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# Structural and Dynamical Properties of $H_2O$ and $D_2O$ under Confinement

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## Structural and Dynamical Properties of $H_2O$ and $D_2O$ under Confinement

by Chenxing Liang

## Report

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# Dedication

To my family for their unconditional trust, support and love.

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#### Abstract

## Structural and Dynamical Properties of $H_2O$ and $D_2O$ under Confinement

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Water  $(H_2O)$  is of great societal importance and there has been a significant amount of research on its fundamental properties and related physical phenomena. Deuterium dioxide  $(D_2O)$ , known as heavy water, also draws much interest as an important medium for medical imaging, nuclear reactors, etc. Although many experimental studies on the fundamental properties of  $H_2O$  and  $D_2O$  have been conducted, they have been primarily limited to understanding the differences between  $H_2O$  and  $D_2O$  in the bulk state. In this report, using path integral molecular dynamics simulations, the structural and dynamical properties of  $H_2O$  and  $D_2O$  in bulk and under nanoscale confinement in a (14,0) carbon nanotube are studied. We find that in bulk, the dipole moment of  $D_2O$  tends to be 4% higher than that of  $H_2O$  and the hydrogen bonding of  $D_2O$  is also stronger than  $H_2O$ . Under nanoscale confinement in a (14,0) carbon nanotube,  $H_2O$  and  $D_2O$  exhibit a smaller bond length and bond angle. The hydrogen bond number decreases, which demonstrates weakened hydrogen bond interaction. Moreover, confinement results in a lower libration frequency, and higher OH(OD) bond stretching frequency with an almost unchanged HOH(DOD) bending frequency. The  $D_2O$ -filled (14,0) carbon nanotube is found to have a smaller radial breathing mode than the  $H_2O$ -filled (14,0) carbon nanotube.

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## Chapter 1: Introduction

#### 1.1 Motivation of Study

Water (H<sub>2</sub>O) is one of the most important molecules in the world. Despite its simple structure, it has many interesting properties such as, for example, the density maximum at 4 °C. [1] The existence of many unique properties of water (H<sub>2</sub>O) is due to the hydrogen bonds (HBs) arising from intermolecular interactions. [2] Because of its importance, numerous experimental and theoretical investigations have been performed over many decades to understand the physical and chemical properties of water. Deuterium oxide (D<sub>2</sub>O), known as heavy water, also draws interest due to its distinct physical and chemical properties, including higher density, higher viscosity, and higher phase transition temperature compared to H<sub>2</sub>O, [3] and its use in versatile applications, including heavy water nuclear reactors, [4] nuclear magnetic resonance spectroscopy, [5] and in the preparation of isotopologues of organic compounds. [6] Thus, there is a great interest in studying the differences between H<sub>2</sub>O and D<sub>2</sub>O especially under confinement.

 $H_2O$  and  $D_2O$  in the bulk state have been widely explored by various experimental methods. Soper et al. [7] investigated the quantum differences between  $H_2O$ and  $D_2O$  using a combination of X-ray diffraction and neutron diffraction and found that  $D_2O$  is a more structured liquid than  $H_2O$ . Tomberli et al. [8] used high-energy electromagnetic radiation scattering to measure the structure of  $H_2O$  and  $D_2O$  and similarly found that heavy water is slightly more ordered than  $H_2O$ . The isotope effect on the local structure of liquid water at room temperature was studied by Bergmann et al. [9] using X-ray Raman spectroscopy and found that  $H_2O$  exhibits a more symmetric hydrogen bonded network. Moreover, there are many numerical simulation studies on  $H_2O$  and  $D_2O$ . Effective models for heavy water in classical molecular dynamics were reported to accurately reproduce its properties. [10, 11] Density functional theory-based molecular dynamics has also been used to study the fundamental properties of water. Lin et al. [12] studied the structure and dynamics of liquid water from ab initio molecular dynamics using BLYP, PBE, and revPBE functions. Zheng et al. [13] utilized SCAN functional-based ab initio molecular dynamics to compute structural, electronic, and dynamical properties of liquid water. By performing first principles path integral simulations of light and heavy water, Machida et al. [14] concluded that the OH bonds can more easily dissociate than OD bonds because of nuclear quantum effects.

Water under nanoscale confinement has been an important research topic because of versatile nanoscale confined environments, including biology, geology, and environmental science, such as biological channels, [15] swelling of clay materials, [16] and novel membranes for water desalination. [17] Moreover, novel physical phenomena of confined water, e.g., high water transport rate through carbon nanotubes attract great interest. [18] Among all types of nanoscale water confinement systems, water-filled carbon nanotubes have been studied experimentally and theoretically to investigate fundamental confined water properties. [19, 20] In this regard, an investigation of the confinement effect on  $H_2O$  and  $D_2O$  and their comparison is required to unveil the differences in fundamental properties.

There have been some investigations on  $D_2O$  when it is under confinement. Sharma et al. conducted a study using first principle calculations to determine the infrared (IR) spectra of  $D_2O$  confined between nonpolar surfaces. [21] Their findings suggested that the frequency shift observed originates from the structure of the hydrogen bonds. Similarly, Cicero et al. [22] conducted a study on the diffusion and hydrogen bonding (HB) of  $D_2O$  under confinement, while Rozsa et al. [23] explored the effects of nanoscale confinement on the structural and dielectric properties of H<sub>2</sub>O using ab initio molecular dynamic simulation. However, there has been no investigation on comparison of H<sub>2</sub>O and D<sub>2</sub>O under nanoscale confinement.

#### **1.2** Path Intergral Molecular Dynamics

Density functional theory (DFT)-based ab initio molecular dynamics (AIMD) simulation has been used as a reliable approach to study physical phenomena in various applications. [24] In AIMD simulations of liquid water, the generalized gradient approximation (GGA) exchange-correlation (XC) functionals are most widely used even though minor inaccuracies have been shown, for example, in the self-interaction error. [25] Although methods based on hybrid XC functions [26] improve the accuracy, these methods are computationally very intensive. [27] GGA is still used to simulate water in this work due to the trade-off between accuracy and computational resources. [24] The properties of water are influenced by nuclear quantum effects (NQEs), such as zero-point energy (ZPE) and tunneling, which arise due to the low mass of the proton and the central role of hydrogen bonding. [28] Despite this, classical first principles molecular dynamics (MD) simulations assume that atoms (nuclei) are classical particles that follow classical statistics, and therefore do not account for the effects of NQEs on thermodynamic properties. [14] However, experimental evidence has shown that isotopic substitution can affect thermodynamic properties, indicating that the classical particle assumption is flawed. [29] Although the Born-Oppenheimer approximation can accurately describe the potential energy of the electronic ground state, NQEs play a crucial role in distinguishing the properties of light and heavy water. Path integral molecular dynamics (PIMD) is a commonly used approach to incorporate nuclear quantum effects (NQEs) into simulations. [30] This method is based on Feynman's imaginary-time path integral formulation of quantum statistical mechanics, which enables the treatment of both the nuclei and electrons involved in electronic structure calculations in a quantum-mechanical manner. [31] The second-order Suzuki-Trotter expansion is utilized to establish an isomorphism between the quantum statistics of a particle and the classical statistics of a ring polymer coupled by harmonic springs. [32] The PIMD approach can be extended to first principles by combining it with electronic structure calculations, which allows for the comprehensive treatment of both the nuclei and electrons based on all-electron calculations.[33, 34]

