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| メタデータ | 言語: eng 出版者: 公開日: 2019-05-21 キーワード (Ja): キーワード (En): 作成者: 三浦, 伸一 メールアドレス: 所属: |
| URL | https://doi.org/10.24517/00054029 |

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Molecular dynamics study of guest hydrogen molecules in filled ices II and Ic

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(Received July 25, 2018 and accepted in revised form August 21, 2018)

Abstract We have performed molecular dynamics calculations on fully occupied and one vacancy systems of hydrogen-filled ices II (C_1) and Ic (C_2) with temperature controlled at 291 K. The pressure of 1 GPa and 4 GPa for C_1 and C_2 , respectively, was adopted, where the fast diffusion of guest hydrogen molecules was experimentally observed. In our calculations, hopping processes between lattice sites were observed only in one vacancy system of C_1 and C_2 , indicating the importance of occupation defect for the fast diffusion. The calculated guest diffusion coefficients for one vacancy systems were found to be in good agreement with experimental results. The guest molecules in C_1 show highly anisotropic diffusion, moving only along the optical c axis. On the other hand, the hydrogen molecules in C_2 are found to diffuse in space isotropically.

Keywords. Filled Ice Ic and II, C_1 , C_2 , hydrogen guest.

1 Introduction

Extensive research of hydrogen hydrates have reported the ability of this compound to store a large amount of hydrogen molecules. The compound can be in the form of classical clathrate hydrates and ice-like structures. In the classical clathrate hydrates, the hydrogen molecules are encapsulated in polyhedral cavities formed by hydrogen-bonded water molecules. The encapsulation only involves physical interaction between cage-like structure and the accommodated gas molecules with no chemical mixing. Theoretical and experimental studies have revealed the potential encapsulation of hydrogen molecules within the classical clathrate hydrates with the dissolution through single and multiple accommodations [1–7]. The hydrogen molecules encasing have been studied within sII structure in the range of atmospheric pressure up to 0.36 GPa at the temperature of 150 K to 240 K [8]. The high-pressure condition to perform the synthesise can be reduced by introducing other molecules such as THF [9] and methane [10].

Similar to the classical clathrate hydrates, the molecule's encapsulation in ice-like structures is performed by filling lattice sites of ice with hydrogen molecules to obtain a stable stoichiometric

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solid-compound. Rather than named as the clathrate hydrate, these hydrogen inclusions are known to be filled ice. A high-pressure condition is needed to compensate the repulsive interaction between the host and guest molecules to keep the compound stable. Not only hydrogen, other light noble gaseous molecules [11–13] can also be occupied. Compared to the respective unfilled ice structures, filled ices are more stable in an extended range of pressure and temperature [14–18].

At low-pressure condition, hydrogen molecules can be stored in hexagonal ice. A theoretical study has revealed the ability to store a weight fraction of hydrogen molecules of 3.8 % [19]. However, the experimental study showed the maximum value only up to 0.1 % [20–22]. It has been reported that under a high-pressure condition, ice II and Ic can accommodate hydrogen molecules to give stable hydrate compounds [23]. These materials are also known as hydrogen hydrate C_1 and C_2 , respectively. The lattice site diameter of these ices is acceptable to enclose hydrogen molecules. The total of $H_2:H_2O$ stoichiometry for C_1 is 1:6 while 1:1 is for C_2 . This guest-host ratio of C_2 is equivalent to 10 % wt of H_2 capacity which is potential to be used as hydrogen storage. Under 2 GPa and 295 K, the hydrate C_1 has been reported to have a hexagonal unit cell containing 36 water molecules [23]. The full arrangement consists of the hexagonal array of hydrogen-bonded water molecules which lies on the surface known as the basal plane. The planes are piled along the optical c axis to form hexagonal tube-like columns in a similar way as the ice II. On the other hand, under 3 GPa of pressure, hydrogen hydrate C_2 has been reported to have a cubic crystal structure [23]. The arrangement of water molecules gives eight faces to form diamond-like crystal structures. Hexagonal-shaped column of hydrogen-bonded water molecules can be viewed on $(1\bar{1}0)$ and (110) plane due to the stacking disorder of (111) layers. The surfaces of (111) are similar to the unoccupied cubic ice structure and perfectly coherent to the basal plane of the hexagonal ice [24].

