

## SHORT COMMUNICATIONS

Molecular dynamics study on the structure I helium hydrate<sup>\*</sup>CHENG Wei, WU Hucai, YE Xiaoqin and ZHOU Hongyu<sup>\*\*</sup>

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**Abstract** A 368-water molecule structure I gas hydrate encased by the number of helium (He) molecules ranging from two to twenty-two, are calculated by molecular dynamical simulations. The potential TIP4P (transferable intermolecular potential with four sites) is used for water interactions and Lennard-Jones for He-He and He-water interactions. He molecules do not affect the water lattice and can stabilize the hydrate when their concentration is small. A trough signature of He encased is found at 80~90 meV in the phonon density of states. He molecules prefer to be more off-center in  $5^{12}6^2$  cages. Heavier isotope He are energetically favorable to be filled in cages.

**Keywords:** molecular dynamics neutron scattering spectra helium hydrate.

Gas hydrates (GHs) are multi-component crystalline compounds with structures consisting of water molecules and encasing gas molecules<sup>[1]</sup>. There are three types of natural GHs called structure I, structure II and structure H. Most of the natural gas molecules which form GH are hydrophobic or water soluble acid<sup>[2]</sup>. Simple gases such as methane and xenon are hydrophobic and can be trapped into water cages to form structure I GHs<sup>[2]</sup>. It is found that helium (He) and neon are virtually not present in the samples from Hydrate Ridge, Cascadia Margin<sup>[3]</sup>. However, He hydrate can be produced in the laboratory, and its effect on the vibrational dynamics of GH is predicted to be small<sup>[4,5]</sup>. Such prediction is tested by inelastic neutron scattering experiment and Lattice Dynamical study<sup>[6]</sup>. It is important to know the relation of stability and He concentration<sup>[2]</sup>. Molecular dynamical simulation (MD) is a powerful tool for studying thermodynamic properties of water and GHs<sup>[7~13]</sup>. By using MD program, time-dependent phenomena, transport properties, and thermodynamic properties can be calculated<sup>[14]</sup>. In this article we use MD simulations to study the thermodynamic properties, phonon density of states (PDOS), and radial distribution functions (RDFs) of GH with different He concentrations. We start from the 368 wa-

ter molecule structure I GH with a cubic cell volume of  $1.25 \times 10^{-26} \text{ m}^3$  with side  $2.32 \text{ nm}$ <sup>[15,16]</sup> and fill two to twenty-two He molecules in the  $5^{12}$  and  $5^{12}6^2$  cages. All the simulations are constant volume simulations just like the simulations of Forrisdahl et al.<sup>[13]</sup>. The total simulation time of 0.12 ns with the time step of 0.6 fs is chosen, and the initial temperatures of simulation are chosen to be 23.5 K of the experimental temperature<sup>[6]</sup>. MD simulation can provide velocities of each atom, and using the velocity data and fast Fourier transformation technique<sup>[17]</sup>, we can provide the PDOS that can be measured by inelastic neutron scattering<sup>[6,8~21]</sup>. PDOS shows that a trough signature of He encased is found at 80~90 meV and He molecules is found to be filled predominantly in one kind of cage. The simulated RDFs which are related to the information obtained from the X-ray scattering experiments<sup>[14,22]</sup> show that for different concentrations the water structure is less affected. The simulated trajectories of He molecule location show that the He molecules are more off-center in large cages.

The force field for water interactions is transferable intermolecular potential with four sites (TIP4P), which is a water molecule model with rigid

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atomic positions. TIP4P can reproduce room temperature bulk properties of water quite well<sup>[23]</sup>. The intermolecular potential for the interaction of a pair of molecule is of the following form

$$V(r_{o-o}) = \frac{A}{r_{\sigma-o}^{12}} - \frac{C}{r_{\sigma-o}^6} + \sum_{i,j} \frac{q_i q_j}{r_{ij}}, \quad (1)$$

where  $i$  and  $j$  label the charge sites,  $r_{o-o}$  is the distance between two oxygen atoms,  $A$  and  $C$  can be found in Ref. [23], and the cut-off radius is 1.82 nm.

The force fields for He-He and water-He interactions are Lennard-Jones potentials of the following form

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (2)$$

where for He-He interactions  $\epsilon_{\text{He}} = 10.22$  K,  $\sigma_{\text{He}} = 0.2556$  nm, and for water-He interactions  $\epsilon_{\text{He-W}} =$

62.3 K,  $\sigma_{\text{He-W}} = 0.260$  nm which are the same as in Ref. [6].

One unit cell of structure IGH contains 46 water molecules. In the 368 atom  $2 \times 2 \times 2$  MD cell there are a total of sixteen  $5^{12}$  and forty-eight  $5^{12}6^2$  cages. We fill only a single He atom in each cage in all the simulations. After eighteen simulations we obtain the radial distribution functions and list the thermodynamical properties in Table 1. The calculated Oxygen-Oxygen, Oxygen-Hydrogen and Hydrogen-Hydrogen radial distribution functions for GH with different number of He molecules are nearly identical to each other and will not be shown here. The result indicates that the water lattice (oxygen sites) is less affected by He molecules at the low temperature of 23.5 K. However, hydrogen sites are affected and will be discussed below.

