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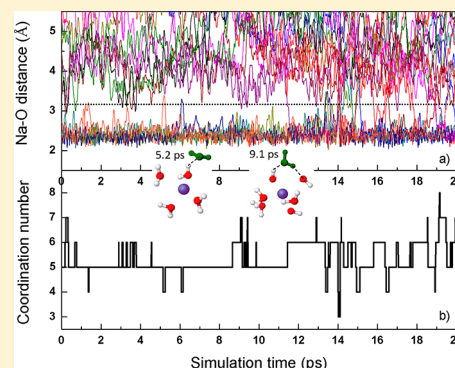
“Structure-Making” Ability of Na⁺ in Dilute Aqueous Solution: An ONIOM-XS MD Simulation Study

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ABSTRACT: An ONIOM-XS MD simulation has been performed to characterize the “structure-making” ability of Na⁺ in dilute aqueous solution. The region of most interest, i.e., a sphere that includes Na⁺ and its surrounding water molecules, was treated at the HF level of accuracy using LANL2DZ and DZP basis sets for the ion and waters, respectively, whereas the rest of the system was described by classical pair potentials. Detailed analyses of the ONIOM-XS MD trajectories clearly show that Na⁺ is able to order the structure of waters in its surroundings, forming two prevalent Na⁺(H₂O)₅ and Na⁺(H₂O)₆ species. Interestingly, it is observed that these 5-fold and 6-fold coordinated complexes can convert back and forth with some degrees of flexibility, leading to frequent rearrangements of the Na⁺ hydrates as well as numerous attempts of inner-shell water molecules to interchange with waters in the outer region. Such a phenomenon clearly demonstrates the weak “structure-making” ability of Na⁺ in aqueous solution.



1. INTRODUCTION

Detailed knowledge of ions solvated in aqueous electrolyte solution has long been desirable for chemists and biologists to understand the role of these ions in chemical and biological processes.^{1,2} When ions are dissolved in liquid water, the effects of the ions can cause substantial modifications in the local structure and changes in the dynamics of the surrounding water molecules. In this respect, the manners in which ions order the structure of their surrounding waters to form their specific ion–water complexes are strongly related to the strength of ion–water interactions. In general, the terms “structure-makers” and “structure-breakers” have been widely used to describe the effect of different ions in ordering the hydrogen bond (HB) network of surrounding water molecules.³ For example, ions with a small size and high charge density, i.e., the ones that can potentially break the HB networks of their nearest-neighbor waters and can order those water molecules to form well-defined ion–water complexes, are classified as “structure-makers”. In contrast, ions with a large size and low charge density are classified as “structure-breakers”; i.e., they are regarded as causing perturbation of the water HBs. In the case of salt solutions, however, it should be realized that the classification of ions as “structure-makers” or “structure-breakers” could also depend on the salt concentration.

For simple alkali metal ions, Na⁺ is abundant in nature and is known as one of the essential elements that play a vital role for all known life. In particular, the contrasting behavior of Na⁺ in aqueous solution, i.e., compared to K⁺, is of special interest concerning the process of ionic pumps across the cell membrane.⁴ During the past several years, the details with respect to the structure and dynamics of Na⁺ in aqueous solution have been studied intensively, both by experiments

and by theoretical investigations.^{5–24} However, some discrepancies among those results still exist, even for the fundamental properties such as the average coordination number and the mean ion–water distance. For example, experimental observations revealed a large variation of coordination numbers, ranging from 4 to 8,^{5–13} which has been attributed mainly to the concentration dependence and the different experimental methods employed. In addition, it has been demonstrated that the concept of “structure-makers/breakers” is not helpful in understanding the effects of ions on water structure, leading to the ambiguous conclusion that Na⁺ can be classified both as a local “structure-maker” and as a long-range “structure-breaker”.¹² In this regard, because the modifications of the HB water structure in particular at a high salt concentration are due partly to the effect of ion pairing, the concept of “structure-makers/breakers” is probably applicable only for the discussion with respect to very dilute aqueous solutions, i.e., the solution containing a single ion.

Theoretical investigations, especially by means of molecular dynamics (MD) simulations, also predicted different hydration numbers of Na⁺, varying from 4.8 to 7.3.^{14–23} With regard to earlier MD studies,^{14–17,21,22} the observed discrepancies could be ascribed to the use of different molecular mechanical (MM) force fields in describing the system’s interactions; i.e., the quality of the simulation results depends crucially on the quality of the ion–water and water–water potentials employed. By several classical MD simulations, Na⁺ has been classified as a strong “structure-maker”.^{14–16} To obtain more reliable

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simulation results, it has been demonstrated that the “quantum effects” are not negligible and that the inclusion of these effects in the simulations through quantum mechanical calculations is nowadays mandatory for studying such condensed phase systems.²⁴ In terms of *ab initio* (AI) MD techniques, first-principles (FP-MD)^{18,19} and Born–Oppenheimer (BO-MD)²⁰ simulations have been carried out for Na⁺ in water, providing detailed descriptions on the structure and dynamics of the Na⁺ hydrate. One major advantage of such AI-MD techniques is that the whole system is treated quantum mechanically, most of which are based on the density functional theory (DFT). However, some severe limitations of the AI-MD techniques come from the use of simple generalized gradient approximation (GGA) functionals, such as BLYP and PBE, and of the relatively small system size.²⁵ According to the FP-MD results, a strong discrepancy in determining the behavior of Na⁺ in water is observed, in which the earlier FP-MD simulation¹⁸ has predicted that Na⁺ is a weak “structure-maker”, whereas the later FP-MD work¹⁹ categorized this ion as a weak “structure-breaker”.

