Theoretical Study of Clathrate Hydrates with Multiple Occupation

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Abstract

In this work, the electronic, structural, dynamic and thermodynamic properties of structure II, H and tetragonal Ar clathrate hydrates have been calculated and the effect of multiple occupancy on their stability has been examined using first-principle and lattice dynamics calculations. The dynamic properties of these clathrates have been investigated depending on the number of guest molecules in a clathrate cage. It has been found that selected hydrate structures are dynamically stable. The calculated cell parameters are in agreement with experimental data. We also report the results of a systematic investigation of cage-like water structures using first-principle calculations. It has been observed that Ar clusters can be stabilized in different water cages and the stability is strongly dependent on the number of argon atoms inside the cages.

Introduction

Clathrate hydrates comprise one type of crystalline inclusion compounds consisting of guest atoms or molecules and host framework of water molecules linked by hydrogen bonds. The clathrate hydrates are formed when water molecules arrange themselves in a cage-like structure around small molecules and hence many of their physical and chemical properties are different from ice [1]. These compounds are a potential source of energy in the future since natural gas (methane) hydrates occur under conditions of high pressure and low temperature in the permafrost regions or below the seafloor. Global estimates of methane in clathrate hydrates may exceed 10^{16} kg, which represents one of the largest sources of hydrocarbons on Earth. Speculations about large releases of methane from clathrate hydrates have raised serious, but unresolved questions about its possible role in climate change. Among many potential applications of clathrate hydrates, these compounds can also be used as gas (such as CO, CO_2, O_2 or H_2) storage materials. Therefore, a good understanding of the chemical and physical properties of clathrate hydrates such as structure, dynamics and stability is essential for practical manipulation of this class of inclusion compounds.

In the early 1950s, two types of gas hydrates known as cubic structures I (CS-I) and II (CS-II) were identified by different authors [2–4]. More recently, the third type of gas hydrates crystal with hexagonal structure H (sH) was de-termined [5, 6]. At the present time, most of recognized gas hydrates existing at moderate pressure (tens MPa) belong to these types of structures. The gas hydrates are acutely sensitive to pressure variation by virtue of friable packing of host framework and relatively weak binding energy between water molecules. Experimental studies [7–11] on different gas-water systems at pressures up to 1.5 GPa showed that the sequential change of hydrate phase is observed by increasing pressure.

There is a well-known general rule that CS-I hydrates are formed by molecules with van der Waals diameters of up to about 0.58 nm while CS-II hydrates are formed by large molecules up to about 0.7 nm in size. The exceptions of this rule are Ar, Kr, N_2, and O_2 molecules with small van der Waals diameters up to about 0.43 nm, which form CS-II hydrates [12, 13]. At a low temperature it had been [14] using solid clathrate solutions theory [15] that these small molecules should favor CS-II. This result was verified by Davidson and co-workers [12].

At the present time, the possibility of double or more occupancy in the large cages of CS-II has been a subject of topical interest. Crystallographic studies of the structure and filling fractions of the small and large cages of N_2, O_2 and air hydrate by high-resolution neutron powder diffraction have shown that the large cages are partly doubly occupied for these hydrates at high pressures [16, 17]. The degrees of filling 1.8 and 2.3 molecules per cage respectively were obtained by powder neutron diffraction at pressure of 0.34 and 0.43 GPa, respectively [11]. The doubly occupied

large cages of CS-II N_2 and Ar hydrates were also examined by molecular dynamics calculations [18–21]. Thus, it was shown that N_2 hydrate in double occupancy is stable at temperature 80 and 273 K below 0.25 GPa [18] and doubly occupied Ar hydrate with may be also stabilized by high external pressure [19]. Recently, the CS-II H_2 clathrate hydrate was synthesized and studied at high pressure [22]. It was proposed that the small cages are doubly occupied and the large cages are quadruply occupied by hydrogen molecules with a diameter of 0.272 nm.

Phase diagram of argon v water system was studied at high pressure and the formation of four hydrates was established [10, 11, 23]. Powder neutron diffraction study showed that in Ar – water system CS-II hydrate exists from ambient pressure up to 0.45 GPa. After increasing the pressure, the phase transition occurs and the Ar hydrate with hexagonal structure is formed up to 0.76 GPa. In the pressure range of 0.76 to 1 GPa, the Ar hydrate with a previously unknown type of structure was obtained and a new tetragonal crystal structure of hydrate with one type of doubly occupied cavity was proposed in [11].

