

# Monte Carlo Calculations of the Free Energy of Binary SII Hydrogen Clathrate Hydrates for Identifying Efficient Promoter Molecules

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## **ABSTRACT**

The thermodynamics of binary sII hydrogen clathrates with secondary guest molecules is studied with Monte Carlo simulations. The small cages of the sII unit cell are occupied by one H<sub>2</sub> guest molecule. Different promoter molecules entrapped in the large cages are considered. Simulations are conducted at a pressure of 1000 atm in a temperature range of 233 K to 293 K. To determine the stabilizing effect of different promoter molecules on the clathrate, the Gibbs free energy of fully and partially

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occupied sII hydrogen clathrates are calculated. Our aim is to predict what would be an efficient promoter molecule using properties such as size, dipole moment, and hydrogen bonding capability. The gas clathrate configurational and free energies are compared. The entropy makes a considerable contribution to the free energy and should be taken into account in determining stability conditions of binary sII hydrogen clathrates.

## I. INTRODUCTION

Clathrate hydrates are of great technological interest because of their capacity to store gas at relatively high density and are therefore considered as prospective candidates for hydrogen storage materials<sup>1</sup>. Clathrate hydrates are crystalline molecular compounds consisting of a water host lattice and guest molecules<sup>2</sup>. The guest molecules are entrapped (enclathrated) into cages (cavities) of the host water structure to stabilize the compounds. The guest molecules can be water-miscible, for instance, tetrahydrofuran or hydrophilic such as cyclopentane. The water molecules forming the host framework are connected by strong hydrogen bonds. The stability of the whole structure is achieved due to the guest molecules interacting with the water molecules of the host lattice through van der Waals forces. When the cages are filled with a sufficient number of guest molecules, the crystalline solid becomes stable. If we change, for instance, either temperature or pressure of the gas hydrate, in such a way that the hydrate dissociates, the enclathrated gas is released.

Different forms of gas hydrates are known of which the cubic structure I (sI), cubic structure II (sII) and hexagonal structure H (sH) are most common. These structures are proton-disordered phases with zero net dipole moment, i.e., the arrangement of the water molecules in the host lattices obeys the Bernal-Fowler ice rules<sup>3</sup>. Clathrate hydrates of hydrogen are mostly of the sII type, although recently the sH hydrogen clathrate hydrate<sup>2,5</sup> has been synthesized. In the present paper we will therefore focus on the sII structure. The unit cell of the sII hydrate, with 136 water molecules, is specified by  $Fd3m$  space group and has sixteen  $5^{12}$  small cavities and eight hexakaidecahedral  $5^{12}6^4$  large cavities. The sII structure can be formed by guest molecules, such as  $C_2H_6$  or  $C_4H_{10}$ , with van der Waals diameters up to  $7.0\text{\AA}$ <sup>2</sup>. Extreme pressures ( $\sim 220$  MPa at 280 K) are required to form stable pure hydrogen clathrate hydrates<sup>4,1</sup>. This makes it impractical to use the pure hydrogen clathrates in technological applications. However, Florusse *et al*<sup>5</sup>. reported that the synthesis pressure of hydrogen hydrates can be significantly decreased ( $\sim 5$  MPa at 274 K) by accommodating tetrahydrofuran (THF) in the large cavities. This second guest molecule is referred to as promoter. The stabilizing impact of THF comes at a cost though, since the promoter molecules occupy a fraction of the large cavities and only the remaining cavities are available for occupancy by hydrogen molecules. Therefore, it is of

great importance to study the relationship between potential promoter molecules and the stability of hydrogen hydrates at a wide range of pressures and temperatures.

