Anomalous thermodynamic properties of ice XVI and metastable hydrates

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A new ice polymorph, called ice XVI, has recently been discovered experimentally by extracting the guest molecules from Ne hydrate. The ice and its filled form (clathrate hydrate) have a unique network topology which results in several interesting properties. Here we provide a theoretical method to calculate thermodynamic properties of a semiopen system in equilibrium with guest gas and thus occupancy of the guest can be varied with temperature and pressure. Experimental observations such as the disappearance of negative thermal expansivity and contraction of the host lattice upon encaging guest molecules are well reproduced, and those behaviors are elucidated in terms of the free energy of cage occupation and its temperature and pressure dependence. We propose an application of the method for preparing ice XVI to create metastable clathrate hydrates having intriguing properties with much lower occupancy of guest molecules than that at equilibrium, which otherwise cannot form.

DOI: 10.1103/PhysRevB.93.054118

I. INTRODUCTION

Ice has many polymorphs in a wide temperature-pressure range [1]. A perfect tetrahedral coordination originating from hydrogen bonds at ambient pressure is distorted by compression. Flexibility of hydrogen bonds enhances versatility of its network by filling void space in hexagonal ice (Ih), resulting in many crystalline forms. Ice XVI is expected to be stable under negative pressure, while much effort has been devoted to find new ice structures stable at high pressures [2]. It was first predicted by computer simulations [3,4], and in fact is metastable under ambient pressure [2]. Ice XVI has the same structure as the host lattice of the clathrate hydrate of CS-II type. Empty hydrate is the reference state for thermodynamic theories on the stability of clathrate hydrates [5,6]. The relationship between CS-II hydrates [5] and ice XVI is the same as that between filled ice C_2 and cubic ice I (Ic) or between filled ice C1 and ice II [7], the latter of which undergoes an anisotropic structural change upon accommodating He [8].

There are several interesting properties observed in ice XVI. While the thermal expansivity of CS-II hydrates is positive as usual solids, ice XVI exhibits negative thermal expansivity below 55 K [2]. The negative thermal expansivity is considered to be a common phenomenon among tetrahedral networkforming substances such as Si, SiO₂, and Ih [9–13]. Quasiharmonic calculations showed that the negative thermal expansivity is associated with the negative Grüneisen parameters of the low-frequency intermolecular vibrations [14,15]. A more sophisticated method by Pamuk et al. was applied to recover the negative thermal expansivity, but qualitative behaviors at low temperature are left mostly unchanged from the quasiharmonic approximation [16].

It was experimentally shown that ice XVI shrinks by accommodating Ne [2]. This effect has been neglected in standard thermodynamic theories of clathrate hydrates, treating them as semiopen systems [5,6]. It was also shown by theoretical studies that clathrate hydrates of small guest species have a smaller volume than the corresponding empty hydrates [17,18]. However, in the early theoretical studies, the occupancy of guest was assumed to be 100%. Clathrate hydrate is a host-guest compound which is usually in equilibrium with a guest species outside of the clathrate hydrate. The equilibrium for a guest species is guaranteed by equivalence of the chemical potential of the guest inside the clathrate hydrate and the outside gas phase. Thus, the occupancy of the guest depends on temperature and pressure. Calculation of volumetric properties of clathrate hydrates should take this equilibrium condition into consideration.

In this study, thermal properties of empty hydrates are examined. We develop a thermodynamic theory based on the van der Waals and Platteeuw (vdWP) theory [6] so as to incorporate the pressure dependence of the volume while keeping clathrate hydrate as a semiopen system. This is important since occupancies of neon and other small guests are significantly dependent on temperature and pressure, and this effect may influence the volume of the clathrate structure. The advantage of this method is discussed by comparing with experimental results. It is also essential to take account of quantum effects because the negative thermal expansivity of ice Ih below 60 K is realized only when a quantum partition function is used [15]. We compare the volume of Ne hydrate calculated with the quantum free energy of cage occupation and that with the classical free energy.

II. METHOD

A. Preparation of hydrate structures

Since ice XVI is reported to be proton disordered [2], we prepare empty CS-II hydrates with 100 different proton arrangements, each containing 1088 water molecules. All the structures obey the Bernal-Fowler's ice rule without net polarization [1]. Thermodynamic properties of ice XVI are calculated as the average over these structures. We also examine other types of hydrate structures, CS-I, TS-I, and HS-I [5]. These structures are

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generated similarly, each containing around 1000 water molecules.