In the present study, the electronic, structural, dynamic and thermodynamic properties of CS-II, sH and tetragonal Ar clathrate hydrates have been investigated and the effect of multiple occupancy on stability of these hydrates has been examined using first-principle and lattice dynamics calculations.

Theoretical methods

First-principle calculations

Full geometry optimization and vibrational analyses of selected cage-like structures of water clusters with and without enclathrated guests were performed at the Hartree–Fock (HF) level. A large yet computationally manageable basis set, 6-31+G(d) including polarization and diffuse functions, was used. The inclusion of diffusion functions in the basis set is necessary for a better description of the structure and energetic of hydrogen bonded complexes [24]. The optimisations were performed using the redundant internal coordinate procedure [25] and the vibrational frequencies were calculated from the second derivative of the total energy with respect to atomic displacement about the equilibrium geometry. If all of eigenvalues of Hessian matrix are positive the corresponding frequencies are real. This means that these structures are indeed (at least local) minima. The stabilization energy (SE) was considered as the difference between the total cluster energy and the energies of separated empty water cages and guest atoms at an infinite distance. All first-principle calculations were carried out using the Gaussian 98 package [26].

Dynamical and thermodynamical properties

The free energy F_{qh} of crystal in this model is calculated within the framework of lattice dynamics (LD) in the quasiharmonic approximation as

$$F_{qh} = U + F_{vib}, \tag{1}$$

where U is the potential energy, F_{vib} is the vibrational contribution:

$$F_{vib} = \frac{1}{2} \sum_{j\mathbf{q}} \hbar \omega_j(\mathbf{q})$$
$$+ k_B T \sum_{j\mathbf{q}} \ln\left[1 - \exp\left(-\hbar \omega_j(\mathbf{q})/k_B T\right) \right], \tag{2}$$

where $\omega_j(\mathbf{q})$ are the frequencies of crystal vibrations. The eigenfrequencies $\omega_j(\mathbf{q})$ of molecular crystal vibrations are determined by solving numerically the following system of equations

$$m_k \omega^2(\mathbf{q}) U_\alpha^t(k, \mathbf{q}) = \sum_{k',\beta} \Big[\tilde{D}_{\alpha\beta}^{tt}(\mathbf{q}, kk') U_\beta^t(k', \mathbf{q}) + $$
$$\tilde{D}_{\alpha\beta}^{tr}(\mathbf{q}, kk') U_\beta^r(k', \mathbf{q}) \Big]$$

$$\sum_\beta I_{\alpha\beta}(k) \omega^2(\mathbf{q}) U_\beta^r(k, \mathbf{q}) = \sum_{k',\beta} \Big[\tilde{D}_{\alpha\beta}^{tt}(\mathbf{q}, kk') U_\beta^t(k', \mathbf{q}) + $$
$$\tilde{D}_{\alpha\beta}^{rr}(\mathbf{q}, kk') U_\beta^r(k', \mathbf{q}) \Big] \tag{3}$$

where $\tilde{D}_{\alpha\beta}^{ii'}(\mathbf{q}, kk')(\alpha, \beta = x, y, z)$ are translational ($i, i' = t$), rotational ($i, i' = r$) and mixed ($i = t, i' = r$ or $i = r, i' = t$) elements of the molecular crystal's dynamical matrix, the expressions for which are presented in [27, 28], $U_\alpha^{i'}(k\mathbf{q})(\alpha, \beta = x, y, z)$ is the amplitude of vibration, m_k and $I_{\alpha\beta}(k)$ are the mass and inertia tensor of kth molecule in the unit cell.

In the quasiharmonic approximation, the free energy of a crystal has the same form as in the harmonic approximation but the structural parameters at fixed volume depend on the temperature. This dependence is determined self-consistently at calculation of the system's free energy. To obtain the equation of state $P(V)$ at fixed temperature, the expression

$$P = -\left(\frac{\partial F_{qh}}{\partial V} \right)_T \tag{4}$$

was used. For calculations of the free energy, the molecular coordinates (the centers of mass positions and orientations of molecules in the unit cell) were determined by the Newton–Raphson method. In this method new coordinates of molecules can be found from the minimum of potential energy of the expanded lattice.