Table 1. Thermodynamic properties of a 368 water molecule structure IGH at 23.5 K with different number of He molecules

	Number of He atoms in $5^{12}$ cages	Number of He atoms in $5^{12}6^2$ cages	Total internal energy (kJ/Mol)	Translational kinetic energy (kJ/Mol)	Rotational kinetic energy (kJ/Mol)	Pressure (GPa)	Enthalpy (kJ/Mol)	Virial (kJ/Mol)
I	0	0	-53.1	0.294	0.293	-0.227	-57.8	14.5
II	2	0	-53.7	0.294	0.291	-0.147	-56.7	9.53
III	3	0	-53.7	0.293	0.290	-0.109	-55.9	7.22
IV	4	0	-53.2	0.293	0.290	-0.177	-56.8	11.3
V	5	0	-52.9	0.293	0.289	-0.175	-56.5	11.2
VI	6	0	-53.2	0.293	0.289	-0.189	-57.0	12.0
VII	6	1	-53.1	0.293	0.287	-0.210	-57.3	13.2
VIII	6	2	-52.5	0.293	0.287	-0.264	-57.7	16.4
IX	6	3	-52.9	0.293	0.286	-0.220	-57.3	13.7
X	6	4	-52.5	0.293	0.285	-0.246	-57.3	15.2
XI	6	5	-52.4	0.293	0.285	-0.161	-55.5	10.2
XII	6	6	-52.1	0.293	0.284	-0.169	-55.5	10.6
XIII	6	7	-51.8	0.293	0.283	-0.222	-56.2	13.7
XIV	6	8	-51.6	0.293	0.282	-0.115	-53.8	7.37
XV	6	16	-50.9	0.293	0.277	-0.241	-55.6	14.5
XVI	0	2	-53.5	0.293	0.291	-0.110	-55.8	7.27
XVII	0	5	-52.9	0.293	0.289	-0.180	-56.6	11.5
XVIII	0	14	-51.7	0.293	0.282	-0.206	-55.7	12.7

In what follows, we calculate the mass weighted power spectrum  $Z(\omega)$  which is identical to the PDOS measured by neutron scattering<sup>[18]</sup>,

$$Z(\omega) = \sum_a m_a \left| \int_0^\infty v_a(t) \exp(-i\omega t) dt \right|^2 = Z_W(\omega) + Z_{\text{He}}(\omega), \quad (3)$$

where the velocity  $v_a(t)$  is obtained by MD simulations, and  $m_a$  is the mass of atom  $a$ . For He hydrate we separate the above sum into two sums, one for the water  $Z_W(\omega)$  and one for He  $Z_{\text{He}}(\omega)$ . There are unambiguously the coupling of guest and water framework vibrations in the range of 0 ~ 10.3 meV for

xenon hydrate<sup>[24,25]</sup>. In this article we concentrate on high frequency effects. The PDOS  $Z_{\text{He}}(\omega)$  is located in the low frequency range. Comparing helium hydrate with empty GH, we only show calculated PDOS  $Z_W(\omega)$  of the 368 water molecules with different He concentrations in Fig. 1. There is a frequency shift of the experimental and the simulated optical band. This is a drawback of the TIP4P potential<sup>[18]</sup>. However, the optical band shape is better than the lattice dynamical (LD) result and closer to the experimental curve<sup>[6]</sup>. There are differences in the 80 ~ 90 meV range in Fig. 1. These differences are caused by both

water-He interactions and simulation pressures since the simulation temperature is the same. Reduction in the vibrational states in the 80 ~ 90 meV range forms a trough in the PDOS. We argue the trough is the signature of gas encased. The experimental curve of pure ice does not show the trough<sup>[18]</sup>, and the experimental curve 1 of He hydrate shows a trough. In our simulations, most curves of He hydrates show a trough, but curve 1 of an empty GH does not show the trough. In curve 2 only small cages are filled; in curve 4 only large cages are filled; in curve 3 both large and small cages are filled, and the number is nearly equal; and in curve 5 the number of large cages is more than that of the small cages. In curves 3 and 4 the concentrations are the same, there is a trough in the experiment and no trough in curve 3, which indicates that He may be filled not evenly but prominently in one kind of cage. Because of He encased, many random motions of hydrogens meet energy barriers, some vibrational energy states ranging in 80 ~ 90 meV are forbidden so that it can result in a trough in PDOS. As the temperature is low enough at 10 K, many hydrogen motions are forbidden, and the trough also appears<sup>[15]</sup>. With the system pressure increasing, hydrogen orientations become random, and the trough will be filled<sup>[19]</sup>.