B. Volume calculation of ices and empty hydrates

The Helmholtz free energy of ice at temperature T is assumed to be the sum of three terms: the interaction energy at T = 0 K, i.e., in the inherent structure [19], the free energy of the intermolecular vibrations, and the residual entropy, as

$$A(T,V) = U_q(V) + F_v(T,V) - TS_r.$$
 (1)

The first term of the right-hand side in Eq. (1) is obtained by averaging the interaction energy of the inherent structures at volume V having various proton orderings. The free energy of the intermolecular vibrational motions is divided into the harmonic and anharmonic contributions as

$$F_v(T,V) = F_h(T,V) + F_a(T,V).$$
 (2)

For the empty hydrate at a low temperature, the anharmonic term is negligible and the free energy is approximated to

$$F_{\nu}(T,V) \approx F_{h}(T,V) = k_{B}T \sum_{j} \ln\left[2\sinh\left(\frac{h\nu_{j}}{2k_{B}T}\right)\right], \quad (3)$$

where k_B and h stand for the Boltzmann and Planck constants, and v_i is the frequency of the *i*th normal mode of the lattice. This is called the quasiharmonic approximation and was applied to ices Ih and Ic [15]. The residual entropy in the third term S_r is given by $k_B N_w \ln(3/2)$, where N_w is the number of water molecules [20]. The mean volume $\langle V \rangle$ is calculated by minimizing the function

$$\Psi(T, p; V) = A(T, V) + pV \tag{4}$$

with respect to the volume at a given pressure p. The Gibbs free energy is given by

$$G(T,p) = A(T,\langle V \rangle) + p\langle V \rangle.$$
(5)

C. vdWP theory combined with the quasiharmonic approximation

Calculation of volumetric properties of a semiopen system is quite different from that of a closed one. We propose here in the first place a way of how to calculate the equilibrium volume at a given pressure for semiopen clathrate hydrate systems. The appearance or disappearance of the negative thermal expansivity upon accommodation of a guest molecule must be argued with a variable occupancy. Thus far, the volume has been obtained by molecular simulations. However, such simulations require occupancy of guest species and their locations in advance. To overcome this difficulty, we develop an extended vdWP theory allowing the occupancy change in which pressure is an independent variable and volume is derived from the thermodynamic condition.

One of the crucial assumptions of the original vdWP theory is that guest motions inside an individual cage are independent of the host vibrational motions. Then, the free energy of accommodating a guest molecule is separated from that of the host water [5,6]. This is legitimate when a guest molecule is small, such as Ar or Ne [21,22].

In the framework of the original vdWP theory, the volume is assumed to be totally unaffected by the accommodation

TABLE I. Lennard-Jones size (σ) and energy (ε) parameters for noble gases.

	$\sigma/0.1\mathrm{nm}$	$\varepsilon/{ m kJ}~{ m mol}^{-1}$
Ne	2.749	0.296
Ar	3.405	0.996
Kr	3.600	1.422
Xe	4.047	1.921

of the guest [6]. Influence of guest accommodation on the lattice constant at a constant pressure is not implemented in the original vdWP theory. However, ice XVI, as a real entity of empty hydrate, though metastable, contracts when guest molecules are accommodated [2]. We have shown how to consider the pressure dependence of the occupancy once volume is given by some means such as simulation [23]. Here we argue a more comprehensive method to calculate both volume and occupancy at a given pressure and temperature. That is, the thermodynamic potential of the clathrate hydrate in equilibrium with the guest gas is obtained by minimizing the following function with respect to volume:

$$\Psi(T,p;V) = A(T,V) + pV - k_B T N_w \sum_i \alpha_i$$
$$\times \ln\left[1 + \exp\left(\frac{\mu_g - f_i(V/N_w)}{k_B T}\right)\right], \quad (6)$$

where α_i stands for the ratio of the number of cages to the number of water molecules, μ_g indicates the chemical potential of the guest, f_i is the free energy of cage occupation, and *i* specifies the large or small cage. The equilibrium volume is calculated by imposing the following condition in Eq. (6):

$$\frac{\partial \Psi}{\partial V} = 0. \tag{7}$$

This method enables us to obtain the temperature dependence of the volume at a fixed pressure where the guest occupancy can be varied with temperature.

