Carbon dioxide occupancies inside ice XVII structure from grand-canonical Monte Carlo simulation

Irwansyah Putra Pradana¹, Diah Mardiana¹, Lukman Hakim¹, *

¹ Department of Chemistry, Faculty of Science, Brawijaya University, Jl. Veteran, Malang, 65145, Indonesia.

*Corresponding author: lukman.chemist@ub.ac.id

Abstract. Clathrate hydrate is a promising material that can be used to trap the carbon dioxide (CO₂) as a mean for the greenhouse-gas emission control. A compromise between experimental findings and density functional theory calculations was recently made to determine the occupancy of the newly reported CO₂ clathrate hydrate of ice XVII structure. In this work, a hybrid isobaric Grand-Canonical Monte Carlo simulation is performed as a direct approach to determine CO₂ occupancy inside ice XVII structure. The simulation results show that the CO₂-to-water ratio starts at about 1:3.55 under lower pressure and ends at about 1:4 under high pressure. The potential energy of CO₂-water interaction as a function of CO₂ molecule displacement inside the voids shows a cage-like character, and the orientation of CO₂ molecules inside the spiral void is shown to be well-ordered. The simulation results support the experimental observation and provide molecular insight into the structure of CO₂ molecules inside the ice XVII structure.

1. Introduction

Investigation of new methods and materials for controlling CO₂ emission to the atmosphere has been widely carried out to reduce the impact of greenhouse gas on global climate change [1–3]. Carbon dioxide clathrate hydrates are non-stoichiometric compounds of ice-like crystalline water whose voids are occupied by CO₂ molecules [4]. The ice-like structure is termed as the host, while the CO₂ is termed as the guest. This material is viewed as a potential candidate to trap the excess CO₂ for long-time storage.

The CO₂ clathrate hydrate has been known to exist as a cubic clathrate-I (CS-I) structure at low-pressure and low-temperature regions [5]. Upon compression, the clathrate then decomposes to ice VI and dry ice at high pressure. However, Hirai and co-workers reported the emergence of a new phase of CO₂ clathrate hydrate under pressure region between the stable CS-I and ice VI-CO₂(s) [6]. Further investigation shows that the structure of this new CO₂ clathrate hydrate is the same with the new hydrogen clathrate-hydrate of the C₀ structure reported by Efimchenko [7]. The extraction of guest molecules from this clathrate-hydrate under vacuum produced a metastable ice structure termed as ice XVII [8,9].

A refined experimental work using neutron and synchrotron X-ray diffraction shows that the water lattice in ice XVII consists of five-membered rings of hydrogen-bonded water molecules. The water molecules form hexagonal helices with a diameter of 0.610 nm, measured from the center of the oxygen atoms, creating a spiral tunnel where guest molecules such as CO₂ and hydrogen can reside. The experimental results, however, encountered by uncertainty in the number of carbon dioxide that occupies the voids of ice XVII due to the mobility of guest molecules, and it was settled to be 1:3.55 with the
results of density functional theory calculation performed at CO$_2$-to-water ratio of 1:4 [10]. This occupancy value describes the capacity of CO$_2$ trapping capacity that can be carried out inside the ice XVII structure, thus an intriguing issue from the industrial perspective, especially since the stable pressure region for this clathrate-hydrate structure is practically feasible at the order of several kbar [11].

In this work, the occupancy of CO$_2$ as a function pressure is directly determined using a hybrid type Monte Carlo (MC) simulation in grand-canonical and isobaric ensembles. The method has been reported to successfully reproduce the occupancy of hydrogen, neon, and carbon dioxide in the clathrate hydrate system [12–15]. The simulations also provide information on the CO$_2$ configuration inside ice XVII, as well as the potential energy profile of CO$_2$ molecule inside the cavity of ice XVII.

2. Research Methods

2.1. Potential Models and Structure of Ice XVII

All potential energies are defined as the sum of intermolecular pair-interaction. The non-bonded interaction is expressed as the summation of Lennard-Jones (LJ) 12-6 term and the electrostatic term. A rigid body model for CO$_2$ according to the work of Zhigang and co-workers [16] is employed and is referred as Z3D model onward. The interaction between water molecules is described by TIP4P/ice potential [17]. This potential model is derived from the TIP4P model that is often used to study water and ice, and the TIP4P/ice is tailored to provide better accuracy in reproducing the phase diagram of ice. Detailed parameters for Z3D and TIP4P/ice models are shown in Table 1. The CO$_2$-water interaction is calculated according to the Lorentz-Berthelot mixing rule. A switching function, starting from separation distance of 0.6655 nm, is applied to the pair potential energy and gives a smooth truncation at 0.8655 nm [18].

