

# Thermodynamic stability of C<sub>3</sub>H<sub>8</sub> hydrate of cubic structure IV using lattice dynamics

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**Abstract** The thermodynamic properties of propane clathrate hydrate with cubic structure IV were studied using a method based on the solid solution theory of van der Waals and Platteeuw but allows one to take into account the influence of guest molecules on the host lattice and guest-guest interactions. The free energies, equations of state, and chemical potentials of this hydrate were estimated using this approach. The proposed theory was used for construction of “guest gas–hydrate–ice I<sub>h</sub>” equilibrium curves of propane hydrates. It was found that the water framework of structure IV was dynamically stable and that the fully C<sub>3</sub>H<sub>8</sub> filled structure was thermodynamically stable in the region of pressure from 43 to 50 MPa as compared with the hexagonal ice. The formation pressure of propane hydrate with structure IV is higher than that of propane hydrate with cubic structure II. However, a structural transformation from structure II to IV of propane hydrate was estimated under a pressure of 78 MPa at 290 K.

**Keywords** Thermodynamic stability · sIV clathrate hydrate · C<sub>3</sub>H<sub>8</sub> · Lattice dynamics

## Introduction

Clathrate hydrate is a special class of inclusion compounds consisting of water and guest molecules, which form a variety of hydrogen-bonded structures. Under certain thermodynamic conditions, water molecules arrange themselves in a cage-like structure around guest molecules and form a crystalline solid with physical and chemical properties that are different from those of ice [1]. Despite the fact that clathrate hydrate was discovered more than 200 years ago, interest in these structures has considerably grown with the discovery of large amounts of natural gas hydrates under conditions of high pressure and low temperature in the permafrost regions or below the ocean floor. At present, most of the recognized gas hydrates have one of three well-known types of structures: cubic structures I (sI) and II (sII) [2–4] and a hexagonal structure (sH) [5, 6]. It has also been proved that gas hydrates are sensitive to pressure variation due to relatively weak binding energy between water molecules; hence, the friable packing of the host framework. The sequential change of the hydrate phase in different gas–water system is observed when the pressure is increased up to 1.5 GPa [7, 8].

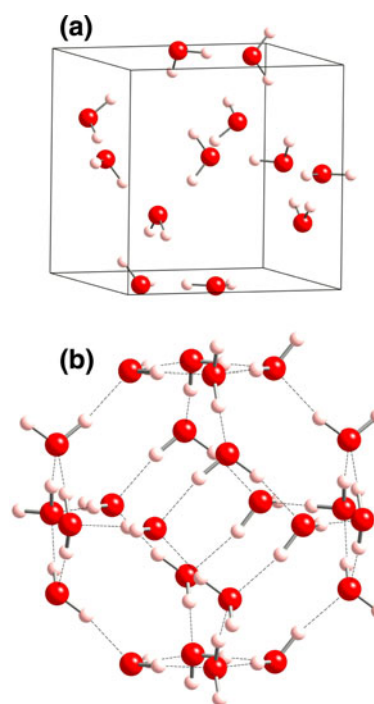
Recently, interest in these compounds has significantly risen after the realization of the hydrogen sII hydrate with high hydrogen content [9], which has been hypothesized several years earlier [10]. The estimated value of hydrogen stored in sII hydrate was 5.3 wt%, which exceeded the 2005 DOE hydrogen storage targets [11]. Subsequently, many experimental and theoretical studies of hydrogen hydrates using different methods were carried out, the most significant achievements having been summarized in recent reviews [12, 13]. A significant part of the works concentrated on accurate estimation of the hydrogen capacity of the sII hydrate and under what conditions the maximum