D. Intermolecular interactions

The interaction between water molecules is described by the TIP4P model [24]. Four noble gas species, Ne, Ar, Kr, and Xe are chosen to elucidate the effect of accommodation of guest molecules. The interaction for noble gases is described by the Lennard-Jones potential. The Lorentz-Berthelot rule is applied to the interaction between water (oxygen) and the guest noble gas. The interaction parameters are listed in Table I [25]. The guest is approximated as an ideal gas to calculate its chemical potential in the gas phase μ_g , unless otherwise mentioned.

E. Free energy of cage occupation

An important issue in calculating the free energy of cage occupation is that motions of a small guest cannot be treated as harmonic vibration. The interaction of a guest molecule inside a cage is given in Fig. 1, which is the interaction energy of the guest with all surrounding water molecules at a radial distance r from the center of each cage. The motion of Xe



FIG. 1. Potential energy curves for Ne (black), Ar (red), and Xe (green) in a larger cage (solid) and in a smaller cage (dotted) against radial distance.

could be approximated as harmonic vibration. In contrast, the potential energy is clearly not a quadratic curve for small Ne. According to classical mechanics, it is possible to calculate the free energy of a guest inside a cage even when the potential is anharmonic by the following expression:

$$f = -k_B T \ln \left[\lambda^{-3} \int \exp\left(-\frac{u(\mathbf{r})}{k_B T}\right) d\mathbf{r} \right], \qquad (8)$$

where λ is the thermal de Broglie wavelength of the spherical guest and $u(\mathbf{r})$ stands for the potential of the guest due to surrounding water molecules at a position *r*. However, the thermodynamic properties of the clathrate hydrate at a low temperature should be calculated based on quantum mechanics in order to compare with the empty counterpart, ice XVI. The quantum-mechanical free energy is given by

$$f = -k_B T \ln \sum_i \exp(-E_i/k_B T), \qquad (9)$$

where E_i is *i*th energy level of the guest molecule in the cage. To evaluate the quantum energy levels, we solve numerically the radial Schrödinger equation under the assumption that the potential of the guest in a cage is isotropic. The radial potential function of a guest, u(r), is obtained by an average of the interaction with surrounding water molecules at a given distance *r* from the center of the cage. The Hamiltonian is discretized using a finite-difference scheme with a mesh size of 0.002 65 Å (0.005 a.u.) [26]. The eigenvalues are obtained from the numerical diagonalization of the Hamiltonian matrix.

F. Double occupancy of Ne

A larger cage in CS-II may accommodate at most two Ne atoms considering its size. This is also expected in experimental work [2]. It is difficult to solve the Schrödinger equation of two Ne atoms mutually interacting. The classical free energy of Ne in a cage is almost identical to the quantum one, as shown below. Encouraged by this fact, the classical free energy of double occupancy is substituted for the quantum one, the former of which is given as [27]

$$f^{(2)} = -k_B T \ln \left[\frac{1}{2!} \lambda^{-6} \right]$$
$$\times \int \int \exp\left(-\frac{u(\mathbf{r}) + u(\mathbf{r}') + \phi(\mathbf{r}, \mathbf{r}')}{k_B T}\right) d\mathbf{r} d\mathbf{r}'], (10)$$

where ϕ is the direct interaction between two guests inside a cage. With this free energy, the thermodynamic potential to be minimized with respect to volume is replaced by

$$\Psi(T,p;V) = A(T,V) + pV - k_B T N_w \sum_i \alpha_i$$

$$\times \ln\left[1 + \sum_{j=1} \exp\left(\frac{j\mu_g - f_i^{(j)}(V/N_w)}{k_B T}\right)\right],$$
(11)

where *j* runs over the possible numbers of guest molecules in a cage.