The purpose of this paper is to obtain the free energy of fully occupied binary sII hydrogen clathrate hydrates to identify efficient promoters and to determine the effect of entropy on stability of the clathrates. We aim to search for possible correlations between the stability of the clathrates and properties of promoter in terms of dipole moment, size and geometry. The thermodynamic stability of any clathrate hydrate can be predicted using, the popular statistical mechanical theory proposed by van der Waals and Platteeuw (vdWP)<sup>6</sup>. The original vdWP model is based on the assumptions that (1) there is no interaction between the guest molecules in different cavities, (2) each cavity cannot contain more than one guest molecule, (3) the free energy contribution of the water molecules is independent of the hydrate occupancy, (4) the guest molecules do not distort the hydrate lattice. Moreover, some phenomenological constants have to be provided for the vdWP calculations<sup>7</sup>. Recently conducted molecular dynamics studies of sI<sup>8</sup>, sII<sup>9,10,11</sup>, and sH<sup>12</sup> showed the hydrogen bonds between the guests and the lattice water molecules affect the rotational dynamics of the guests in the large cages and lead to the formation of Bjerrum L-defects resulting in greater rotational freedom for neighboring water molecules. This implies that vdWP cannot be applied to determine relative stability of these hydrates and free energy calculations are needed in this case<sup>8</sup>. Nevertheless, regardless of its restrictive assumptions, the vdWP approach was successfully applied to estimate phase behavior of clathrate hydrates with one and more types of guest molecules<sup>7</sup>. To evaluate the stability, i.e., the free energy of clathrate hydrate with multiple cage occupancy, the generalized vdWP theory combined with Monte Carlo (MC) was proposed by Tanaka *et al.*<sup>13,14</sup> This theory is based on the assumptions that molecular motions can be approximated as a collection of harmonic oscillators. The model takes into account the host water-guest interactions. However, due to the underlying assumption, the application of the theory is restricted to the temperature region where the harmonic approximation is valid. Belosludov *et al.*<sup>15,16,17</sup> developed another extended vdWP method that calculates thermodynamic properties of hydrates with multiple filling of the cages. The technique uses the quasiharmonic lattice dynamics method<sup>18,19</sup> which determines the Helmholtz free energy of clathrate hydrate as the sum of the potential energy of the hydrate and the vibrational contribution under the assumption that structural

parameters depend on temperature at constant pressure. The proposed method accounts for guest-host and guest-guest interactions, although it is limited to the temperature range where the lattice dynamics approach is correct.

To overcome limitations of approximate theories it is important to calculate the free energy of clathrate hydrates assuming only the potential surface of intermolecular interactions. Computer simulations of binary gas hydrate systems can help to explore stability, structural details at the molecular level with as only input the intermolecular potential. Furthermore, studies of free energies are of great importance for determining crystal phase diagrams. Monte Carlo and molecular dynamics simulations<sup>20,21,22,23,24,25,26</sup> have been reported on the thermodynamic stability of hydrates in terms of free energy.

A problem with free energy calculations is that a reference state with known free energy is needed. Probably the most widely used and proven method for determining the free energy of crystals was introduced by Frenkel and Ladd<sup>27</sup> (FL). The reference state of the method is an Einstein crystal. However, it is not straightforward to apply the method to complex molecular crystals. Using Monte Carlo techniques based on the FL method, Wierzchowski *et al.*<sup>21</sup> calculated the Helmholtz free energy of the zero-occupancy and fully occupied structure-I methane clathrates. Jensen *et al.*<sup>20</sup> carried out Monte Carlo calculations based on thermodynamic integration from an Einstein crystal<sup>27</sup> to obtain the three-phase liquid water – hydrate – methane vapour equilibrium based only on the knowledge of interaction potential.

In this paper the Helmholtz free energy calculations are carried out using the self-referential (SR) method<sup>28</sup>. The SR technique utilizes the principle that the free energy is an extensive quantity. The crystal of interest is taken as the reference state. The only difference between the state of interest and the reference state is their size. This makes the transition from the reference state to the tertiary molecular crystal more straightforward than the transition from an Einstein crystal. The drawback is that a cell of double size should be simulated. The present work addresses hydrogen storage in binary sII gas hydrates. We assume these hydrates to be fully filled. In Sec. IV A we will justify this choice by performing a series of semigrand Monte Carlo (SGMC) simulations of partially occupied hydrogen hydrates with THF promoters.

The remainder of this paper is organized as follows. In Sec. II we provide computational details. In Sec. III tested molecules are listed. In Sec. IV the results are presented and discussed. We summarize with conclusions.