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capacity can be achieved. The sII structure has two types of cavities classified as small ( $5^{12}$ ) and large ( $5^{12}6^4$ ) cages. The possibility of fourfold filling of large cages and twofold filling of small cages by hydrogen molecules proposed by Mao et al. [9] has been analyzed in detail by several groups [13]. Neutron diffraction studies of the composition of sII hydrogen hydrate have been performed [14]. The occupancy of large cavities by four hydrogen molecules was confirmed but only the single occupancy of the small cavity was found at low temperature and high pressure ( $\sim 200$  MPa), which was recently confirmed by other methods [13]. This has resulted in the hydrogen storage capacity reduction of sII hydrate up to 3.77 wt%. Other studies have focused on the formation of hydrogen hydrates at lower pressure because pure hydrogen sII hydrate can be formed only at high pressure. Thus, it has been found that the introduction of the tetrahydrofuran (THF) molecules into the hydrogen–water system significantly reduces the hydrate formation pressure [15, 16]. Moreover, after low pressure formation of binary THF + hydrogen hydrate, it is possible to realize hydrogen storage of around 4 wt% at low THF concentrations by increasing pressure due to the “composition tuning mechanism” proposed by Lee et al. [16] and recently confirmed by another group [17] who reported a smaller  $H_2$  storage amount, i.e., 3.4 wt%.

Despite numerous experimental and theoretical investigations [13], the problem of the possible existence of hydrates with hydrogen content exceeding that in the hydrogen sII hydrates and hence comparable with the revised 2015 DOE target of 5.5 wt% is still remains. In addition to the most common sI, sII and sH structures, there is another set of structures proposed by Jeffery [18]. Most of these structures have been experimentally verified and among of them there is cubic clathrate hydrate IV (sIV) that can be considered as a structure with an estimated storage capacity exceeding the 2015 DOE target. Structure IV clathrate has a cubic structure with space group  $Im\bar{3}m$  and lattice parameter  $a = 7.6 \text{ \AA}$  composed of 12 water molecules per unit cell with only one type of cavity ( $4^66^8$ ) formed by 24  $H_2O$  molecules and an average of cavity radius equal to 4.29  $\text{\AA}$  (Fig. 1). However, this structure has been observed only for hexafluorophoric acid as a guest with the composition  $(HPF_6 \cdot 6H_2O)$  [19], and according to Jeffery’s classification, can be referred to as ionic clathrates, in which some of the vertex of the polyhedral host lattice can be cationic (or anionic) parts of guest molecules [18]. Despite of the fact that ionic clathrates themselves exhibit many peculiar features such as metal ion engagement, co-host inclusion, or excellent thermal stability for gas storage [20], it is interesting to consider the possibility to realize similar frameworks based only on water molecules. To our knowledge, there have been no experimental reports to date on the realization of true (each vertex of host polyhedrons is a water oxygen) clathrate hydrate with sIV.



**Fig. 1** Structure of clathrate hydrate IV indicating the unit cell (a) and the structure of ( $4^66^8$ ) cage (b). Note that *large* and *small* spheres are oxygen and hydrogen atoms, respectively

In this work, we analyze the possibility of realizing true sIV clathrate hydrate using an original approach based on the statistical model of ideal solid clathrate solutions of van der Waals–Platteeuw (vdWP) [21] with modifications that take into account the influence of the guest molecules on the host lattice as well as the guest–guest interaction in the description of thermodynamics properties recently proposed by our group [22]. The curves of the “guest gas–hydrate–ice  $I_h$ ” phase equilibrium for propane sIV hydrate were calculated at various pressures and temperature conditions. Moreover, the structural transformation from structure II to IV of propane hydrate was estimated in order to support experimentalists in the practical realization of true sIV hydrate.

### Theory and computational details

The mathematical formalism of the present model for the general case and in the cases of clathrate hydrates with two types of cavities with one and two types of guests has been described in our previous studies [22–24]. The approach is based on one of the assumptions of the vdWP theory: the contribution of guest molecules to the free energy is independent of the mode of occupation of the cavities at a designated number of guest molecules. This assumption allows separation of the entropy part of free energy, and in

the case of one type of cavities which can be occupied one type of guest, the expression for the free energy  $F$  takes the following form:

$$F = F_1(V, T, y_1) + kTN_t[(1 - y_1) \ln(1 - y_1) + y_1 \ln y_1], \tag{1}$$

where  $F_1$  is the part of the free energy at a given arrangement  $\{y_1\}$  of guest molecules in the cavities and the second term is the entropic part of the free energy arising from the guest subsystem,  $y_1 = N_1/N_t$  is the fraction of filled,  $N_1$ , to the total number,  $N_t$ , of cavities. The free energy  $F_1(V, T, y_1)$  of the molecular crystal can be calculated within the framework of a lattice dynamics approach [24] and yields