An alternative QM-based MD approach is to apply a so-called combined quantum mechanics/molecular mechanics (QM/MM) technique,^{26–28} which treats the active-site region, i.e., a small subsystem that contains most interesting particles, quantum mechanically, whereas the rest of the system is described by classical MM potentials. Recently, a series of QM/MM MD simulations has been performed for the systems of Na⁺ in aqueous solution,^{21–23} revealing results which are also in good accord with previously published experimental and theoretical studies. All QM/MM MD simulations had led to the similar conclusion that Na⁺ showed a clear “structure-making” ability, and that only a single layer of hydration is formed; i.e., the influence of the ion beyond the first hydration shell is definitely very weak. With regard to the QM/MM MD technique, however, a smoothing function is applied only for the exchanging particles that are crossing the QM/MM boundary. Such treatment clearly implies the methodical weakness because an immediate exchange of particles between the QM and MM regions also affects the forces acting on the remaining QM particles. In addition, the conventional QM/MM framework cannot clearly define the energy expression during the solvent exchange process.^{29,30} To solve these problems, a more sophisticated QM/MM MD technique based on the ONIOM-XS method (which will be abbreviated throughout this work as “ONIOM-XS MD”) has been proposed.^{29,30} This technique allows forces on all QM particles to be smoothed during particle exchange and, thus, better defines the system’s energy expression. By the ONIOM-XS MD technique, it is worth noting that both energies and forces can be smoothed, whereas only forces were handled in the conventional QM/MM MD scheme. Recently, the ONIOM-XS MD technique has been successfully applied for various systems, such as Li⁺ and Ca²⁺ in liquid ammonia,^{29,30} K⁺ and Ca²⁺ in aqueous solution,³¹ and pure water.³² Interestingly, it has been demonstrated that the ONIOM-XS MD technique becomes more effective for the situation where the number of ligands that are crossing the QM/MM boundary is large, i.e., a system in which the ion–water interactions are weak and water molecules surrounding the ion are labile.³¹ In this study, the ONIOM-XS MD technique will be applied to investigate the characteristics of Na⁺ hydrate, in particular those related to the “structure-making” ability of Na⁺ in aqueous solution.

2. METHOD

On the basis of the ONIOM-XS MD technique,^{29,30} the system is composed of a “high-level” QM region, i.e., a sphere that contains the Na⁺ ion and its surrounding water molecules, and the remaining “low-level” MM bulk waters. A thin switching layer located between the QM and MM regions is employed to smooth the energy and forces of the combined system according to the solvent exchange. Given n_1 , l , and n_2 as the number of particles in the QM region, the switching layer, and the MM region, respectively, and N as the total number of particles (i.e., $N = n_1 + l + n_2$), the potential energy of the system can be written in two ways with respect to the ONIOM extrapolation scheme.³³ If the switching layer is included into the “high-level” QM sphere, the energy expression is written as

$$E^{\text{ONIOM}}(n_1+l;N) = E^{\text{QM}}(n_1+l) - E^{\text{MM}}(n_1+l) + E^{\text{MM}}(N) \quad (1)$$

If the switching layer is considered as part of the “low-level” MM region, the energy expression is

$$E^{\text{ONIOM}}(n_1;N) = E^{\text{QM}}(n_1) - E^{\text{MM}}(n_1) + E^{\text{MM}}(N) \quad (2)$$

According to eqs 1 and 2, the E^{QM} and E^{MM} terms refer to the interactions derived by means of QM calculations and by the classical MM potentials, respectively. In this respect, the interactions between the QM and MM regions are described by means of MM potentials, and thus, these contributions are already included into the $E^{\text{MM}}(N)$. In practice, when a particle moves into the switching layer (from either the QM or MM region), both eqs 1 and 2 will be evaluated. The potential energy of the entire system is then taken as a hybrid between both energy terms 1 and 2,

$$E^{\text{ONIOM-XS}}(\{r_i\}) = (1 - \bar{s}(\{r_i\})) \cdot E^{\text{ONIOM}}(n_1+l;N) + \bar{s}(\{r_i\}) \cdot E^{\text{ONIOM}}(n_1;N) \quad (3)$$