#### **1.3 Report Overview**

In this report, the structural and dynamical properties of  $H_2O$  and  $D_2O$  confined in the (14,0) carbon nanotube are systematically studied using the GGA approximation in PIMD simulations. We study the structural properties of  $H_2O$  and  $D_2O$ , including the bond angles, bond lengths, radial distribution functions, number and length of hydrogen bonds, dipole moments, and the differences in dynamical properties, including the vibrational frequencies, diffusion coefficients, and the radial breathing mode of water filled (14,0) carbon nanotube. The PIMD simulation results are also compared with AIMD simulation results to show the nuclear quantum effects on the structural and dynamical properties of  $H_2O$  and  $D_2O$ . The majority of the contents in this report are from my publication. [35]

Chapter 2 describes the system geometry and computational modeling process in detail.

In Chapter 3, we delve into various properties of interest. These encompass bond angles, bond lengths, radial distribution functions, hydrogen bond count and length, dipole moments, vibrational frequencies, diffusion coefficients, and the radial breathing mode of water within a (14,0) carbon nanotube. Each property's significance and its computation through PIMD simulation are succinctly outlined. Additionally, a comparison is drawn between  $H_2O$  and  $D_2O$  in both bulk and confined states. This is followed by an in-depth discussion of the comparison, offering insights into the dissimilarities and thereby enhancing our comprehension of the core attributes of  $H_2O$  and  $D_2O$ .

Lastly, Chapter 4 provides a conclusion and summarizes the impact of nuclear quantum effects on the fundamental properties of  $H_2O$  and  $D_2O$ .

## Chapter 2: System Modeling and Simulation

#### 2.1 Parameter Settings and geometry modeling

To study the difference in fundamental properties of H<sub>2</sub>O and D<sub>2</sub>O in bulk and under confinement, ab initio path integral molecular dynamics (PIMD) simulations were conducted using the CP2K (version 2022.1) package [36] based on density functional theory. [37] Perdew-Burke-Ernzerhof (PBE) [38] exchange correlation functional and the Goedecker-Teter-Hutter (GTH) pseudopotentials [39] were used. The energy cutoff was 500 Ry and Dispersion corrections were accounted for by Grimme's third-generation corrections DFT-D3. [40] The wave function was optimized by the orbital transformation (OT) method with a convergence criterion of  $1 \times 10^{-6}$  a.u. The PINT module in CP2K is used to perform the PIMD simulation. In all the PIMD simulations, an imaginary time slice of the second-order Suzuki-Trotter expansion (the number of beads) of P = 16 was employed. [14] According to Poltavsky et al., the beads number need to be larger than 12 to get the converged structural properties of liquid water using PIMD simulation. [41] The time step for PIMD simulations is set to be 0.5 fs and the temperature was maintained at 300 K.

The unit cell is composed of  $32 \text{ H}_2O(D_2O)$  molecules with the same dimensions in the x-, y-, and z-directions of 9.97 Å. Geometry of the bulk H<sub>2</sub>O(D<sub>2</sub>O) is shown in Figure 2.1. The initial structure of the unit cell for PIMD simulation of bulk H<sub>2</sub>O and D<sub>2</sub>O was first obtained from classical molecular dynamics (MD) simulation using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). [42] The SPC/E water model [43] was used, and the classical MD simulation was equilibrated for 2 ns to get the well-equilibrated initial structure for PIMD. The PIMD simulation for both bulk H<sub>2</sub>O and bulk D<sub>2</sub>O was run for 40 ps. The subsequent property calculation is based on the 20-ps trajectory of the PIMD simulation, with the initial 20-ps PIMD simulation for equilibrium. For the PIMD simulation of H<sub>2</sub>O and D<sub>2</sub>O in the (14,0) carbon nanotube, we used the same energy cutoff. The unit cell consists of 12.762 Å long water-filled CNTs with a total of 207 atoms. The initially water-filled carbon nanotube structure was obtained by equilibrating an empty carbon nanotube (14,0) in bulk water for 2 ns using classical molecular dynamics simulation in LAMMPS [42] and force fields from Wu et al. [44] were employed for the classical MD simulation. Subsequently, the structure was relaxed using density functional theory for the PIMD simulation. The relaxed structure of confined  $H_2O(D_2O)$  in a (14,0) carbon nanotube can be seen in Figure 2.1. The PIMD simulation for  $H_2O(D_2O)$  under confinement was run for 30 ps. The initial 10 ps PIMD trajectory was taken as an unequilibrated simulation and the subsequent 20-ps PIMD trajectory was used to calculate the properties of  $H_2O(D_2O)$  in (14,0) carbon nanotube.



Figure 2.1: Simulation geometries for bulk and confined  $H_2O(D_2O)$  systems. (a) Cubic simulation box used for the bulk  $H_2O(D_2O)$  simulations with dimensions of 9.97 Å in each direction. (b) Simulation box for the confined  $H_2O(D_2O)$  system, which is a (14,0) carbon nanotube with dimensions of 26.00 Å in the x and y directions to avoid interaction with periodic images, and 12.762 Å in the z direction.

#### 2.2 Simulation Validation

The radial distribution function (RDF) of bulk  $H_2O$  has been extensively studied and reported in both experimental and simulation literature. In this study, we

validate the accuracy of our PIMD and AIMD simulations (without NQE) by comparing the calculated RDFs with previously reported results. We compare our results with those obtained by Marsalek et al., who employed a revised PBE functional with DFT-D3 correction to perform the PIMD simulation of  $H_2O$  in the bulk state. [45] Figure 2.2 shows that our PIMD simulation (black solid line) agrees well with Marsalek et al.'s results (blue dashed line) with regards to the first peak. However, the differences in the first valley and the second peak suggest that different exchange-correlation functionals used in the simulations (our PIMD simulation used PBE functional, while Marsalak et al. used revised PBE functional) may account for the discrepancies. Furthermore, our calculated RDF agrees better with experimental results compared to Marsalak et al.'s calculation, indicating the accuracy of our PIMD simulation. [46] In the appendix, we include the properties calculated from AIMD without nuclear quantum effect and discuss the nuclear quantum effect based on the comparison between PIMD and AIMD in this report. We validate our AIMD simulation by comparing our results with Pham et al.'s work. [24] As shown in Figure 2.2, our AIMD simulation (red solid line) agrees well with Pham et al.'s RDF (purple dashed line).