$$F_1(V, T, y_1) = U + F_{\text{vib}}, \tag{2}$$

where  $U$  is the potential energy of clathrate hydrate, and  $F_{\text{vib}}$  is the vibrational contribution,

$$F_{\text{vib}} = \frac{1}{2} \sum_{\vec{q}} \hbar \omega_j(\vec{q}) + k_B T \sum_{\vec{q}} \ln(1 - \exp(-\hbar \omega_j(\vec{q})/k_B T)), \tag{3}$$

where  $\omega_j(\vec{q})$  is the  $j$ th frequency of crystal vibration, and  $\vec{q}$  is the wave vector.

The equation of state can be found by numerical differentiation of free energy:

$$P(V, T) = - \left( \frac{\partial F(V, T, y_1)}{\partial V} \right)_0 \tag{4}$$

The subscript “0” implies constancy of all thermodynamic parameters except those relative to which the differentiation is performed.

Using these values, the chemical potential,  $\mu_1$ , of guest molecules which are located in cavities can be obtained as follows:

$$\begin{aligned} \mu_1(P, T, y_1) &= \left( \frac{\partial F(V(P), T, y_1)}{\partial N_1} \right)_0 \\ &= \tilde{\mu}_1(P, T, y_1) + kT \ln \frac{y_1}{(1 - y_1)}, \end{aligned} \tag{5}$$

and  $\tilde{\mu}_1$  can be found using the following approximation:

$$\begin{aligned} \tilde{\mu}_1(P, T, y_1) &= \left( \frac{\partial F_1(V(P), T, y_1)}{\partial N_1} \right)_0 \\ &\cong \frac{F_1(V(P), T, N_1) - F_1(V(P), T, N_1 - \tilde{N}_1)}{\tilde{N}_1}, \end{aligned} \tag{6}$$

where  $\tilde{N}_1$  is number of guest molecules removed from clathrate hydrate. The chemical potential of the host water molecules  $\mu_Q$  can be calculated using the following expressions:

$$\begin{aligned} \mu_Q(P, T, y_1) &= \frac{1}{N_Q} \{F(V(P), T, y_1) + PV(P) - N_1 \mu_1\} \\ &= \tilde{\mu}_Q(P, T, y_1) + kT v_t \ln(1 - y_1), \end{aligned} \tag{7}$$

$$\begin{aligned} \tilde{\mu}_Q(P, T, y_1) &= \frac{PV(P)}{N_Q} + \frac{1}{N_Q} F(V(P), T, y_1) \\ &\quad - \frac{N_1 \partial F_1(V(P), T, y_1)}{N_Q \partial N_1}, \end{aligned} \tag{8}$$

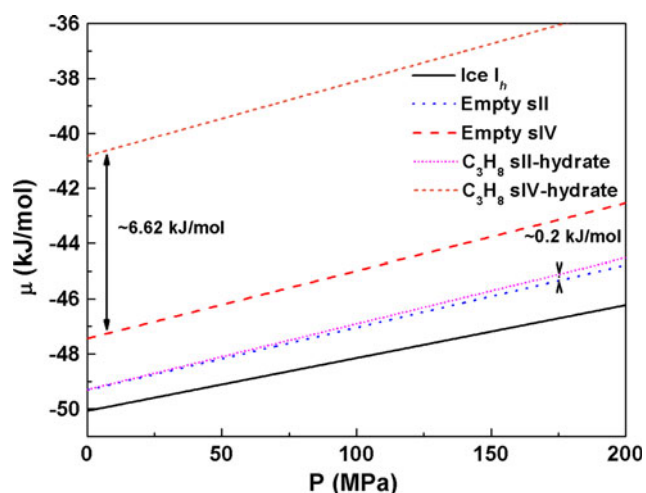
where  $N_Q$  is number of host molecules.

If the chemical potentials are known, the different phase equilibria of hydrates can be obtained. The corresponding equations have been presented in our previous studies [23–25].

