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Dynamics of hydrogen bonds and vibrational spectral diffusion in liquid methanol from first principles simulations with dispersion corrected density functional

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ABSTRACT

The effects of dispersion interactions on the dynamics of hydrogen bonds and vibrational spectral diffusion in liquid methanol are investigated through first principles simulations with a dispersion corrected density functional. Calculations are done at two different temperatures of 300 and 350 K and the results are compared with those of an earlier study where no such dispersion corrections were included. It is found that inclusion of dispersion interactions slightly increases the number of molecules held through non-hydrogen-bonded dispersion interactions in the neighborhood which, in turn, makes the dynamics faster. The inclusion of dispersion corrections gives rise to a faster hydrogen bond dynamics compared to the case when no such dispersion corrections are made. Also, the time scale of vibrational spectral diffusion obtained with the dispersion corrected density functional is found to be in better agreement with experiments.

1. Introduction

In a recent paper [1], we presented an *ab initio* molecular dynamics study of liquid methanol within density functional theory using the well-known BLYP functional [2]. The calculated dynamics of hydrogen bonds and vibrational spectral diffusion [3] in the liquid were found to be slower than the experimentally reported results at room temperature [4]. A somewhat slower dynamics of vibrational spectral diffusion was also reported earlier for liquid water with the same BLYP functional [5,6]. The extent of slowing down of molecular motion was found to be even stronger for the long-time diffusion and orientational relaxation processes in water calculated with the BLYP or other similar functionals belonging to the class of generalized gradient approximation (GGA) [7–14]. In recent years, a number of first principles studies on liquid water have concluded that the calculated slower dynamics of water with BLYP and other similar functionals arise, at least in part, from the fact that these functionals do not capture the dispersion interactions properly [15–17]. In fact, there have been a number of studies on water and also methanol in recent years which have shown the importance of incorporating dispersion interactions in describing the liquid structure and dynamics of these liquids correctly [15–20]. For water, these studies have shown that the dispersion-corrected BLYP functional significantly improves the phase diagram, structure and dynamics of the liquid when compared with the corresponding results obtained with the pure dispersion uncorrected BLYP functional [15–18]. Similar studies on methanol have also been carried out for the phase diagram and structure [19,20] and the general conclusion has been that, for methanol also, the dispersion interactions provide improved results for the thermodynamic and structural properties. In this work, we look at the effects of dispersion interactions on the dynamics of liquid methanol through first principles simulations.

In the present study, we have carried out *ab initio* molecular dynamics simulations of liquid methanol using the dispersion corrected BLYP functional, also known as the BLYP-D functional. In this functional, the dispersion corrections are incorporated to the BLYP functional [2] empirically by using the scheme of Grimme [21,22]. The simulations have been carried out at two different temperatures of 300 and 350 K. Thus, by comparing the earlier results of Ref. [1] at 300 K, we could examine the significance of dispersion interactions in the dynamics of hydrogen bond and frequency fluctuations and, by comparing the results at 300 and 350 K for the same BLYP-D functional, we could study the temperature effects on such dynamics. The *ab initio* simulations have been carried out using the Car–Parrinello method [23] and the frequency fluctuations have been calculated using the wavelet method [24] of time series analysis. Generally, it is found that the inclusion of dispersion interactions improves the dynamics and produces results which are in closer agreement with experiments [4] than those obtained earlier with the pure BLYP functional [1].

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The rest of the Paper is organized as follows. The details of *ab initio* molecular dynamics are presented in Section 2. In Section 3, we discuss the results of the structure of methanol and also of the hydrogen bonds and vibrational frequencies. The results of the dynamics of hydrogen bond fluctuations and vibrational spectral diffusion are presented in Section 4. Finally, our conclusions are briefly summarized in Section 5.

2. Ab initio molecular dynamics simulations

The *ab initio* molecular dynamics simulations were carried out by using the Car–Parrinello method [23,25] and the CPMD code [26]. Our simulation systems contain 32 deuterated methanol molecules at two different temperatures of 300 and 350 K. The length of the cubic simulation box is 12.9Å which corresponds to the experimental density of methanol at room temperature [27]. The simulation box was replicated periodically in three dimensions and the electronic structure of the extended system was represented by the Kohn–Sham (KS) [28] formulation of quantum density functional theory. The KS orbitals were represented using a plane wave basis. The core electrons were treated through Troullier-Martins [29] pseudopotentials and the plane wave expansion of the KS orbitals were truncated at 70 Ry. A fictitious mass of μ = 800 a.u. was assigned to the electron orbitals and a time step of 5 a.u. (0.125 fs) was used to propagate the system dynamics. All hydrogen atoms were assigned the mass of deuterium to reduce the influence of quantum effects on the dynamical properties. Our choice of CD_3OD in place of CH_3OH ensured that electronic adiabaticity and energy conservation were maintained throughout the simulations for the chosen values of the fictitious electronic mass parameter and time step. Since the main goal of the present work was to look at the effects of dispersion interactions on the dynamics of liquid methanol, we employed the dispersion corrected BLYP-D density functional in our calculations. This functional includes dispersion corrections to the pure BLYP functional [2] as introduced by Grimme [21]. We prepared the initial configurations at both temperatures through classical molecular dynamics simulations. Subsequently, we equilibrated each system through *ab initio* molecular dynamics for 15 ps in canonical ensemble and then ran each system for another 45 ps in microcanonical ensemble for the calculations of various equilibrium and dynamical properties. After the simulation trajectories were generated, we carried out a time series analysis of the coordinates and momenta of OD bonds to calculate their stretch frequencies. Specifically, we have used the wavelet method [24] 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 [1,5,6,30–32].