III. RESULTS AND ANALYSES

A. Negative thermal expansivity of the empty hydrates

Inspired by the experiment on ice XVI, we search for the most stable empty clathrate hydrate structure among the known clathrate hydrates, i.e., CS-I, CS-II, HS-I, and TS-I. The volumes of those empty hydrates are plotted against temperature along with those of ice Ih and ice Ic in Fig. 2. The most stable and bulky structure at ambient pressure is CS-II according to the chemical potential, which is obtained in the calculation of the equilibrium volumes. All four empty hydrates at atmospheric pressure exhibit the negative thermal expansivity below 55 K as well as ice Ih below 60 K, which has been known as one of the anomalous properties of ice [10].



FIG. 2. Volumes for empty CS-I (magenta), CS-II (dark blue), HS-I (light blue), and TS-I (green) clathrate hydrates (left axis) together with those for (right axis) ice Ih (black) and ice Ic (black dotted) against temperature.



FIG. 3. Temperature dependence of molar volume of water in CS-II (solid) encaging species Ne (black, double occupancy), Ne (orange, single occupancy), Ar (red), Kr (light blue), and in CS-I (dashed) encaging Xe (green) in equilibrium with the gas phase of the guest at 0.1 MPa together with empty CS-II and CS-I (blue and magenta, respectively). The molar volume with the classical free energy of Ne guest (orange dotted line) is also plotted but is indistinguishable from that with the quantum free energy (orange solid line).

The thermal expansivity α is defined as

$$3\alpha = \left(\frac{\partial \ln V}{\partial T}\right)_p = -\left(\frac{\partial \ln V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V = -\kappa_T \left(\frac{\partial^2 A}{\partial T \partial V}\right),\tag{12}$$

where κ_T is isothermal compressibility. For ices composed of the fixed number of molecules, κ_T is always positive. Thus, the negative thermal expansivity for ice is associated with the positive $(\partial^2 A/\partial T \partial V)$. In ices Ih and Ic, this is caused by the negative Grüneisen parameters of low-frequency modes [15]. It is not surprising that the empty hydrates exhibit negative thermal expansivity at low temperature because it has a porous structure similar to ice Ih: the open tetrahedral structure results in the negative Grüneisen parameters for the O-O-O bending modes in the hydrogen bond network [2,15,28]. The magnitude of negative thermal expansivity for any empty hydrate examined is similar to that for ice Ih.

B. Contraction caused by accommodation of guest

It is possible to calculate the volume of clathrate hydrates as a function of pressure applying the extended vdWP theory [Eq. (6)]. In fact, the observed contraction upon accommodation of Ne is reproduced as shown in Fig. 3. The volume becomes smaller by 0.5% when Ne atoms are accommodated, which should be compared with experimental observation of 0.4% [2]. Comparison is also made for various guest species in Fig. 3 in which each clathrate hydrate is in equilibrium with a gas phase of guest species at 0.1 MPa. In general, guest species having stronger attractive interaction seems to have smaller volume. Contraction is also observed for CS-I containing Xe, although the relative magnitude is smaller than that for CS-II containing Ar.



FIG. 4. Molar volume of water in CS-II clathrate hydrate at 0.1 MPa with and without guests against temperature. The guest is either Ar (red), repulsive Ar (magenta), or small Ar (green). The dashed (orange) lines are those of the fixed occupancy of 0.9, 0.5, 0.4, 0.3, 0.2, 0.1 (from the bottom to top) containing only Ar.

Falenty *et al.* suggested that the contraction is caused by the attractive interaction between the host lattice and the guest molecule [2]. This is examined by a clathrate hydrate encaging a hypothetical "repulsive argon" that has no attractive interaction, i.e., the Lennard-Jones interaction for host-guest interaction is truncated at the minimum of the potential energy function, which resides at $r = 2^{1/6}\sigma$, and the potential function is shifted upward by adding ε in order to converge to zero at that distance [29]:

$$\phi_r(r) = 4\varepsilon [(\sigma/r)^{12} - (\sigma/r)^6] + \varepsilon \quad \text{for } r \leq 2^{1/6}\sigma$$

$$\phi_r(r) = 0 \quad \text{for } r \geq 2^{1/6}\sigma. \tag{13}$$

As shown in Fig. 4, the volume becomes even larger than the empty hydrate when the repulsive Ar is accommodated and the guest occupancy is set to that corresponding to Ar. This result demonstrates that the volume contraction is indeed caused by the attractive interaction. This is also confirmed by another hypothetical guest, "small Ar," in which the size parameter σ is set to that of Ne. It is obvious that the magnitude of volume contraction is rather insensitive to the size of the guest, but the strength of the attractive interaction is essential.