The interactions between water molecules in hydrate were described by the modified empirical TIP4P potential [29]. The protons were placed according to the Bernal–Fowler rule and the water molecules were oriented so that total dipole moments of the unit cells of the hydrates are equal to zero. The long-range electrostatic interactions were

computed by the Ewald method. The free energy and the derivatives of free energy were calculated using $3 \times 3 \times 3$ k-points inside the Brillouin zone. The guests were considered as spherically symmetric Lennard–Jones particles. The potential parameters for the argon-argon interactions were taken from [15].

Results and discussion

Dynamic of CS-II, sH and tetragonal Ar clathrate hydrates with different filling of cavities

The phonon density of states (the number of vibrational modes in a given frequency interval) is the most widely discussed and best understood dynamical property of molecular crystal. To calculate this property for CS-II, sH and tetragonal Ar clathrate hydrates, the LD method was used. The clathrate hydrate of CS-II consists of two fundamental cages (small (5^{12}) and large ($5^{12}6^4$)) with radius of about 0.391 and 0.473 nm, respectively. The unit cell of the CS-II hydrate contains 136 water molecules, forming 16 small and 8 large cavities. For comparison, the calculations of phonon density of states (DOS) of the CS-II hydrate have been performed for various fillings: empty host lattice, single occupancy of the large and small cages and double occupancy of the large cages and single occupancy of the small cages. The results are shown in Figure 1. The peculiarity of this plot is a gap of about 7.2 THz which divides the low- and high-frequency vibrations of lattice. For empty host lattice, the analysis of the eigenvectors derived from the LD method revealed that the low-frequency region (0–9 THz) consists of translation modes of water and the high-frequency region (15.6–30 THz) consist of libration modes of water host framework. Argon atoms influence the vibrations of the host water framework only slightly and guest vibrations are located in the vicinity of the peaks of phonon density of states at 0–1.2 THz. The peak in the negative region, in the case of the single occupancy of both types of cages, corresponds to the motions of argon in large cages with imaginary frequencies. This means that the argon atoms are not localized in potential minima and can be freely moved inside the large cages. However, the all frequencies of water framework are positive in all the cases and hence both the single and the double occupancies do not disrupt the dynamical stability of the host lattice.

The unit cell for sH hydrate contains 34 water molecules, forming 3 small, 2 medium and one large cavities. Radius of small (5^{12}), medium ($4^35^{12}6^3$) and large ($5^{12}6^8$) cages are of about 0.391, 0.406 and 0.571 nm, respectively [5]. We examine the dynamical properties only for two cases. There are dynamic of empty host lattice and dynamic of Ar hydrate of sH with maximum experimentally predicted [11] number of guest atoms (fivefold occupancy of the large cages and single occupancy of the small and medium cages). The DOS calculations have been done using the experimental values of cell parameters at $T = 293$ K. The results are shown in Figure 2. The large intensive peak at 0.6 THz corresponds to translation of the guest atoms. After inclusion of argon
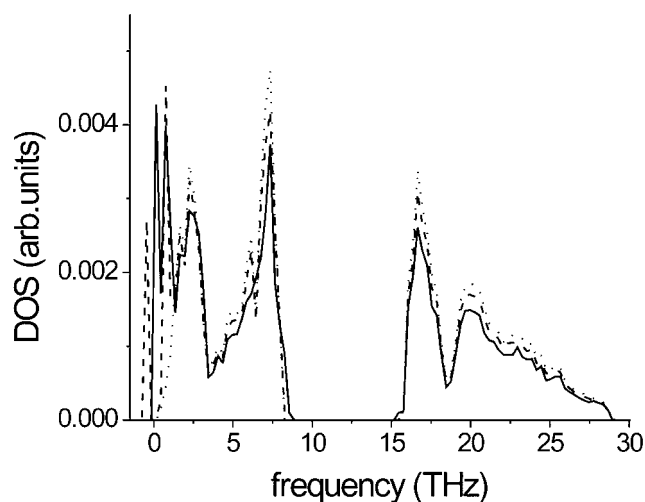

