Structure and dynamics of water-CO_2 mixtures at elevated temperatures and pressures: Insights from classical and quantum molecular dynamics.

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Abstract

A combination of classical and Born-Oppenheimer molecular dynamics simulations was used to investigate the thermodynamic, structural and dynamic properties of water-CO_2 mixtures at elevated temperatures and pressures in the range 1073-1973 K and 1-2.2 GPa. The results obtained indicate that weak hydrogen bonding interactions among water and CO_2 molecules still exist at these conditions. Interestingly, although the number of water-water hydrogen bonds decreases with the temperature increase, the CO_2 – water one slightly increases. This effect is more pronounced in the case of the Born-Oppenheimer simulations, which predict stronger CO_2-water and weaker water-water interaction in comparison with the classical simulations.

Graphical Abstract
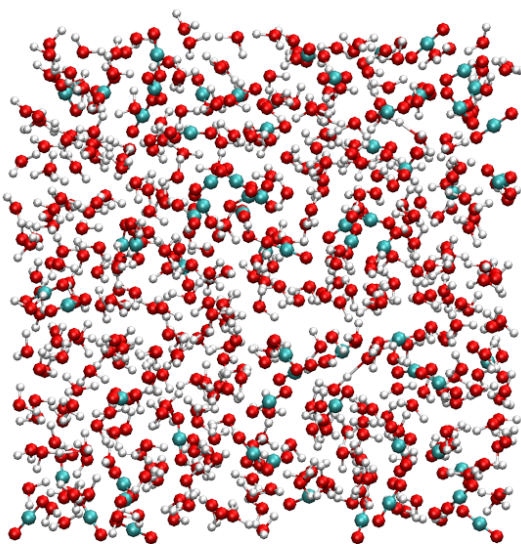
Keywords: Water, Carbon dioxide, mixtures, Born-Oppenheimer, molecular dynamics, supercritical, high temperature, high pressure, hydrogen bonding

Highlights

- The structure of CO_2-water mixtures has been studied at elevated temperatures and pressures.

- Classical and quantum Born-Oppenheimer molecular dynamics simulations have been performed.

- The quantum simulations predict weaker water-water and stronger CO_2-water hydrogen bonding interactions.

- The number of water-water hydrogen bonds decreases upon the increase of the temperature, whereas the CO_2-water one increases.

1. Introduction

The properties of water – carbon dioxide mixtures have attracted the attention of the scientific community due to its crucial role and importance in a wide range of geochemical and environmental processes. Aqueous mixtures of CO_2 are among the most frequently encountered fluid mixtures in and around the Earth, widely existent in various geospheres [1-7]. In general, the investigation of these mixtures can provide a

good approximation for the description of the behavior of most of the Earth's crustal and mantle fluids. Apart from their effect on heat and mass transfer processes, these fluid mixtures play a key role in element fractionation processes in the Earth's lithosphere, such as volcanism and ore deposit formation [8].

In general, most of the experimental studies reported so far for aqueous CO_2 mixtures correspond to thermodynamic conditions in the temperature range 276 - 1000 K and pressure range 1- 600 MPa [9-23] . Only a very small set of data corresponds to higher temperatures and pressures, up to 1673 K and 1.94 GPa [2, 3, 24, 25]. Due to the lack of available experimental data at extreme temperature and pressure conditions, molecular level computer simulation techniques can play a very crucial role toward the extending up to a wide range of temperatures and pressures[1]. However, for the CO_2-water mixture only a few molecular simulation studies have reported up to know and mainly for temperatures much lower than 1000 K [26-35]. Only two classical molecular dynamics (MD) simulations have been reported for higher temperatures and pressures, to the best of our knowledge, focusing on the description of the PVTx properties of the mixtures [1, 35].

Recent studies have underlined the importance of *ab initio* quantum molecular simulations in opening the way to study geochemical processes beyond the reach of current experiments in the Earth's mantle [6-8]. With these methods it is possible to incorporate quantum effects in MD simulations of condensed phase molecular systems by combining finite temperature atomistic MD with internuclear forces obtained from electronic structure calculations performed "on the fly" as the simulation proceeds [36]. For reasons of computational efficiency, the most commonly employed approach to represent the electronic structure and corresponding interactions is based on density functional theory (DFT).

