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# Dynamics and equation of state of hydrogen clathrate hydrate as a function of cage occupation

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## Abstract

The recent discovery of hydrogen clathrate hydrate with potential for efficient storage of molecular hydrogen at modest pressure has initiated significant scientific interest. Of critical importance for the amount of hydrogen that can be stored is the number of hydrogen molecules that occupy the cages in the hydrate clathrate host structure. The experimental data of cage occupancy is controversial, and the reproducibility of the initial experiment has been questioned. Therefore, in the present report we study the dynamic and thermodynamic properties of hydrogen clathrate hydrate as a function of cage occupancy using lattice dynamics calculations in order to determine the most favored occupancy at different external conditions. Lattice dynamics investigations show that all hydrogen hydrates with multiple species per cage are dynamically stable and phonon spectra strongly depend on the cage occupancy. As a result all thermodynamic functions vary significantly with cage occupancy. It is shown that quantum zero-point vibrations are of fundamental importance for the thermodynamic properties. The equation of state has been estimated as a function of temperature and cage occupancy.

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## 1. Introduction

Clathrate hydrates are a special class of inclusion compounds consisting of water and small guest molecules which form an ice-like hydrogen-bonded structure. These compounds are formed when water molecules arrange themselves in a cage-like structure around guest molecules and hence many of their physical and chemical properties differ from ice [1]. In recent years clathrate hydrates have attracted considerable interest because

large accumulations of natural gas hydrates have been discovered in ocean floor sediments and in permafrost regions. The fact that hydrate clathrates can contain several hundred times their own volume in gas has drawn attention. For instance, hydrogen clathrate hypothetically contains 500 times its volume in H<sub>2</sub> gas (under standard conditions 0.1 MPa and 273 K) while stable at 145 K at a pressure 0.01 MPa. At this temperature hydrogen hydrate clathrate contains as much H<sub>2</sub> as pure H<sub>2</sub> gas at a pressure of 25 MPa at 145 K. From a fundamental point of view hydrogen hydrate is interesting as it is the only known clathrate in which cages are multiple occupied.

Almost all known hydrate clathrate structures can be classified as cubic structure I (sI), cubic structure II (sII),

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and hexagonal (sH). In these structures the cages are much too large for an individual  $\text{H}_2$  molecule and therefore the existence of hydrogen hydrate with single cage occupancy was not suspected. The existence of hydrogen hydrate had been recognized in high-pressure experiments [2,3] but the crystal structure of the host lattice and the cage occupancy was not characterized. Recently, it had been reported that this hydrate has an sII type structure with a lattice parameter  $a = 1.7047 \pm 0.001$  nm at  $220 \pm 30$  MPa and 234 K with 4 (2)  $\text{H}_2$  molecules in the large (small) cage [4]. At variance with these data are the recent results of Lokshin et al. [5] who observed sII type  $\text{H}_2$  hydrate with a small cage occupancy of 1 and a large cage occupancy of 4 at a pressure of 2 kbar. At atmospheric pressure the observed large cage occupancy changes from 4 to 2 and the small cage remains singly occupied even when the temperature is increased.

Electronic local density functional simulations have shown that the enclathration of hydrogen molecules is based on physisorption with the  $\text{H}_2$  molecules in a cage each individually binding to the cage wall, and that  $\text{H}_2$ – $\text{H}_2$  interaction plays a role in the case of crowding only [6]. The stability of hydrate clathrate as function of hydrogen occupancy has been examined in a cluster approximation with a statistical mechanical model in conjunction with first-principles quantum chemistry calculations [7]. Zero-point quantum vibrations were accounted for only partially. Quantum effects of the rotational movement only were considered and translational motions were neglected. Therefore, it is of interest to study the structural, dynamic and thermodynamic properties of sII hydrogen hydrate crystal as a function of cage occupancy taking into account all types of molecular vibrations. In the present study we investigate these properties within the framework of the lattice dynamics approach in the quasiharmonic approximation.

