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Formaldehyde-mediated spectroscopic properties of heavy water from first principles simulation

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*Water shows incredible ability to form a rich variety of hydrogen bonded structure when encountered atmospheric solute. We have presented a first-principle Born-Oppenheimer molecular dynamics simulation for deuterated formaldehyde-water ($D_2CO - D_2O$) system with dispersion corrected density functional (BLYP-D3). We explicitly focus on the relaxation and spectroscopy associated with the CO mode of D_2CO and its interaction with surrounding water molecules through deuterated-hydrogen bonding. Our study enables us to compare and contrast our findings with earlier calculations on formaldehyde in water, and thereby explore the effect of solvent on the structural and dynamical properties of the solute. Inside the first solvation shell of deuterated formaldehyde, we find that the higher frequency of OD modes of water is a result of weak interaction. The frequency fluctuations of the CO mode of solute and OD modes of the solvent water are also investigated. Our calculation with the inclusion of dispersion correction in density functional produces much better results compared with the earlier *ab initio* approach [Mugnai et al., Mol. Phys. 105, 2203-2210 (2007)].*

1 Introduction

Formaldehyde is a class of most abundant carbonyl compounds found in the atmosphere and is involved in various atmospheric chemical processes due to its higher solubility in water¹⁻⁵. The chemical composition of formaldehyde contains both the hydrophobic methylene (CH_2) and hydrophilic carbonyl (CO) groups and the latter group appears frequently in peptides and proteins. Theoretical calculations have revealed that an HCHO molecule forms hydrogen bonds with maximum two water molecules in the water-rich region⁶. The characteristics of these hydrogen bonds greatly influence the energetics, dynamics and vibrational features of both HCHO and water molecules. Explicitly, the solvation dynamics of small organic solute at the microscopic level through *ab initio* molecular dynamics attracted significant interest in providing the solute-solvent structure and dynamics around the solute molecule⁷⁻⁹.

Earlier classical molecular dynamics simulations (Using MCY potential for the water-water and 12-6-1 potential for formaldehyde-water interaction) have been performed for an infinitely dilute solution of formaldehyde in water^{10,11} and reported that the presence of formaldehyde enhances the 'cage effect' in the structure of the solvent. In addition, they also observed strong interaction between the solute and solvent molecules, which was shown to hinder the translational and rotational degree of freedom of formaldehyde. Blair¹² and coworkers reported well-defined solvation structure around the oxygen atom of formaldehyde which gets disrupted in the excited state^{13,14}. Through classical approach, the formaldehyde electronic vertical excitation in water has been reproduced at normal to ele-

vated temperature by introducing the perturbed matrix method (PMM)¹⁵ providing a rather accurate prediction when compared to the experimental data. In general, polar solvents like water induces high energy shift in the $S_0 \rightarrow S_1$ transition state of the carbonyl containing molecules¹⁶ and this transition induces the blue shift in energies and leads to the weakening of hydrogen bonding between carbonyl oxygen and hydrogen atoms of water. This high energy shift is more pronounced in formaldehyde compared with larger solute like acetone^{17,18}. Different level of the theory (Monte Carlo, QM/MM method with CC/MM model, mixed quantum-classical methods based on the dielectric continuum DC model) has been reported and employed to understand this blue shift of the electronic transition for formaldehyde-water system¹⁹. Solvent induced structural and electronic properties of formaldehyde²⁰ have also been explored by using the electronic absorption spectra calculation at ambient conditions. Low-temperature molecular dynamics (200-273 K) was performed to study the diffusion mechanisms of formaldehyde in ice at the molecular level at atmospheric pressure.²¹ Mugnai and coworkers²² performed *ab initio* molecular dynamics simulations on the formaldehyde-water system at room temperature and explained the solvation shell dynamics. Their calculation reveals a hydrogen bond lifetime of 3 ps between formaldehyde and water.

We have organized the rest of the paper as follows. In Simulations details, we provide the detailed explanation of the methodology employed for the present study. In Results and Discussion, the information on the structural and dynamical features associated with the solvation shell and bulk water molecules have been described under sub-section "Structural and Dynamical Properties". In sub-sections "Spectroscopic Properties" and "Electronic Structure of the Aqueous Formaldehyde", we discussed the spectroscopic and electronic properties associated with formaldehyde and water, respectively. We conclude the paper in the last section with a brief summary of the main results of the current study.

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