The main aim of the present study is to provide information about the structure of CO_2-water mixtures at high temperatures and pressures by employing ab initio and classical MD simulations. The only available structural study of these mixtures in the literature has been performed at 673 K, using a combination of neutron diffraction and reverse modeling [5]. Therefore, the present study is the first one reported in the literature aiming to provide information about the structure and dynamics of CO_2-water mixtures at temperatures up to 1973 K and pressures higher than 2 GPa.

One of the main characteristics of water and aqueous mixtures, which significantly affects their properties, is the formation of hydrogen bonds [37]. Several studies have revealed that hydrogen bonds in supercritical water exist even at high temperatures and pressures [38-40]. Quite recent neutron diffraction studies, combined with reverse modeling and classical molecular dynamics, suggest also that hydrogen bonding exists at CO_2-water mixtures with low CO_2 concentration at 673 K and 1300 bar [5,41].

The main aim of the present study is therefore to investigate the local structure and corresponding dynamics of CO_2-water mixtures at a low CO_2 concentration at much higher temperatures and pressures by employing classical and DFT-based quantum Born-Oppenheimer molecular dynamics (BOMD) techniques. Particular emphasis has been given to the investigation of the existence or not of hydrogen bonds at these conditions. It is also known that commonly used density functionals do not describe the long-range dispersion interactions accurately and cannot provide the correct radial dependence of the dispersion interatomic interaction energy. Therefore in the present study, two different methods to account for London dispersion forces in the framework of DFT-MD have been used and tested in comparison with a classical force field which provides accurate descriptions of PVTx properties of CO_2-water mixtures up to 2500 K and 10 GPa.

2. Computational Details

A combination of classical and BOMD simulations of a CO_2-water binary mixture with a CO_2 mole fraction X=0.146 at fixed molar volume (22.54 cm^3/mol) was performed in the present study for a series of temperatures in the range 1073-1973 K.

In the case of the classical simulations, ten NVT-MD simulations have been performed starting from a temperature of 1073 K and increasing the temperature value by 100 K each time in the subsequent simulation runs. A cubic box with 427 water and 73 CO_2 molecules was used in each simulation and periodic boundary conditions were also employed. The force fields suggested by Duan and Zhang [1] have been used in the present study to model the interactions between the species in the mixtures. In their study Duan and Zhang predicted the equation of state for CO_2-water mixtures up to 2500 K and 10 GPa, reporting a very good accuracy in comparison with the available PVTx experimental data. The simulated systems were equilibrated

for 5 ns and the system properties were obtained in subsequent 5 ns production runs. The equations of motion were integrated using a leapfrog-type Verlet algorithm and the integration time step was set to 1 fs. A Nose-Hoover thermostat with a temperature relaxation time of 0.5 ps was used to constrain the temperature during the simulations. A cut-off radius of 12.0 Å has been applied for Lennard-Jones and electrostatic interactions and long-range corrections have been also taken into account. The Ewald method has been employed to account for long-range electrostatic interactions.

In the case of the BOMD simulations, six simulations have been performed in total at three different temperatures, 1073, 1373 and 1973 K. A cubic box with 55 water and 9 CO_2 molecules was used in each simulation, employing also periodic boundary conditions. At each simulated state point two different simulations were performed, using two different density functionals in each case. The density functionals employed in the present study were the PBE [42] with the D3 dispersion correction suggested by Grimme et al [43] (PBE+D3) and the non-local van der Waals vdW-DF2 functional [44]. A hybrid Gaussian and plane waves methodology, as implemented in the Quickstep [45] part of the cp2k code [46], was employed in the BOMD simulations. The DZVP-MOLOPT basis set [47] and the Goedecker-Teter-Hutter pseudopotentials [48] were used for the electronic structure calculations. The density cutoff was set to 480 Ry to yield well converged calculations. The simulated systems were initially equilibrated by performing classical molecular dynamics for a period of 10 ns, using the force fields suggested by Duan and Zhang. Afterwards BOMD equilibration run of 4 ps duration were performed. Thermal equilibration in the canonical ensemble was achieved using the CSVR thermostat with a strong coupling. Subsequent 12 ps NVT runs, where the canonical ensemble was sampled using a weaker coupling to the bath, were performed to obtain the properties of the systems. The time step used for the integration of the equations of motion was 0.5 fs, using the Velocity-Verlet algorithm.