#### 2.3 Size Effect Correction on Diffusion Coefficient

Due to the long-range interactions, there is a significant system size effect on the diffusion of water in a small periodic box. Yeh et al. [47] investigated the systemsize dependence of diffusion coefficient in molecular dynamics simulations and presented a theoretical approach to correct the calculated diffusion coefficient in a small periodic water box. The correction equation is expressed as  $\Delta D_w = K_B T \zeta / (6\pi \eta L)$ , where  $\Delta D_w$  is the difference between corrected diffusion coefficient and calculated diffusion coefficient from small box,  $K_B$  is the Boltzmann's constant, T is the temperature,  $\zeta$  is 2.83729, and  $\eta$  is the experimental viscosity of water. To investigate the size effect on the diffusion coefficient, we used the LAMMPS package [42] to perform



Figure 2.2: The Radial Distribution Function (RDF) of oxygen. The black and red lines correspond to the RDF obtained from Path Integral Molecular Dynamics (PIMD) and Ab Initio Molecular Dynamics (AIMD without nuclear quantum effects) in this work, respectively. The blue dashed line represents the PIMD result from Marsalek et al., [45] the green dashed line represents the experimental RDF of oxygen, and the purple dashed line shows the AIMD (without nuclear quantum effect) result from Pham et al. [24]

classical MD simulations of bulk water boxes with dimension sizes ranging between 10 and 70 Å. The corrected and uncorrected diffusion coefficient values are compared in Figure 2.3. We find that when the box dimension is larger than 60 Å, the uncorrected diffusion coefficient converges, and the difference between the corrected and uncorrected diffusion coefficient decreases to less than 5%. Thus, the correction equation is appropriate in elucidating the size effect on the diffusion of water. Although the correction equation was validated using classical MD, the physics behind the size effects should not depend on the simulation methods and would remain unchanged for classical MD and PIMD. In summary, the correction equation is used to correct the diffusion coefficient calculated from PIMD.



Figure 2.3: Study of system size effect on the diffusion coefficient. The black line is the diffusion coefficient calculated from the MD simulation. The blue line represents the diffusion coefficient using the correction equation for the size effect. The difference between the corrected value and the uncorrected value is within 5% when the box dimension is larger than 60 Angstroms.

## Chapter 3: Results and Discussion

In this chapter, we summarize the results obtained from our PIMD and AIMD simulations and provide a detailed discussion on the comparison of the properties of  $H_2O$  and  $D_2O$  under confinement and in bulk, as well as the nuclear quantum effect on the structural and dynamical properties

#### 3.1 Bond Length and Bond Angle

The bond length and bond angle are important structural information of molecules at the quantum level. The probability distribution functions of bond lengths and bond angles of  $H_2O$  and  $D_2O$  in the bulk state and under confinement are calculated based on the PIMD trajectory and are shown in Figure 3.1 a and 3.1 b. The bond lengths and bond angles are listed in Table 3.1, where we observe that differences in the bond lengths and bond angles of  $H_2O$  and  $D_2O$  in the bulk state amount to 0.0026 Å and 0.3486°, respectively, which is around 0.3% of the values for  $H_2O$ . This result leads us to conclude that H<sub>2</sub>O has a slightly larger bond length and bond angle than  $D_2O$ , which agrees well with the conclusion in Machida et al.'s work. [14] Similarly, when both  $H_2O$  and  $D_2O$  are confined, bond lengths and bond angles of  $H_2O$  are 0.0038 and 0.398 larger than  $D_2O$ . The difference of the bond angle and bond length of  $H_2O$  and  $D_2O$  can be observed through the shift in the peak of the distribution shown in Figure 3.1 a and 3.1 b. Thus, the bond angles and bond lengths of  $H_2O$  are slightly larger than  $D_2O$  whether they are in bulk or under confinement. Although in the experimental study by Soper et al., the covalent bond length of bulk  $H_2O$  is around 3% longer than  $D_2O$ , [7] other experimental studies using neutron scattering reported that the differences in bond lengths are significantly smaller. According to Ceriotti et al., large uncertainties exist in the experimental measurement of RDF for  $H_2O$  and  $D_2O$ . [28] Based on our PIMD simulations, the covalent bond length for  $H_2O$  is around 0.3% larger than  $D_2O$  in bulk and confined states. However, comparing  $H_2O$  ( $D_2O$ ) in bulk state to  $H_2O$  ( $D_2O$ ) under confinement, the nanoscale confinement from the (14,0) carbon nanotube makes the structure of both  $H_2O$  and  $D_2O$  more compact with the bond lengths and bond angles being around 1.5% smaller, as observed by the shift in the peak of the bond length and bond angle distribution in Figure 3.1 a and 3.1 b.



Figure 3.1: The comparison of the relative probability distribution of HOH (DOD) bond angle and OH (OD) bond length in bulk state and under (14,0) CNT confinement and the nuclear quantum effect on the bond length and bond angle of  $H_2O$  in bulk state and under (14,0) CNT confinement (a) The comparison of the OH (OD) bond length distribution of bulk  $H_2O$ , confined  $H_2O$ , bulk  $D_2O$  and confined  $D_2O$ . (b) Comparison of the HOH (DOD) bond angle distribution of bulk  $H_2O$ , confined  $H_2O$ , bulk  $D_2O$  and confined  $D_2O$ . (c) Nuclear quantum effect on the bond length distribution of bulk  $H_2O$  and confined  $H_2O$ . (d) Nuclear quantum effect on the bond angle distribution of bulk  $H_2O$  and confined  $H_2O$ .