## II. NUMERICAL AND SIMULATIONS DETAILS

### A. Potential energy

Calculations of the free energy of an empty and a fully occupied binary sII clathrate promoter+H<sub>2</sub> systems are carried out in the canonical (NVT) ensemble. Simulations of the Gibbs free energy of partially filled binary sII clathrate are conducted in the isobaric semigrand ensemble. It is assumed that all molecular interactions are pairwise additive. The van der Waals interactions between molecules are represented by the Lennard-Jones (LJ) potential. Coulomb interactions are calculated using the Ewald summation method<sup>29</sup>. The intermolecular potential is given by

$$U = \sum_{i=1}^{N-1} \sum_{j>i}^N 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{i=1}^{M-1} \sum_{j>i}^M \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad , \quad (1)$$

where  $N$  is the number of LJ sites and  $M$  is the number of Coulomb charges. Note that the charges are not necessarily located at LJ sites. Both the cutoff of the van der Waals interactions and the cutoff for the real-space part of the Ewald sum equal half of simulation box. Standard long range corrections<sup>29</sup> for LJ potential are taken into account. For the guest H<sub>2</sub> a linear rigid model with a bond length of 0.7414 Å is used.<sup>25</sup> For the water molecules in the host lattice the TIP4P/2005<sup>30</sup> model is employed. It has recently been shown that this potential is capable to correctly predict the density of the clathrate hydrates sI, sII, and sH at temperatures above 150 K.<sup>31</sup>

Since many tested promoter molecules (see Table 1) have chemical rings, molecular models of these guest molecules are treated as rigid bodies. For the sake of consistency, the promoter molecules without rings are assumed to be rigid as well. The aim of this work is to compare efficiencies of various promoter molecules, therefore we obtained geometries, point charges and force field parameters for each promoter following the same recipe. For promoter interactions GAAF-like<sup>32</sup> model potentials are used, similar to those used in the simulation studies of binary

clathrate hydrates<sup>25,26,33</sup>. To represent the electrostatic interactions, partial charges are placed on atomic sites. The partial charges are fitted with the CHELPG method<sup>34</sup> implemented in Gaussian 03<sup>35</sup> using *ab initio* calculations of the electrostatic potential of the promoter molecules at the MP2/aug-cc-pVQZ level (except for cyclopentane and fluorocyclopentane where the MP2/aug-cc-pVTZ level is used) with the total charge constrained to zero. The atomic positions are optimized at the same level. For promoter molecules exhibiting symmetry, the symmetry inherent in the rectangular geometric constructions of the CHELPG method yields different charges for symmetry-equivalent atoms. In these cases the calculated charges have been averaged over the symmetry-equivalent sites. The parameters of the Lennard-Jones potential for different promoter molecules are taken from Cornell *et al.*,<sup>36</sup> except for bromine and chlorine whose parameters are taken from Mayo *et al.*<sup>37</sup> The calculated atomic positions, fitted charges and the LJ parameters of the promoter molecules are provided in the supplementary information. The Lorentz-Berthelot combining rule is applied for unlike site-site interactions.

## B. Simulations details

The initial positions of oxygens in the sII structure are obtained from the experimental X-ray crystallographic clathrate structure<sup>38</sup>. Buch's algorithm<sup>39</sup> is used to generate initial proton-disordered configurations satisfying the ice rules<sup>3</sup> (each oxygen atom is chemically bonded to two hydrogen atoms and the oxygen in each molecule forms two hydrogen bonds with other water molecules) and the configuration with nearly zero net dipole moment is selected following the method proposed by Rick and Haymet<sup>40</sup>. For free energy calculations of an empty and a fully occupied hydrate, the simulated cell is composed of one unit cell ( $a=17.31$  Å) containing 136 water molecules in the host framework with 16 small cages and 8 large cages. The total number of molecules  $N$  in the one unit cell system is 160. Single occupancy of the large and the small cages is assumed. In the initial configuration the centre of mass of each promoter molecule is located in the centre of the large cage whereas the centre of mass of each H<sub>2</sub> guest molecule is placed in the centre of the small cages. Simulations in the isobaric semigrand ensemble are conducted in the eight unit 2x2x2 supercell.