We consider why the lattice contracts by the accommodation of the guest. The equilibrium volume of the system is obtained from the minimization of Ψ in Eq. (6) with respect to the volume. This is equivalent to finding the volume satisfying the following equation:

$$p = -\frac{\partial a(T,v)}{\partial v} - \sum_{i} \alpha_{i} x_{i} \frac{\partial f_{i}}{\partial v}, \qquad (14)$$

where a(T,v) is $A(T,V)/N_w$ with $v = V/N_w$, and x_i is the occupancy of type-*i* cage given by

$$x_i = \frac{\exp[(\mu_g - f_i)/k_B T]}{1 + \exp[(\mu_g - f_i)/k_B T]}.$$
 (15)



FIG. 5. Free energy of cage occupancy f against temperature at three volume values of CS-II (black (20.974) < blue (22.967) < red (24.959 cm³ mol⁻¹)) encaging Ne, for a large cage (solid line) and for a small cage (dotted line). Free energies according to classical mechanics for a large cage (solid green) and for a smaller cage (dotted green) with the intermediate volume (corresponding to blue lines) are plotted. The classical free energy of double occupancy by Ne in a larger cage is also shown by the orange line (right axis).

Without guests, the second term in the right-hand side of Eq. (14) vanishes and the pressure p is equal to the total external pressure p_0 . The second term in Eq. (14), i.e.,

$$p^{\text{ex}} = -\sum_{i} \alpha_{i} x_{i} \frac{\partial f_{i}}{\partial v}, \qquad (16)$$

can be regarded as an excess pressure by the guest. Since both α_i and x_i are positive, the sign of the excess pressure depends solely on $\partial f_i / \partial v$. Higher free energy indicates the lower affinity of a guest molecule to the cage. In general, a larger volume makes weaker attractive interaction between a small guest and a water cage because the distance between the guest and each water molecule in the cage becomes longer. This leads to $\partial f_i / \partial v > 0$. Figure 5 shows that this is indeed the case and thus negative excess pressure is exerted inside the filled hydrate. As a result, the volume of the filled hydrate becomes smaller than the corresponding empty hydrate.

Figure 3 shows that the negative thermal expansivity disappears upon containing any guest species. This result is in agreement with the experimental observation. As shown in Fig. 4, the thermal expansivity of the fictitious repulsive Ar hydrate is also positive, indicating that the attractive interaction is not the origin of the disappearance of negative thermal expansivity. In fact, it is originated by the contribution from $-\sum_{i} \alpha_i x_i (\frac{\partial^2 f_i}{\partial T \partial v}) = \sum_{i} \alpha_i x_i (\frac{\partial s_i}{\partial v})_T$ derived from Eq. (14), which we find is positive and so large as to cancel the negative expansivity arising from the first term, $-\frac{\partial^2 a(T,v)}{\partial T \partial v}$. The equilibrium volume is calculated from Eqs. (6) and

The equilibrium volume is calculated from Eqs. (6) and (7). Any noble gas is assumed to be ideal in calculating its chemical potential. Below the boiling temperature at a given pressure (0.1 MPa), this is of course not true. However, the cage occupancy is almost unity just above the boiling point in any noble gas. We can take advantage of this fact in obtaining

the equilibrium volume. That is, Eq. (16) does not contain the chemical potential of a guest except for x_i , which is $x_i \approx 1$ below the boiling point, and the volume variation from the empty state is simply determined by $(\partial f_i/\partial v)$, which is irrelevant to the chemical potential of the guest outside of the clathrate hydrate.

Since the quantum free energy for intermolecular vibration is essential to recover the negative thermal expansivity in ice XVI, its disappearance in the filled one should also be investigated using the quantum free energy of cage occupation. In effect, no appreciable free energy difference between quantum and classical is seen except for the very low temperature range as shown in Fig. 5. Figure 3 shows that the molar volume of water containing Ne using the classical free energy overlaps that using the quantum free energy. Figure 3 also shows that only a small discrepancy appears at low temperatures if double occupancy is considered.

