Preliminary Molecular Dynamics Simulations
of the OSS2 Model for the Solvated Proton in Water

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Received May 14, 2001

The OSS2(Ojäme-Shavitt-Singer 2)[L. Ojäme *et al.*, *J. Chem. Phys.* **109**, 5547 (1998)] model as a dissociable water model is examined in order to study the dynamics of H^+ in water. MD simulations for 216 water system, 215 water + H^- ion system, and 215 water + OH^- ion system using the OSS2 model at 298.15 K with the use of Ewald summation are carried out. The calculated O-H radial distribution functions for these systems are essentially the same and are in very good agreement with that obtained by Ojäme.

Keywords : Molecular dynamics simulation. OSS2 potential, Solvated proton. Grotthus chain mechanism.

Introduction

The large difference of the limiting molar conductances between H^+ and other monovalent cations (H^-: 350. Li^+: 39. Na^+: 50, K^-: 77. Br^-: 78. and Cs^-: 77 Scm^2/mol) in ambient water is also found in those between OH^- and other monovalent anions (OH^-: 199. F^-: 55, Cl^-: 76. Br^-: 78, and I^-: 77 Scm^2/mol). The transport of H^- in water is well-known as the Grotthus chain mechanism that does not involves its actual motion through the solution. Instead of a single. highly solvated proton moving through the solution. it is believed that there is an effective motion of a proton which involves the rearrangement of bonds through a long chain of water molecules as shown Figure 1(a). A closer insight into the transport of OH^- reveals that the large value of the limiting molar conductance of OH^- is also related to the Grotthus chain mechanism as shown Figure 1(b) in addition to its actual motion through the solution.

The anomalously high mobility of H^+ and OH^- in water is owing to the transfer of H^- by the Grotthus mechanism and normal ionic diffusion can be considered to play a secondary role in this kind of process. As the role of hydrogen bonding in aqueous systems became clear. the Grotthus chain mechanism was refined by assuming that the transport of H^+ occurs preferentially along hydrogen bonds.[1,2] Spectroscopic

experiments in solution[3-5] and diffraction studies of hydrated crystals[6] were able to show that the charge defects introduced by excess or missing protons in water occur naturally in the form of simple. relatively long-lived hydronium (H_3O^+) and hydroxyl (OH^-) ions. The proton transfer process along a hydrogen bond described by the Grotthus chain mechanism (Figure 1) is interpreted as fast exchange reactions of H^+ forming these ions consecutively.

In order to study the dynamics of H^+ in water, it is essential to have models capable of describing how water solvent molecules can participate in ionic chemistry through dissociation and reassociation of H^+ in OH^-. H_2O, and H_3O^-. Several attempts at dissociating water potentials have been made in the past. beginning with the work of Stillinger, David and Weber.[7] Recently Ojäme. Shavitt, and Singer reported progress in the design of a family of potentials for describing $H^-(H_2O)_n$. called OSS (Ojäme-Shavitt-Singer)n (n = 1-3).[8,9] The models were generated by fitting to results of *ab initio* electronic structure calculations for the $H_5O_2^-$ ion. the H_2O molecule, and the H_3O^- ion. as well as some results for the neutral water dimer. The potential models could well reproduce *ab initio* results for the $H_5O_2^-$ ion. and could provide formation energies and structures of both protonated-water and water-only clusters that agree favorably with *ab initio* MP2 calculations.
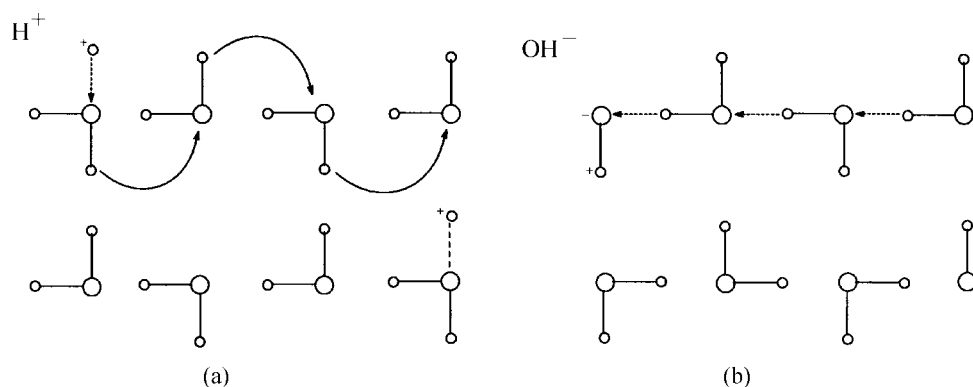

Figure 1. Grotthus chain mechanism.

