6	3.4	9.2	7.1
	2	1.2	1.6	2.1	2.2	4.8	2.5
$\vec{u}_3$	1	1.2	2.2	2.1	2.8	3.8	3.2
	2	0.7	1.0	1.5	1.6	2.5	1.8
$\vec{u}_4$	1			19.3	15.1	24.0	13.0
	2			7.2	5.2	8.4	4.4

motions in addition to the translational and vibrational ones. This kind of information is usually given through a set of reorientational time-correlation functions defined as<sup>31</sup>

$$C_l(t) = \langle P_l(\vec{u}_l(t) \cdot \vec{u}_l(0)) \rangle \quad (3)$$

where  $P_l$  is the  $l$ th Legendre polynomial and  $\vec{u}_l$  is a unit vector that characterizes the orientation of the molecule. These  $C_l(t)$  functions may not only be calculated from molecular dynamics simulations,<sup>32,33</sup> but they are also related to the results of spectroscopic experiments,<sup>34,35</sup> and they can be used to compare the predictions for different theoretical approximations.<sup>31,36</sup>

We considered three different unit vectors in the water molecules of the hydration shells, i.e.,  $\vec{u}_1$  in the direction of the dipole vector,  $\vec{u}_2$  in the intramolecular proton-proton direction, and  $\vec{u}_3 = \vec{u}_1 \times \vec{u}_2$  orthogonal to the plane of the water molecule. For the study of the orientation of the hydrate complexes, we also considered the unit vector  $\vec{u}_4$  along the ion-oxygen direction. The reorientational times were calculated by assuming an exponential decay of  $C_l(t)$  functions at long times (as is shown in Figures 11 and 12, except for  $\vec{u}_4$  the initial  $C_l(t)$  decay differs notoriously from an exponential as a consequence of the librational motions of the molecule)

$$C_l(t) \simeq \exp(-t/\tau_l) \quad (4)$$

(31) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*, 2nd ed.; Academic Press: London, 1986; Chapter 12.

(32) Impey, R. W.; Madden, P. A.; McDonald, I. R. *Mol. Phys.* **1982**, *46*, 513.

(33) Szász, G. I.; Heizinger, K. *J. Chem. Phys.* **1983**, *79*, 3467.

(34) Tildesley, D. J. In *Molecular Liquids: Dynamics and Interactions*; Barnes, et al., Eds.; Reidel: Dordrecht, 1984.

(35) Pottel, R. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 3, Chapter 8.

(36) Lynden-Bell, R. M. In *Molecular Liquids: Dynamics and Interactions*; Barnes, et al., Eds.; Reidel: Dordrecht, 1984.

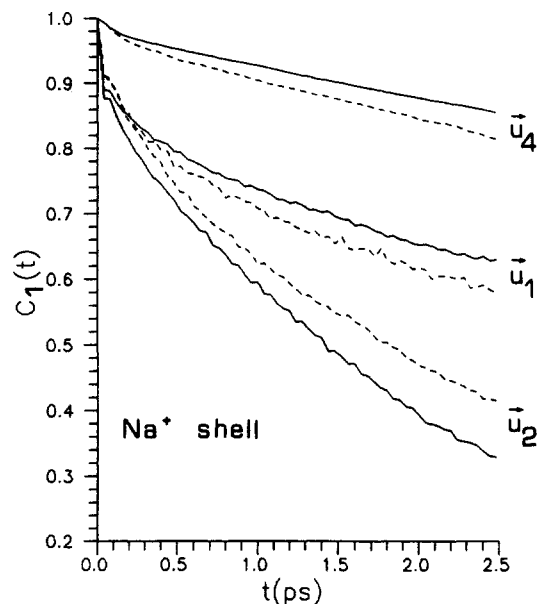


Figure 11. Reorientational time correlation functions  $C_1(t)$  for the water molecules in the first hydration shell of Na<sup>+</sup>. —, flexible water; ---, rigid water.