Figure 1. Phonon density of vibrational states (DOS) of CS-II Ar hydrates for various fillings: empty host lattice (dotted line); double occupancy of the large cages (solid line) and single occupancy of the large cages (dashed line). For the small cages, only single occupancy is considered.
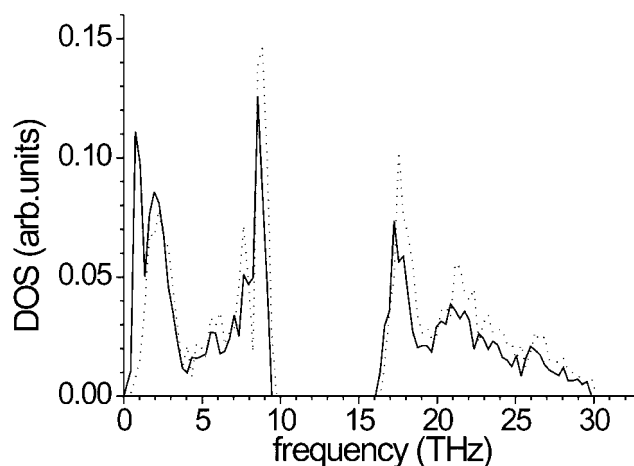

Figure 2. Phonon density of vibrational states (DOS) of structure sH Ar hydrates for various fillings: empty host lattice (dotted line), fivefold occupancy of the large cages and single occupancy of the small and medium cages (solid line).

atoms, the vibrational spectrum of host lattice has practically same features as in the case of the empty hydrate structure and hence the dynamical stability of H hydrate is not significantly changed even for fivefold occupancy of the large cages.

The unit cell for the argon hydrate with the tetragonal structure contains 12 water molecules, forming one cavity ($4^25^86^4$) [2]. The DOS calculations have been performed both for empty host lattice and double occupancy of the cages using the experimental values of cell parameters at $T = 293$ K. The results are shown in Figure 3. The empty host lattice is dynamically stable because all frequencies of water framework are positive. Dynamical stability of water lattice preserves after inclusion two guest atoms in each cage. The density of vibrational states of the empty tetragonal hydrate has same features as the density of vibrational states of ice Ih [30], hydrates of CS-I [31], CS-II and sH. The frequency region of molecular vibrations is
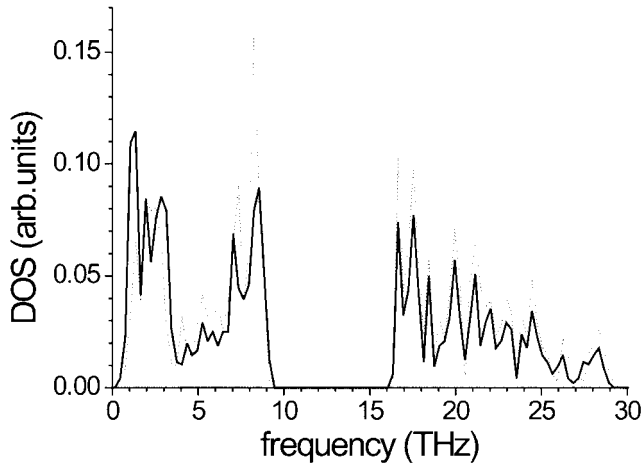
Figure 3. Phonon density of states of empty host lattice (dotted line) and doubly occupied tetragonal Ar clathrate (solid line).

divided into two zones. In the lower zone (0–9.45 THz) water molecules mainly undergo translational vibrations, whereas in the upper one (16.2–29.4 THz) the vibrations are mostly librational. In comparison with hydrates of CS-I, the frequency spectrum of tetragonal argon hydrate is shifted towards higher frequencies, which may be explained by greater density of a new tetragonal crystal argon hydrate compared to hydrates of CS-I. Vibrational frequencies of argon atoms in the cavities lay in the region 0.6–1.35 THz and 1.8–3.3 THz. The guest atoms influence the phonon spectrum of host framework, diminishing the density of states in upper zone of translational vibrations and the density of states of librational vibrations.

