Dynamics of vibrational spectral diffusion in water: Effects of dispersion interactions, temperature, density, system size and fictitious orbital mass

Anwesa Karmakar[1], Amalendu Chandra*

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

ARTICLE INFO

ABSTRACT

We have carried out a series of *ab initio* molecular dynamics simulations to investigate the effects of dispersion interactions, temperature, density, system size and fictitious orbital mass on the dynamics of vibrational spectral diffusion and other dynamical properties of liquid water. While most of the simulations are performed at room temperature, the effects of temperature are looked at by carrying out additional simulations at 25 K above the reported melting point of *ab initio* water for our chosen density functionals. Apart from the dynamical properties, we have also looked at some of the equilibrium properties such as structure, frequency distributions and frequency-structure correlations for all the systems. In general, it is found that the inclusion of dispersion interactions makes the dynamics faster. The effects of system size, orbital mass and temperature are also discussed for the systems considered here.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Vibrational frequencies of water molecules in liquid water are known to be sensitive to its surrounding environment. In particular, the stretch frequency of a water molecule fluctuates rather strongly with fluctuations in the local environment such as breaking and reformation of hydrogen bonds. Studies of time dependence of these frequency fluctuations, the so-called vibrational spectral diffusion, within the stretch band of water have proved to be a very powerful means to unearth the molecular dynamics in aqueous medium [1–4]. Such studies have been a topic of tremendous interest in recent years from both experimental [1–19] and theoretical [20–33] points of view. On the theoretical side, most of the existing *ab initio* simulation studies of vibrational spectral diffusion in liquid water have used the well-known BLYP [34] functional. It was found that this functional produces a slower dynamics for some of the long-time dynamical properties such as diffusion and orientational relaxation [30,35-41]. Subsequently, it has been shown that the inclusion of dispersion interactions can significantly improve the phase diagram, equilibrium density, structure and also dynamical properties of water [42–47] compared to those given by the corresponding functional without any dispersion corrections. It is also known that

system size, density and temperature are important parameters for molecular simulations. Besides, the fictitious orbital mass plays an important role in *ab initio* molecular dynamics simulations using the Car-Parrinello method [48]. Earlier studies have looked at the roles of the orbital mass in correct evaluation of the atomic forces and the atom-atom structures of liquid water [49,50]. Clearly, the correct choice of the fictitious mass parameter is important in maintaining adiabaticity during the Car-Parrinello simulations. Besides, how various dynamical properties, especially the vibrational spectral diffusion in the current context, are affected by the choices of system size, density and temperature are also important issues worth looking at. The present study makes a contribution toward this end. The purpose of the present study is to investigate the effects of dispersion interactions, temperature, density, system size and fictitious mass of electronic orbitals on the vibrational spectral diffusion and other related dynamical properties and also to compare our results with available experimental and other simulation results wherever possible.

In the present study, we have performed Car-Parrinello molecular dynamics simulations [48] of liquid water at varying temperature using BLYP and also its dispersion corrected variant, namely the BLYP-D functional. In the BLYP-D functional, the dispersion interactions are incorporated by using the D2 scheme of Grimme [51,52]. We have performed simulations at the room temperature of 298 K and also at a temperature of 25 K above the previously reported melting temperature (T_m) of *ab initio* water for BLYP and BLYP-D functionals to see the effect of temperature. We note that such a study of water at $T_m + 25K$ was performed earlier for investigations

---

* Corresponding author.
E-mail address: amalen@iitk.ac.in (A. Chandra).
[1] Present address: Physics and Chemistry of Materials, Theoretical Division (T-1), Los Alamos National Laboratory, NM 87545, USA.

of structure and diffusion [44]. It may also be noted that a recent study by DiStasio et al. [53] also looked at the dispersion effects on structural and dipolar properties of water using a different density functional. The temperature of the simulation system was raised by 30 K to take into account approximately the nuclear quantum effects. Their results clearly showed the importance of the collective influence of exact exchange, dispersion interaction and choice of temperature on the equilibrium properties of liquid water.

Here we have extended such studies further to look at spectral diffusion, hydrogen bond dynamics and other dynamical properties such as rotational diffusion. Earlier studies have shown that the equilibrium liquid density of water at 298 K and 1 bar pressure is about 0.8 g cm^{-3} for the BLYP functional [46]. This can be brought closer to the experimental liquid density of 1 g cm^{-3} upon inclusion of dispersion corrections in the density functional. It has also been found from recent *ab initio* simulation studies [44] that inclusion of dispersion interaction improves both the melting temperature and density of liquid water at room temperature and 1 bar pressure. Here, we have run simulations for different system sizes (32 and 108 water molecules) using the BLYP-D functional and, to see the effects of orbital mass on the dynamics, we ran simulations for bigger system with two different values of the fictitious orbital mass (400 and 800 a.u.) for the BLYP-D functional. In all cases, we have calculated the dynamical properties and have compared our results with some of the existing simulation and experimental results. The main purpose of the present study was to study the effects of dispersion interactions, temperature, density, system size and fictitious mass of electronic orbitals on the structural and dynamical properties, in particular the vibrational spectral diffusion, of liquid water. Calculations for the effects of dispersion interaction and temperature are carried out for a particular system size (32 water molecules). For these simulations, both BLYP and BLYP-D functionals are considered at different temperatures of 298 K and $T_m + 25$ K where T_m is the melting point of the *ab initio* water which is taken from the results reported in previous studies [44]. Also, we have looked at the effect of density on the vibrational spectral diffusion of liquid water for the BLYP functional at room temperature.