The proton-disordered ice XVII structure, containing 1296 water molecules, is generated according to the Bernal-Fowler rule using the GenIce package [19]. The simulation cell of CO$_2$ hydrate of ice XVII is considered a rectangular prism with a dimension of 3.7381 nm × 3.2906 nm × 3.5787 nm. The periodic boundary condition for all simulations are implemented in all directions.

2.2. Simulation Methods

2.2.1. MD Simulations and the Chemical Potential of CO$_2$ Fluid

The grand canonical ensemble corresponds to the equilibrium state between CO$_2$ inside the voids of ice XVII structure with CO$_2$ in the fluid phase outside, marked by the equality of CO$_2$ chemical potential in both phases. The chemical potential of ideal-gas is not appropriate to describe the CO$_2$ fluid under high pressure and low temperature; thus, an isobaric-isothermal molecular dynamics (MD) simulations are carried out using GROMACS 2018.7 package [20] to obtain the isotherm pressure-density curves of CO$_2$ fluid. The equation motion is settled using the algorithm of velocity-verlet at 2 fs time step. The temperature is maintained using the Nosé-Hoover thermostat, while the pressure is maintained using the Parrinello-Rahman barostat. The sampling is done over the 1.0 ns time evolution.

For a single-component and single-phase system, the Helmoltz energy per molecule, $a$, is given by the sum of ideal and non-ideal parts as

$$a = k_B T \left[ \ln \left( \frac{h^2}{2\pi m k_B T} \right)^{3/2} \right] - 1 + \ln \left( \frac{h^2}{4\pi^2 I k_B T} \right) + \int_0^\rho \frac{P - \rho k_B T}{\rho^2} d\rho. \tag{1}$$

where $m$ and $I$ are the mass and moment of inertia of CO$_2$, respectively. The chemical potential of CO$_2$, $\mu_g$, is then given as

$$\mu_g = a + \frac{P}{\rho}. \tag{2}$$

where density $\rho$ at a given pressure, $P$ is obtained from the NPT MD simulation results.
Table 1. Parameters for CO$_2$ and water potential models used in this research. In TIP4P/ice, M refers to the negative charge located on a bisector of two OH bonds.

| Model      | Site | $\sigma$ / 0.1 nm | $\varepsilon$ / kJ mol$^{-1}$ | $q$ / e  |
|------------|------|-------------------|-------------------------------|---------|
| CO$_2$/Z3D | C    | 2.7918            | 0.2398                        | +0.5888 |
|            | O    | 3.0000            | 0.6871                        | -0.2944 |
| TIP4P/ice  | H    | -                 | -                             | +0.58970|
|            | O    | 3.1668            | 0.8822                        | -       |
|            | M    | -                 | -                             | -1.17940|

2.2.2. Isobaric Grand-Canonical Monte Carlo Simulation

The occupancy of CO$_2$ molecules inside the cavity of ice XVII structure is directly investigated using a hybrid-type of Monte Carlo simulation in grand-canonical isobaric-isothermal ensemble (GC/NPT MC). The attempts to insert or eliminate CO$_2$ are carried out with the same probability under constant chemical potential. A trial insertion of the CO$_2$ is performed on random position and orientation represented by polar ($\theta$) and azimuthal ($\phi$) angles. The insertion of CO$_2$ is conducted with the probability

$$\max \left\{ \exp [\beta (\mu'_g - w)] \frac{V \sin \theta (2\pi \beta m_g / h^2)^{3/2}}{N_g + 1}, 1 \right\},$$

where $w$ is the interaction energy between CO$_2$ and the surrounding water molecules, $\mu'_g$ is the chemical potential of CO$_2$ that does not include the contribution from the free-rotational motion. A trial elimination of CO$_2$ is conducted by choosing an existing CO$_2$ randomly, and the trial is accepted with the probability

$$\max \left\{ \exp [\beta (\mu'_g + w)] \frac{N_g}{V \sin \theta (2\pi \beta m_g / h^2)^{3/2}}, 1 \right\}.$$

In this Monte Carlo simulation, one MC step consists of a trial CO$_2$ molecule insertion or elimination with an equal probability, followed by five attempts to move a guest molecule or a water molecule that is randomly chosen, and a trial volume change based on the pressure. Each simulation is performed for at least $10^8$ MC steps.