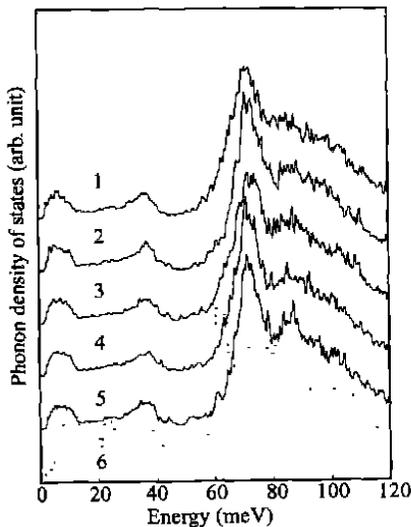


Fig. 1. The PDOS  $Z_w(\omega)$  calculated with the same parameters (23.5 K) for a 368 water hydrogen disordered structure I GH with cubic simulation cell length of 2.32 nm. (1) The PDOS of an empty GH; (2) two He molecules at small cages; (3) six He molecules at small and eight He molecules at large cages; (4) fourteen He molecules at large cages; (5) six He molecules at small and sixteen He molecules at large cages; (6) the experimental spectrum taken from Ref. [6]. The signature of He encased is a trough ranging in 80 ~ 90 meV.

As shown in Table 1, the total internal energy (TIE) increases but it does not monotonously increase with more He molecules encased. Most GH with less than seven He molecules are more stable than an empty one. For large He concentrations the He hydrate is less stable than an empty one. Although PDOS suggests that one kind of cage is occupied by He molecules, it is not energetically favored. The TIE depends a little on what kind of cages He molecules occupy after rolling averages by comparing cases II with XVI, V with XVII, and XIV with XVIII. The energy differences of GH with small  $5^{12}$  and large  $5^{12}6^2$  cages occupied is in the range of  $-0.2 \sim 0.2$  kJ/Mol. Gas molecules are predicted to be located off-center near the cavity wall<sup>[2]</sup>. From the He molecule trajectories shown in Fig. 2, we found that the He molecule in  $5^{12}6^2$  cage is significantly off-center while in  $5^{12}$  cage slightly off-center, because He molecule is a simple molecule with diameter of 0.228 nm, the ratios of He diameters and small  $5^{12}$  and large  $5^{12}6^2$  cage diameters are 0.454 nm and 0.342 nm, respectively. The translational kinetic energy does not depend on the number of He molecules encased, and it depends only on the temperature. In

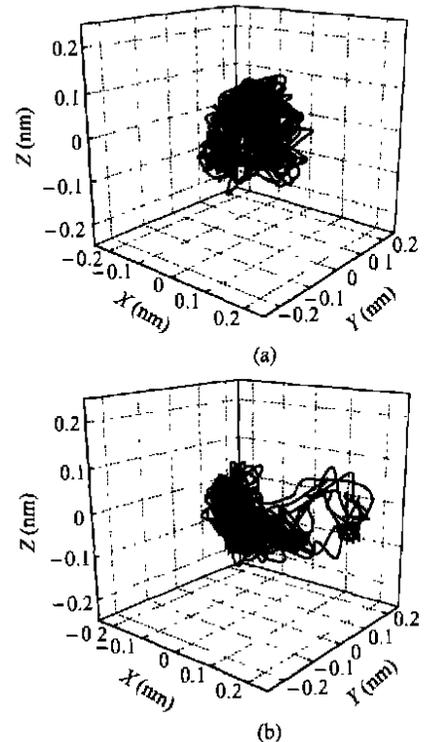


Fig. 2. The trajectories of a He molecule in  $5^{12}$  (a),  $5^{12}6^2$  (b) cage. The starting point is at the origin which is the center of the cage. The average positions calculated over 10000 steps are at (0.002, 0.015, 0.013) for (a) and (0.070, -0.055, 0.005); (b) in unit of nm.

the simulations we do not include a potential to treat He internal molecular rotation. The rotational temperature is equal, as the average rotational kinetic energy decreases with the increase of the number of He encased. Other thermodynamic properties such as pressure, enthalpy and virial are all dependent on the occupation of the cage. The pressure variation on the occupancy cannot be described by an ideal solution behaviour and is consistent with experiments<sup>[5]</sup>. The negative pressures indicate that the difference between the contributions to the virial function from attractive and repulsive forces is greater than the kinetic energy contribution. In order to enlarge the small isotope effects we further simulate two and three He molecule GHs with the mass thirty times heavier and other parameters the same in 5<sup>12</sup> cages. The results show that for the same force field, heavier isotope He molecules are energetically favorable to be filled in cages.

In conclusion, we have studied PDOS of different He hydrates by MD simulations and found a trough at 80 ~ 90 meV in PDOS. The trough is caused by water and He interactions.

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