Compared to the diffusion coefficient of the hydrogen molecule in the solid hydrogen, fast diffusion of hydrogen molecules has experimentally been observed in the dense C_1 and C_2 at highly compressed systems [25, 26]. Another interesting feature is provided by the mode of the H_2 molecules to diffuse concerning the crystallographic planes. It has been suggested that the hydrogen molecules diffuse anisotropically in the hydrate C_1 while isotropically in the C_2 [25]. However, the molecular mechanism of the guest diffusion has not been studied theoretically. This knowledge could be valuable in delivering useful features to design more efficient hydrogen-storage systems [27].

In this paper, we report the molecular dynamics (MD) simulation results of the hydrogen hydrate C_1 and C_2 . We aim to provide microscopic information on inter-site diffusion mechanism of hydrogen molecule regarding the experimental observations in C_1 and C_2 structures [25, 26]. We have performed long MD calculations to investigate the hopping events of accommodated hydrogen molecules. We prepared two types of setups on each of the filled ices. Full occupation systems were set to adopt experimental $H_2:H_2O$ stoichiometry, in which 1:6 for C_1 and 1:1 for C_2 [23]. In a similar way to the previous study [28–30], we also simulated the one vacancy system prepared by taking out a hydrogen molecule from a randomly chosen lattice site of the full occupied system; here, one lattice site left empty is considered as an occupation defect that plays an essential role for the hydrogen diffusion in the filled ices.

The rest of this paper is organized as follows. In Sec. 2, we describe the MD methods, systems setup complemented with potential parameters and pair-potential energy calculation. In Sec. 3, we present the results and discussion. Finally, concluding remarks are given in Sec. 4.

2 Computational Details

We carried out molecular dynamics (MD) calculations of hydrogen hydrate C_1 and C_2 systems by using LAMMPS molecular dynamics package [33]. The system's pressure was 1 GPa for C_1 and 4 GPa for the C_2 . Meanwhile, the temperature for all simulated system was controlled to be 291 K. These thermodynamic values were derived from experimental conditions where the fast diffusion of H_2 molecules was found [25, 26]. The NPT condition was applied by the LAMMPS standard procedure [34–39]. Subsequently, the desired temperature and pressure were controlled by implementing a chain of 4 thermostats coupled to the system particles, while the other four to the barostat variables.

To model the intermolecular interaction, Lennard-Jones (LJ) and the Coulomb potential

$$\phi = \sum_{i,j} \left[4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + \frac{q_i q_j e^2}{r_{ij}} \right] \quad (2.1)$$

were used; long-range Coulomb interaction was evaluated by using a particle-particle particle-mesh method [40]. To describe the guest molecules, one site H_2 model [31] was chosen with TIP4P/Ice [32] to specify the water-water interaction. SHAKE algorithm [41] was used to handle rigid water molecules. All of the potential parameters are listed in Table 1. The parameters of intermolecular interaction between water and hydrogen guest molecules were given by using Lorentz-Berthelot combination rules [42, 43].