The nuclear quantum effects have an impact on the bond angle and bond length of  $H_2O$  and  $D_2O$ , as depicted in Figure 3.1 c and 3.1 d. This observation is consistent with the findings presented in Table 3.1 using PIMD and in Table A.1 using AIMD. Specifically, the bond angle and bond length of bulk  $H_2O$  and  $D_2O$  are shown to increase, with a broader distribution. These results align with those reported by Machida et al. and are attributed to quantum fluctuations in PIMD simulations. [14]

and under commement in a (14,0) carbon nanotube.			
Confined $H_2O$	Bulk $H_2O$	Confined $D_2O$	Bulk $D_2O$
$0.9863 {\pm} 0.03376$	$1.0000 \pm 0.03655$	$0.9825 {\pm} 0.03643$	$0.9974 {\pm} 0.03356$
$104.6287 \pm 6.3026$	$105.4314 \pm 6.0601$	$104.2307 \pm 6.1795$	$105.0828 \pm 6.3417$
$2.6674 {\pm} 0.3650$	$3.0179 {\pm} 0.3532$	$2.8125 \pm 0.3884$	$3.1289 {\pm} 0.3724$
$1.5512{\pm}0.9557$	$3.0316 \pm 1.0772$	$1.7805 {\pm} 0.9574$	$3.2082{\pm}1.0018$
$2.00955 \pm 0.2670$	$2.0381 \pm 0.8768$	$2.0366 \pm 0.2686$	$2.0915 \pm 0.9316$
3769.66	3622.87	2793.42	2601.53
1613.32	1647.97	1147.61	1180.93
$14.796 \pm 2.7964$	$2.704 \pm 0.9472$	$10.981 \pm 2.6592$	$2.294{\pm}0.9514$
$213.50 \pm 0.7246$	NA	$209.05 \pm 0.7925$	NA
	$\begin{array}{c} \text{ment in a (14,0)}\\ \hline \text{Confined H}_2\text{O}\\ \hline 0.9863 \pm 0.03376\\ \hline 104.6287 \pm 6.3026\\ \hline 2.6674 \pm 0.3650\\ \hline 1.5512 \pm 0.9557\\ \hline 2.00955 \pm 0.2670\\ \hline 3769.66\\ \hline 1613.32\\ \hline 14.796 \pm 2.7964\\ \hline 213.50 \pm 0.7246\\ \end{array}$	Siment in a (14,0)carbon nanotConfined $H_2O$ Bulk $H_2O$ $0.9863 \pm 0.03376$ $1.0000 \pm 0.03655$ $104.6287 \pm 6.3026$ $105.4314 \pm 6.0601$ $2.6674 \pm 0.3650$ $3.0179 \pm 0.3532$ $1.5512 \pm 0.9557$ $3.0316 \pm 1.0772$ $2.00955 \pm 0.2670$ $2.0381 \pm 0.8768$ $3769.66$ $3622.87$ $1613.32$ $1647.97$ $14.796 \pm 2.7964$ $2.704 \pm 0.9472$ $213.50 \pm 0.7246$ NA	Siment in a (14,0) carbon nanotube.Confined $H_2O$ Bulk $H_2O$ Confined $D_2O$ $0.9863\pm0.03376$ $1.0000\pm0.03655$ $0.9825\pm0.03643$ $104.6287\pm6.3026$ $105.4314\pm6.0601$ $104.2307\pm6.1795$ $2.6674\pm0.3650$ $3.0179\pm0.3532$ $2.8125\pm0.3884$ $1.5512\pm0.9557$ $3.0316\pm1.0772$ $1.7805\pm0.9574$ $2.00955\pm0.2670$ $2.0381\pm0.8768$ $2.0366\pm0.2686$ $3769.66$ $3622.87$ $2793.42$ $1613.32$ $1647.97$ $1147.61$ $14.796\pm2.7964$ $2.704\pm0.9472$ $10.981\pm2.6592$ $213.50\pm0.7246$ NA $209.05\pm0.7925$

Table 3.1: Structural and Dynamical Properties of  $H_2O$  and  $D_2O$  in bulk and under confinement in a (14,0) carbon nanotube.

#### 3.2 Radial Distribution Function(RDF)

Other than the bond angle and bond length, the radial distribution function gives information on the overall structure of  $H_2O$  and  $D_2O$ . Based on the radial distribution function calculated from PIMD, we observe that  $D_2O$  is a more structured liquid than  $H_2O$  in bulk. The first peak in the RDF of oxygen for  $D_2O$  in Figure 3.1 a is about 5% higher than that of  $H_2O$ , which is consistent with the result from first principles simulations showing that the first peak of  $g_{oo}$  for  $H_2O$  is smaller than that of  $D_2O$ . [14] Additionally, for the first valley and second peak of the RDF for oxygen,  $D_2O$  is lower and higher, respectively, than that of  $H_2O$ . Similarly, for the RDF of oxygen-hydrogen and RDF of hydrogen-hydrogen,  $D_2O$  tends to have higher peak values and lower valleys, as shown in Figure 3.1 b and 3.1 c. These simulation results agree with the experimental conclusion that  $D_2O$  is slightly more ordered than  $H_2O$ . [8]

The role of nuclear quantum effects in determining the radial distribution function (RDF) of water molecules has been a subject of much interest in the literature. Our PIMD simulations reveal that the RDF of H2O and D2O significantly deviates from that obtained through AIMD simulations that neglect nuclear quantum effects. In Figure 3.1, we find that the first peak of the oxygen RDF from PIMD simulations is much lower than that from AIMD simulations, consistent with experimental results. While the AIMD simulations in this study were carried out at an elevated temperature of 400 K, which is a common practice to enhance diffusion and avoid over-structuring in water simulations, [24] they fail to accurately capture the effects of nuclear quantum motion. Similar findings have also been reported by Li et al. [48]



Figure 3.2: The comparison of the oxygen-oxygen radial distribution function  $g_{oo}$  (r), oxygen-hydrogen radial distribution function  $g_{oh}$  (r) and hydrogen-hydrogen radial distribution function  $g_{hh}$  (r) of bulk H<sub>2</sub>O and D<sub>2</sub>O with nuclear quantum effect.