3. Results and Discussion

Before calculating the structural properties of the simulated mixtures, the reliability of the used methodologies in predicting the PVT properties of the mixtures was first validated by comparing the calculated pressure of the system at 1373 K with available experimental data. As it can be seen in Figure 1, the pressure obtained by the BOMD

simulations with the PBE+D3 and the vdW-DF2 functionals and by the classical simulation (1.53, 1.51 and 1.57 GPa, respectively) come in good agreement with the experimental value of 1.45 GPa [2] at the molar volume of 22.54 cm^3/mol. Note also that in the case of the classical simulations, test runs performed at several temperatures with 64 and 500 molecules in the simulation box showed that the deviation in the calculated pressures in both cases is in the range of around 2 %. Such a finding indicates that finite system size effects are not strong and BOMD simulations using small simulation boxes and number of molecules can provide reliable estimation of the pressure of the mixtures at these conditions. The dependence of the calculated pressure on the temperature, for this fixed molar volume and composition, has been found to be almost linear, as it can be seen in the Supporting Information (Figure S1). The calculated pressures obtained by classical MD and by BOMD with the use of the PBE+D3 and vdw-DF2 functional are very similar at 1073 and 1373 K; however their differences slightly increase at 1973 K where the classical MD predicts a higher pressure in comparison with the values obtained with the PBE+D3 and vdW-DF2 functionals, respectively.

Note also that during the BOMD simulations no reactions between the molecules in the mixtures were observed. Therefore in this range of thermodynamic conditions and compositions both classical and BOMD simulations can be used to predict the properties of these mixtures. However, at even higher temperatures and pressures the possibility to observe reactions will be increased and these effects can be treated only by the use of ab initio MD methods. The finding that BOMD simulations can provide reliable descriptions of PVT properties of CO_2-water mixtures even for small system sizes indicates that such kind of simulations might be used in order to predict PVTx equations of state at more extreme conditions.

The intermolecular structure of the simulated systems was investigated in terms of calculating the appropriate atom-atom pair radial distribution functions (RDF). Some representative atom-atom RDF for water-water and CO_2-water pairs at 1373 K are presented in Figure 1. By inspecting this figure it can be observed that in the case of the O_w-H_w RDF (the w subscript denotes the water molecules) the typical first peak observed at about 2.4 Å, which is a characteristic of liquid and supercritical water, has shrunk and has been replaced by a shoulder. This behavior is a clear indication of the weakening of hydrogen bonding (HB) interactions between the water molecules at the

investigated thermodynamic conditions. Interestingly, this shoulder is more pronounced in the case of the classical MD simulation, signifying that the classical force field favors the interaction between the water molecules in comparison with the DFT-based MD simulations. This finding is further supported by the shape of the calculated O_w-O_w RDF, whose first peak calculated intensity is higher in the case of the classical force field. In the case of the BOMD simulations, the shoulder in the O_w-H_w RDF predicted by the PBE+D3 functional is slightly more pronounced in comparison with the one obtained by the vdW-DF2 functional, indicating that the vdw-DF2 predicts a slightly weaker HB interaction between the water molecules.

In the case of the O_c-H_w (the c subscript denotes the carbon dioxide molecules) and C-O_w RDF the BOMD simulations predict that the first non-zero values of the RDF are observed at smaller distances in comparison with the classical simulation. This is an indication that, in contrast with the water-water interactions, the BOMD simulations favor CO_2-water interactions in comparison with classical MD. The peaks of the O_c-H_w and C-O_w RDF are also lower in comparison with the corresponding O_w-H_w and O_w -O_w ones, in all simulations, signifying that water-water hydrogen bonds are more pronounced in comparison with the CO_2-water ones.

Regarding the temperature dependence of the intermolecular structure in the mixture, temperature effects are more pronounced in the case of the water-water pair correlations. In Figure 2 the temperature dependence of the calculated O_w-H_w RDF is presented. From this figure it can be seen that as the temperature increases the shoulder observed in the O_w-H_w RDF at the distance range around 2.0-2.4 Å starts to shrink and disappear. On the other hand, regarding the temperature effect on the shape and behavior of the O_c-H_w RDF, the main feature observed as the temperatures increases is that in the case of the BOMD simulations the first non-zero values of the RDFs shift to lower distances at higher temperatures (Figure 3). This effect is not observed in the classical MD simulations, indicating thus the importance of using quantum simulations at higher temperatures in order to model the interactions between CO_2 and water molecules. At even higher temperatures it is very likely that CO_2 and water molecules will approach each other even more closely and after a temperature range chemical reactions will start taking place. In the investigated temperature and pressure range no reactions have been observed, but the shift observed for the first non-zero values of the O_c-H_w RDF indicates that at the highest

temperature studied we approach the limit where the CO_2-water system at this particular volume and composition will become reactive.