Equation of state of the CS-II, sH and tetragonal argon clathrate hydrates

The thermodynamic functions $P(V)$ of three types of hydrate structures can be estimated using obtained vibrational spectrum within the LD method. The equation of state $P(V)$ has been calculated at 293 K. It has been found that the studied hydrates are thermodynamically stable in selected range of pressure. Moreover, these results can be compared with experimental $P(V)$ data for Ar hydrate of three structural types [11]. In the case of Ar hydrate of CS-II type, the calculated $P(V)$ for single occupancy of the large and small cages is most closely correlated with experimental points as shown in Figure 4. The largest difference between theory and experiment has been obtained for sH hydrate using the experimental proposed multiply (5 Ar atoms) occupation of large cages [11] (see Figure 5). In this case, the $P(V)$ function of sH Ar hydrate with Ar·4.87H$_2$O stoichiometry, for which the occupancy of the large cages is double is closer to experiment.

The good agreement with experimental data has been observed in the case of double occupancy of Ar atoms in the hydrate cages of tetragonal structure. Figure 6 shows that at the experimental determined lattice parameters ($a = 0.634$ nm, $c = 1.061$ nm) the calculated value of pressure is $P = 0.98$ GPa, which correlates well with the experimental value ($P = 0.92$ GPa) [11].
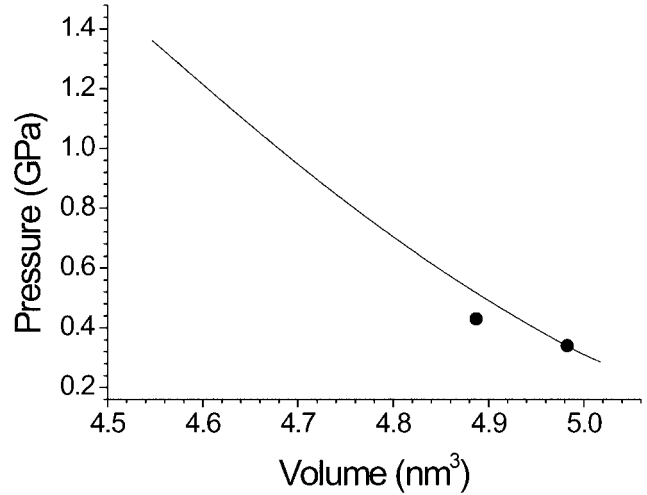

Figure 4. Equation of state of single occupied CS-II Ar hydrate at $T = 293$ K (solid line) and ● experiment [11].
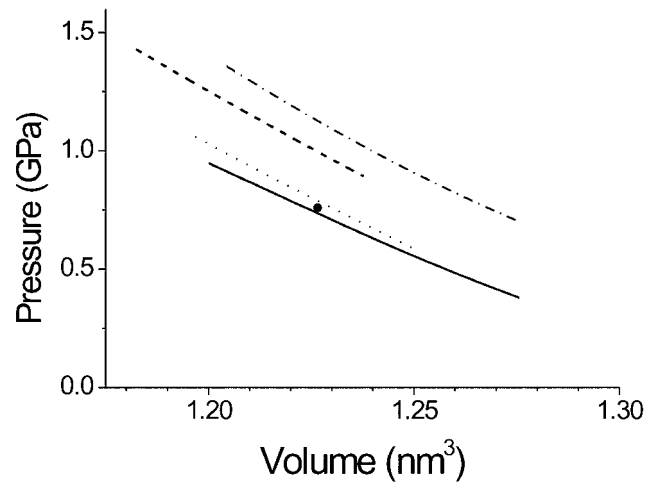

Figure 5. Equation of state of sH Ar hydrate: empty host lattice (solid line); fivefold (dotted and dashed line); threefold (dashed line) and double (dotted line) occupancy of the large cages (in all the cases, except empty host, the occupancy of the small and medium cages are single) at $T = 293$ K and ● experiment [11].
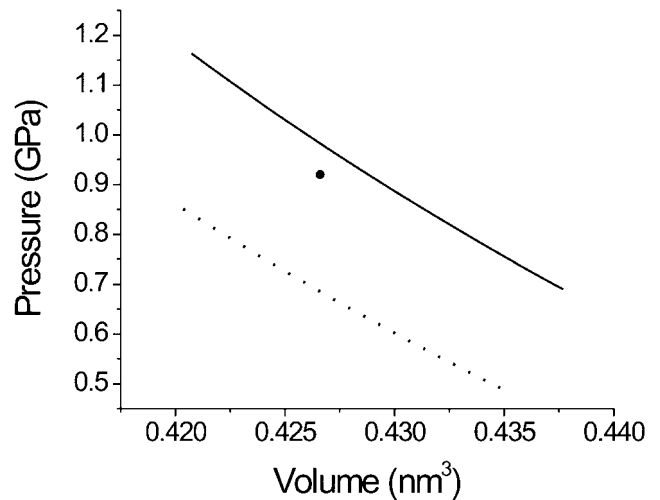