#### 3.3 Dipole Moment

A dipole moment develops when there is a charge delocalization along the direction of the total angular momentum of the system. [49] A larger dipole moment implies a larger difference in electronegativity and stronger interaction with other particles. The electric dipole moment distribution was calculated using the maximally localized Wannier functions (MLWFs) in the Wannier 90 program [50] and the dipole moment distributions of  $H_2O$  and  $D_2O$  in bulk state and confinement state are shown in Figure 3.3. We observe that  $D_2O$  has a higher dipole moment than  $H_2O$ , regardless of whether it is in the bulk state or under confinement, which agrees with the trends observed in experiment work. [51] From Table 1, the dipole moment of  $D_2O$  is approximately 4% higher than that of  $H_2O$  in the bulk and confinement states. To understand the origin of higher dipole moment, the partial charges of the oxygen atom and hydrogen (deuterium) atom in  $H_2O$  and  $D_2O$  are calculated and shown in Table 3.2. We see that all atoms in  $D_2O$  have slightly higher partial charges than  $H_2O$ . Thus, the electrostatic interaction between oxygen and deuterium is stronger than that between oxygen and hydrogen. The dipole moments of both  $H_2O$  and  $D_2O$  are significantly influenced by the nanoscale confinement of the (14,0) carbon nanotube. From Figures 3.3 b and 3.3 c, the peaks of the dipole moment distribution shift to the left when  $H_2O$  and  $D_2O$  are under confinement, which shows around 10% decrease in dipole moment. Table 3.2 also shows that the partial charge of both oxygen and hydrogen (deuterium) is reduced by approximately 11% due to confinement. This trend has been consistently observed in other studies as well. For example, Dellago et al. utilized AIMD to calculate the dipole moment of water confined in narrow pores and observed an average dipole moment of about 2.7 D, nearly 10% lower than the dipole moment of bulk water. [52] Similarly, Cicero et al. measured the dipole moment of  $D_2O$  under both bulk conditions and confinement within a (14,0) carbon nanotube, obtaining values of 3.10 D and 2.87 D, respectively. [22] In our PIMD calculations, we found that the dipole moment of bulk  $D_2O$  was 3.1289 D, while that of  $D_2O$  confined within a (14,0) carbon nanotube was 2.8125 D, which is in good agreement with the previously reported values. Additionally, Rozsa et al. found that water molecules confined within a 1.1 nm carbon nanotube exhibit a 9% reduction in molecular dipole moments relative to bulk values, which further supports our findings. [23] By comparing the result we obtained from PIMD simulation (Table 3.1) and AIMD simulation (Table A.1), it is found that the nuclear quantum effects can slightly increase the dipole moment regardless of bulk or under nanoscale confinement of carbon nanotube. The distribution of  $H_2O$  and  $D_2O$  is much broader due to quantum fluctuations in PIMD simulation.

Table 3.2: Oxygen and hydrogen (deuterium) partial charges of  $H_2O$  and  $D_2O$  in bulk and confined states.

Atom Type	Bulk $H_2O$	Bulk $D_2O$	Confined $H_2O$	Confined $D_2O$
0	1.0379 e	$1.0746~{\rm e}$	0.9216 e	0.9712 e
H(D)	$0.5190 \ e$	$0.5373 \ e$	0.4608 e	$0.4856~{\rm e}$

#### 3.4 Hydrogen Bonds

Hydrogen bonds, which are interactions between the hydrogen atom covalently bound to an electronegative donor and the lone pair of electrons of an acceptor [53], are one of the most important features of aqueous systems. Moreover, hydrogen bonds play an important role in life sciences including the protein geometry and protein transport process. [54] The hydrogen bond number as well as the hydrogen bond length are calculated from the AIMD simulation. The hydrogen bonds in the simulated water box are identified using the geometry criteria in which a hydrogen bond exists between two water molecules when the distance between oxygen atoms is less than 3.5 Å and the O—H...O angle is smaller than 30°. [55] The distribution histogram for the hydrogen bond number of each water is plotted in Figure 3.4. From Figure 3.4 a, 3.4 d, and Table 3.1, it has been observed that  $H_2O$  exhibits a higher probability of having fewer than three hydrogen bonds, whereas  $D_2O$  displays a lower



Figure 3.3: The comparison of the probability distribution of dipole moment of  $H_2O$  and  $D_2O$  in bulk state and under (14,0) CNT confinement. The probability distribution is calculated based on Wannnier90 results of 20 different frames in PIMD. (a) The dipole moment distribution comparison between bulk  $H_2O$  and bulk  $D_2O$  (b) The dipole moment distribution comparison between bulk  $H_2O$  and confined  $H_2O$ . (c) The dipole moment distribution comparison between bulk  $D_2O$  and confined  $D_2O$ . (d) The dipole moment distribution comparison between confined  $H_2O$  and confined  $D_2O$ .

having four or more hydrogen bonds. This results in a lower average number of hydrogen bonds in H<sub>2</sub>O compared to D<sub>2</sub>O. The number of hydrogen bonds for H<sub>2</sub>O is around 0.18 smaller than D<sub>2</sub>O in bulk and around 0.1451 smaller in the confinement state. The analysis reveals that hydrogen bonding in bulk and confined D<sub>2</sub>O is stronger compared to H<sub>2</sub>O, consistent with previous theoretical and experimental studies.[28, 56] Furthermore, our simulations reveal that the hydrogen bond length of bulk H<sub>2</sub>O is 0.0534 smaller than that of D<sub>2</sub>O, which is consistent with the trend observed in Soper et al.'s experimental findings. [7] Moreover, we found that when both H<sub>2</sub>O and D<sub>2</sub>O are confined in a (14,0) carbon nanotube, the hydrogen bond length of H<sub>2</sub>O is 0.0271 smaller than that of D<sub>2</sub>O.



Figure 3.4: The comparison of the probability distribution of hydrogen bonds number of  $H_2O$  and  $D_2O$  in bulk state and under (14,0) CNT confinement.(a) Comparison of the distribution of the number of hydrogen bonds between bulk  $H_2O$  and bulk  $D_2O$  (b) Comparison of the distribution of the number of hydrogen bonds between bulk  $H_2O$  and confined  $H_2O$ . (c) Comparison of the distribution of the number of hydrogen bonds between bulk  $D_2O$  and confined  $D_2O$ . (d) Comparison of the distribution of the number of hydrogen bonds between confined  $H_2O$  and confined  $D_2O$ .

Because of the dehydration effect inside a carbon nanotube, the number of neighboring water molecules decreases, which makes it relatively more difficult to form hydrogen bonds between water molecules. Thus, as shown in Figures 3.4 b and 3.4 c, the number of hydrogen bonds for confined  $H_2O$  and  $D_2O$  molecules decreases considerably. Research on the hydrogen bond network of  $H_2O$  or  $D_2O$  under nanoscale confinement or perturbations from ions has been conducted. Cicero et al. investigated the number of hydrogen bonds along the radial distance in carbon nanotubes with a diameter of 1.1 nm and observed a decrease in hydrogen bonds near the carbon nanotube wall. [22] Likewise, Rozsa et al. observed a reduced number of hydrogen bonds in the first shell when ions were present. [23] Joseph et al. reported that the number of hydrogen bonds in  $H_2O$  confined within a carbon nanotube reduces in

the depletion layer. [18] These findings support our conclusion that the number of hydrogen bonds is reduced when  $H_2O$  and  $D_2O$  are subjected to confinement. The confined  $H_2O$  and  $D_2O$ , therefore, have fewer hydrogen bonds compared to the bulk state, showing that confinement in (14,0) carbon nanotube can significantly weaken the overall hydrogen bonding interaction between  $H_2O$  ( $D_2O$ ) molecules.