To provide a quantitative description of HB interactions in the mixtures studied, standard geometric criteria [49, 50] were employed in order to estimate the average number of water-water and CO_2-water hydrogen bonds per water and CO_2 molecules, as well as the corresponding hydrogen bond statistics. According to this criteria a hydrogen bond between two water molecules exists if the interatomic distances are such that $R_{O...O} \leq 3.6$ Å, $R_{H...O} \leq 2.4$ Å and the donor-acceptor angle H-O...O $\leq 30°$ (the symbol ... corresponds to intermolecular distances). Similarly a hydrogen bond between a CO_2 and a water molecule exists if the interatomic distances are such that $R_{Oc...Ow} \leq 3.6$ Å, $R_{Oc...H} \leq 2.6$ Å and the donor-acceptor angle H-O_w...O_c $\leq 30°$.

Using these geometric criteria, the fractions of molecules forming from 0-4 hydrogen bonds, as well as the average number of hydrogen bonds formed per water and CO_2 molecules were calculated and are presented in Figures 4, 5. From these figures in can be seen that in the case of water-water hydrogen bonds, the temperature increase mainly affects the fraction of molecules forming 2-4 bonds, as well as the fraction of the HB-free molecules in all cases (Figure 4). The increase of the fraction of HB-free molecules combined with the decrease of the fractions of molecules forming 2-4 bonds is the main reason for the decrease of the average number of water—water hydrogen bonds per water molecules (Figure 5). The fraction of water molecules forming one hydrogen bond with a water neighbor molecule is not very strongly affected by the increase of the temperature in all cases. When comparing the values obtained by the classical force field and by BOMD using the PBE+D3 and vdW-DF2 functionals, the average number of hydrogen bonds and the fractions of molecules forming 1-4 bonds are higher in the case of the classical MD and the lowest values are obtained when using the vdW-DF2 functional. This finding is a quantitative verification of our previous finding, based upon the behavior of the calculated RDFs, that indeed the vdW-DF2 functional predicts weaker HB interactions between the water molecules in comparison with PBE+D3 and the classical force field.

On the other hand, in the case of the CO_2-water hydrogen bonds the temperature dependence of the fraction of CO_2 molecules forming 1-3 hydrogen bonds and of the average number of hydrogen bonds formed per CO_2 molecule is the opposite, with

these values slightly increasing with the temperature increase (Figures 5,6). This effect is more pronounced in the case of the BOMD simulations, especially when using the vdw-DF2 functional. This observation comes also in agreement with the behavior of the calculated O_c-H_w RDFs and further validates our previous statement that at higher temperatures CO_2 and water molecules approach each other even more closely. The fact that the values obtained by BOMD are higher than the ones obtained by classical MD signifies the importance of using first principles MD at temperatures even higher than the ones investigated in the present, where the possibility to observe chemical reactions between water and CO_2 molecules will be significantly increased.

Apart from the static description of the hydrogen bonds formed in the investigated mixtures, the dynamics of the water-water and CO_2-water hydrogen bonds have been investigated in terms of the intermittent HB time correlation functions:

$$C_{HB}(t) = \frac{\left\langle h_{ij}(0) \cdot h_{ij}(t) \right\rangle}{\left\langle h_{ij}(0)^2 \right\rangle} \tag{1}$$

The corresponding intermittent HB lifetime is defined as:

$$\tau_{HB} = \int_0^\infty C_{HB}(t) \cdot dt \tag{2}$$

The variable h_{ij} has been defined in the following way:

a) $h_{ij}(t) = 1$, if molecule j is hydrogen bonded with molecule i at times 0 and t

b) $h_{ij}(t) = 0$, otherwise

The calculated intermittent HB time correlation functions obtained by the classical simulations at 1073 K and 1973 K are presented in the Supporting Information (Figure S2). The intermittent water-water HB time correlation functions calculated with the classical force fields and the PBE+D3 functional decay slightly slower in comparison with the ones calculated with vdW-DF2 functional; however these differences become almost negligible at the highest temperature studied (1973 K).