Initially, random orientations are chosen for promoter and H<sub>2</sub> molecules inside all the cages. Maximum displacements as well as rotations for the host water molecules differ from those for the enclathrated guest molecules and are chosen to ensure suitable acceptance rates<sup>41</sup>. Periodic boundaries are employed.

Initial MC simulations were conducted in the isothermal isobaric ensemble (NPT) to equilibrate a system to the correct density and lattice parameters corresponding to given temperature and pressure. Then two types of free energy calculations were performed: using the self-referential and SGMC method. The former can treat only empty or fully filled hydrates; the latter works with partially/fully filled hydrates but is limited to small promoter molecules.

Free energy calculations of an empty and a fully occupied hydrate were conducted in the canonical (NVT) ensemble to determine relative stability of the hydrogen hydrates filled with various promoters. Each MC free energy run for a fixed value of constraint parameter  $\alpha$  involves 400000-700000 cycles to achieve equilibrium and 60000-70000 production cycles to compute ensemble averages. A cycle is defined as  $2N$  attempts to change a current configuration. Translational and rotational moves are chosen at random with equal probability whereas in the NPT simulations volume trial changes were attempted with probability  $1/N$ . More computational details on the Helmholtz free energy calculations of general molecular crystals are provided in Ref. <sup>28</sup>. The Gibbs free energy is related to the Helmholtz free energy via the thermodynamic expression

$$G = F + PV \quad (2)$$

where  $P$  is the pressure,  $V$  is the unit-cell volume of hydrate.

In isobaric semigrand simulations of partially/fully filled hydrates, translational, rotational, and volume-changing moves were performed in the same way as in the NPT ensemble calculations. However, trial insertion and deletion moves were additionally conducted to sample the concentration of guest molecules of the hydrate. Insertion moves were attempted with randomly orientated guest molecules. Simulation lengths were typically  $5 \times 10^5$  trial configurations for equilibration and the same number cycles for taking averages. SGMC simulations were carried out for a series of promoter and H<sub>2</sub> chemical potentials. Starting values of guest chemical potentials were chosen to



keep the occupancy of the large and small cages close to zero. By gradually increasing values of the chemical potentials, a clathrate hydrate is being filled with guest molecules until the state of full occupancy. The final configuration obtained at the end of each SGMC simulation at a fixed chemical potential was then used as the initial configuration for the simulation at higher value of the chemical potential.

### **C. Free energy calculations of empty and fully occupied clathrate hydrates**

The free energy calculations of empty and fully occupied clathrate hydrates are carried out using the self-referential (SR) technique recently extended to general molecular crystals<sup>28</sup>. The SR method was validated in study<sup>28</sup> by comparing the free energy results for hexagonal ice, cubic ice, ice VII, empty sI clathrate and fully occupied methane sI clathrate with available literature data obtained with the FL method. The technique is based on the principle that the Helmholtz free energy scales linearly with system size, i.e., doubles if the system size doubles. The SR method has two stages: a ‘replication’ and a ‘relaxation’. The replication stage produces a self-similar double-size system by adding a replica, to within a self-similarity constraint, to the original single-size system of interest. The replication simulation calculates the free energy difference between the small single-size system and a highly constrained double-size system. The relaxation procedure gradually relaxes this self-similarity constraint imposed at the replication stage until the constraint is no longer felt by the molecules of the crystal. The relaxation simulation calculates the free energy difference between the fully constrained double-size system and fully relaxed double-size system which has twice the Helmholtz free energy of the single-size system of interest. The total free energy difference between the single-size and double-size system is the sum of the free energies differences of the two stages. Because of the linear scaling this difference equals the free energy of the single-size system. The SR technique works only for a periodic system. Since the SR method requires the replica to reside in a cage exactly a cell length separated from the original cell of the single system, it is correct only for completely empty and fully occupied clathrates. Applying the technique to a clathrate hydrate, we take advantage that the system is periodic and avoid interfaces. The SR method is advantageous when

compared to other techniques because it takes the crystalline solid of interest as the reference state which makes the transition between the two states relatively straightforward. The disadvantage of the SR approach compared, for example, to the FL method is that the simulation cell during the relaxation stage contains twice as many molecules as the original crystal of interest has.