The rest of the Paper is organized as follows. We have presented the details of simulations and various systems in Section 2. In Section 3, we have described various structural properties. The current results of the frequency-structure correlations are discussed in Section 4. In Section 5, we have presented the current results of vibrational spectral diffusion and hydrogen bond dynamics. The results of orientational relaxation and diffusion are discussed in Section 6. Finally, our conclusions are briefly summarized in Section 7.

2. Computational details

We have carried out a series of *ab initio* molecular dynamics simulations of water using the Car-Parrinello method [48,54] and the CPMD code [55] for varying system size, density, temperature and fictitious orbital mass. We have used both BLYP [34] and dispersion corrected BLYP-D functionals [51,52]. Here we have used the damped atom-pairwise dispersion correction of the C_6r^{-6} form to include the dispersion interactions in the system where r represents the distance between two atoms and C_6 is the prefactor that determines the strength of dispersion interaction. This is the Grimme-D2 version [51,52] of dispersion correction scheme where three body interactions are not taken into account. The effect of dispersion interaction were studied only at ambient condition and to see the effect of temperature, we have carried out simulations at 25 K above the calculated melting temperatures. Since the calculated melting points of both BLYP and BLYP-D water have been found to be significantly higher than that of experimental water, theoretical results at 298 K

may not be directly comparable with those of experiments at the same temperature. Hence, in addition to looking at the effects of dispersion interactions at room temperature, we have also investigated the dynamics at 25 K above the calculated melting temperatures. The details of the functional and temperature of the seven systems, which are marked as Systems 1–7, are included in Table 1. The length of the cubic box for each simulation system was 9.8652 Å for 32 and 14.782 Å for 108 liquid water molecules. These box lengths are determined from the experimental density of water at room temperature [56]. Periodic boundary condition was applied in all three dimensions and the quantum electronic structure of the simulation system was treated by the Kohn-Sham (KS) [57] formulation of density functional theory. A plane wave basis with a cut-off of 80 Ry was used to represent the KS orbitals and Troullier-Martins [58] pseudopotential was used to treat the core electrons. A fictitious mass of $\mu = 800$ a.u. was given to the electron orbitals and a time step of 5 a.u. (0.125 fs) was used to integrate the equations of motion. For System 4, we have chosen $\mu = 400$ a.u. and time step of 4 a.u. The deuterium mass was used for all the hydrogen atoms to maintain the electronic adiabaticity throughout the simulations. We note, however, that the density of various systems as shown in Table 1 are calculated for normal water with hydrogen mass for convenience. The initial configurations of the simulation systems were prepared through classical molecular dynamics simulations using an empirical potential model of water [59]. Subsequently, each system was equilibrated through *ab initio* molecular dynamics for 15 ps in canonical ensemble and then the simulations were run for each system for another 30–70 ps in microcanonical ensemble for calculations of various equilibrium and dynamical properties. Once the time dependent trajectories were generated, we carried out a time series analysis of the instantaneous OD bond distance and the corresponding momentum along the OD bond of deuterated water molecule to calculate its stretch frequency. We repeated this method for the entire trajectory and for all OD bonds which are there in the present simulation. In particular, we used the wavelet method [60–63] of time series analysis for this purpose. The details of this method have been discussed elsewhere for calculations of fluctuating OD bond frequencies from simulation trajectories [27-30,64,65].

3. Structural properties

We have investigated the effects of dispersion interactions, temperature, density, system size and fictitious mass of electronic orbital on the structural correlations and hydrogen bonding by calculating the oxygen-oxygen and oxygen-hydrogen radial distribution functions for all cases. Also, the average number of hydrogen bonds was calculated for each case by integrating the first peak of the oxygen-hydrogen radial distribution function for all the systems

$$N_{HB} = 4\pi\rho \int_0^{R_c} g_{OH}(r)r^2 \, dr \tag{1}$$

where ρ is the average number density and R_c is the cut-off distance which corresponds to the location of the first minimum of the oxygen-hydrogen correlation.

The results of radial distributions showing the effects of dispersion interactions, temperature and density are included in Fig. 1 for 298 K and $T_m + 25$K for the BLYP and BLYP-D functionals, respectively. The results shown in these figures are for the system size of $N = 32$. At the room temperature, it is seen that the height of the first minimum of the oxygen-oxygen correlation increases slightly with the inclusion of dispersion interactions whereas that of the first minimum of the oxygen-hydrogen correlation remains essentially unchanged. This means a slight enhancement in the number of non-hydrogen-bonded water molecules at the boundary of the