These results further verify our previous statements that the vdw-DF2 functional predicts weaker HB interactions between the water molecules in comparison with PBE+D3 and the classical force field. The calculated intermittent HB lifetimes at 1073 K are 0.22 ps in the case of the classical force fields and the PBE+D3 functional and 0.17 ps for the vdW-DF2 one. These values are about 50% lower in comparison with the HB intermittent lifetimes calculated for pure supercritical water very close to its critical temperature and comparable densities [50]. At 1973 K the corresponding lifetimes for the classical force fields, the PBE+D3 and vdW-DF2 functional are 0.11, 0.10 and 0.09 ps, respectively.

In the case of the CO_2-water hydrogen bonds the decay of the intermittent HB time correlation functions is much faster in comparison with the ones corresponding to the water-water hydrogen bonds. Note also that the differences in the time decay of the calculated time correlation functions for the classical and first principles simulations are very small, giving also very similar values for the intermittent CO_2-water HB lifetime. The values obtained at 1073 K for the classical force fields, the PBE+D3 and vdw-DF2 functional are 0.08, 0.07 and 0.07 ps, respectively. The temperature dependence on these very fast dynamics is not strong at all. The lifetimes obtained by the classical force fields and the PBE functional are the same at 1973 K. Interestingly, a small increase of the lifetime is observed in the case of the vdW-DF2 functional, where the calculated value at 1973 is 0.09 ps, equal to the value obtained by this functional for the water-water hydrogen bonds. However, this finding is in accordance with the conclusions drawn from the structural data, where in the case of the vdW-DF2 functional it has been found that at higher temperatures CO_2 and water molecules approach each other more closely to each other.

4. Conclusions

In the present study, classical and *ab initio* (DFT-based) BOMD simulations have been employed to study the structure and related dynamics in carbon dioxide-water mixtures, with CO_2 mole fraction $X_{CO2}=0.146$, at elevated temperatures and pressures, in the range of 1073-1973 K and about 1.1-2.2 GPa. The *ab initio* MD simulations have also confirmed the absence of chemical reactions between the molecules in the mixture at the investigated range of thermodynamic conditions and have provided very reasonable descriptions of the thermodynamic properties of the mixtures.

The results obtained indicate that weak hydrogen bonding interactions among water and CO_2 molecules still exist at these conditions. Interestingly, although the number of water-water hydrogen bonds decreases with the temperature increase, the CO_2 – water one slightly increases. This effect is more pronounced in the case of the *ab initio* MD simulations, which predict stronger CO_2-water and weaker water-water interaction in comparison with the classical simulations. In the case of the *ab initio* MD simulations, two different density functionals were compared; the PBE with the D3 dispersion correction (PBE+D3) and the non-local van der Waals vdW-DF2 functional. The results obtained have also revealed that the vdW-DF2 functional predicts weaker water-water HB interactions and stronger CO_2-water ones in comparison with the PBE+D3 functional. The investigation of the corresponding HB dynamics has further verified the conclusions drawn from the structural data, predicting also a decrease in the calculated HB lifetimes in comparison with previous values reported for supercritical water close to its critical temperature.

The results and trends observed in the present study have confirmed that the methodologies employed in the present *ab initio* MD simulations can be used to model supercritical CO_2-water mixtures at elevated temperatures and pressures. Therefore these methods could be used in future studies to predict the mixture properties at even more extreme conditions, in order to study and interpret several geochemical processes taking place in the Earth's crust and mantle.