where $\bar{s}(\{r_i\})$ is an average over a set of switching functions for individual exchanging particles in the switching layer $s_i(x_i)$,

$$\bar{s}(\{r_i\}) = \frac{1}{l} \sum_{i=1}^l s_i(x_i) \quad (4)$$

Basically, the switching function in eq 4 can have any form. In this study, a polynomial expression is employed,

$$s_i(x_i) = 6\left(x_i - \frac{1}{2}\right)^5 - 5\left(x_i - \frac{1}{2}\right)^3 + \frac{15}{18}\left(x_i - \frac{1}{2}\right) + \frac{1}{2} \quad (5)$$

where $x_i = [(r_i - r_0)/(r_1 - r_0)]$, and r_0 and r_1 are the radius of the inner and outer surfaces of the switching shell, respectively, and r_i is the distance between the ion and the oxygen atom of the exchanging water molecule. Note that the above polynomial form and parameter sets were derived to have an S-shape that converges to 0 and 1 at r_0 and r_1 , respectively.²⁹ This polynomial form is preferred over the ST2 switching function³⁴ usually employed in the conventional QM/MM MD scheme because its first and second derivatives are both continuous. Finally, the gradient of the energy can be expressed as

Table 1. Optimized Parameters of the Analytical Pair Potentials for the Interactions of Water with Na⁺ (Interaction Energies in kcal·mol^{−1} and Distances in Å)

pair	A (kcal mol ^{−1} Å ⁴)	B (kcal mol ^{−1} Å ⁸)	D (kcal mol ^{−1})	D (Å ^{−1})
Na–O	−663.2089588	967.45544406	28536.783215	3.2925018407
Na–H	148.8680902	605.89247202	−7143.0151207	3.5661952849

$$\begin{aligned} \nabla_{\mathbf{R}} E^{\text{ONIOM-XS}}(\{r_i\}) \\ = (1 - \bar{s}(\{r_i\})) \cdot \nabla_{\mathbf{R}} E^{\text{ONIOM}}(n_i + l_i N) + \bar{s}(\{r_i\}) \cdot \\ \nabla_{\mathbf{R}} E^{\text{ONIOM}}(n_i; N) + \frac{1}{(r_i - r_0)} \nabla \bar{s}(\{r_i\}) \cdot \\ (E^{\text{ONIOM}}(n_i; N) - E^{\text{ONIOM}}(n_i + l_i N)) \end{aligned} \quad (6)$$

In this work, because the correlated QM calculations, even at the simple MP2-level, are rather too time-consuming for our current computational feasibility, all interactions within the QM region were evaluated by performing ab initio calculations at the Hartree–Fock (HF) level of accuracy using DZP³⁵ and LANL2DZ^{36,37} basis sets for H₂O and Na⁺, respectively. With regard to the fact that the HF method could produce an error due to the neglect of electron correlation effects, it is assumed that the use of this method with sufficiently large QM size and basis sets can achieve a sufficient level of accuracy, compromising between the quality of the simulation results and the requirement of CPU time.²⁴ The DFT methods, such as B3LYP, are not taken into account for this work because these methods often yielded overestimation of the ion–water interactions as well as considerably shorter ion–water distances.^{22,23} For the QM size, a QM radius of 4.2 Å and a switching width of 0.2 Å were chosen, corresponding to the ONIOM-XS parameters r_0 and r_1 of 4.0 and 4.2 Å, respectively. This QM size is considered to be large enough to include most of the many-body contributions and the polarization effects, i.e., at least within the first hydration shell of Na⁺, and the remaining interactions beyond the QM region could be well accounted for by the MM potentials. As can be seen in the next section (cf. Figure 1), the smooth shape of the Na–O radial distribution function (RDF) between 4.0 and 4.2 Å clearly supplies information that transition of water molecules between the QM and MM regions occurs smoothly. For the interactions within the MM and between the QM and MM regions, a flexible BJH–CF2 model, which describes intermolecular³⁸ and intramolecular³⁹ interactions, was employed for water. This flexible water model allows explicit hydrogen movements and, thus, ensures a smooth transition when water molecules move from the QM region with its full flexibility to the MM region and vice versa. The pair potential functions for describing Na⁺–H₂O interactions were newly constructed. The 2424 HF interaction energy points for various Na⁺–H₂O configurations, obtained from Gaussian03⁴⁰ calculations using DZP³⁵ and LANL2DZ^{36,37} basis sets for H₂O and Na⁺, respectively, were fitted to the analytical form of

$$\Delta E_{\text{Na}^+-\text{H}_2\text{O}} = \sum_{i=1}^3 \left(\frac{A_{ic}}{r_{ic}^4} + \frac{B_{ic}}{r_{ic}^8} + C_{ic} \exp(-D_{ic} r_{ic}) + \frac{q_i q_c}{r_{ic}} \right) \quad (7)$$