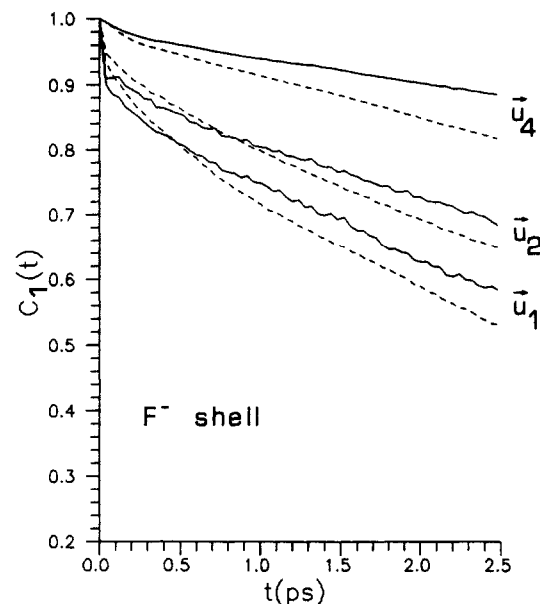


Figure 12. Same as Figure 11, except for F<sup>-</sup>.

The results for  $l = 1$  and  $l = 2$  are summarized in Table V.

The results of Table V show a satisfactory qualitative agreement with the ones from the experiments<sup>28,35</sup> or from the other computer simulations.<sup>32,33</sup> The reorientational motions of the hydration water are significantly slower than the ones for pure water, and important deviations from the predictions of the Debye model for the rotational diffusion<sup>31</sup> may be observed, i.e., the values of  $\tau_1/\tau_2$  are clearly smaller than 3 (except in the case of  $\vec{u}_1$  for Na<sup>+</sup>, which are larger).

A quantitative comparison of the reorientational times is very difficult. The strong sensitivity of these data to the temperature and concentration<sup>28,32,33</sup> of the solution only allows us comparisons in identical conditions. Moreover, in the case of experimental results there is an additional difficulty because the establishment of a relationship between the data obtained from the measurements and the reorientational times requires the consideration of approximate microscopic models. Although the proportionality factor between the experimental and simulation data is not well established,<sup>33</sup> we obtained  $\tau_1$  values for  $\vec{u}_1$  in pure water that were too small when compared with the 8.25 ps resulting from the dielectric relaxation measurements.<sup>35</sup> In the case of  $\vec{u}_2$  for pure water and

TABLE VI: Residence Times and Hydration Numbers

	$\tau_{1W}$ , ps		$hn_{1W}$	
	Na <sup>+</sup>	F <sup>-</sup>	Na <sup>+</sup>	F <sup>-</sup>
F model	38.5	21.4	5.4	5.7
R model	23.8	15.8	5.2	5.4
ref 6 <sup>a</sup>	9.9	20.3	3.8	4.6
from expt <sup>37</sup>			5 ± 1	4 ± 1

<sup>a</sup> Data of ref 6 correspond to computer simulations at different temperatures, i.e., 282 K for Na<sup>+</sup> and 278 K for F<sup>-</sup>.

$\bar{u}_4$  for F<sup>-</sup> hydrate complex, the agreement of our results with the data from the experiments<sup>28</sup> (2.5 and 10–14 ps, respectively) is better.

As a result of the anisotropy of water molecules, the decay of  $C_i(t)$  functions for  $\bar{u}_1$  and  $\bar{u}_2$  directions depends notoriously on the geometrical arrangement of molecules. Thus, in the case of Na<sup>+</sup> the decay for  $\bar{u}_1$  is slower than the one for  $\bar{u}_2$  whereas for F<sup>-</sup> the decay is slower for  $\bar{u}_2$ .

The influence of the intramolecular degrees of freedom on the reorientational correlation times is significant (see Table V and Figures 11 and 12). As in the work of Teleman et al.,<sup>16</sup> the flexibility of water increases the speed of the reorientational times and the values of  $\tau$  for pure water are smaller for the F model. In contrast to this behavior the water molecules close to an ion, in general, reduce their reorientational times when internal motions are considered. Thus, except in the case of  $\bar{u}_2$  and  $\bar{u}_3$  for the Na<sup>+</sup> hydration water, the  $\tau$  values are larger for the F model. These results are consistent with the conclusions of the preceding section. The anomalous behavior for  $\bar{u}_2$  and  $\bar{u}_3$  in the Na<sup>+</sup> shell may be associated with the geometrical arrangement of water around Na<sup>+</sup>. In this case the reorientational motions in the  $\bar{u}_2$  and  $\bar{u}_3$  directions would be weakly influenced by the formation of hydrate complexes.