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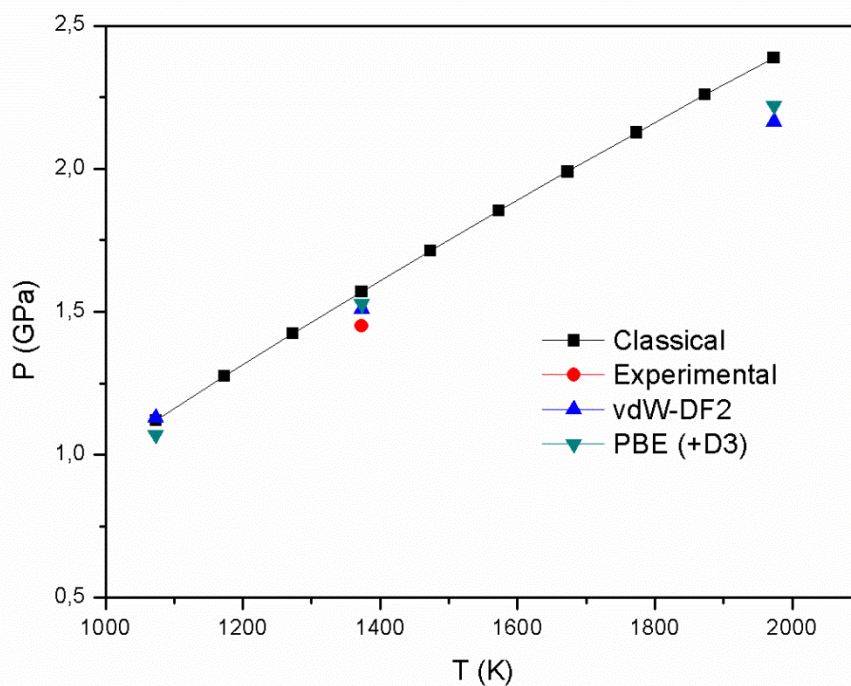
Supporting Information

Figure S1: Calculated pressure at the simulated state points, obtained by the classical and Born-Oppenheimer molecular dynamics methods. Comparison with available experimental data is provided at 1373 K.
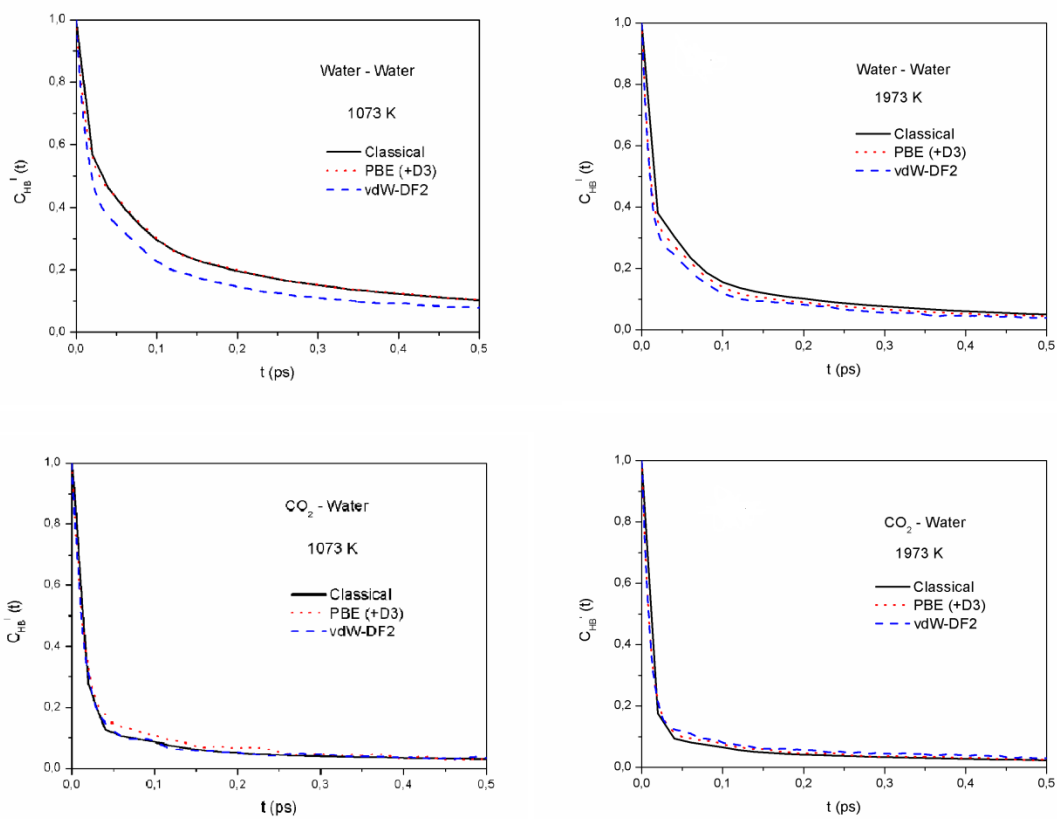
Figure S2: Calculated intermittent hydrogen bonding time correlation functions for water-water and CO_2-water hydrogen bonds at 1073 K and 1973 K.