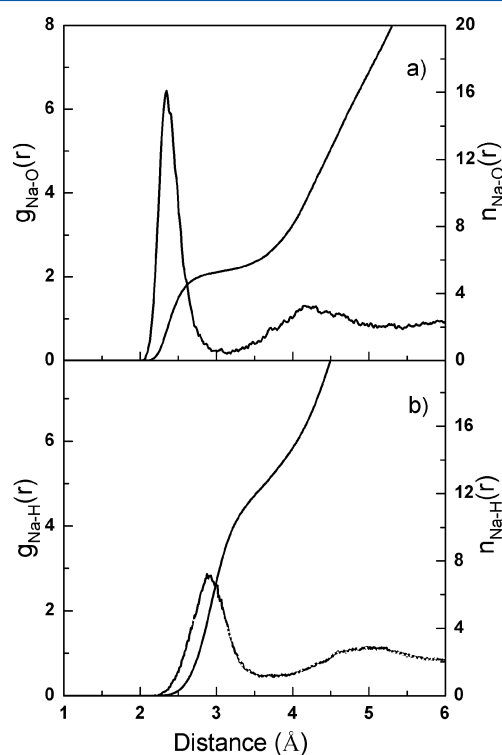
where A , B , C , and D are fitting parameters (Table 1), r_{ij} denotes the distances between the ion and the i th atoms of water molecule, and q are the atomic net charges. In this work, the charge for Na⁺ was set to 1.0, and the charges for O and H

atoms of water were set with respect to the BJH–CF2 model, i.e., −0.6598 and +0.3299 for O and H atoms, respectively.

The ONIOM-XS MD simulation was performed in a canonical ensemble at 298 K with periodic boundary conditions. The system's temperature was kept constant using the Berendsen algorithm.⁴¹ A periodic box, with a box length of 18.19 Å, contains one Na⁺ and 199 water molecules, corresponding to the experimental density of pure water. The reaction-field method⁴² was employed for the treatment of long-range interactions. The Newtonian equations of motions were treated by a general predictor-corrector algorithm. The time step size was set to 0.2 fs, which allows for the explicit movement of the hydrogen atoms of water molecules. The ONIOM-XS MD simulation was started with the system's re-equilibration for 30 000 time steps, followed by another 205 000 time steps to collect configurations every 10th step.

3. RESULTS AND DISCUSSION

The hydration shell structure of Na⁺ can be described by means of Na–O and Na–H RDFs, together with their corresponding integration numbers, as depicted in Figure 1. With regard to the ONIOM-XS MD simulation, a well-defined first Na–O peak with a maximum centered at 2.35 Å is observed. Interestingly, the nonzero minimum following the first Na–O peak clearly suggests some exchange processes between first-shell waters and water molecules in the outer region. Integration up to the

**Figure 1.** (a) Na–O and (b) Na–H radial distribution functions and their corresponding integration numbers.

first minimum of the Na–O RDF yields an average coordination number of 5.4 ± 0.1 . This observed value is in good agreement with the recent ND experiments¹² and AI-MD studies,^{13,18,19} which reported the coordination numbers of 5.3 and 5.2, respectively. The second peak of the Na–O RDF is less pronounced, indicating that the influence of Na⁺ beyond the first hydration layer is relatively weak; i.e., only a single layer of Na⁺ hydration is formed. The ONIOM-XS MD results are in good accord with the interpretation of X-ray absorption spectroscopy (XAS) experiments, which indicated that there is no long-range effect on the HB network of water due to the presence of monovalent cations.⁴³ With regard to the XAS results, it has been demonstrated that the changes in the XA spectra observed upon addition of monovalent cation halide salts are due mainly to the interactions of water molecules with the halide anions. In addition, according to the recent femtosecond pump–probe spectroscopy study,⁴⁴ it has been suggested that the effect of alkali ions on the structure and dynamics of water is limited to the first hydration shell of ions; i.e., the HB network beyond the first shell is not different from that of bulk water.