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In Section II, we present the molecular models and MD simulation method. We discuss our simulation results in Section III and present the concluding remarks in Section IV.

Molecular Models and Molecular Dynamics Simulation Methods

We have chosen the OSS2 model for the preliminary molecular dynamics (MD) of the solvated proton in ambient water. It is reported that the best results were obtained using the OSS3 potential and that the OSS2 model potential also gave good results, but usually exhibited too large bond angles for water molecule.[8] When that deficiency was not a serious problem for the application at hand, the OSS2 model was a preferred choice for simulation studies, because of the faster and less elaborate computer-code implementation as compared to the OSS3 model, which contains a dipole-three-body coupling term which depends both on the induced dipole moment and the geometry. The induced dipole moment at each oxygen site in the OSS2 model can be obtained self-consistently by imposing the conditions $dV_{el}/d\mu_k = 0$ ($k = 1$, 2, ..., n_O), where n_O is the number of oxygen atoms[8]:

$$\mu_i = \alpha \left[\sum_{j,j \neq i}^{n_O+n_H} \frac{r_{ij}q_j}{r_{ij}^3} S_{ij}^{cd}(r_{ij}) + \sum_{j,j \neq i}^{n_O} \frac{T_{ij} \cdot \mu_j}{r_{ij}^3} S_{ij}^{dd}(r_{ij}) \right]. \quad (1)$$

where $S_{ij}^{cd}(r_{ij})$ and $S_{ij}^{dd}(r_{ij})$ are the electric field cutoff functions for charge-dipole and dipole-dipole interactions, respectively. This method to calculate the induced dipole moment at each oxygen site is exactly the same as that used in the revised polarized (RPOL) model[10-14] for a rigid water model except the use of Ewald summation.[15,16] The use of the Ewald summation for the induced dipole moment is rather complicated. The double summation for particles i and j in the reciprocal-space cannot be reduced to one summation due to the electric field cutoff functions. We do not apply the Ewlad summation in the reciprocal-space and this is reasonable since the electric field cutoff functions are for short ranged interactions and the distances dealing in the reciprocal-space are larger than the length of the simulation box. Ojäme *et al.*, however, used a different method[17] for the Ewald summation in the calculation of the induced dipole moment.

A canonical ensemble of fixed N (number of particles), V (volume of fixed zeolite framework), and T (temperature) is chosen for the simulation ensemble. Gauss's principle of least constraint[18-21] is used to maintain the system at a constant temperature. The ordinary periodic boundary condition in the x-, y-, and z-direction and Gear's fifth order predictor-corrector method[22,23] is used to solve the equations of translational motion of the framework atoms with a time step of 2.00×10^{-16} second (0.2 fs). The equilibrium properties are averaged over five blocks of 200,000 time steps, for a total of 1,000,000 time steps after 500,000 time steps to reach an equilibrium state. The configuration of each ion is stored every 10 time steps for further analyses.

