Insights into the structure and dynamics of liquid water: A comparative study of conventional QM/MM and ONIOM-XS MD simulations

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ABSTRACT

Structural and dynamical properties of liquid water have been investigated through molecular dynamics (MD) simulations based on conventional QM/MM scheme and ONIOM-XS method. The region of highest interest, i.e., a sphere which contains a central water molecule and its nearest-neighbor waters, was treated at the Hartree–Fock (HF) level of theory using DZP basis set, while the rest of the system was described by the flexible BJH-CF2 model. With regard to both the HF/MM and ONIOM-XS simulations, the arrangement of hydrogen bonds (HBs) in liquid water is found to be rather flexible, in which the nearest-neighbors are either "loosely" or "tightly" bound to the central water molecule. Consequently, this leads to numerous water exchange mechanisms, with either "short-live" or "long-live" exchange periods, as well as to large fluctuations in the number of HBs, ranging from 2 to 6, with the prevalent value of 4. By means of the ONIOM-XS simulation, it is observed that the structural arrangement of liquid water with respect to 4 HBs decreases significantly and that the distributions of 2- and 3-fold HB species become more visible, i.e., compared to the HF/MM results. Overall, the observed differences between the HF/MM and ONIOM-XS simulations clearly indicate the important treatment of the ONIOM-XS method in describing the properties of liquid water.

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1. Introduction

Water, the most abundant substance on earth, is known to play a central role in many areas of science, including physics, chemistry, biology and geology. In solid phase, each water molecule simply conducts four hydrogen bonds (HBs) with its neighboring waters, forming a well-defined tetrahedral structure. In liquid phase, however, the pattern and dynamics of the HB network are not fully understood. Experimental techniques, such as X-ray and neutron scattering, have been carried out to investigate the structural properties of liquid water, most of which reported the tetrahedral arrangement with coordination number near 4 [1–6]. This observed phenomenon is consistent with X-ray absorption spectroscopy (XAS) results by Smith and his group [7], which reported the XAS spectral of tetrahedral-like liquid water. However, this standard picture of liquid water has been challenged by Wernet and co-workers [8], who used XAS and X-ray emission spectroscopy (XES) techniques to investigate the structure of liquid water.

Of particular interest, they proposed that most water molecules in liquid phase form only two strong HBs with one donor and one acceptor, consisting mainly of chain or ring structures and with very few tetrahedral structures. These observations are in good accord with an early XAS study by Myneni and co-workers [9], who reported a coordination number as small as 2.4. In addition, the results from a high resolution XES experiment also showed that the liquid water consists of both a distorted structure and tetrahedral structure with the ratio of 2:1 [10]. With regard to these observed discrepancies, some researchers claimed that the results may be affected by the specifics of each experimental technique [11]. In this respect, since the time scales for HBs forming and breaking in liquid water are extremely fast, i.e., in femto to picoseconds, it should be realized that a complete set of structural and dynamical data of liquid water cannot be obtained from a single experimental technique [12]. For example, X-ray and neutron scattering are only useful in providing structural details, while the infrared (IR) and Raman techniques are instead preferred in order to obtain dynamics information.

In conjunction with experiments, numerous theoretical efforts have been devoted to elucidate such details. During the past decades, several water models have been proposed and employed in molecular dynamics (MD) and Monte Carlo (MC) simulations, most of which fairly provided good correlations with experimental data [13–19]. However, some serious problems still exist such as the effects of many-body contributions, since most of the potential functions employed in the simulations are usually derived from water

dimer, i.e., based on pairwise-additive approximations [20,21]. Nowadays, as a consequence of the rapid development in computer capacity and performance, these problems can be solved by performing quantum-mechanics-based simulations. In terms of ab initio (AI) MD techniques, Car–Parrinello (CP-MD) and Born–Oppenheimer (BO-MD) are well-known. Based on AI-MD techniques [22], the whole system is treated quantum mechanically using density functional theory (DFT), with common exchange correlation functions BLYP and PBE. For the earlier AI-MD studies, several CP-MD simulations have been carried out for systems of 32 and 64 water molecules [23–27]. With regard to the CP-MD results, however, it has been demonstrated that some properties of the liquid water are quite sensitive to the density functionals chosen, i.e., several of them were found to overestimate the water–water interactions [25,28]. Consequently, some dynamics properties of water obtained from numerous CP-MD simulations, such as self-diffusion coefficients, showed significantly smaller value than that of experiments, implying that the liquid water simulated by the CP-MD technique under ambient condition is super-cooled or glassy [26]. In this respect, inclusion of van der Waals (vdW) forces, e.g., BO-MD simulations with BLYP functional including dispersion correction [29], has been shown to lower the melting points of water, i.e., from >400 K with the BLYP functional to 360 K. However, this is still significantly higher than the normal melting point (273 K) of real water. Recently, BO-MD simulations using new vdW density functionals, i.e., using exchange-correlation functionals optPBE-vdW [30] and vdW-DF2 [31], have been performed for water, demonstrating that inclusion of the more isotropic vdW interactions significantly shifts the balance of resulting water structures from directional HBs to higher packing, i.e., leading to a softening of the microscopic structure of water [32].