The present formalism was used to calculate the  $P(T)$  equilibrium curves of the “gas–hydrate–ice  $I_h$ ” phases for propane sII and sIV hydrates. A single unit cell of sII hydrate with 136 water molecules and a supercell of sIV hydrate containing 96 molecules were selected in the present calculations. In the case of ice  $I_h$ , the calculations were performed using a supercell with 128 water molecules. Additional computational details, such as orientation of water molecules in hydrates and ice, as well as the empirical parameters of host–host, host–guest and guest–guest interactions, can be found elsewhere [25].

### Results and discussion

As a first step, the calculations of the free energies of the sII and sIV hydrates were performed after full structure optimization of both the host framework and the position of the propane molecules inside the cavities. Based on these data, the equation of state  $P(V)$  and the Gibbs free energy  $\Phi(P, T, \{y\})$  expressed in terms of chemical potentials of host and guest molecules were determined. It can be seen from Fig. 2 that without guest molecules, both hydrate structures are metastable as compared with hexagonal ice. At zero pressure, the difference between the chemical potentials of  $I_h$  ice and sII hydrate is about 0.7 kJ/mol, and in the case of sIV hydrate, this difference is nearly four times larger and becomes equal to be 2.62 kJ/mol. Thus, structure II of hydrate clathrate is more energetically stable than structure IV. It can also be expected that the hydrate structure IV is possibly stabilized at higher pressure than the sII one. It is well known that in Ar, Kr,  $N_2$ ,  $O_2$ ,  $CH_4$ , Xe and  $H_2S$  clathrate hydrates, the guest molecule can occupy both the small and large cages of the sII structure. However large molecules, such as  $C_3H_8$  or THF can only be accommodated in large cavities. Comparing the average cavity radius of small  $5^{12}$  cage forming sII hydrate with the  $4^6 6^8$  cage of structure IV ( $3.91 \text{ \AA} < 4.29 \text{ \AA}$ ), we consider that a propane molecule can occupy this cage. Fig. 2 also



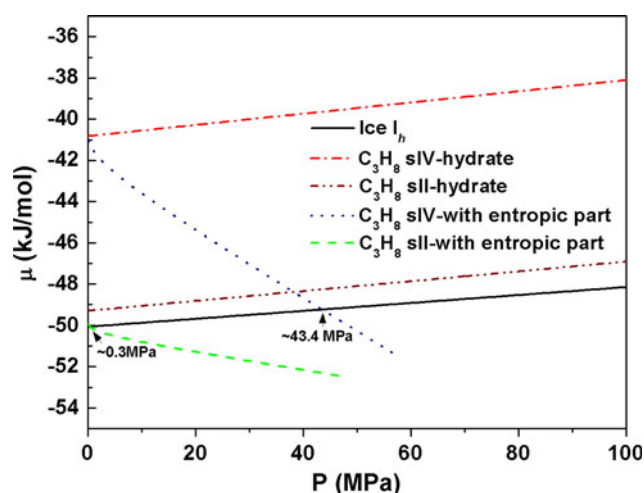
**Fig. 2** Pressure dependence of chemical potentials of ice  $I_h$ , sIV and sII hydrate including and excluding propane at  $T = 250$  K

shows the effect of the selected guest on the water host framework. Including the propane molecules in hydrate cavities, leads to an increase in the difference in the chemical potentials of  $I_h$  ice and hydrate structures. In the case of sII hydrate, the inclusion of propane slightly increases the difference in chemical potentials, but a significant effect of propane on the chemical potential of water from the host framework of sIV hydrates has been found.