## 2. Computational details

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

$$F_{qh} = U + F_{\text{vib}}, \quad (1)$$

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

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

where  $\omega_j(\mathbf{q})$  are the frequencies of crystal vibrations.

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 and temperature are determined self-consistently by minimization of the free energy. To obtain the equation of state  $P(V)$  at fixed temperature, the expression

$$P = - \left( \frac{\partial F_{qh}}{\partial V} \right)_T \quad (3)$$

was used. For calculations of the free energy and the phonon spectra, the molecular coordinates (the centers of mass positions and orientation of molecules in the unit cell) were optimized by the conjugate gradient method. The initial positions of the oxygen atoms of the host molecules are from the X-ray analysis of the double hydrate of tetrahydrofuran and hydrogen sulfide performed by Mak and McMullan [8].

The modified TIP4P potential [9] was used to describe the interaction between water molecules in the hydrate. The protons were placed according to the Bernal–Fowler rule and the water molecules were oriented such that the total dipole moment of the unit cell of the hydrate vanishes. Long-range interactions were computed by the Ewald method. The guests were considered as spherically symmetric particles and their interaction potential is formulated as

$$U_{\text{H}_2-\text{H}_2} = \frac{D_0}{\zeta - 6} \left( 6 \exp \left( \frac{\rho - r}{\rho} \zeta \right) - \zeta \left( \frac{\rho}{r} \right)^6 \right), \quad (4)$$

where  $r$  is intermolecular separation,  $D_0$  is the potential well depth,  $\rho$  is the intermolecular distance at the minimum of the potential (i.e., where  $U_{\text{H}_2-\text{H}_2} = -D_0$ ), and  $\zeta$  is a dimensionless “steepness factor”. We used this kind of intermolecular potential instead the well-known Lennard–Jones (LJ) form because the repulsive term in the LJ potential is known to be much too hard (ie, the repulsive core is too steep) at small intermolecular distances. The exponential-6 (exp-6) potential used here is a more realistic potential as it agrees with molecular beam scattering data and gives the correct functional form at small intermolecular separations [10]. For modeling the  $\text{H}_2\text{O}$ – $\text{H}_2$  interaction the LJ part of the TIP4P potential has been fitted by a exp-6 potential and host–guest interaction potential parameters are represented as

$$\begin{aligned} D_{\text{H}_2\text{O}-\text{H}_2} &= \sqrt{D_{\text{H}_2\text{O}-\text{H}_2\text{O}} D_{\text{H}_2-\text{H}_2}} \\ \zeta_{\text{H}_2\text{O}-\text{H}_2} &= \sqrt{\zeta_{\text{H}_2\text{O}-\text{H}_2\text{O}} \zeta_{\text{H}_2-\text{H}_2}} \\ \rho_{\text{H}_2\text{O}-\text{H}_2} &= (\rho_{\text{H}_2\text{O}-\text{H}_2\text{O}} + \rho_{\text{H}_2-\text{H}_2})/2 \end{aligned} \quad (5)$$

We analyzed the effect of the  $\text{H}_2$ – $\text{H}_2$  interaction potential parameters by considering two potentials; the first set (P1) was taken from [11], and in the second set (P2) the long-distance dispersion interaction part was

Table 1  
Potential parameters of the exp-6 potential as described in the text

Parameter	$D_0$ (kJ/mol)	$\rho$ (nm)	$\zeta$
H <sub>2</sub> –H <sub>2</sub> (P1)	0.16742	0.2886	12
H <sub>2</sub> –H <sub>2</sub> (P2)	0.7295	0.2967	10.92
H <sub>2</sub> O–H <sub>2</sub> O	0.25113	0.35	21

taken from [12] and the short-range repulsion part was estimated with a *density functional* calculation using the mixed basis method [13]. Potential parameters of the H<sub>2</sub>–H<sub>2</sub> and fitted LJ part of host–host interaction are listed in Table 1.