We performed MD calculations in several stages. Firstly, guest molecules were inserted into the lattice site of ice structure to subsequently entering energy minimization step. All of the chosen ice configurations satisfy Bernal-Fowler [44] rules on $3 \times 3 \times 3$ unit cells, containing 324 water molecules for C_1 while 216 for C_2 [45]. We simulated two different setups for every filled ice system, namely full occupation and one vacancy implemented with periodic boundary conditions. For the maximumly occupied system, the ratio between water and guest molecules for C_1 was 6:1 while 1:1 for C_2 . For comparison, one vacancy was prepared by letting a single lattice site unoccupied. Secondly, all minimum energy configurations were equilibrated for 50 ps. During the equilibration process, energy conservation and controlled thermodynamic conditions were carefully observed. Finally, long MD calculation of 100 ns was performed for full occupation setup, while 50 ns for the one vacancy; longtime simulation run was needed to study the diffusion process in C_1 and C_2 systems. In the equilibrium and production run, thermostat and barostat were implemented with 0.1 ps and 1.0 ps of relaxation time, respectively. We used 1 fs time step for the production run of all simulated systems. A van der Waals cut off radius of 10.0 Å was used in all simulated systems and stages. All of the system's structure presented here were drawn by using Visual Molecular Dynamics (VMD) [46].

Table 1: The potential parameters for water and hydrogen molecules are collected. For H_2 molecules, LJ site is located at the center of mass [31]. For water molecules, TIP4P/Ice water model is adopted [32]. A negative charge is placed at an M site, located between the center of H-H and oxygen.

| Model | Site | $q(e)$ | $\sigma(\text{Å})$ | $\epsilon(\text{kcal/mol})$ |
|----------------|--------|----------|--------------------|-----------------------------|
| H_2 [31] | Center | 0.0 | 2.96 | 0.067962 |
| TIP4P/Ice [32] | H | 0.5897 | | |
| | O | | 3.1668 | 0.21084 |
| | M | -1.1794 | | |

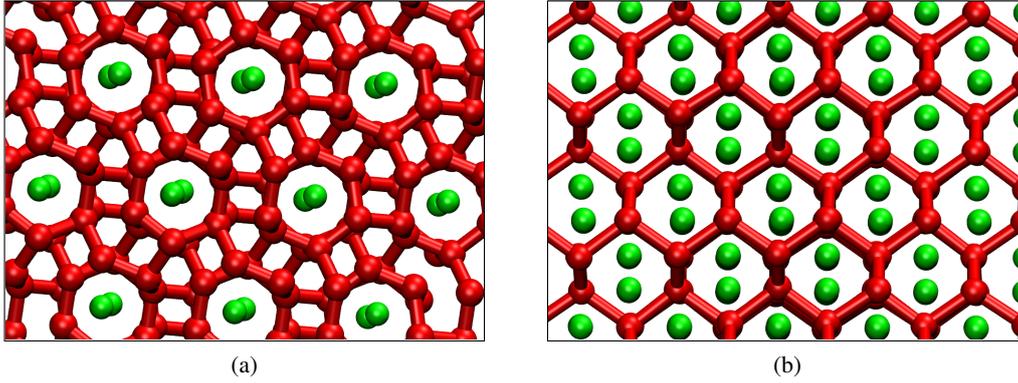


Figure 1: The arrangement of oxygen atoms (red spheres) and H_2 molecules (green spheres) in (a) hydrate C_1 and (b) C_2 . Hydrate C_1 is viewed parallel to the basal plane and C_2 on (110) plane. Bond connecting the adjacent oxygen atoms are drawn to clarify the structural configuration with the distance criteria 3.0 \AA for hydrate C_1 and 2.8 \AA for C_2 .

3 Results and Discussion

We first mention the molecular dynamics results in full occupation setups. In these arrangements, each lattice site accommodates one hydrogen molecule. The structure can be considered to be ideally synthesized filled ices in which no site left unoccupied. Initially, the guest molecules have been placed in the center of each site in the ice structure. During 100 ns of simulation time, all the guest molecules are found to oscillate only inside its site. Eventually, we observed no inter-site movement during the simulation time on neither hydrate C_1 nor C_2 .