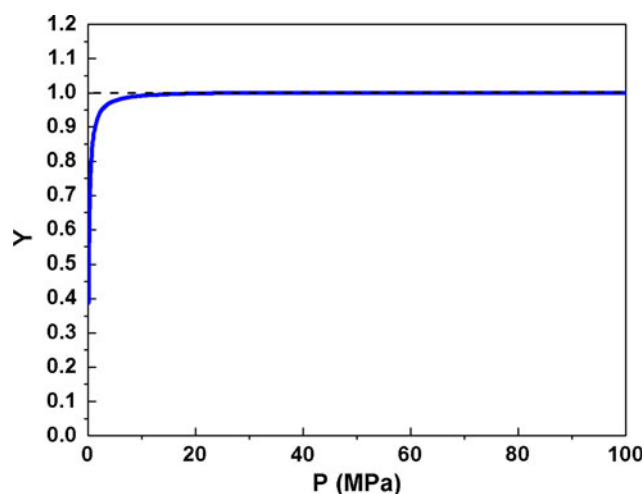
The calculated difference is three times larger than the difference between chemical potentials of the empty host lattice of hydrate and ice that is commonly used in the construction of phase diagrams within framework of the van der Waals and Platteeuw theory [21]. Thus, it is important to include of both guest–host and guest–guest interactions in the description of the thermodynamic properties of clathrates.

In order to reproduce the formation pressure and the region of the stable phase of hydrate, the entropic terms of the chemical potentials of host molecules in Eqs. (7) and (8) related to the guest subsystem need to be considered. Taking into account the entropic terms of the chemical potential of the host molecules related to the guest subsystem, the  $P$ – $T$  curve for “gas phase–ice  $I_h$ –hydrate phase” equilibrium of propane hydrate can be constructed. The intersection of the chemical potential curves of ice  $I_h$  and both hydrate structures has been found (see Fig. 3), which defines the formation pressure of the propane hydrates at a given temperature.

The propane sIV hydrate exists in a metastable phase at low pressure and stabilizes with pressures greater than  $P = 43.4$  MPa at  $T = 250$  K. It is important to note that the stabilization of sIV propane clathrate occurs after the full occupation of cavities by guest molecules as shown in Fig. 4.



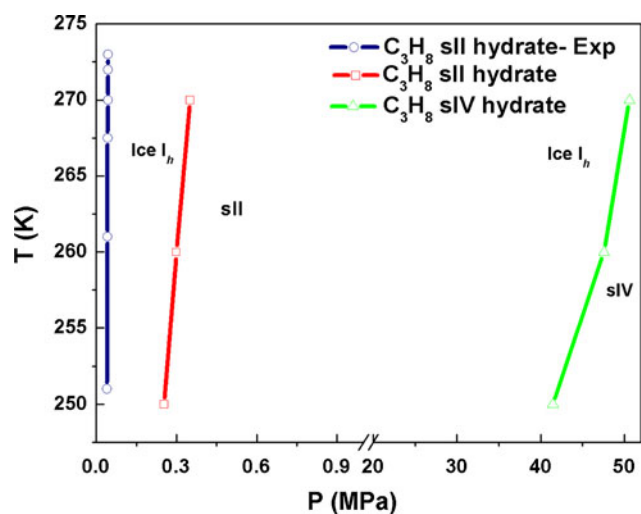
**Fig. 3** Pressure dependence of the chemical potential of water molecules at  $T = 250$  K for  $I_h$  (solid line),  $C_3H_8$ -sIV hydrates including (dotted line) and excluding (dash-dotted line) the entropy term,  $C_3H_8$ -sII hydrates including (dashed line) and excluding (dash-dot-dotted line) the entropy term



**Fig. 4** Degree of filling of sIV by propane at  $T = 250$  K

Moreover, at the same temperature, the formation pressure of propane sII hydrate is equal to 0.3 MPa, which is significantly smaller than the formation pressure of sIV hydrates. The calculated  $P$ – $T$  curve for “gas phase–ice  $I_h$ –propane hydrate phase” equilibrium in the temperature region of 250–270 K is displayed in Fig. 5.