In the SR method the position of the center of mass and the angular coordinates of a rigid molecule  $i$  are specified by  $\mathbf{r}_i$  and the Euler angles  $\mathbf{\Omega}_i = \{\varphi_i, \theta_i, \psi_i\}$ , respectively. The orientation of each replicated molecule can be expressed relative to that of the corresponding partner molecule in the single-size crystal with the number of molecules  $N_s$ . For a double-size system  $\mathbf{\Omega}_{i+N_s}$ , for  $i = 1, \dots, N_s$  is described relative to  $\mathbf{\Omega}_i$  rather than space-fixed axes so that  $\mathbf{\Omega}_{i+N_s} = \{\nu_i, \tau_i, \chi_i\}$  where  $\nu_i, \tau_i, \chi_i$  are the relative Euler angles formed by the axes of molecule  $i$  and its partner molecule  $i+N_s$ . The self-similarity translational constraint on the molecular centers of mass of the molecules  $N_s+1, \dots, 2N_s$  of double-size system is expressed by

$$r_i = \left| \mathbf{r}_i - (\mathbf{r}_{i+N_s} - \mathbf{L}_x) \right| \leq \hat{r}(\alpha), \quad (3)$$

where  $\mathbf{L}_x$  is a vector in the duplication direction with the length of the single-size box,  $\hat{r}(\alpha)$  is the tolerance constraint for the displacement of the centres of mass of molecules,  $\alpha$  controls the self-similarity constraint for relative translational and orientational molecular degrees of freedom. When  $\alpha = \alpha_1$  is very small, the double-size system is almost perfectly self-similar; when  $\alpha$  is sufficiently large the double-size system is fully relaxed. It is convenient to introduce a similar orientational constraint  $-\pi \leq \kappa(\alpha) \leq \pi$  for relative Euler angle  $\chi_i$  and the constraint  $0 \leq \eta(\alpha) \leq 2$  for  $(1 - \xi)$ , where  $\xi$  is the cosine of relative angle  $\tau_i$ , i.e.,  $1 - \xi \leq \eta(\alpha)$ . The relative angle  $\nu_i$  should not be constrained.

Since the Helmholtz free energy is related to partition function  $\Phi$  via the expression

$$\beta F = -\ln(\Phi) \quad (4),$$

the Helmholtz free energy difference for the replication stage can be calculated analytically and given by

$$\Delta(\beta F_{rep}) = -\ln\left(\frac{\Phi_{\alpha_1}}{\Phi_s}\right) \approx -N_s \ln(V_{\hat{r}_1} V_{\hat{\eta}_1} V_{\hat{\kappa}_1}), \quad (5)$$

where  $\Phi_s$  and  $\Phi_{\alpha_1}$  are the partition functions of the single-size system of interest and the highly constrained, self-similar, double-size system, respectively,  $\beta^{-1} = k_B T$  ( $k_B$  is Boltzmann's constant and  $T$  is temperature),  $V_{\hat{r}_1} = 4\pi\hat{r}_1^3/3$ ,  $V_{\hat{\eta}_1} = 2\pi\hat{\eta}_1$  and  $V_{\hat{\kappa}_1} = 2\hat{\kappa}_1$  are the phase volumes available to each replicated particle when the system is fully constrained. Here, the temperature of the highly constrained double-size system is twice as much as the temperature of the original single-size system,  $\beta_{\alpha} = \beta/2$ . It is convenient to keep the density of the constrained double-size crystal similar to that of the single-size crystal in order to avoid any phase transitions. This is achieved by changing the temperature of the constrained double-size system during the relaxation simulation. It is straightforward to show that the error in the approximation in Eq. (3) is proportional to  $\hat{r}_1^2$ .

To be consistent with results in Ref. <sup>42</sup>, we use the normalized angular coordinates and add  $\ln(V_{\Omega}) = \ln(8\pi^2)$  to the right hand side of Eq. (5) to obtain

$$\Delta(\beta F_{rep}) \approx -N_s \ln\left(\frac{2}{3} \hat{r}_1^3 \hat{\eta}_1 \hat{\kappa}_1\right) \quad (6)$$

The relaxation free energy term can be obtained using thermodynamic integration

$$\Delta(\beta F_{rel}) = \int_{\alpha_1}^{\alpha_m} d\alpha \frac{d(\beta_{\alpha} F_{\alpha})}{d\alpha}, \quad (7)$$

where  $\alpha_m$  is the value of constraint when double-size system is completely relaxed.