We then present diffusion process occurred in one vacancy setups. As can be seen in the full occupation, the lattice site is supposed to be engaged by one hydrogen molecule. In contrast with the full encapsulation, during 50 ns of simulation, many inter-site jumping events were observed for the hydrogen molecules. The inter-site hopping schemes are noticeable in hydrate C_1 and C_2 . The movement involving only the hydrogen molecules located next to the empty site was observed. This clearly indicates the need for the vacancy to facilitate the inter-site translation of the encapsulated guest molecules. To quantitatively investigate the process, we calculated the mean square displacement of a tagged hydrogen guest molecule in one vacancy systems as a function of time t , $\langle |\Delta \mathbf{r}(t)|^2 \rangle$. The mean square displacement is linked with the diffusion coefficient D by

$$\langle |\Delta \mathbf{r}(t)|^2 \rangle = 6Dt \quad (3.1)$$

in a long time regime. In the case of the C_1 structure, the hydrogen molecules are anisotropically coordinated by other hydrogen molecules as shown in Fig. 1 (a). Since the lattice site distance along the c axis is about three times shorter compared to the adjacent neighboring distance on the basal plane, the molecules are found to move only along the optical c axis. We observed that the inter-site diffusion of the hydrogen molecules could be seen only in a specific channel where the vacancy is initially set up. To take account of this observation to evaluate the diffusion coefficient, the mean square displacement was calculated for the hydrogen molecules in the specific channel. On the other hand, as shown in Fig. 1 (b) for the hydrate C_2 , the hydrogen molecules are tetrahedrally coordinated by other hydrogen molecules. The molecules are supposed to move along the direction of the coordinated molecules. Under this circumstances, hydrogen molecules would travel along the tetrahedral direction on the inter-site translation. Therefore, all of hydrogen molecules movements are considered to contribute to the diffusion process. The calculated mean square displacements are presented in Fig. 2. For 2 ns, all plots show linearly increasing MSD.

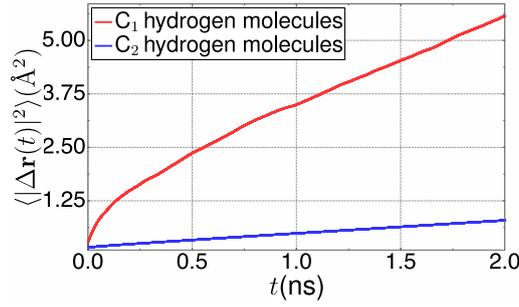


Figure 2: Mean square displacement of the hydrogen molecule as a function of time t in one vacancy configurations.

The evaluated diffusion coefficients are collected in Table 2. The diffusion coefficients for the hydrate C_1 and C_2 are found to be in good agreement with the experimental results [25, 26]; here, the fast diffusion of hydrogen molecules is successfully reproduced by our simulations.

The guest jumping among sites occur sequentially. In more details, these inter-site movements are presented in Fig. 3. Time evolution of one tagged hydrogen molecule on each filled ice system is selected to demonstrate details of the inter-site movement. In the case of the hydrate C_1 , the inter-site translation only occurred along the optical c axis; an example of this anisotropic hydrogen diffusion is depicted in Fig. 3 (a). The figure shows the time evolution of a tagged hydrogen molecule from 110.8 ps to 111.0 ps pictured along the basal plane of ice II structure. Shown by yellow spheres, the movement of a tagged hydrogen molecule in the channel took 200 fs to complete. During the first 100 fs, the hydrogen molecule already on its halfway towards the new lattice site position. Distance covered from this early stage is 2.55 \AA while the second is 1.49 \AA . With only one vacancy in the whole system, most of the hydrogen molecules oscillate within its lattice site. Inter-site movement is observed only when the adjacent lattice site is unoccupied.