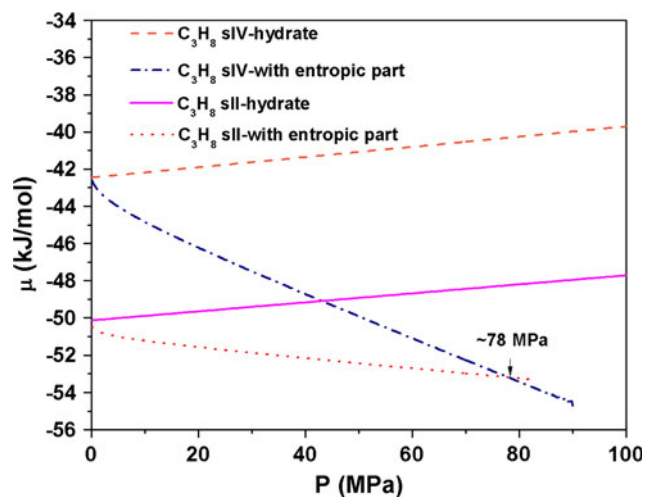
Reasonable correlation between the calculated and experimental [26] curves of the hexagonal ice–sII propane hydrate phase transformation confirm the validity of the selected potential used for propane molecules. In the case of propane sIV hydrate, the formation pressure is significantly greater than that of the propane hydrate of structure II in the calculated temperature region. This can be explained by several facts. First, the size of the large cavity



**Fig. 5**  $P$ - $T$  phase diagram of  $C_3H_8$ - $H_2O$  system related to sII (experimental and theoretical data) and sIV

in the sII is larger than that of the cavity in the sIV, and hence the host-guest interaction is less significant. Second, the sIV hydrate has only one type of cavity, which leads to closer packing of propane molecules in the host framework, which is energetically unfavorable. Despite the fact that propane sII hydrate is stabler than the propane IV hydrate in the pressure region up to 60 MPa (see Fig. 3), the slope of both curves indicates that at high pressure, a possible line crossing corresponds to the structure phase transition in the propane-water system. The sII-sIV phase transition was estimated at a pressure of about  $P = 78$  MPa and  $T = 290$  K as shown in Fig. 6.

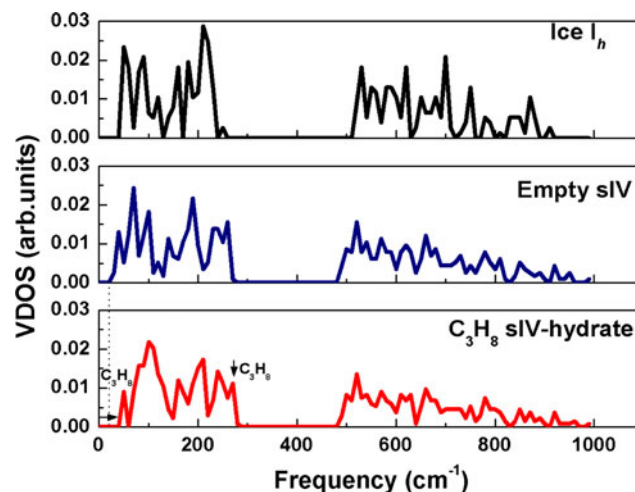
Recently, an sII-sVI structural transformation in  $t$ -BuNH<sub>2</sub> hydrates upon pressurization with methane at 0.7 MPa and 283.65 K has been reported [26]. According to Jeffery's classification, the sVI can be referred to as



**Fig. 6** sII-sIV phase transition point at  $T = 290$  K

hydrate with cubic structure III [18]. Moreover, as previously mentioned, the water framework in a true hydrate can be varied up to 1.5 GPa [7, 8] which is larger than the proposed pressure for sII-sIV structural transition in the propane-water system. The obtained results indicate the possibility of the formation of a true sIV hydrate with propane as a guest molecule and could serve as guidance in the design of future experiments in order to confirm or refute the possibility of formation of propane sIV hydrate.

The fundamental existence of a host lattice with structure IV can be also proved by analysis of its dynamic properties, especially the phonon density of states (VDOS), the number of vibrational modes in a given frequency interval, the most widely used and discussed value. The VDOS of sIV clathrate hydrates with  $C_3H_8$  and those without  $C_3H_8$  were calculated and are compared to those of ice  $I_h$ , the results being shown in Fig. 7. It was found that the frequencies of water framework as well as enclathrated propane are positive in the cases of empty and propane-filled sIV structures. This means that the empty sIV structure is dynamically stable and propane does not disrupt the dynamical stability of the host lattice. The common peculiarity of these plots is a gap of about  $250\text{ cm}^{-1}$  which divides the low- and high-frequency vibrations of the crystal lattice of both hydrates and ice. Frequency analysis revealed that the low-frequency region consists of translation modes of the host as well as translation and librations modes of propane molecules. The high-frequency region consists of libration modes of the water host framework. As compared with hexagonal ice, several peaks appeared in the  $950\text{--}1000\text{ cm}^{-1}$  region, which indicates that the water framework in sIV hydrates is less dynamically stable. The propane molecules influence the vibrations of the host water framework, resulting in



**Fig. 7** Phonon density of states of ice  $I_h$ , empty sIV and  $C_3H_8$ -sIV hydrate

rearrangement of peak intensity in the low-frequency region.