### 3. Results and discussion

#### 3.1. Dynamics of sII hydrogen hydrate at different cage occupancy

As the phonon density of states (VDOS) is the most widely discussed and best understood dynamical property of molecular crystals we analyze it in some detail as a function of cage occupancy. The clathrate hydrate of sII 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 sII hydrate contains 136 water molecules, forming 16 small and 8 large cavities. Cage occupancies of  $n\text{H}_2$  in the large cage (L) and  $m\text{H}_2$  in the small cage (S) are indicated as  $n\text{H}_2@\text{L} + m\text{H}_2@\text{S}$ . The calculations of phonon density of states (VDOS) of the sII hydrate have been performed for various cage occupancies:  $0\text{H}_2@\text{L} + 0\text{H}_2@\text{S}$ ,  $2\text{H}_2@\text{L} + 1\text{H}_2@\text{S}$ ,  $3\text{H}_2@\text{L} + 1\text{H}_2@\text{S}$ ,  $4\text{H}_2@\text{L} + 1\text{H}_2@\text{S}$ , and  $4\text{H}_2@\text{L} + 2\text{H}_2@\text{S}$ . The VDOS calculations have been performed at the experimental lattice parameter at  $T = 234$  K [4]  $a = 1.7047$  nm, see Fig. 1. The VDOS of the empty sII hydrate has the same feature as that of ice Ih [14], a gap of about 7.2 THz which divides the low- and high-frequency vibrations of lattice. Analysis of the eigenvectors of the dynamical matrix revealed that the low-frequency region (0–9 THz) consists of translation modes of water and the high-frequency region (15.6–30 THz) consists of libration modes of the water host framework.

All cage occupancies considered are found to be dynamically stable because all frequencies of water and hydrogen molecules are positive. Guest molecules influence the vibrations of the host water framework only slightly and guest vibrations are located in the vicinity of the peaks of the phonon density of states at 0–1.7 THz. The influence of hydrogen molecules on the VDOS depends on the cage occupancy and the H<sub>2</sub>–H<sub>2</sub> intermolecular interaction potential. In the case of  $1\text{H}_2@\text{S}$  the host VDOS is influenced only slightly, rather independent of the occupancy of the large cage.

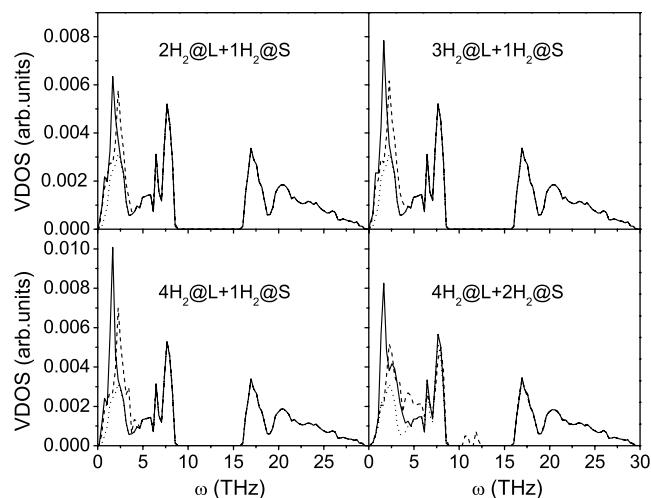


Fig. 1. Phonon density of states (VDOS) of H<sub>2</sub> hydrate at various cage occupancies calculated by using two different H<sub>2</sub>–H<sub>2</sub> intermolecular interaction potentials (P1—solid line and P2—dashed line) as compared with the VDOS of the empty sII lattice (dotted line).

For the P1(P2) potential the effects of the guest H<sub>2</sub> are in the frequency range of 0–1.7 THz (0–2.3 THz).