Nuclear quantum effects (NQEs) have a significant impact on the hydrogen bonding properties of  $H_2O$  and  $D_2O$ , affecting both the hydrogen bond number and length. Our PIMD simulation results show that the NQE leads to a 10% reduction in the number of hydrogen bonds, a 11% enlargement of the hydrogen bond length, and a broader distribution of both the hydrogen bond number and length due to quantum fluctuations, compared to AIMD simulations. These findings suggest that the NQE weakens the hydrogen bonding interaction between  $H_2O$  and  $D_2O$  molecules. Many experiments have shown that NQEs act to weaken the hydrogen bond, leading to a less structured liquid and a more mobile hydrogen-bonded network, which further supports our findings. [28]

#### 3.5 Power Spectra

The vibrational spectroscopy are calculated from the fast Fourier transform of the velocity autocorrelation of hydrogen (deuterium) atoms and it includes the low vibrational frequency modes, the HOH (DOD) bending mode as well as the OH(OD) stretching mode. [57] The low vibrational frequency mode, which is usually from the collective motion of water molecules in the H-bond network [58] includes the hindered translational mode (approximately  $60 \text{ cm}^{-1}$ ) and libration mode (from approximately  $100 \text{ cm}^{-1}$  to approximately  $1000 \text{ cm}^{-1}$ ). The libration model is composed of rocking, wagging and twist motion of the water molecule. [59]

From the plot of the power spectra comparison of  $H_2O$  and  $D_2O$  in the bulk state and under confinement in Figures 3.5 a and 3.5 d, we find that all mode frequencies (including hindered translational mode, libration mode, bond angle bending mode, and bond stretching mode) of  $D_2O$  are smaller than those of  $H_2O$  when they are in the bulk and confined states, which is attributed to the heavy mass of deuterium. The frequency of each mode is summarized in Table 3.1. The confinement in (14,0) carbon nanotube has a different influence on different vibrational modes. Figures 3.5 b and 3.5 c show that the libration mode frequency decreases, the bond stretching frequency increases, and the bond angle bending frequency remains almost unchanged. Previous studies have investigated the vibrational spectra of confined  $D_2O$  in a (14,0) carbon nanotube. For instance, Cicero et al. utilized first-principles calculations to obtain the power spectra of  $D_2O$  in confinement and observed an increase in the high-frequency signal due to the increased surface-to-volume ratio of the liquid. [22] In addition, the low-frequency band showed a red shift in more confined samples, suggesting a weakening of the hydrogen bond strength, while the bending frequency of the power spectra remained unchanged. Similarly, Sharma et al. reported an increase in the O-D stretching frequency and a decrease in the librational mode of  $D_2O$  under confinement. [21] These findings are consistent with experimental investigations, which have also reported a red shift in the librational mode and an increase in the stretching mode frequency of confined  $H_2O$ . [60] Our study aligns with these previous results and contributes to the understanding of the vibrational spectra of confined  $H_2O$  and  $D_2O$ .

For bulk  $H_2O$ , the HOH bending frequency can be an accurate marker of the physical details of the hydrogen bonding network. Compared to the OH stretching frequency, it is less sensitive to the frequency coupling between intermolecular interactions, and it provides the same physical insights into the hydrogen bonding system. [61] However, it is not reliable to detect the hydrogen bond strength of confined  $H_2O$  and  $D_2O$  using bending mode frequency, since the bending mode remains unchanged under confinement in (14,0) carbon nanotube while the hydrogen bond interaction becomes weaker under confinement.



Figure 3.5: The Power spectra comparison of  $H_2O$  and  $D_2O$  in bulk state and under (14,0) CNT confinement.(a) The power spectra comparison between bulk  $H_2O$ and bulk  $D_2O$  (b) The power spectra comparison between bulk  $H_2O$  and confined  $H_2O$ . (c) The power spectra comparison between bulk  $D_2O$  and confined  $D_2O$ . (d) The power spectra comparison between confined  $H_2O$  and confined  $D_2O$ .

#### 3.6 Self-diffusion coefficient

The calculation of the self-diffusion coefficient gives direct information on the dynamic properties of the aqueous system. The self-diffusion coefficients of  $H_2O$  and  $D_2O$  are calculated using the PIMD simulation data. The mean-squared displacement (MSD) of oxygen atoms is first obtained, and the diffusion coefficient can be subsequently calculated using the Einstein relation. [62]

$$\lim_{t\to\infty}\frac{1}{2dt}<[\mathbf{r(t)}-\mathbf{r(0)}]^2>$$

where d is the dimension of the system, and  $\mathbf{r}(\mathbf{t})$  is the coordinate of the oxygen atom at time t. The mean-squared displacement (MSD) plot is obtained by averaging 3 different ensembles of the PIMD trajectory. From Figures 3.6 a and 3.6 b, H<sub>2</sub>O has a higher slope for the MSD plot compared to D<sub>2</sub>O for both bulk and confined states, which implies that  $H_2O$  has a higher self-diffusion coefficient than  $D_2O$ . Due to the size effect from the small simulation box, the diffusion coefficients of  $H_2O$  and  $D_2O$  in the bulk state are corrected using the Y-H equation. [47] The corrected diffusion coefficients for  $H_2O$  and  $D_2O$  for bulk and confined states are summarized in Table 3.1. Statistical Error for the calculated diffusion coefficient is also attached. Based on the calculated results, the diffusion coefficient of bulk  $D_2O$  is 15.16% lower than that of bulk  $H_2O$ , while the diffusion coefficient of confined  $D_2O$  is 25.78% lower than that of confined  $H_2O$ , which shows that confinement enlarges the difference in the diffusion of  $H_2O$  and  $D_2O$ .



Figure 3.6: The MSD (mean-squared displacement) comparison of  $H_2O$  and  $D_2O$  in bulk state and under (14,0) CNT confinement. (a) Comparison of the MSD between bulk  $H_2O$  and bulk  $D_2O$  (b) Comparison of the MSD between confined  $H_2O$  and confined  $D_2O$ . The MSD is calculated by averaging AIMD data from 3 ensembles for bulk and confined water. The statistical errors, which are calculated based on different ensembles, are indicated by the width of the curves.