Results and Discussion

The oxygen-oxygen and oxygen-hydrogen radial distribution functions (RDF) are shown in Figures 2 and 3, respectively. The calculated O-O RDF of the OSS2 model has more structures than that of the RPOL mode.[24] The O-O RDF of the OSS2 model for N = 32 water system shows a weird structure near r = 5 nm due to the small size of the simulation box when compared with that for N = 216 water system. This is also found in the O-H RDF of the OSS2 model for N = 32. But the O-H RDF of the OSS2 model obtained by Ojäme[17] looks reasonable even though that is for N = 32. In his MD simulation within the Ewald summation, the real-space interactions are considered to go beyond the "minimum image convention". That is, for the pair, dipole, and Coulomb interactions it is necessary to include more neighbours in the real-space summation than just the neighbours within half of the box length. All the interactions from neighbours within a distance of up to 8 unit boxes away are summed explicitly.
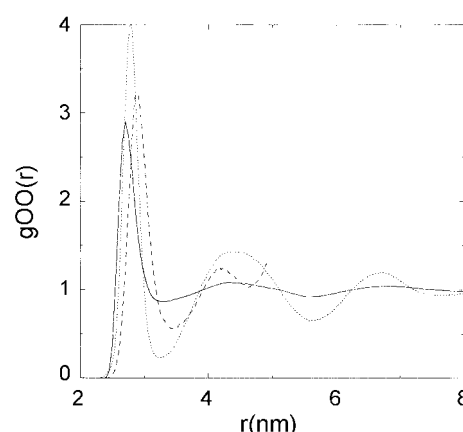

Figure 2. Oxygen-oxygen radial distribution functions: The solid line is the RPOL results without Ewald summation (Ref. 24), the dashed line is the results of this work for N = 32 water system, and the dotted line is for N = 216 water system.
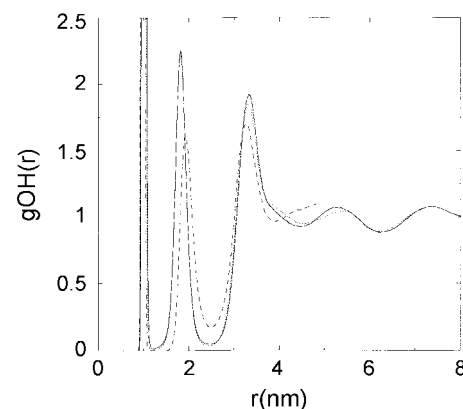

Figure 3. Oxygen-hydrogen radial distribution functions: The solid line is the OSS2 results by Ojäme,[17] the dashed line is the results of this work for N = 32 water system, and the dotted line is for N = 216 water system.

The first peak of the O-H RDF is due to two H atoms directly bonded to O atom in a water molecule and the second peak is due to the hydrogen-bonded H atoms of different water molecules. The calculated O-H RDF of the OSS2 model for N = 216 is in very good agreement with that obtained by Ojäme[17] except the small discrepancy at r = 3.5-5.5 nm. The discrepancy is a minor problem and the excellent agreement indicates that our method to calculate the induced dipole moment at each oxygen site within the Ewald summation is valid even though our method for the Ewald summation is different from that of Ojäme.

Replacing a water molecule by H⁻ and adjusting the length of the simulation box, a system of H⁻ among 215 water molecules is obtained. The immediate formation of H_3O^+ is observed and during a long equilibration simulation the exchange of H^+ is also observed. Similarly replacing a water molecule by OH⁻ and adjusting the length of the simulation box again. a system of OH⁻ among 215 water molecules is also obtained. During a long equilibration simulation the transfer of H^+ from a water molecule to the OH⁻ is occasionally observed. The calculated O-O and O-H RDF's of the OSS2 model for these systems are essentially the same as those for N = 216 water system.

For these systems, using our method for the Ewald summation of the OSS2 model, investigation of the dissociation and reassociation of H⁻ in OH⁻, H_2O, and H_3O^- is in progress for the study of the ionic mobilities of H^+ and OH⁻. Applying the path-integral method for quantum effect on H atoms and H⁻ is also in progress.

Concluding Remarks

In this paper. we have chosen the OSS2 model as a dissociable water model in order to study the dynamics of H^+ in water. We have carried out MD simulations for 216 water system, 215 water + H⁻ ion system, and 215 water + OH⁻ ion system using the OSS2 model at 298.15 K with the use of Ewald summation. The calculated O-H radial distribution functions for these systems are essentially the same and are in very good agreement with that obtained by Ojäme.[20] It is worth reporting that the transfer of H⁻ ion is observed in the 215 water + H^+ ion and 215 water + OH⁻ ion systems. Confirming the validity of our method for the Ewald summation of the OSS2 model. a systematic investigation of the dissociation and reassociation of H⁻ in OH⁻, H_2O, and H_3O^- is in progress.

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