As can be seen in Figure 1, the shape and height of the first Na–O and Na–H peaks clearly indicate the “structure-making” ability of Na⁺ in aqueous solution, i.e., the ability by which the ion can order the HB structure of its surrounding waters to form its specific Na⁺–water complexes. In this study, it should be clarified at the beginning that all discussion with respect to the “structure-making” ability of Na⁺ in water assumes a sufficiently dilute aqueous solution, i.e., the solution in which the influences of either counterion or ion-pairing are negligible. The “structure-making” effect of Na⁺ in aqueous solution has been discussed in detail in the recent QM/MM and quantum mechanical charge field (QMCF) MD studies²³ using the HF method and the same basis sets as employed in the present ONIOM-XS MD simulation. In fact, the QMCF framework⁴⁵ has been formulated to neglect the construction of non-Coulombic interaction potentials between solute and solvent particles. Nevertheless, it has been shown that the QMCF method with a sufficiently large QM size, i.e., where all exchange processes between the first and second hydration layer occur within the QM region, and a suitable embedding scheme has several advantages over the conventional QM/MM technique.²³ In particular, because the smoothing zone takes place at a relatively large distance to the ion, the error introduced by the nonconservation of momenta, as pointed out by Truhlar et al.,⁴⁶ becomes nearly negligible. In this work, as compared to the QMCF MD results,²³ the ONIOM-XS MD simulation reveals rather similar structural parameters for the Na⁺ hydrate, such as the average ion–water distance and the coordination number. However, the feature of the ONIOM-XS MD’s Na–O and Na–H RDFs are somewhat different, especially in terms of the half-width and intensity of the first-shell peaks. On the basis of ONIOM-XS MD simulation, the increased intensity of the first Na–O and Na–H peaks can be ascribed to the artificial “pressure” of the MM molecules on the QM region; i.e., the Coulombic interactions of the QM–MM coupling are computed according to fixed charges for both the QM and MM atoms. In this respect, a formal charge of +1.0 assigned to Na⁺ results in a slightly too strong ion–water interactions. Comparing to results from the QMCF MD technique, the partial charges of the QM particles are newly derived via population analysis in every step of the simulation.²³ In addition, the observed differences between the ONIOM-XS

and QMCF MD simulations could be due partly to the use of different QM size, i.e., of the QM radii of 4.2 and 5.7 Å, respectively. With regard to this point, it could be demonstrated that further improvement of the ONIOM-XS MD results is achievable by performing the simulation in conjunction with the use of larger QM size and a suitable embedding methodology, such as the partial charge schemes employed in the QMCF framework.

Figure 2 displays the probability distributions of the coordination numbers of Na⁺, calculated up to first minimum

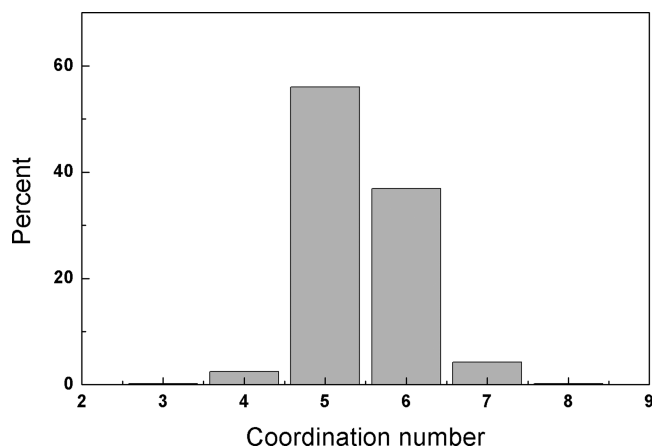


Figure 2. Distributions of the coordination numbers of Na⁺, calculated within the first minimum of the Na–O RDF.

of the Na–O RDF. It is obvious that this ion prefers the coordination numbers of 5 and 6, with the probability distributions of 56% and 37%, respectively, whereas the distributions of 4-fold and 7-fold coordinated complexes appear to be quite rare. This supplies information that only Na⁺(H₂O)₅ and Na⁺(H₂O)₆ complexes are the most prevalent species formed in aqueous solution. The flexibility of Na⁺ hydration can be described by the distributions of O---Na---O angle, as shown in Figure 3. In addition, the orientation of water molecules in the vicinity of Na⁺ is also given in Figure 4. In this context, the angle θ is defined by the Na---O axis and the dipole vector of first-shell water molecules. According to

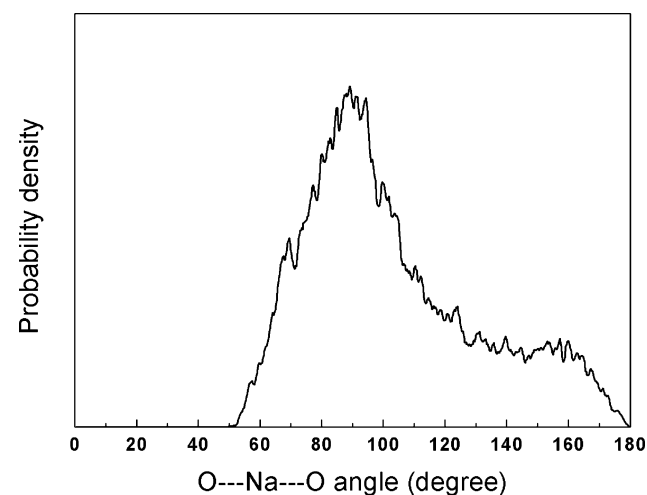


Figure 3. Distributions of the O---Na---O angle, calculated within the first minimum of the Na–O RDF.