3. Results and Discussion

The isotherm pressure-density curve of CO$_2$ modeled here at 273.15 K in the range of 10 to 2000 MPa is depicted in Figure 1. At low pressure, the chemical potential of CO$_2$ fluid is shown to be less than its ideal gas counter-part, emphasizing the intermolecular attractive-force that tends to lead to CO$_2$ condensation. As the pressure increases beyond 100 MPa, the chemical potential of CO$_2$ deviates rapidly from the ideal gas curve due to the strong intermolecular repulsion. The curves shape provides a realistic representation of CO$_2$. In GCMC simulation, the chemical potential of CO$_2$ at a certain pressure is fixed according to this isotherm.
Figure 1. Pressure dependence of chemical potential of CO$_2$ fluid. The ideal gas curve (dashed-line) is provided here as a reference.

The typical depiction of clathrate hydrate where guest molecules are encaged inside the host structure is somewhat less relevant in the case of CO$_2$ hydrate of ice XVII structure because of the cavity shape in ice XVII that resembles a spiral tunnel. Figure 2 shows the potential energy curve arising from the interaction of a single CO$_2$ molecule with the surrounding water molecules inside the cavities of ice XVII. The potential energy is calculated as a function of CO$_2$ displacement from its equilibrium position, obtained by quenching the system at 0 K, and averaged over all CO$_2$ molecules. The displacement is classified according to each axis direction. As shown in Figure 2, as the CO$_2$ molecule moves 1 Å away from its equilibrium position, at any axis direction, the rapid increase of potential energy resembles a cage-like profile whose radius is between 1.0 - 1.5 Å. Figure 2(c) also suggests that the movement along z-axis is also limited with similar cage-like property. The description may be confusing because the voids in ice XVII have a spiral-tunnel shape that stretches along the z-axis. However, those potential energy curves are built under the absence of thermal motion of water molecules; thus, it should not be interpreted that CO$_2$ cannot move across the tunnel. Nevertheless, the information provided by Figure 2 is useful to understand the size of the cavities of ice XVII, whose size may change due to the thermal motion of water molecules. Figure 2 also shows that the orientation of CO$_2$ molecule does not significantly alter the profile of cage-like cavity. Note that the shift of potential energy curve due to orientational change in Figure 2 is due to the way that the displacement is always measured from the center carbon. At certain orientation, e.g. at $\theta = \pi/2$, the oxygen atom becomes very close to the tunnel “wall” along x-axis; thus, the displacement on x-axis direction becomes more limited.

The Isobaric Grand-Canonical Monte Carlo simulations of CO$_2$ inside ice XVII at 273.15 K are carried out in the pressure range between 0.05 and 2.0 GPa. The occupancy of CO$_2$ is expressed as the ratio of the number of CO$_2$-to-water molecules, $N_w/N_g$ and is shown in Figure 3. The occupancy of CO$_2$ inside ice XVII is found near 1:3.55 at low pressure, which is similar to the experimental finding. However, uncommon to clathrate hydrate, Figure 3 shows a slight increase in the $N_w/N_g$ curve with the increase of pressure, which means that the number of CO$_2$ inside ice XVII decreases during the course of compression. The possible cause is that the shrinking of system size due to compression increases the free energy of occupancy to a degree that is not favorable even with the increase of chemical potential. The simulation also suggests that the CO$_2$ hydrate of ice XVII is mechanically stable at a range of 0.05 - 1.6 GPa. Further compression beyond 1.6 GPa, although it increases the CO$_2$ occupancy due to the increase in chemical potential of CO$_2$ fluid, leads to a distortion in the ice XVII structure. This observation is consistent with the stable region of CO$_2$ clathrate hydrate of ice XVII structure in the phase diagram that was reported by Michl [11]. It is reasonable to argue that further distortion at higher pressure may lead to a phase separation that develops into the formation of ice VI and dry ice.
The potential energy curve of interaction between a CO$_2$ molecule with the surrounding water molecules in ice XVII. The potential energy is shown as a function of CO$_2$ displacement from its equilibrium position along the (a) x-direction, (b) y-direction, and (c) z-direction.

Figure 2. The potential energy curve of interaction between a CO$_2$ molecule with the surrounding water molecules in ice XVII. The potential energy is shown as a function of CO$_2$ displacement from its equilibrium position along the (a) x-direction, (b) y-direction, and (c) z-direction.