Figure 6. Equation of state of single (dash line) and double (solid line) occupied tetragonal Ar hydrate at $T = 293$ K and ● experiment [11].
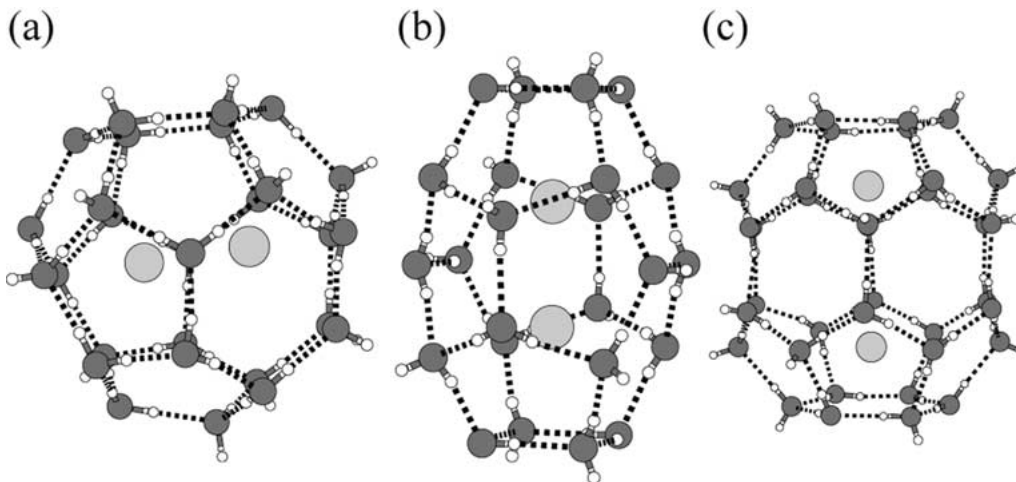
Figure 7. Structures of the water cages with double occupancy: (a) hexakaidecahedron ($5^{12}6^4$); (b) icosahedron ($5^{12}6^8$); and (c) tetradecahedral ($4^25^86^4$) cages.

Stability of argon clusters in large cages of clathrate hydrates CS-II, sH and tetragonal structures

Since the multiple occupation for Ar hydrate has been proposed only for the large cages and the large cavities of selected clathrate hydrates have different number of water molecules, the hexakaidecahedron ($5^{12}6^4$), icosahedron ($5^{12}6^8$) and tetradecahedral ($4^25^86^4$) water cages with enclathrated Ar atoms have been optimised using first-principles calculations (see Figure 7). The energy values for all investigated structures are presented in Table 1. The interaction between one Ar and the hexakaidecahedron cage $(H_2O)_{28}$ is equal to -1.72 kJ/mol. In the case of the icosahedron cage $(H_2O)_{36}$, the interaction between one argon atom and the cage is equal to -1.21 kJ/mol. The negative value of SE means that Ar has positive stabilization effect on these cages and hence single occupations can be achieved without applying high external pressure.

The analysis of calculated frequencies shows that the translation of Ar atom in these two cages is characterized by imaginary frequency that is in agreement with LD calculations (see Figure 1). Moreover, other calculated vibrational frequency of an Ar atom in both cavities is ≈ 0.6 THz, which is also close to the value obtained by the LD method. To calculate the H-bond energy (HBE), we assumed the binding energy (difference between the total cluster energy without guest atoms and the separate H_2O monomers at infinite distance) for the water cluster is solely due to H-bonding. The value of HBE was determined as the binding energy divided by the number of H-bonds. In these cases, we found the HBE values for the respective empty cages. Moreover, the structural features of the water cavities (distances, angles, etc.) are very similar to those existing in the empty cages, and hence, they represent the cage structures with no distortion.