In the case of the hydrate C_2 system, the evolution of a tagged hydrogen molecule from 24.8748 ns to 42.3493 ns is depicted in Fig. 3 (b). All of the molecules are viewed on the hexagonal puckered-plane of the cubic ice structure. The trajectory drawn in the figure corresponds to the pathway of one hydrogen molecule when performing inter-site jumping during the time period. To clarify the jumping process, three different sphere colors are used to describe the trajectory taken by the guest molecule on performing inter-site movement at a consecutive time. The yellow and blue spheres show the jumping parallel to the (011) plane observed at 24.8748 ns and 42.3491 ns, respectively. The green particles are used to demonstrate the movement along the (0 $\bar{1}$ 1) plane at 36.2858 ns. All of the inter-sites translation took 200 fs to complete with distinctive covered distance throughout stages in the period; here, the guests are hopping between the adjacent hexagonal vertex formed by tetrahedrally coordinated hydrogen molecules as shown in Fig. 1 (b). The inter-site diffusion is terminated since no available vacancy to prohibit the occupation. In the meantime, the hydrogen molecule oscillates inside its new lattice site during the time interval

Table 2: Diffusion coefficient of hydrogen molecules (D) in units of cm^2s^{-1} . C_1 and C_2 are for filled ice II and Ic, respectively.

| System | D | Exp. |
|--------|----------------------------|---------------------------|
| C_1 | $3.852(3) \times 10^{-8}$ | 1.3×10^{-8} [25] |
| C_2 | $5.1798(9) \times 10^{-9}$ | $\simeq 10^{-9}$ [26] |

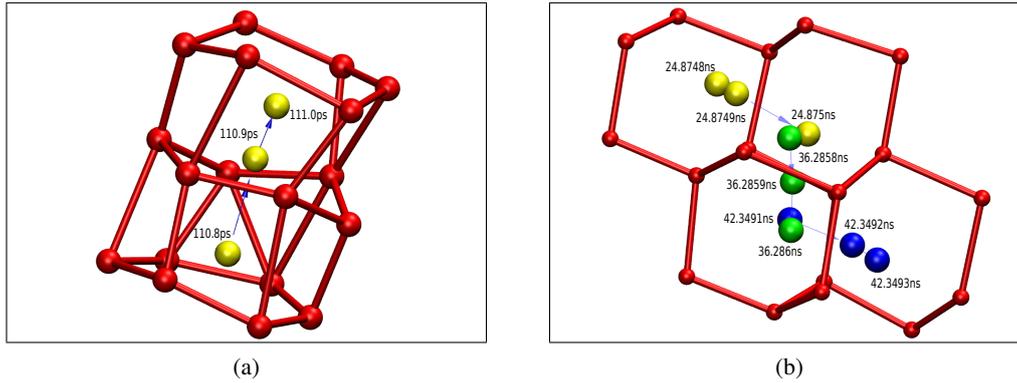


Figure 3: Diffusion mechanism of a tagged hydrogen molecule in (a) hydrate C_1 viewed along ice II basal plane and (b) hydrate C_2 drawn parallel to (110) plane of ice Ic. Red spheres are drawn to describe oxygen atoms of water molecules, connected by hydrogen bond shown by the red stick. Blue arrows indicate the direction of movement along the trajectory. Colored spheres (green, blue and yellow) are for hydrogen molecules. In both figures, similar color is used to represent the same hopping scheme in successive time. In the case of hydrate C_1 , yellow spheres indicate the hydrogen movement along the optical c axis. In hydrate C_2 , the inter-site diffusion mechanism parallel to the $(0\bar{1}1)$ plane is shown by the yellow and blue spheres, while for the scheme parallel to the (011) plane, it is represented by the green spheres.

between the observed jumping process.