Since the thermodynamic behavior of the propane–hydrogen–water system is similar to that of the THF–hydrogen–water system [27] as well as the fact that at a low concentration of THF molecules in gas phase, the 3.4 wt% H<sub>2</sub> storage amount can be achieved in binary THF + hydrogen hydrate with structure II by increasing pressure [17], the same scenario can be expected for binary propane + hydrogen hydrates. This has been recently confirmed theoretically [24]. Thus, the possible structural transformation in binary propane + hydrogen upon pressurization with hydrogen can lead to formation of sIV hydrates with hydrogen storage capacity greater than that observed in sII hydrate. This is currently being investigated and the obtained results will be submitted for publication in the future.

## Conclusion

Based on the present results, it can be concluded that true sIV hydrate can exist due to its dynamic stability. Propane molecules are stabilized in this structure and high-pressure conditions are necessary for the formation of propane sIV hydrate. Moreover, a structural transformation from structure II to IV of propane hydrate predicted in this study can provide necessary information to support experimentalists in the practical realization of this clathrate hydrate. This can be considered as the first step of sIV hydrate in hydrogen storage application.

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## References

- Sloan, E.D., Koh, C.A.: *Clathrate Hydrates of Natural Gases*, 3rd edn. CRC/Taylor Francis, Boca Raton (2008)
- Von Stackelberg, M., Muller, H.R.: Feste gas hydrate II. Struktur und racmchemie. *Z. Elektrochem.* **58**, 25–28 (1954)
- Claussen, W.F.: A second water structure for inert gas hydrate. *J. Chem. Phys.* **19**, 1425–1426 (1951)
- Pauling, L., Marsh, R.E.: The structure of chlorine hydrate. *Proc. Natl. Acad. Sci. USA* **38**, 112–118 (1952)
- Ripmeester, J.A., Tse, J.S., Ratcliffe, C.I., Powell, B.M.: A new clathrate hydrate structure. *Nature* **325**, 135–136 (1987)
- Udachin, K.A., Ratcliffe, C.I., Enright, G.D., Ripmeester, J.A.: Structure H hydrate: a single crystal diffraction study of 2,2-dimethylpentane 5(Xe, H<sub>2</sub>S)·34H<sub>2</sub>O. *Supramol. Chem.* **8**, 173–176 (1997)
- Dyadin, Y.A., Larionov, E.G., Mirinski, D.S., Mikina, T.V., Starostina, L.I.: Clathrate formation in the Ar–H<sub>2</sub>O system under pressures up to 15000 bar. *Mendeleev Commun.* **1**, 32–34 (1997)
- Dyadin, Y.A., Larionov, E.G., Mikina, T.V., Starostina, L.I.: Clathrate formation in Kr–H<sub>2</sub>O and Xe–H<sub>2</sub>O systems under pressures up to 15 kbar. *Mendeleev Commun.* **2**, 74–76 (1997)
- Mao, W.L., Mao, H.K., Goncharov, A.F., Struzhkin, V.V., Guo, Q., Hu, J., Shu, J., Hemley, R.J., Somayazulu, M., Zhao, Y.: Hydrogen storage in molecular compounds. *Science* **297**, 2247 (2002)
- Dyadin, Y.A., Larionov, E.G., Manakov, A.Y., Zhurko, F.V., Aladko, E.Y., Mikina, T.V., Komarov, V.Y.: Clathrate hydrates of hydrogen and neon. *Mendeleev Commun.* **5**, 209 (1999)
- Mao, W.L., Mao, H.K.: Hydrogen storage in molecular compounds. *Proc. Natl Acad. Sci.* **101**, 708 (2004)