An insight to the CO$_2$ configurations inside the ice XVII cavities is obtained by analyzing the angular distribution CO$_2$ molecules at its maximum occupancy. The orientation of a linear molecule such as CO$_2$ can be simply expressed in terms of two angles in spherical coordinate: $\theta$ and $\phi$. The $\theta$ angle describes the orientation of CO$_2$ against the z-axis, and the $\phi$ angle describes the orientation of CO$_2$ on the $xy$-plane. Figure 4 shows that CO$_2$ molecules tend to arrange themselves in configurations with $\theta = \pi/4$ and $3\pi/4$. These angles indicate a zig-zag orientation of CO$_2$ inside the tunnel. The distribution also suggests that CO$_2$ molecules tend not to align themselves closely parallel to z-direction ($\theta = 0$, or $\theta = \pi$). Furthermore, Figure 2 suggests that the cavity size is too small for stacking two or more CO$_2$ in the circular plane of the tunnel; thus, the only plausible configuration is to have CO$_2$ molecules lining across the tunnel in the z-direction with zig-zag orientation. In addition, the orientation of CO$_2$ in $xy$-plane described by $\phi$ angle is less defined as the orientation angle is broadly distributed, except for a peak between $\pi/2$ and $3\pi/4$. 
Figure 3. Pressure dependence of CO$_2$-to-water molar ratio in CO$_2$ hydrate of ice XVII structure, obtained from isobaric grand-canonical Monte Carlo simulation.

Figure 4. Distribution of orientational angles of CO$_2$ molecules inside ice XVII structure.

4. Conclusion
The isobaric grand-canonical MC simulation is useful as a direct approach to determine the occupancy of CO$_2$ hydrate and provide an insight into the CO$_2$ configurations. The occupancy of CO$_2$ inside ice XVII structure from simulations results is found to be aligned with the experimental findings, but the number of CO$_2$ molecules inside ice XVII is shown to be unusually decreasing during the course of compression. The simulations further show that CO$_2$ hydrate of ice XVII structure is mechanically stable at the low-pressure region up to 1.6 GPa, which is in line with the hydrate stable region in the phase diagram.

References
[1] Sanz-Pérez E S, Murdock C R, Didas S A and Jones C W 2016 Chem. Rev. 116 11840–76
[2] Ekwurzel B, Boneham J, Dalton M W, Heede R, Mera R J, Allen M R and Frumhoff P C 2017 Clim. Change 144 579–90
[3] Pradana I P and Hakim L 2019 IOP Conf. Ser. Earth Environ. Sci. 239 1–7
[4] Sloan E D and Koh C 2007 Clathrate Hydrates of Natural Gases, Third Edition vol 20074156
[5] Loveday J S and Nelmes R J 2008 Phys. Chem. Chem. Phys. 10 937–50
[6] Hirai H, Komatsu K, Honda M, Kawamura T, Yamamoto Y and Yagi T 2010 J. Chem. Phys. 133 12–5
[7] Efimchenko V S, Kuzovnikov M A, Fedotov V K, Sakharov M K, Simonov S V. and Tkacz M 2011 J. Alloys Compd. 509 860–3
[8] del Rosso L, Celli M and Ulivi L 2016 Nat. Commun. 7 13394
[9] del Rosso L, Grazzi F, Celli M, Colognesi D, Garcia-Sakai V and Ulivi L 2016 J. Phys. Chem. C 120 26955–9
[10] Amos D M, Donnelly M E, Teeratchanan P, Bull C L, Falenty A, Kuhs W F, Hermann A and Loveday J S 2017 J. Phys. Chem. Lett. 8 4295–9
[11] Michl J, Sega M and Dellago C 2019 J. Chem. Phys. 151 104502
[12] Hakim L, Koga K and Tanaka H 2010 Phys. Rev. Lett. 104 115701
[13] Hakim L, Koga K and Tanaka H 2010 Phys. A Stat. Mech. its Appl. 389 1834–8
[14] Hakim L, Koga K and Tanaka H 2010 Phys. Rev. B 82 144105
[15] Matsuo M, Takii Y, Matsumoto M and Tanaka H 2012 J. Phys. Soc. Japan 81 1–6
[16] Zhang Z and Duan Z 2005 J. Chem. Phys. 122 1–15
[17] Abascal J L F, Sanz E, Fernández R G and Vega C 2005 J. Chem. Phys. 122 1–9
[18] Ohmine I, Tanaka H and Wolynes P G 1988 J. Chem. Phys. 89 5852–60
[19] Matsumoto M, Yagasaki T and Tanaka H 2017 J. Comput. Chem. 61–4
[20] Hess B, Kutzner C, Van Der Spoel D and Lindahl E 2008 J. Chem. Theory Comput. 4 435–47

Acknowledgments
The research work is supported by research grants from DPRM Indonesian Ministry of Research, Technology, and Higher Education.