3. Structure of methanol, hydrogen bonds and vibrational frequencies

We have looked at the effects of dispersion interactions and temperature on the structure of methanol by calculating the radial distribution functions between different pairs of atoms such as oxygen–oxygen, oxygen-hydrogen and carbon–carbon pairs. The results of these correlation functions are shown in Fig.1. It is seen that at 300 K, the inclusion of dispersion interactions slightly increases the height of the first minimum of oxygen–oxygen correlation which means a slight enhancement of the number molecules at the boundary of the neighborhood of hydroxyl group. These molecules are held through weaker non-hydrogen-bonded dispersion interactions. The enhanced dispersion interaction also shifts the first peak of carbon–carbon correlation to a slightly shorter distance. These non-hydrogen-bonded molecules are relatively

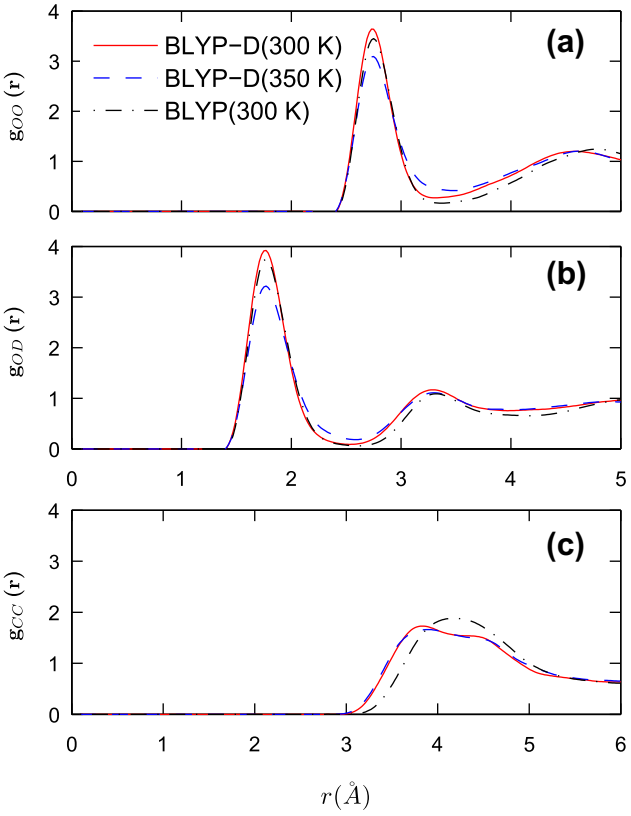

Fig. 1. The atom–atom radial distribution functions of methanol molecules. The plots of (a), (b) and (c) are for oxygen–oxygen, oxygen-hydrogen and carbon–carbon correlations. The solid and dashed curves represent the BLYP-D results at 300 and 350 K. The corresponding results for BLYP functional without dispersion corrections at 300 K, as calculated from the simulation trajectory of Ref. (1), are shown by dashed-dotted curves.

loosely held, hence increase the dynamics as discussed later in Section 4. We note that a similar, rather more pronounced, structural effect was also found for water upon inclusion of dispersion effects [15–18]. We calculated the number of hydrogen bonds per methanol molecule by integrating the corresponding oxygen-hydrogen RDF up to its first minimum. With this geometrical definition of hydrogen bonds, the average number of hydrogen bonds per methanol molecule is found to be 1.9 for BLYP-D at 300 K. The corresponding number for pure BLYP without any dispersion corrections at the same temperature is 1.95. When the temperature is raised to 350 K, peak heights of all the correlations decrease showing a reduction of structure around methanol molecules. The number of hydrogen bonds per molecule is found to be 1.82 at the elevated temperature. We note that a decrease in the hydrogen bond number with increase of temperature was also reported in an earlier *ab initio* Monte Carlo study of liquid methanol [20].

We next discuss the distributions of our calculated stretch frequencies of OD bonds. In particular, we focus on the correlations between the stretch frequencies and the hydrogen bonded structure between molecules. In Fig. 2, we have shown the contour plots of the conditional probability of observing a particular frequency for a given O··D distance for both the systems. It is clear from the contour plots that one can not assign a single instantaneous frequency to a given O··D bond because of the substantial dispersion present in the probability distributions. A comparison between Figs. 2a and 2b reveals that, at the higher temperature, the distribution is more elongated towards the longer distance. The dashed lines in these plots represent the average behavior of stretch frequencies with change of hydrogen bond distance. On average, it