For the P2 potential the peaks in VDOS associated with the guest H<sub>2</sub> are slightly wider than those for the P1 potential. For  $4\text{H}_2@\text{L}$  the P2 potential gives two additional small peaks in the VDOS at 3.4 and 4.5 THz. As Fig. 1 indicates the influence of the cage occupancy on the VDOS is significant for  $4\text{H}_2@\text{L}$  and  $2\text{H}_2@\text{S}$ . In these cases the VDOS changes noticeably for all translational modes and in the VDOS calculated with the P2 potential there appear frequencies in the gap between translational and vibrational modes. Eigenvector analysis shows that these extra frequencies in the gap correspond to resonating translational vibrations of pairs of H<sub>2</sub> molecules located in the small cages. The VDOS calculated with H<sub>2</sub>–H<sub>2</sub> intermolecular interaction potentials P1 differs from that obtained with P2 because P1 is a much softer potential than P2.

#### 3.2. Equation of state of the hydrogen clathrate hydrate as a function of cage occupancy

The thermodynamic function  $P(V)$  of hydrogen hydrate can be estimated with the calculated VDOS as a function of cage occupancy. The equation of state  $P(V)$ , calculated at 234 K, shows that the hydrates considered here can be thermodynamically stable in a range of pressure. These results can be compared with experimental  $P(V)$  data for H<sub>2</sub> hydrate [4], see Fig. 2. In all  $1\text{H}_2@\text{S}$  cases the calculated  $P(V)$  depends weakly on the kind of H<sub>2</sub>–H<sub>2</sub> intermolecular interaction potential. However, for  $4\text{H}_2@\text{L} + 2\text{H}_2@\text{S}$  the dependence on the H<sub>2</sub>–H<sub>2</sub> potential is much stronger. This can be associated with the strong repulsion between the two guests molecules in the small cage. For none of the cases

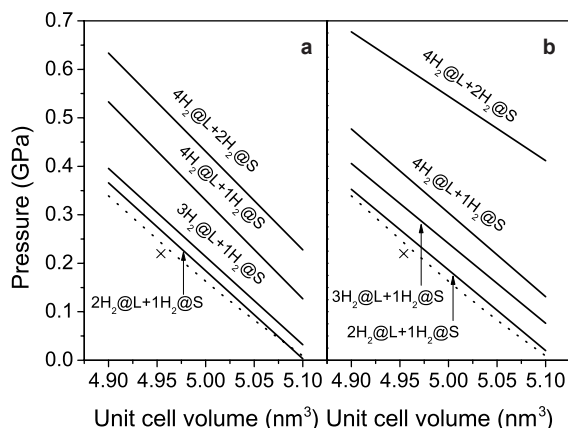


Fig. 2. Equation of state of hydrogen hydrate at various cage occupancies as compared with the empty sII lattice (dotted line) using two different  $H_2$ – $H_2$  intermolecular interaction potentials at  $T = 234$  K: (a) potential P1 and (b) potential P2.

considered do the calculated results coincide with the experimental data of Mao et al. [4]. Our calculations agree better with the measurements of Lokshin et al. [5] who found that the large cages are occupied by  $4H_2$  molecules at a pressure of 200 MPa up to a temperature of 190 K, with gradually decreasing occupancy as the temperature is raised, while the small cage was found to be singly occupied at all temperatures considered (Fig. 3).

### 3.3. Thermal expansion of hydrogen hydrate at atmospheric pressure

The lattice parameter of hydrogen hydrate as a function of temperature as calculated and as measured at the experimental cage occupancies [5] are displayed in Fig. 4. The calculated lattice parameters are in good agreement with the experimental data and the relative error is not more than 0.2% for both  $H_2$ – $H_2$  potentials considered. At temperatures above 120–130 K the lattice

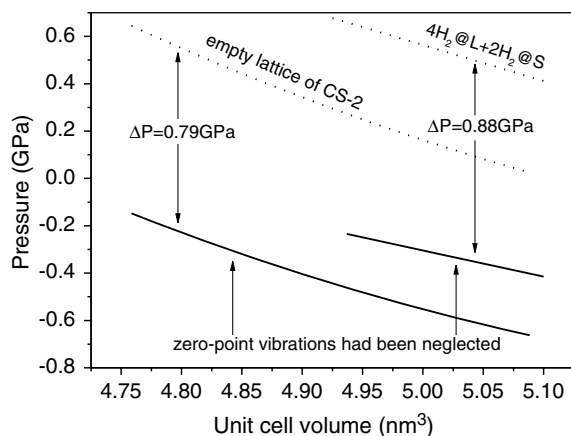


Fig. 3. Influence of zero-point quantum vibrations on the equation of state of the empty sII lattice and  $H_2$  hydrate at  $T = 234$  K.