It was reported that the small cage contracts more than the large cage when Ne is accommodated at 5 K [2]. The cage volumes of two types are calculated at a fixed total volume to verify the experimental result. It is found that small cages shrink by 0.1% and large cages expand by 0.2% when encaging Ne. This also accounts for rather smaller contraction for CS-I Xe hydrate than for CS-II Ar hydrate (see Fig. 3): the number of small cages contributing to contraction is fewer in CS-I than in CS-II.

The cell dimensions of empty CS-II and Ne hydrates obtained in the present and early studies are compared in Fig. 6. The absolute value of the volume of empty CS-II is reproduced better in the previous theoretical work by Belosludov *et al.* [17] than in the present study because Belosludov *et al.* employed a water force field which was parameterized to reproduce the volume of ice Ih. However, as shown in Fig. 7, the negative thermal expansivity is not recovered in the work of Belosludov *et al.*, while it is clearly seen in the present study. The origin of discrepancy between the result of Belosludov



FIG. 6. Cell dimension against temperature at 0.1 MPa for CS-II (blue), Ne hydrates allowing double (black) and only single (orange) occupancies, and Ne hydrate fully filled (green), with experimental for CS-II (magenta) and Ne hydrate (red) [2]. A previous calculation for empty CS-II (circles) is also plotted [17].



FIG. 7. Thermal expansivity of empty CS-II (ice XVI) in the present work (blue), experimental (magenta), and the previous calculation (light blue).

et al. and the present study is not clear, but it may be caused by the difference in the water-water interaction, the system size, or the number of generated structures satisfying the Bernal-Fowler rule. The discrepancy between the experiment and our study in Fig. 7 is larger at higher temperature, probably because anharmonic effects, which are not included in the quasiharmonic approximation, become significant with increasing temperature.

In the previous works, the number of guest species is fixed to obtain the volume, although the occupancy depends on temperature in real systems [17,18]. We here examine the effect of the change in the occupancy on the volume of Ne hydrate. In the experimental study of Falenty et al., a fairly large volume difference between the empty and filled hydrate is observed at T = 0 K, and the difference decreases with increasing temperature as shown by the magenta and red curves in Fig. 6 [2]. This is associated with a gradual decrease in the occupancy of guest Ne. In our method, this decrease is taken into consideration. In fact, the volume difference between CS-II (blue) and Ne hydrate (orange) becomes smaller with increasing temperature in a way similar to the experimental result. When the occupancy of Ne in the hydrate is unchanged, the increase in the volume of Ne hydrate with increasing temperature becomes much smaller, as shown by the green curve.

C. Metastable clathrate hydrates

It is possible to make a binary clathrate hydrate of Ne and a larger (second) guest species at a high pressure. The method to produce metastable ice XVI suggests that only Ne can be removed by decompression of it at low temperature. Thus, we can create a metastable clathrate hydrate with a lower occupancy than the threshold one, which cannot form in a usual method. The occupancy of the second guest species is adjusted by choosing an appropriate composition in the binary gas mixture in equilibrium with the clathrate hydrate. In practice, the cage-to-cage jumps for removing Ne will certainly be hindered by the presence of larger molecules in the pathways [2] and only a binary hydrate with a small amount of the second guest may be formed.

We show that the metastable clathrate hydrates prepared by this method have a unique property. The initial composition of the mixed gas of Ne and Ar (second guest species) determines the occupancy of these guest species in the Ne+Ar binary hydrate. Extraction of Ne from the Ne+Ar binary hydrate yields pure Ar hydrate with quite low occupancy, though this would be impractical in a realistic experiment because of its very slow process [2]. The thermodynamic potential of the partially filled clathrate hydrate, G(T, p, y), is given with the equilibrium volume $\langle V \rangle$ as

$$G(T, p, y) = A(T, \langle V \rangle) + p \langle V \rangle + k_B T N_w \sum_i \alpha_i y_i f_i(T, \langle V \rangle / N_w), \quad (17)$$

where the occupancy of Ar, y_i , could be much smaller than the equilibrium occupancy x_i . The occupancy to be aimed at is attained by adjusting the partial pressure of Ar. The molar volumes of water in the metastable Ar hydrates are shown for various occupancies in Fig. 4 as a function of temperature. The metastable clathrate hydrate has a nearly constant volume for mean occupancy, y = 0.3. Thus, it could be plausible to obtain a metastable clathrate hydrate having intermediate properties between the empty and the stable clathrate hydrate.