To provide more information, we present a potential field map of pair interaction between a tagged H_2 molecule and its surrounding water molecules. The calculation was performed by using a system snapshot at a consecutive time before an inter-site jumping process is observed. We adopted a similar method developed in Ref. [47]. We calculated the map as follows. Firstly, a snapshot of the filled ice system is selected. Then, the projection surface is calculated concerning the hexagonal-puckered plane of ice structure. We then divided the surface into small rectangular spaces of 0.1 \AA . Subsequently, we move the tagged molecule to the grid on the projection surface and calculate the total potential energy. Finally, the energy values are contoured with the interval defined by $a \times 4^n$, where a is the starting value of potential energy, and n is the number of the contour line. The results are presented in Figs. 4 and 5. We calculate the potential maps to show the availability of a pathway through sites concerning the potential energy. This information will lead to the chosen jumping trajectories performed by hydrogen molecules, and the track indeed comparable to the unit cells of hydrogen hydrate. Within these figures, the local maxima are shown when the trial tagged hydrogen molecule position coincides with the occupied lattice site location and every water molecules coordinate along the calculated crystallographic plane. On the other hand, the local minima area can be found when the trial position of a tagged hydrogen molecule post in an unoccupied calculation grid of lattice point and its actual position. It also can be seen in the figure that there are energy barriers found between local minima's points and the position of a tagged hydrogen molecule. This feature inhibits the tagged molecule to move across the confinement to accommodate other low potential energy areas. The similar pattern is observed on all calculated planes. However, we find relatively wide-flat-area that covers tagged hydrogen molecule location. This low potential field area encompasses the surface where the vacancy is located. The area can be found in Fig. 4 (b), Fig. 5 (a) and Fig. 5 (b) where hydrogen molecules perform inter-site diffusion along the depicted crystallographic planes. To connect the localized area of potential minima feature with the inter-site translation, we observed the path followed by the tagged molecule in the next consecutive time-frame. It is found that the diffusing molecule

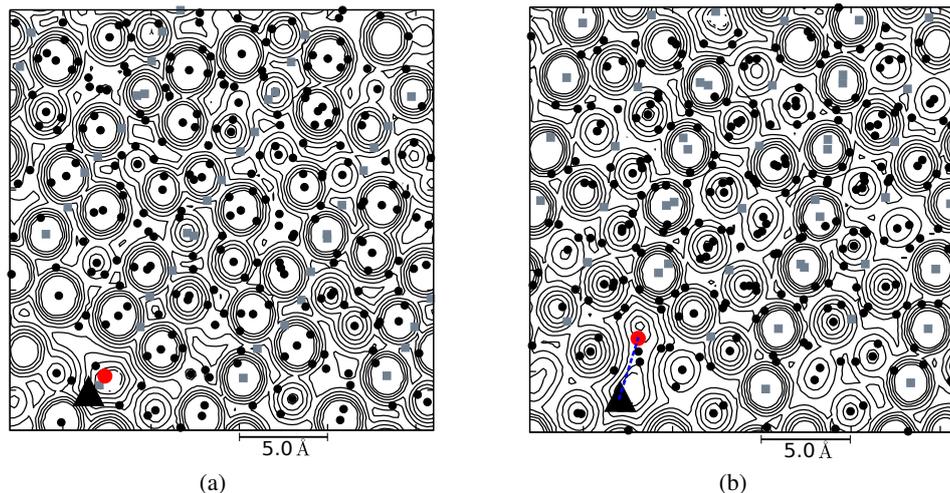


Figure 4: Potential energy contour of one vacancy C_1 system, snapshots are drawn at 0.36619 ns on the surface parallel to (a) basal and (b) optical plane. On the basal plane, ten contour lines are used with the lowest represent energy value of 1 kcal/mol and the highest is 2.6×10^5 kcal/mol. Meanwhile, there are 14 contour lines used on the optical plane; here, the lowest energy line represents 6.25×10^{-3} kcal/mol. Projected hydrogen molecules and oxygens of water molecules are represented by gray rectangles and black spheres, respectively. The tagged hydrogen molecule to perform inter-site translation is represented by a black triangle, and the vacancy location is described by a red sphere. The dashed blue line shows the path taken by the tagged hydrogen molecule when performing inter-site jumping in the next consecutive time.

moves across this low potential field area. In contrast, a slightly different pattern occurred in the basal surface of the hydrate C_1 . As can be seen in Fig. 4 (a), energy barriers are built between the tagged hydrogen molecule and the vacancy location, thus prohibiting the inter-site movement along the plane; the guest hopping is only noticeable along the optical c axis.