## 7. Residence Times and Hydration Numbers

The times of residence of water molecules in the first coordination shell and the hydration numbers were studied according to the procedure described in ref 6. During simulations we computed the time-dependent  $cn_{1W}(t)$ , function which is defined as the number of water molecules that having initially been in the first coordination shell still remain there after a time  $t$ . We allowed temporary absences for continuous time intervals smaller than  $t^* = 1$  ps. The initial value of  $cn_{1W}(t)$  is precisely the coordination number  $cn_{1W}$  defined in section 3. The positions of the  $g_{1W}(r)$  first minima were taken as the radii of the corresponding hydration shells.  $cn_{1W}(t)$  functions show an exponential decay at sufficiently long times, and the characteristic time of residence of molecules in the hydration shell ( $\tau_{1W}$ ) was determined by fitting  $cn_{1W}(t)$  to the function

$$cn_{1W}(t) = cn_{1W} \exp(-t/\tau_{1W}) \quad (5)$$

Table VI compares our results with those obtained by Impey et al.<sup>6</sup> using a MCY rigid model for water. The discrepancies, which are especially significant for Na<sup>+</sup>, indicate that the influence of the interaction model on  $\tau_{1W}$  may be important. On the other hand, the residence times for the F model are higher than the ones for the R model, which is consistent with the greater stability of

the hydrate complexes allowed by the intramolecular atomic motions as has already been commented in the last two sections.

The hydration number is conventionally defined as the number of solvent molecules that are associated with an ion in a solution. However, this definition is ambiguous since the concept of association is not rigorously established. Moreover, the experimental estimations of the hydration numbers are widely divergent and they depend both on the property used for their determination and on the way followed for the interpretation of the experimental data. We calculated the dynamic hydration numbers  $hn_{1W}$ , which were defined<sup>6</sup> as the mean number of water molecules that remain within the hydration shell over a period of time in which the first coordination shell in pure water is renewed:

$$hn_{1W} = cn_{1W} \exp(-\tau_{WW}/\tau_{1W}) \quad (6)$$

where  $\tau_{WW}$  is the residence time in the first coordination shell of a water molecule in pure water.  $\tau_{WW}$  values were obtained during the simulations of pure water by the same procedure used for the determination of  $\tau_{1W}$  for ions in solution.

We obtained  $hn_{1W}$  values that are in reasonable accord with the hydration numbers given by Conway,<sup>37</sup> which are based on the experimental results for several ionic properties (Table VI). As for the residence times, we found noticeable discrepancies with the results of Impey et al.<sup>6</sup> for other interaction models. We did not observe significant differences due to the flexibility of the water molecules.

## 8. Conclusions

We analyzed the effect of the intramolecular motions of water on the microscopic properties of dilute aqueous solutions when these motions were modeled according to oscillatory hydrogen-hydrogen and hydrogen-oxygen intramolecular potentials. The results reported in the preceding sections show that these effects are, in general, important. The changes in the ion-water structure are always noticeable, and they are bigger for the anions (F<sup>-</sup>). However, in the case of more averaged equilibrium properties, such as the coordination numbers or the mean ion-water orientation angles, the influence of the intramolecular motions is negligible. The molecular motions in pure water are speeded up when the flexible model is considered, but in the case of ions and water molecules of their hydration shells both translational and reorientational motions are slowed down as a result of the formation of more stable ion-water complexes.

Although MD simulations allowing for intramolecular motions are in principle more realistic, the disagreements of our simulation results with the experimental data ( $cn_{1O}$ ,  $D_1$ ,  $D_O$ ,  $hn_{1W}$ ) are somewhat bigger for the flexible model. This fact suggests that the simple intramolecular potential of Toukan and Rahman<sup>18</sup> should be notoriously refined to achieve an accurate reproduction of the properties of aqueous ionic solutions.

**Acknowledgment.** Financial support by DGICYT, Project PS 87-0026-C02, is acknowledged. We thank R. Rey for his help in the computational work.

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