The term  $d(\beta_{\alpha} F_{\alpha})$  can be found taking into account the thermodynamic relation (4)

$$d(\beta_{\alpha} F_{\alpha}) = -d(\ln(\Phi(\alpha))) = -\frac{d\Phi(\alpha)}{\Phi} = -\frac{1}{\Phi} \left( \left( \frac{\partial \Phi}{\partial \alpha} \right) d\alpha \right) \quad (8)$$

The relaxation contribution to the Helmholtz free energy difference has been derived in paper 28 and is given by

$$\Delta(\beta F_{rel}) = \int_{\beta_s/2}^{\beta_s} d\beta_\alpha \langle H_\alpha \rangle - 4\pi N_s \int_{\ln(\hat{r}_1)}^{\ln(\hat{r}_m)} d \ln(\hat{r}) g_r(\hat{r}, \hat{r}) \hat{r}^3 - N_s \int_{\ln(\hat{\eta}_1)}^{\ln(\hat{\eta}_m)} d \ln(\hat{\eta}) g_\xi(1-\hat{\eta}, \hat{\eta}) \hat{\eta} - N_s \int_{\ln(\hat{\kappa}_1)}^{\ln(\hat{\kappa}_m)} d \ln(\hat{\kappa}) g_\kappa(\hat{\kappa}, \hat{\kappa}) 2\hat{\kappa} \quad (9)$$

where the Hamiltonian  $\langle H_\alpha \rangle$  of the double-size system of the relaxation stage depends of the translational constraint  $\hat{r}$  and the orientational constraints  $\hat{\eta}$  and  $\hat{\kappa}$ ,  $g_r(r, \hat{r})$  is the probability distribution function for the reduced separation,  $r$  as given by Eq.(2), when the tolerance is  $\hat{r}(\alpha)$ ,  $g_\xi(\eta, \hat{\eta})$  and  $g_\kappa(\chi, \hat{\kappa})$  are the probability distributions for the cosine of relative Euler angle  $\tau$ , i.e. for  $\xi = \cos(\tau)$ , and relative Euler angle  $\chi$ , respectively, when the orientational constraints are  $1-\hat{\eta}(\alpha)$  and  $\hat{\kappa}(\alpha)$ , respectively. The integrands in Eq. (9) are obtained with MC simulations and the integrals are evaluated numerically.

Putting the replication and relaxation free energy contributions (6) and (9) together gives the Helmholtz free energy per particle of a general molecular crystal

$$\frac{\Delta(\beta F)}{N_s} = -\ln\left(\frac{2}{3} \hat{r}_1^3 \hat{\eta}_1 \hat{\kappa}_1\right) + \frac{1}{N_s} \int_{\beta_s/2}^{\beta_s} d\beta_\alpha \langle H_\alpha \rangle - 4\pi \int_{\ln(\hat{r}_1)}^{\ln(\hat{r}_m)} d \ln(\hat{r}) g_r(\hat{r}, \hat{r}) \hat{r}^3 - \int_{\ln(\hat{\eta}_1)}^{\ln(\hat{\eta}_m)} d \ln(\hat{\eta}) g_\xi(1-\hat{\eta}, \hat{\eta}) \hat{\eta} - \int_{\ln(\hat{\kappa}_1)}^{\ln(\hat{\kappa}_m)} d \ln(\hat{\kappa}) g_\kappa(\hat{\kappa}, \hat{\kappa}) 2\hat{\kappa} \quad (10)$$

For disordered ice phases, i.g., for clathrate hydrate structures,  $\beta(S_{res}T)/N_s = -\ln(3/2)$ , where  $S_{res}$  is the Pauling degeneracy entropy<sup>43</sup>, has to be added to the expression (10).