- Struzhkin, V.V., Miltzer, B., Mao, W.L., Mao, H.K., Hemley, R.J.: Hydrogen storage in molecular clathrates. *Chem. Rev.* **107**, 4133 (2007)
- Strobel, T.A., Hester, K.C., Koh, C.A., Sum, A.K., Sloan, E.D.: Properties of the clathrates of hydrogen and developments in their applicability for hydrogen storage. *Chem. Phys. Lett.* **478**, 97 (2009)
- Lokshin, K.A., Zhao, Y., He, D., Mao, W.L., Mao, H., Hemley, R.J., Lobanov, M.V., Greenblatt, M.: Structure and dynamics of hydrogen molecules in the novel clathrate hydrate by high pressure neutron diffraction. *Phys. Rev. Lett.* **93**, 125503 (2004)
- Florusse, L.J., Peters, C.J., Schoonman, J., Hester, K.C., Koh, C.A., Dec, S.F., Marsh, K.N., Sloan, E.D.: Stable low-pressure hydrogen clusters stored in a binary clathrate hydrate. *Science* **306**, 469 (2004)
- Lee, H., Lee, J.W., Kim, D.Y., Park, J., Seo, Y.T., Zeng, H., Moudrakovski, I.L., Ratcliffe, C.I., Ripmeester, J.A.: Tuning clathrate hydrates for hydrogen storage. *Nature* **434**, 743 (2005)
- Sugahara, T., Haag, J.C., Prasad, P.S.R., Warntjes, A.A., Sloan, E.D., Sum, A.K., Koh, C.A.: Increasing hydrogen storage capacity using tetrahydrofuran. *J. Am. Chem. Soc.* **131**, 14616 (2009)
- Jeffrey, G.A.: Hydrate inclusion compounds. In: MacNicol, D.D., Toda, F., Bishop, R. (eds.) *Comprehensive Supramolecular Chemistry*, vol. 6, pp. 757–788. Pergamon Press, Oxford (1996)
- Bode, H., Teufer, G.: Die Kristallstruktur der hexafluorophosphorsäure. *Acta Crystallogr.* **8**, 611–614 (1955)
- Shin, K., Cha, J.-H., Seo, Y., Lee, H.: Physicochemical properties of ionic clathrate hydrate. *Chem. Asian J.* **5**, 22 (2010)
- Van der Waals, J.H., Platteeuw, J.C.: Clathrate solutions. *Adv. Chem. Phys.* **2**, 1 (1959)
- Belosludov, V.R., Subbotin, O.S., Krupskii, D.S., Belosludov, R.V., Kawazoe, Y., Kudoh, J.: Physical and chemical properties of gas hydrates: theoretical aspects of energy storage application. *Mater. Trans.* **48**, 704–710 (2007)
- Subbotin, O.S., Adamova, T.P., Belosludov, R.V., Mizuseki, H., Kawazoe, Y., Kudoh, J., Rodger, P.M., Belosludov, V.R.: Theoretical study of phase transitions in Kr and Ar clathrate hydrates from structure II to structure I under pressure. *J. Chem. Phys.* **131**, 114507 (2009)
- Belosludov, R.V., Subbotin, O.S., Mizuseki, H., Kawazoe, Y., Belosludov, V.R.: Accurate description of phase diagram of clathrate hydrates at the molecular level. *J. Chem. Phys.* **131**, 244510 (2009)
- Belosludov, R.V., Igumenov, I.K., Belosludov, V.R., Shpakov, V.P.: Dynamical and thermodynamical properties of the acetylacetonates of copper, aluminium, indium, and rhodium. *Mol. Phys.* **82**, 51–66 (1994)
- Yasuda, K., Ohmura, R.: Phase equilibrium for clathrate hydrates formed with methane, ethane, propane, or carbon dioxide at temperatures below the freezing point of water. *J. Chem. Eng. Data* **53**, 2182–2188 (2008)
- Skiba, S.S., Larionov, E.G., Manakov, A.Y., Kolesov, B.A., Ancharov, A.I., Aladko, E.Y.: Double clathrate hydrate of propane and hydrogen. *J. Incl. Phenom. Macromol. Chem.* **63**, 383 (2009)