NQEs have a significant influence on the diffusion coefficient. Comparing PIMD result and AIMD result, it is found that the diffusion coefficient of bulk  $H_2O$ increases around 20% when we take nuclear quantum effects into consideration. It is known that GGA results in over structuring of the liquid phase, which is accompanied by slower molecular diffusion. [63] However, by considering the nuclear quantum effects, the hydrogen bonds get weakened and both  $H_2O$  and  $D_2O$  become less structured and more diffusive.

## 3.7 Radial Breathing Mode (RBM) of the (14,0) carbon nanotube

Raman spectroscopy has been widely used to characterize single-wall carbon nanotubes [64] and the radial breathing mode (RBM) is one of the best-known features in the Raman spectra of carbon nanotubes. [65] In this vibration, the entire tube has a breathing-like deformation due to the radial velocity of the carbon atoms, which is frequently utilized to detect carbon nanotube diameters. In addition, the radial breathing mode (RBM) is sensitive to the local environment of carbon nanotubes [66] which enables the detection of fluid properties inside carbon nanotubes. The radial breathing mode frequency of both H<sub>2</sub>O-filled and D<sub>2</sub>O-filled single-wall carbon nanotubes are calculated to show the different influences of H<sub>2</sub>O and D<sub>2</sub>O molecules on the carbon nanotube. The radial breathing mode frequency is calculated by performing a Fourier transform of the radial velocity autocorrelation (VACF), which is given by [44]

$$C(t) = \frac{\langle v_r(t)v_0(t) \rangle}{\langle v_r(0)v_r(0) \rangle}$$

where  $v_r(t)$  is the radial velocity averaged over all carbon atoms, and  $\langle \rangle$  denotes ensemble average. In our calculation, we used PIMD trajectories of 3 different ensembles and averaged all RBMs to obtain the final RBM value and the standard deviation. The fast Fourier transform of C(t) yields the RBM frequency of the carbon nanotube. The RBMs of H<sub>2</sub>O-filled and D<sub>2</sub>O-filled carbon nanotubes are compared in Figure 3.7. The D<sub>2</sub>O-filled carbon nanotube has a smaller radial breathing mode frequency than the H<sub>2</sub>O-filled one. NQEs lead to a slightly larger radial breathing mode and the difference between D<sub>2</sub>O-filled carbon nanotubes and H<sub>2</sub>O-filled carbon nanotubes

The  $H_2O$  and  $D_2O$  interaction energy with the (14,0) carbon nanotube was calculated to study the origin of the different RBMs. The interaction energy between



Figure 3.7: The comparison of the RBM of  $H_2O$ -filled and  $D_2O$ -filled carbon nanotubes (CNTs). The blue line represents the RBM of  $H_2O$  in CNT and the orange line represents the RBM of  $D_2O$  in CNT.

 $H_2O(D_2O)$  and the (14,0) carbon nanotube is calculated as:

$$E_{interaction} = E_{CNT} + E_{H_2O(D_2O)} - E_{CNT+H_2O(D_2O)}$$

where  $E_{interaction}$  is the interaction energy between H<sub>2</sub>O (D<sub>2</sub>O) and the (14,0) carbon nanotube,  $E_{CNT}$  is the total energy of the (14,0) carbon nanotube and  $E_{CNT+H_2O(D_2O)}$ is the total energy of the H<sub>2</sub>O (D<sub>2</sub>O) filled (14,0) carbon nanotube. The interaction energy is summarized in Table 3.3. It is observed that the interaction of D<sub>2</sub>O and (14,0) carbon nanotube is slightly smaller than the interaction energy between H<sub>2</sub>O and (14,0) carbon nanotube. Based on the studies by Longhurst et al., [66] the upshift of the radial breathing mode frequency is smaller if the fluid and carbon nanotube interaction is weaker. Thus, the result of our PIMD simulation of  $H_2O$  ( $D_2O$ )-filled CNTs leads to the same conclusion.

rabie 0.0. interaction	$\mathbf{Linei}\mathbf{g}  \mathbf{or}  \mathbf{n}_2 \mathbf{o}  \mathbf{una}  \mathbf{p}_2 \mathbf{o}$	
Energy(eV)	H <sub>2</sub> O	$D_2O$
Pure $H_2O/D_2O$	-187.6850	-186.8716
Pure CNT	-1545.1228	-1544.4838
$H_2O/D_2O + CNT$	-1734.7421	-1733.2700
Interaction Energy	-1.9343	-1.9147

Table 3.3: Interaction Energy of  $H_2O$  and  $D_2O$  with a (14,0) CNT

## Chapter 4: Conclusion

In this report, we discuss the fundamental property differences of  $H_2O$  and  $D_2O$  in bulk and confined states considering nuclear quantum effects. PIMD simulation shows that the bond angles and bond lengths of  $H_2O$  are slightly larger than  $D_2O$  in bulk and confined states. The dipole moment of  $D_2O$  is approximately 4%higher than that of  $H_2O$ , which comes from slightly higher partial charges of each atom in  $D_2O$ . The dipole moments of both  $H_2O$  and  $D_2O$  are significantly reduced under confinement due to the decreased partial charges of oxygen and hydrogen (deuterium) atoms.  $H_2O$  has fewer hydrogen bonds than  $D_2O$  in bulk and confinement, which demonstrates stronger hydrogen bonding interaction in  $D_2O$ . The effect of confinement from (14,0) carbon nanotube reduces the hydrogen bond number, which means weakening of the hydrogen bonds. All vibrational mode frequencies of  $D_2O$ are lower than those of  $H_2O$  in the bulk and confined states.  $H_2O$  and  $D_2O$  inside carbon nanotubes have lower libration mode frequencies, higher bond stretching frequencies, and unchanged bond bending frequencies compared to the bulk state. The radial breathing mode of the D<sub>2</sub>O-filled carbon nanotube has a smaller radial breathing mode frequency due to a slightly smaller interaction energy with (14.0) carbon nanotube than  $H_2O$ -filled ones. The inclusion of NQEs in our simulations has allowed us to observe several changes in the structural and dynamical properties of both bulk  $H_2O$  and  $D_2O$ , as well as confined  $H_2O$  and  $D_2O$  in carbon nanotubes. NQEs lead to a slightly increased bond length and bond angle for both  $H_2O$  and  $D_2O$ , resulting in a broader distribution due to quantum fluctuations. The presence of NQEs also promotes a less structured and more diffusive behavior of both  $H_2O$  and  $D_2O$ , as observed through the radial distribution function (RDF) and diffusion coefficient. Moreover, the weakening of hydrogen bond interactions is evident from the reduced hydrogen bond number and enlarged hydrogen bond length upon inclusion of NQEs. Additionally, we observe a slight increase in the dipole moment and radial breathing mode for  $H_2O$  - and  $D_2O$  -filled carbon nanotubes due to the presence of NQEs. Importantly, our simulations highlight the isotopic effect, whereby the differences between the structural and dynamical properties of  $H_2O$  and  $D_2O$  are magnified by the inclusion of NQEs.