The integrals in the final free energy formula (10) are estimated numerically using the trapezoidal rule with equal intervals  $\ln(r(\alpha))$ , where  $r(\alpha_{i+1}) = \lambda r(\alpha_i)$ ,  $i = 1, \dots, 19$  and  $\lambda$  is constant. To calculate integrands in Eq. (10), the distribution functions  $4\pi g_r(r, \hat{r}) \hat{r}^3$ ,  $g_\xi(\xi, \hat{\eta}) \eta$  and  $g_\kappa(\chi, \hat{\kappa}) 2\chi$  are divided into  $n_b = 30$  bins. Since we are interested only in the values of the distributions at the constraint distances  $r = \hat{r}$ ,  $\xi = 1-\hat{\eta}$  and  $\kappa = \hat{\kappa}$ , during each MC simulation we evaluated  $4\pi g_r(\hat{r}, \hat{r}) \hat{r}^3$ ,  $g_\xi(1-\hat{\eta}, \hat{\eta}) \hat{\eta}$  and  $g_\kappa(\hat{\kappa}, \hat{\kappa}) 2\hat{\kappa}$  by two point linear extrapolation using the values of bins  $n_b$  and  $n_{b-1}$ . It is important for the upper integration limit  $\ln(\hat{r}_m)$ , when the double size system is fully relaxed,  $\hat{r}_m$  is chosen large enough to ensure that  $g_r(r = \hat{r}_m, \hat{r}_m) \sim 0$ . For the

lower limit  $\ln(\hat{r}_1)$ , when the double size system is highly constrained, it is known that  $g_r(r = \hat{r}_1, \hat{r}_1) \hat{r}_1^3 \rightarrow 3$  in the limit  $\hat{r}_1 \rightarrow 0$ . Similarly, for the orientation constraint  $\xi$ , the limit  $\hat{\eta}_m$  is sufficiently large if  $g_\xi(\xi = 1 - \hat{\eta}_m, \hat{\eta}_m) \sim g_{\xi \min}$ , where  $g_{\xi \min}$  is some average value of  $g_\xi$  when constraint  $\xi$  is not felt by the system;  $\hat{\eta}_1$  should be such that  $g_\xi(\xi = 1 - \hat{\eta}_1, \hat{\eta}_1) \hat{\eta}_1 \sim 1$ . For the orientation constraint  $\kappa$  the limit  $\hat{\kappa}_m$  is sufficiently large if  $g_\kappa(\kappa = \hat{\kappa}_m, \hat{\kappa}_m) \sim g_{\kappa \min}$ , where  $g_{\kappa \min}$  is the value of  $g_\kappa$  when the system is fully relaxed, and  $\hat{\kappa}_1$  should be such that  $g_\kappa(\kappa = \hat{\kappa}_1, \hat{\kappa}_1) 2\hat{\kappa}_1 \sim 1$ . Adequate integration limits for integrals with respect to  $d \ln(\hat{r})$ ,  $d \ln(\hat{\eta})$  and  $d \ln(\hat{\kappa})$  in Eq. (10) have been found for all cases discussed here.

#### **D. Free energy calculations of partially/fully occupied clathrate hydrates**

A technique for determining the free energies and chemical potentials of hydrate solids as a function of hydrate occupancy is presented in paper 21. The method employs Monte Carlo simulations in the isobaric semigrand ensemble to calculate the hydrate occupancies, i.e., hydrate composition, as a function of the chemical potentials of guest molecules at a fixed temperature, pressure, number of water molecules, and chemical potentials of guest molecules. The water chemical potential is then determined by carrying out the thermodynamic integration over the hydrate composition. The empty hydrate is used as the reference state for calculating the water chemical potential. To validate thermodynamic consistency of the results obtained with the isobaric SGMC simulations, the Gibbs free energy of the empty and completely filled hydrates can be calculated using the FL or SR method.

To derive an expression for determining the Gibbs free energy of a partially/fully filled hydrate, we begin by considering a system consisting of  $i$  chemical components. The total number of molecules in the system  $N = \sum_i N_i$  is fixed, but the composition can change. The system is not subject to the operation of external forces. The thermodynamic relation for changes the internal energy of such a system is given by

$$dU = TdS - PdV + \sum_i \mu_i dN_i, \quad (11)$$

where  $U$  is the internal energy,  $P$  is the pressure,  $V$  is the volume,  $S$  is the entropy,  $\mu_i$  is the chemical potential of the  $i$ th chemical component,  $N_i$  is the number of molecules composing the  $i$ th chemical component, changes  $dN_i$  results from an influx or outflux of molecules.