In the case of double occupancy, the negative value of SE was obtained only in the case of $5^{12}6^8$ cage. The positive values of SE are found for hexakaidecahedron and tetradecahedral cavities. However, these energies are very small and hence the double occupancy may be possible in the case of CS-II and tetragonal structures under applying the external

Table 1. Stabilization energy for Ar clusters in the different large hydrate cages, H-bond energy (HBE) for the studied hydrate cages, number of Ar atoms and stoichiometry of the studied Ar hydrate

Type of water cage	Number of Ar atoms	Stoichiometry[a]	SE (kJ/mol)	HBE (kJ/mol)
Cage ($5^{12}6^4$)	0			-25.36
	1	Ar·5.67H_2O	-1.72	-25.36
	2	Ar·4.25H_2O	8.96	-25.36
	3	Ar·3.40H_2O	38.72	-25.07
Cage ($5^{12}6^8$)	0			-24.99
	1	Ar·5.67H_2O	-1.21	-24.95
	2	Ar·4.87H_2O	-2.26	-24.95
	3	Ar·4.25H_2O	-0.17	-24.90
	4	Ar·3.78H_2O	14.82	-24.86
	5	Ar·3.40H_2O	23.36	-24.86
	6	Ar·3.10H_2O	49.60	-24.69
Cage ($4^25^86^4$)	0			25.82
	1	Ar·6H_2O	4.14	25.82
	2	Ar·3H_2O	10.46	25.78
	3	Ar·1.5H_2O	112.21	24.57

[a] The occupation in the small and medium cages in the cases of CS-II and sH hydrates are single.

pressure. Moreover, the HBE as well as shape of cages are not changes as compared with the HBE and the structure of the respective empty cavities. Addition one more Ar atom leads to significant increasing the SE and decreasing the HBE values for hexakaidecahedron and tetradecahedral cages because of the distortion of the water cages. Moreover, the imaginary frequencies are found. The analysis of these frequencies shows that the Ar clusters are strongly interacting with the water cages since there is a strong coupling between the vibrations of guest and host molecules.

In the case of sH hydrate, the Ar_n (n up to 5) clusters can be stabilized in the icosahedron cavity. Frequency calculations reveal that all frequencies are real and so these structures are in local minima. The SE value is increased to 23.77 kJ/mol and HBE is not significantly changed (see

Table 1). Stabilization of the Ar_6 cluster inside this cage is energetically unfavorable since the value of SE is twice as larger as for the Ar_5 cluster.

The present calculations results can support to observed experimental data [11]. Thus, the double occupancy of the large cage of CS-II hydrates can be achieved under external pressure. The following increasing pressure with changing of stoichiometry form $Ar \cdot 4.25H_2O$ to $Ar \cdot 3.4H_2O$ leads to phase transition of hydrate structure and formation of sH hydrates with fivefold occupancy of icosahedron cages as observed in experiment. After further pressure increasing the formation of high dense tetragonal phase with stoichiometry $Ar \cdot 3H_2O$ is preferable. The disagreement between the LD results and experimental data on $P(V)$ diagram can be explained by fact that in the LD calculations all the cages were filled. However, in real situation, it is difficult to realize the full occupation of hydrate cavities. Moreover, it is experimentally known that it is not necessary to occupy all cavities by guest molecules and even a small number of guests is enough to form the clathrate structure [1]. Therefore, the multiple occupation for sH which was predicted experimentally [11], may be realized by only in a limited number of large cavities.

Conclusion

The electronic, structural, dynamic and thermodynamic properties of CS-II, sH and tetragonal Ar clathrate hydrates were investigated. The LD calculations showed that the selected hydrate structures with the different filling fractions are dynamically stable. The systematic investigation of the large cage of CS-II, sH and tetragonal structures with different number of Ar atoms was also performed using first-principle calculations. It has been found that in the studied hydrates the multiple occupancies of the large cages is possible. Moreover, the stability of Ar clusters in the large cages is correlated well with experimental phase transition from CS-II to a new tetragonal hydrate structure [11].

Acknowledgements

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