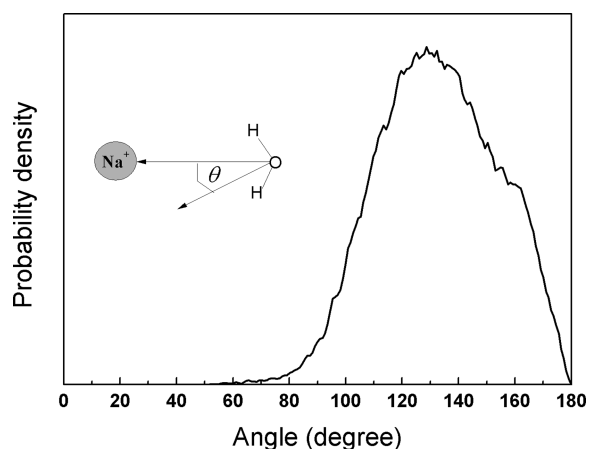


Figure 4. Probability distributions of θ angle in the first hydration shell of Na^+ , calculated within the first minimum of the Na–O RDF.

Figures 3 and 4, the observed broad distributions of both O---Na---O and θ angles clearly indicate a less ordered orientation of first-shell water molecules, i.e., showing that the hydration shell structure of Na^+ is somewhat flexible and that the “structure-making” effect of Na^+ in aqueous solution might not be strong.

The details with respect to the dynamical properties of the Na^+ hydrate can be visualized from plots of time dependence of the Na–O distance and number of first-shell waters, as depicted in Figure 5. During the ONIOM-XS MD simulation, it is

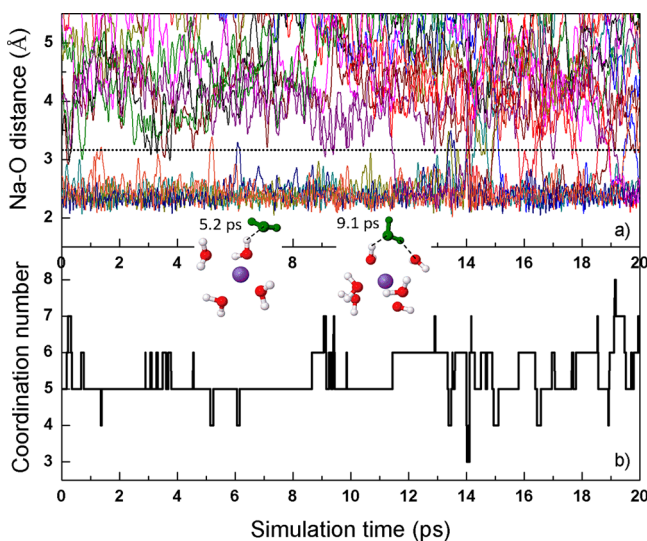


Figure 5. Time dependence of (a) Na^+ ---O distance and (b) number of first-shell waters, as obtained from first 20 ps of the ONIOM-XS MD simulation. In (a), the dashed line parallel to the x -axis indicates the first minimum of the Na–O RDF.

observed that the structure of the hydrated Na^+ complexes is rather flexible in which the most favorable $\text{Na}^+(\text{H}_2\text{O})_5$ species can convert back and forth to the lower probability $\text{Na}^+(\text{H}_2\text{O})_6$ complexes. This leads to several rearrangements of the hydrated Na^+ complexes, as well as numerous attempts of first-shell waters to interchange with water molecules in the outer region. For example, at the simulation time of 5.2 ps, the arrangement of $\text{Na}^+(\text{H}_2\text{O})_4(\text{H}_2\text{O})$ complexes ($\text{CN} = 4$) can temporarily be formed; i.e., one first-shell water molecule (labeled in “green”) moved as far as 1 Å away from its optimal distance but it forms

a hydrogen bond to an inner-shell water molecule. In addition, other transition complexes, such as of the types $\text{Na}^+(\text{H}_2\text{O})_5(\text{H}_2\text{O})_2$ and $\text{Na}^+(\text{H}_2\text{O})_6(\text{H}_2\text{O})$ ($\text{CN} = 7$), can transiently be formed (e.g., at the simulation time of 9.1 ps, in which a “green” water molecule from the outer region approaches as close as 3 Å to the Na^+ ion and form hydrogen bonds to some inner-shell water molecules, forming $\text{Na}^+(\text{H}_2\text{O})_6(\text{H}_2\text{O})$ intermediate). The presence of such intermediates can be ascribed to the polarized first-shell waters, whose hydrogen atoms can form hydrogen bonds to the outer-shell water molecules, once they are arranged in a suitable geometrical position.

According to Figure 1a, the nonzero first minimum of the Na–O RDF implies that water molecules in the hydration shell of Na^+ are somewhat labile and they can possibly exchange with those in the outer region. The lability of water molecules in the hydration shell of Na^+ can be interpreted through the self-diffusion coefficient (D). In this study, the D value for first-shell waters was calculated from their center-of-mass velocity autocorrelation functions (VACFs) using the Green–Kubo relation,⁴⁷

$$D = \frac{1}{3} \lim_{t \rightarrow \infty} \int_0^t C_v(t) dt \quad (8)$$

On the basis of the ONIOM-XS MD simulation, the D value for water molecules in the vicinity of Na^+ is estimated to be $1.75 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, which is not much different from the value of $2.23 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ of pure water derived by the similar ONIOM-XS MD scheme.³² In this respect, it could be demonstrated that water molecules in the hydration shell of Na^+ are not strongly attached to the ion, i.e., they diffuse only slightly slower than those in the bulk. Such a phenomenon clearly corresponds to the weak “structure-making” ability of Na^+ in water. Regarding the ONIOM-XS MD results, it should be emphasized that the correct degree of lability of the first-shell waters is a crucial factor in determining the reactivity of Na^+ in aqueous solution.