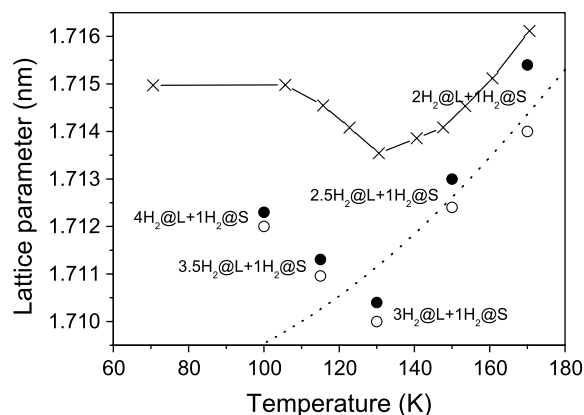


Fig. 4. Lattice parameter of hydrogen hydrate and of the empty sII lattice (dotted line) at atmospheric pressure as calculated with potentials P1 (○) and P2 (●) and as measured experimentally (x) [5].

parameter of the hydrate almost coincides with that of the empty lattice of sII. At lower temperatures the encathrated hydrogen molecules expand the water framework which can be interpreted as an effective chemical pressure of the guest molecules on the host lattice. The value of this pressure can be estimated using the equation of state  $P(V)$  as a function of temperature [15]. Such an analysis reveals that the host lattice parameter is not affected at a large cage occupancy of 3 and fewer  $H_2$  guest molecules. The effective chemical pressure is negative for both  $H_2$ – $H_2$  potentials because in both cases the guest molecules expand the hydrate lattice. At a temperature of 100 K the effective chemical pressure is –38 and –45 MPa for potentials P1 and P2, respectively.

It must be emphasized that the hydrate clathrates are quantum substances. This is evidenced by calculating  $P(V)$  at  $T = 234$  K of the empty lattice of sII and of  $4H_2@L + 2H_2@S$  hydrate using the free energy with and without the zero-point quantum vibrations (using Eq. (1) with and without the first term on the right side), as shown in Fig. 3. The contribution of the zero-point quantum motion of the water molecules on  $P(V)$  for the empty sII lattice is 790 MPa while for  $4H_2@L + 2H_2@S$  it is 880 MPa. The quantum character of molecular the vibrations in  $H_2$  hydrate is so significant because of the small mass of guest and host molecules. Our calculations indicate that the zero-point quantum vibrational part of the free energy is about 25–30% of the potential energy at low temperatures and therefore its consideration is essential for a correct description of the thermodynamic properties of such molecular crystals as ices and gas hydrates.

## 4. Conclusion

Dynamical properties of hydrogen hydrate as a function of cage occupancy has been investigated using lattice dynamics calculations in the quasiharmonic



approximation. Two different guest–guest intermolecular interactions potentials have been examined and both are shown to give similar results for all occupancies of the large and small cages. Notable differences occurred in the case of double occupancy of the small cage only. All investigated hydrates are dynamically stable and the phonon spectra and equation of state depend on the cage occupancy. Lattice dynamics calculations at the experimentally measured cage occupancy and temperature agree well with the equilibrium pressure of  $H_2$  hydrate reported by Lokshin et al. [5] but do not agree with those of another experiment [4]. An examination of the lattice parameter as a function of temperature at the experimentally measured cage occupancy shows that at temperatures above approximately 125 K and for large-cage occupancies of 3  $H_2$  or less, the guest molecules do not affect the host lattice. The quantum zero-point vibrations are shown to be of fundamental importance for the thermodynamic properties of water clathrate hydrates.

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