This kind of metastable clathrate hydrate may deserve a close scrutiny for a gas storage. For this purpose, we pick up ozone hydrate. Ozone is an explosive gas which is dangerous to preserve in high density. In ozone hydrate, each ozone molecule is isolated in a cage and collisions are prevented, but the amount of ozone can be fairly small compared with the number of the available cages. Although the formation of clathrate hydrates containing ozone has been reported, help molecules, such as CCl₄ or Xe, are inevitable [30]. We may examine a possibility to form pure ozone hydrate in a way similar to the formation of ice XVI. A Ne + O₃ hydrate is formed under high pressure and then Ne is removed at low pressure and temperature below 140 K, although it may not be practical considering the elapse in time to remove Ne and control of temperature. A small amount of ozone is expected to remain in this hydrate after the removal of Ne. We evaluate the thermodynamic properties of the pure ozone hydrate. When the initial formation is processed at 244 K and a total pressure of 350 MPa with an additional small amount of ozone, competition of cage occupation between Ne and ozone occurs. The occupancy of ozone for each type of cage (denoted by *i*) is given by

$$x_{i} = \frac{\exp[(\mu_{\text{O}_{3}} - f_{i,\text{O}_{3}})/k_{B}T]}{1 + \exp[(\mu_{\text{Ne}} - f_{i,\text{Ne}})/k_{B}T] + \exp[(\mu_{\text{O}_{3}} - f_{i,\text{O}_{3}})/k_{B}T]}.$$
(18)

The chemical potential of Ne at 350 MPa is calculated from the Redlich-Kwong equation of state [31]. In the case of a nonlinear rigid molecule having the symmetry number s, the



FIG. 8. Mean occupancy of ozone (weight fraction) against the partial pressure of O_3 when the clathrate hydrate is formed at total pressures of 300 (blue), 350 (black), or 400 (red) MPa of gas mixture.

free energy f is given by

$$f = -k_B T \ln\left[\frac{1}{s}\lambda^{-3}\prod_{j=1}^{3}\left(\frac{2\pi I_j k_B T}{h^2}\right)^{1/2} \times \int \exp\left(-\frac{u(\mathbf{r},\Omega)}{k_B T}\right) d\mathbf{r} d\Omega\right],$$
(19)

where *I* is the inertia moment and Ω denotes orientational parameters with the appropriate intermolecular interaction [32]. The mean occupancy of the ozone is plotted in Fig. 8 as a function of the partial pressure of ozone when it is formed. Although the help guest species are different from the experimental work, the occupancy of ozone (weight fraction, see Fig. 8) agrees fairly well with the experimental value of 0.003–0.007 at the ozone partial pressure of roughly 0.03 MPa [30].

IV. CONCLUDING REMARKS

Thermodynamic properties of clathrate hydrates and their empty counterparts have been calculated from the relevant thermodynamic potentials. We propose a theoretical approach based on the quasiharmonic approximation and the extended vdWP theory. All the volumetric properties obtained by experiments [2], especially the temperature dependence of volume for the Ne hydrate, are reproduced by the method presented here with reliable intermolecular potentials. It is found that the quantum effects, which are essential for the lattices to recover the negative thermal expansivity of ices and empty clathrate hydrates, are insignificant for the free energy of cage occupation to calculate the volumetric properties of filled clathrate hydrates.

This theoretical treatment enables us to calculate the volumetric properties of clathrate hydrates in a wide temperaturepressure range while leaving them as semiopen systems, which takes account of variation of the occupancy of guest molecules. This method can be applicable to not only clathrate hydrates but also filled ices whose phase behaviors at high pressures and occupancies of guest molecules have not been established.

The experimental method to prepare ice XVI suggests a way to form metastable clathrate hydrates having lower occupancy than those at equilibrium conditions, and we show that such a clathrate hydrate has an intermediate property between empty and stable clathrate hydrates.

ACKNOWLEDGMENTS

The present work was supported by a Grant-in-Aid by JSPS (Grant No. 25288008), by HPCI Strategic Programs for Innovative Research (SPIRE), and the Computational Materials Science Initiative (CMSI), MEXT, Japan.

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