The rates of water exchange processes at Na^+ were evaluated through mean residence times (MRTs) of the first-shell water molecules. In this work, the MRT data were calculated using the “direct” method,⁴⁸ as the product of the average number of water molecules in the first shell with the duration of the ONIOM-XS MD simulation, divided by the observed number of exchange events lasting a given time interval t^* . In general, a t^* value of 0.0 ps is recommended for the estimation of hydrogen bond lifetimes, whereas a t^* value of 0.5 ps is chosen as a good measure for water exchange processes.⁴⁸ The calculated MRT data with respect to t^* values of 0.0 and 0.5 ps are summarized in Table 2. To provide a useful discussion with respect to the “structure-making” ability of Na^+ , the MRT data

Table 2. Number of Water Exchange Events (N_{ex}) and Mean Residence Times (MRTs) of Water Molecules in the Bulk and in the Vicinity of Na^+ , K^+ , and Ca^{2+} , Obtained by ONIOM-XS MD Simulations

ion/solute	CN	t_{sim}	$t^* = 0.0 \text{ ps}$		$t^* = 0.5 \text{ ps}$	
			$N_{\text{ex}}^{0.0}$	$\tau_{\text{H}_2\text{O}}^{0.0}$	$N_{\text{ex}}^{0.5}$	$\tau_{\text{H}_2\text{O}}^{0.5}$
Na^+	5.4	41.0	164	1.35	36	6.18
K^{+31}	6.3	30.0	445	0.42	105	1.80
Ca^{2+31}	7.6	40.0	30	10.13	14	21.71
H_2O^{32}	4.7	30.0	607	0.23	65	2.17

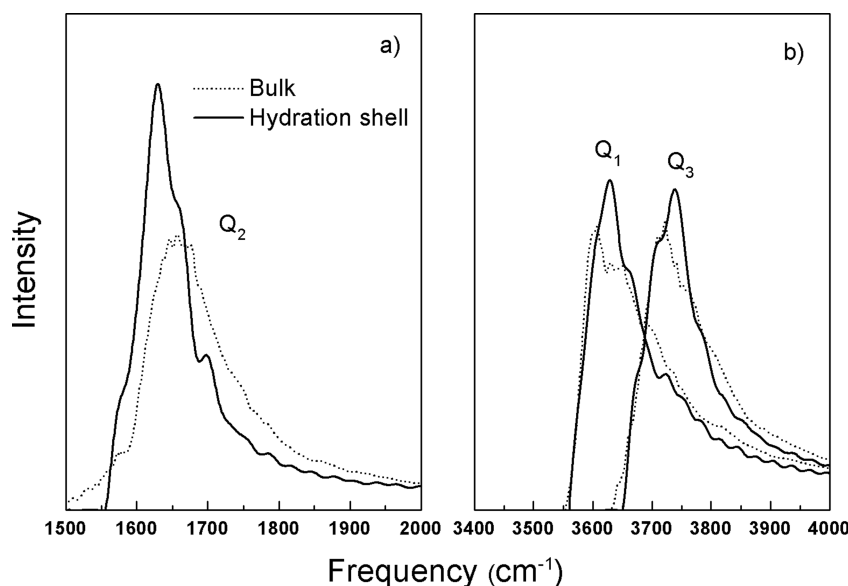


Figure 6. (a) Bending vibrations (Q_2) and (b) symmetric and asymmetric stretching vibrations (Q_1 and Q_3) of water molecules in the first hydration shell of Na^+ and in the bulk, obtained by ONIOM-XS MD simulations.

for water molecules in the vicinity of K^+ and Ca^{2+} , as derived by the similar ONIOM-XS MD framework,³¹ were also given for comparison. For both $t^* = 0.0$ and 0.5 ps, the MRT values of water molecules in the hydration shell of Na^+ are higher than those of bulk waters, showing a clear “structure-making” ability of Na^+ in aqueous solution. However, the ability of Na^+ in ordering the structure of its surrounding waters is much less than that of stronger “structure-makers”, like Ca^{2+} . In the case of K^+ , the MRT values of first-shell waters are close to the corresponding data for bulk waters, suggesting that K^+ may not be able to form any specific geometrical order of its hydration shell. In biological processes, the contrasting behaviors of Na^+ and K^+ are of special interest in determining the ability of ions to abandon their hydration shell to be pumped into the cell membrane.