# Appendix A: Structural and dynamical properties calculated from Ab initio Molecular Dynamics Simulation



Figure A.1: The comparison of the relative probability distribution of HOH (DOD) bond angle and OH (OD) bond length in bulk state and under (14,0) CNT confinement from AIMD without nuclear quantum effect. (a) The comparison of the OH bond length distribution between bulk  $H_2O$  and confined  $H_2O$ . (b) Comparison of the HOH bond angle distribution between bulk  $H_2O$  and confined  $H_2O$ . (c) Comparison of the OD bond length distribution between bulk  $D_2O$  and confined  $D_2O$ . (d) Comparison of the DOD bond angle distribution between bulk  $D_2O$  and confined  $D_2O$ .



Figure A.2: The comparison of the probability distribution of dipole moment of  $H_2O$  and  $D_2O$  in bulk state and under (14,0) CNT confinement from AIMD without nuclear quantum effect. The probability distribution is calculated based on Wannier90 results of 10 different frames in AIMD. (a) The dipole moment distribution comparison between bulk  $H_2O$  and bulk  $D_2O$  (b) The dipole moment distribution comparison between confined  $H_2O$  and confined  $D_2O$ . (c) The dipole moment distribution comparison between bulk  $H_2O$  and confined  $H_2O$ . (d) The dipole moment distribution comparison between bulk  $H_2O$  and confined  $H_2O$ . (d) The dipole moment distribution comparison between bulk  $D_2O$  and confined  $H_2O$ .



Figure A.3: The comparison of the probability distribution of hydrogen bonds number of  $H_2O$  and  $D_2O$  in bulk state and under (14,0) CNT confinement from AIMD without nuclear quantum effect. (a) Comparison of the distribution of the number of hydrogen bonds between bulk  $H_2O$  and bulk  $D_2O$  (b) Comparison of the distribution of the number of hydrogen bonds between confined  $H_2O$  and confined  $D_2O$ . (c) Comparison of the distribution of the number of hydrogen bonds between bulk  $H_2O$  and setween bulk  $H_2O$  and confined  $H_2O$ . (d) Comparison of the distribution of the number of hydrogen bonds between bulk  $D_2O$  and confined  $D_2O$ .



Figure A.4: The Power spectra comparison of  $H_2O$  and  $D_2O$  in bulk state and under (14,0) CNT confinement from AIMD without nuclear quantum effect. (a) The power spectra comparison between bulk  $H_2O$  and bulk  $D_2O$  (b) The power spectra comparison between confined  $H_2O$  and confined  $D_2O$ . (c) The power spectra comparison between bulk  $H_2O$  and confined  $H_2O$ . (d) The power spectra comparison between bulk  $D_2O$ and confined  $D_2O$ .



Figure A.5: The MSD (mean-squared displacement) comparison of  $H_2O$  and  $D_2O$ in bulk state and under (14,0) CNT confinement from AIMD without nuclear quantum effect. (a) Comparison of the MSD between bulk  $H_2O$  and bulk  $D_2O$  (b) Comparison of the MSD between confined  $H_2O$  and confined  $D_2O$ . The MSD is calculated by averaging AIMD data from 5 ensembles for bulk and confined water.

Table A.1: Structural and Dynamical Properties of  $H_2O$  and  $D_2O$  in bulk and under confinement in a (14,0) carbon nanotube calculated from AIMD without nuclear quantum effect

Properties	Confined $H_2O$	Bulk $H_2O$	Confined $D_2O$	Bulk $D_2O$
Bond Length (Å)	$0.9872 {\pm} 0.0292$	$0.9969 {\pm} 0.0329$	$0.9871 {\pm} 0.0309$	$0.9964{\pm}0.0321$
Bond Angle (°)	$104.8583 \pm 5.6973$	$105.7973 \pm 5.9433$	$104.9187 \pm 6.0996$	$105.8286 \pm 5.9042$
Dipole (D)	$2.5932{\pm}0.2265$	$3.0079 \pm 0.2739$	$2.7325 \pm 0.3032$	$3.1225 \pm 0.2865$
HBs Number	$2.2382{\pm}0.8398$	$3.5602 {\pm} 0.7812$	$2.2867 {\pm} 0.8393$	$3.5794{\pm}0.7609$
HBs Length (Å)	$1.9671 {\pm} 0.2745$	$1.8829 \pm 0.2302$	$1.9471 {\pm} 0.2480$	$1.8775 \pm 0.2294$
Stretching $(cm^{-1})$	3742.01	3538.42	2715.91	2589.68
Bending $(cm^{-1})$	1626.70	1624.66	1180.83	1176.76
Diffusion $(\times 10^{-9}m^2/s)$	$9.7521 {\pm} 0.8613$	$2.2090 \pm 0.4755$	$7.7141 \pm 0.8787$	$1.8878 \pm 0.4154$
$RBM (cm^{-1})$	$206.445 \pm 0.5576$	NA	$205.627 \pm 0.5732$	NA



Figure A.6: The comparison of the RBM of  $H_2O$ -filled and  $D_2O$ -filled carbon nanotubes (CNTs) from AIMD without nuclear quantum effect. The blue line represents the RBM of  $H_2O$  in CNT and the orange line represents the RBM of  $D_2O$  in CNT.

Table A.2: O and H (D) partial charges of  $H_2O$  and  $D_2O$  in bulk and confined states from AIMD without nuclear quantum effect.

Atom Type	Bulk $H_2O$	Bulk $D_2O$	Confined $H_2O$	Confined $D_2O$
0	1.0419 e	1.0827 e	$0.8975~{\rm e}$	$0.9465 \ e$
H(D)	$0.5210 \ e$	$0.5413 \ e$	0.4488 e	$0.4732 \ e$

Table A.3: Interaction Energy of  $H_2O$  and  $D_2O$  with a (14,0) Carbon Nanotube from AIMD without nuclear quantum effect.

<b>1</b>					
Energy(eV)	$H_2O$	$D_2O$			
Pure $H_2O/D_2O$	-190.9961	-190.9218			
Pure CNT	-1554.3045	-1554.3182			
$H_2O/D_2O + CNT$	-1747.2613	-1747.1619			
Interaction Energy	-1.9607	-1.9219			

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## Vita

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