4 Concluding Remarks

In the present study, we have performed molecular dynamics calculations for the hydrogen hydrate filled ice II and Ic; the former is called C_1 , and the latter is C_2 . Our calculated diffusion coefficients are found to be in good agreement with experimental results; the fast diffusion of the hydrogen molecules has successfully been reproduced. We observed the anisotropic diffusion of the hydrogen molecules for C_1 and the isotropic for C_2 . We found that the occupation defect of guest molecules or vacancy is essential to facilitate the inter-site translation; no energy barrier on the movement is seen when the adjacent nearest neighbor lattice site is unoccupied.

Our next work would be the hydrogen hydrates at a low temperature. The recent experimental study has revealed the ability to synthesize filled ice system at low temperature and pressure with partial occupation [48]. Under the low-temperature condition, quantum effect of hydrogen molecule dynamics is expected to be significant. It has been reported in hexagonal ice that quantum effect at 220 K gives noticeable contrast in lattice vibrations and potential energy in comparison to the classically approximated systems [49]. This issue will be addressed in the near future.

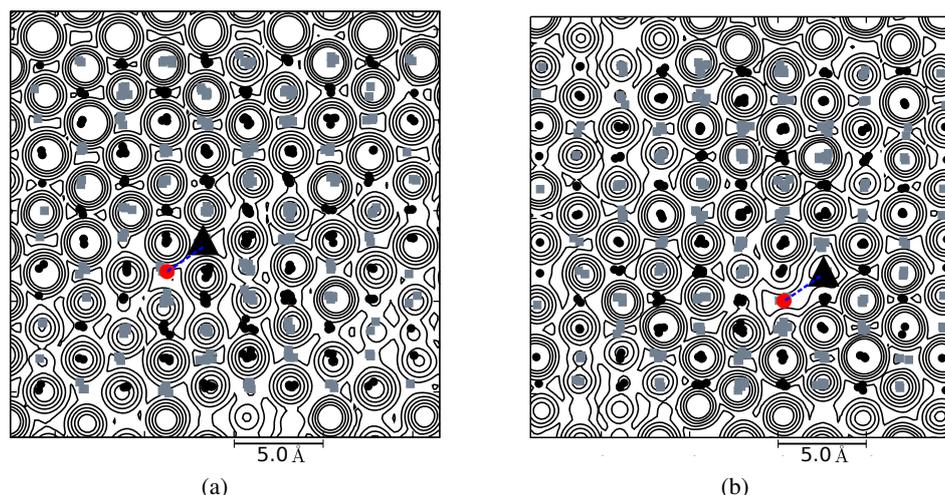


Figure 5: Contour plot of one vacancy hydrogen hydrate C_2 potential energy drawn on the (a) (110) surface and (b) $(\bar{1}10)$ plane of cubic ice. The snapshot is depicted at 0.40106 ns for the (110) surface while on the $(\bar{1}10)$ is at 0.60572 ns. There are eight isolines to describe potential energy map for the (110) surface, with the lowest value is 64 kcal/mol. Similarly, eight increasing contour lines are used to describe the potential field on the $(\bar{1}10)$ face. The line represents energy value started at 16 kcal/mol. In both figures, the tagged hydrogen molecule is represented by a black triangle and the vacancy position is denoted by a red sphere. Black spheres and gray rectangles indicate the projected oxygen position of water molecules and other hydrogen molecules on the plane, respectively. The dashed blue line indicates the inter-site diffusion path followed by the tagged hydrogen molecule at the next consecutive time.

Acknowledgments

YA would like to show his gratitude to Directorate General of Higher Education, Ministry of National Education, Indonesia for the support.

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