Besides the AI-MD techniques, an alternative approach is to apply a so-called combined quantum mechanics/molecular mechanics (QM/MM) technique [33–36], which treats the active-site region, i.e., a small subsystem which contains most interesting particles, quantum mechanically, while the rest of the system is described by classical molecular mechanical potentials. Recently, a series of QM/MM MD simulations, namely HF/MM, B3LYP/MM and MP2/MM, have been performed for liquid water [37,38], showing that the use of the HF method with enlarged QM size can provide simulation results in good agreement with those obtained by the correlated MP2 calculations, while the B3LYP method predicted a too rigid water structure as well as too slow exchange rates. Regarding the HF/MM simulation with enlarged QM size [38], the results clearly indicated an enormous flexibility of the HB network in liquid water, suggesting that each water molecule forms (on average) only 2.8 HBs. These HF/MM results are in good accord with the recent experimental observations, in which the number of 4-fold HBs in liquid water is found to be rather small in comparison to 2- and 3-fold HB species [8–10].

With regard to the conventional QM/MM technique, however, only the exchanging particles are treated by a smoothing function when they are crossing the QM/MM boundary. In practice, this is not realistic since the immediate addition or deletion of a particle in the QM region due to the interchange also affects the forces acting on the remaining QM particles. Furthermore, the conventional QM/MM framework cannot clearly define the energy expression during the exchange process. To solve those problems, a more sophisticated QM/MM MD technique based on ONIOM-XS method (which will be abbreviated throughout this work as "ONIOM-XS MD") has been proposed [39,40]. This technique allows the forces on all QM particles to be smoothed during particle exchange, and thus, clearly defines the system's energy expression. In this work, MD simulations based on the conventional QM/MM scheme and ONIOM-XS method will be performed to study the local structure and dynamics of HBs in liquid water. Of particular interest, the results obtained by the ONIOM-XS simulation can be expected to provide more reliable data of liquid water, i.e., compared to those obtained by the conventional QM/MM scheme, leading to further understanding the properties of this peculiar liquid in many areas of science.

2. Methods

2.1. Conventional QM/MM MD

By the conventional QM/MM MD technique [33–36,41–43], the system is divided into two parts, namely the QM and MM regions. The total interaction energy of the system is defined as:

$$E_{total} = \left\langle \Psi_{QM} \middle| \hat{H} \middle| \Psi_{QM} \right\rangle + E_{MM} + E_{QM-MM}, \tag{1}$$

where $\left\langle \Psi_{QM} \middle| \hat{H} \middle| \Psi_{QM} \right\rangle$ refers to the interactions within the QM region, and E_{MM} and E_{QM-MM} represent the interactions within the MM and between the QM and MM regions, respectively. The QM region, the most interesting part which contains a central H_2O and its nearest-neighbor waters, is treated quantum mechanically, while the rest of the system (i.e., the E_{MM} and E_{QM-MM}) is described by classical MM potentials. By this scheme, the total force of the system is described by the following formula:

$$F_{tot} = F_{MM}^{sys} + \left(F_{QM}^{QM} - F_{MM}^{QM} \right), \tag{2}$$

where F_{MM}^{sys}, F_{QM}^{QM} and F_{MM}^{QM} are the MM force of the total system, the QM force in the QM region and the MM force in the QM region, respectively. In this respect, the F_{MM}^{QM} term accounts for the coupling between the QM and MM regions.

During the QM/MM simulation, since the interchange of water molecules between the QM and MM regions can take place frequently, the forces acting on each particle in the system are switched according to which region the water molecule is entering or leaving and can be defined as:

$$F_i = S_m(r)F_{QM} + (1-S_m(r))F_{MM}, \tag{3}$$

where F_{QM} and F_{MM} are the quantum mechanical and molecular mechanical forces, respectively. $S_m(r)$ is a smoothing function [44],

$$\begin{aligned} S_m(r) &= 1, & \text{for } r \leq r_0, \\ S_m(r) &= \frac{\left(r_1^2-r^2\right)^2\left(r_1^2+2r^2-3r_0^2\right)}{\left(r_1^2-r_0^2\right)^3}, & \text{for } r_0 < r \leq r_1, \\ S_m(r) &= 0, & \text{for } r > r_1, \end{aligned} \tag{4}$$

where r_0 and r_1 are the distances characterizing the start and the end of the QM region, respectively, and applied within an interval of 0.2 Å (i.e., between the distances of the central H_2O's oxygen and the oxygen atoms of the surrounding waters of 4.0 – 4.2 Å) to ensure a continuous change of forces at the transition between the QM and MM regions.

2.2. ONIOM-XS MD

Based on the ONIOM-XS method [39,40], the system is comprised of a "high-level" QM region, i.e., a sphere which contains the central H_2O and its nearest-neighbor waters, and the remaining "low-level" MM bulk waters. A thin switching shell located between the QM and MM regions is employed to detect the exchanging particles and help in smoothing the energy and forces of the combined system. 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 $N = n_1 + l + n_2$ as the total number of particles, the potential energy of the system can be written in two ways based on the ONIOM extrapolation scheme [45]. If the switching layer is included into the high-level QM sphere, the energy expression is written as

$$E^{ONIOM}(n_1 + l; N) = E^{QM}(n_1 + l) - E^{MM}(n_1 + l) + E^{MM}(N). \tag{5}$$