More details regarding the dynamics of water molecules in the vicinity of Na^+ can be gained by computing the velocity autocorrelation functions (VACFs) of first-shell waters and their Fourier transformations. In this work, the normal-coordinate analysis developed by Bopp^{49,50} was used for obtaining three quantities Q_2 , Q_1 , and Q_3 , which are defined for describing bending vibration, and symmetric and asymmetric stretching vibrations of water molecules, respectively, as depicted in Figure 6. By the ONIOM-XS MD technique, because all atomic motions of first-shell water molecules are generated according to QM force calculations, the calculated vibrational spectra are usually scaled by an empirical factor, i.e., an approximate correction for errors in the force constants and for anharmonic effects.^{51–53} With regard to the systematic error of HF frequency calculations, all frequencies obtained by the ONIOM-XS MD simulation were multiplied by an appropriate scaling factor of 0.905.⁵¹ To reliably illustrate the “structure-making” ability of Na^+ in water, the corresponding Q_1 , Q_2 , and Q_3 frequencies obtained from the ONIOM-XS MD simulation of liquid water³² were utilized for comparison. All intramolecular vibrational frequencies (Q_1 , Q_2 , and Q_3) of water molecules in the hydration shell of Na^+ and in the liquid water are given in Table 3. For liquid water, all the bending and stretching vibrational frequencies showed peaks with recogniz-

Table 3. Vibrational Frequencies (Q_1 , Q_2 , and Q_3) of Water Molecules in the First Hydration Shell of Na^+ and in the Bulk, Obtained by ONIOM-XS MD Simulations (Numbers for the Shoulders in Parentheses)

phase	frequency (cm^{-1})		
	Q_2	Q_1	Q_3
hydration shell of Na^+	1629	3628	3738
pure water ³²	1660	3606 (3650)	3720 (3755)

able shoulders, especially for the symmetric and asymmetric vibrational modes. These observed spectra have been ascribed to the presence of several kinds, with varying strengths, of HBs formed in liquid water.³² In the hydration shell of Na^+ , water molecules are less mobilized and are arranged with respect to the influence of the ion, leading to more intense and better defined vibrational frequencies. As compared to bending frequencies of liquid water, the bending frequency of first-shell waters shows a clear “red-shift”, i.e., by about 31 cm^{-1} , whereas the symmetric (Q_1) and asymmetric (Q_3) stretching frequencies are found to be exhibited between the main peaks and the shoulders of the respective Q_1 and Q_3 frequencies of liquid water. These observed data, in particular the positions of Q_1 and Q_3 frequencies of first-shell waters, clearly demonstrate that Na^+ acts as weak “structure-maker” in aqueous solution. The results are consistent with the assignment of “structure-makers/breakers” according to Marcus,⁵⁴ indicating that Na^+ should be a weak “structure-maker”, i.e., it is considered as a borderline ion dividing “structure-makers” from “structure-breakers”. In terms of thermodynamics evidence, the details with respect to ion hydration entropies can provide a direct connection to ordering effects due to the insertion of ions into bulk water.^{55,56} For Na^+ , the hydration entropy of this ion analyzed via energetic partitioning of the potential distribution theorem free energy suggested that Na^+ is indeed a weak “structure-maker” and that the effect is relatively local around the ion.⁵⁶ Very recently, the hydration of Na^+ in aqueous solution has been studied by large angle X-ray scattering (LAXS) and double difference infrared spectroscopy (DDIR),

suggesting that this ion is weakly hydrated with only a single shell of water molecules and that it may be a “structure-breaker” even though its interactions with water are stronger than bulk water molecules interacting internally.⁵⁷ In this context, the results obtained by the ONIOM-XS MD simulation clearly provide more insights into the behaviors of Na⁺ hydrate, which are very crucial to correctly understand the reactivity of Na⁺ in aqueous solution.

4. CONCLUSIONS

In this study, an ONIOM-XS MD simulation has been performed to investigate the hydration shell structure and dynamics of Na⁺ in dilute aqueous solution. Regarding the detailed analyses of the ONIOM-XS MD trajectories, Na⁺ clearly acts as a “structure-maker” that can order the structure of waters in its surroundings to form two prevalent Na⁺(H₂O)₅ and Na⁺(H₂O)₆ species, with the probability distributions of 56% and 37%, respectively. Of particular interest, it is observed that these two probable hydrated Na⁺ complexes are rather flexible, in which the most stable Na⁺(H₂O)₅ species can convert back and forth to the lower probability Na⁺(H₂O)₆ complexes. This results in frequent structural rearrangements of the Na⁺(H₂O)₅ and Na⁺(H₂O)₆ complexes as well as numerous attempts of inner-shell water molecules to interchange with water molecules in the outer region. The overall observed data derived by means of the ONIOM-XS MD simulation clearly demonstrate the weak “structure-making” ability of Na⁺ in aqueous solution.

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Notes

The authors declare no competing financial interest.

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