Applying Legendre transform to  $U$ , we get

$$U = TS - PV + \sum_i \mu_i N_i \quad (12)$$

Taking the total differential of Eq. (12) and substituting  $dU$  with the right hand side of Eq. (11), we have

$$\sum_i N_i d\mu_i = -SdT - VdP \quad (13)$$

For the hydrogen clathrate filled with promoter molecules, Eq. (13) can be written as

$$N_w d\mu_w + N_h d\mu_h + N_p d\mu_p = -SdT - VdP, \quad (14)$$

where  $\mu_w$ ,  $N_w$ ,  $\mu_p$ ,  $N_p$ ,  $\mu_h$ ,  $N_h$  are the chemical potential and the number of water, hydrogen, and promoter molecules, respectively.

Integrating Eq. 14 at fixed temperature and pressure, we get the expression for the water chemical potential relative to that of the empty hydrate  $\mu_w^{(0)}$

$$\mu_w - \mu_w^{(0)} = -\frac{1}{N_w} \left( \int_{\mu_p^{(0)}}^{\mu_p} N_p d\mu_p' + \int_{\mu_h^{(0)}}^{\mu_h} N_h d\mu_h' \right), \quad (15)$$

where  $N_p$ , and  $N_h$  denote isobaric semigrand ensemble averages.

For the empty hydrate reference state,  $\mu_p^{(0)} = -\infty$  and  $\mu_h^{(0)} = -\infty$ .

Taking into account Eq. (15), the Gibbs free energy of a general hydrate filled partly or fully with promoter and hydrogen molecules is then

$$G = \sum_{i=1}^3 \mu_i N_i = \mu_p N_p + \mu_h N_h + \mu_w N_w = \mu_p N_p + \mu_h N_h + \mu_w^{(0)} N_w - \int_{\mu_p^{(0)}}^{\mu_p} N_p d\mu_p' - \int_{\mu_h^{(0)}}^{\mu_h} N_h d\mu_h', \quad (16)$$

where for an empty hydrate  $\mu_w^{(0)} N_w = G_w$ , the Gibbs free energy can be obtained, for example, using the SR method.

The probability density that a hydrogen clathrate filled with promoter molecules resides in the state specified by given temperature, pressure, and composition in the isobaric semigrand ensemble is given by

$$p(\mathbf{r}, V, N_p, N_h) \propto \frac{V^N}{N_p! N_h!} \exp\left(-\frac{PV}{k_B T}\right) \exp\left(\frac{\mu_p N_p}{k_B T}\right) \exp\left(\frac{\mu_h N_h}{k_B T}\right) \exp\left(-\frac{U(\mathbf{r})}{k_B T}\right), \quad (17)$$

where  $U(\mathbf{r})$  denotes the configurational potential energy function.

In the isobaric semigrand ensemble pressure, temperature, and the total number of molecules are constant. Similarly to the isothermic-isobaric ensemble simulations, in our isobaric SGMC simulations volume changes, and molecule displacement moves, i.e., translations and rotations, are attempted and then accepted or rejected in the usual<sup>29</sup>. Additionally, two composition changes are performed: insertions and deletions of guest molecules. Trial insertions and deletions of promoter molecules are allowed only in the large cages. Insertions and deletions of hydrogen molecules are permitted only in the small cages.

The acceptance probability of trial insertion can be derived from Eq. 17 and is given by

$$P_{ins} = \frac{V}{N_m + 1} \exp\left(\frac{\mu_m}{k_B T}\right) \exp\left(-\frac{\Delta U}{k_B T}\right), \quad (18)$$

where  $N_m=N_p$ ,  $\mu_m=\mu_p$  for trial promoter insertion, and  $N_m=N_h$ ,  $\mu_m=\mu_h$  for trial hydrogen molecule insertion,  $\Delta U$  is the potential energy difference between the new and old configurations.

Similarly, a trial deletion is accepted with probability

$$P_{del} = \frac{N_m}{V} \exp\left(-\frac{\mu_m}{k_B T}\right) \exp\left(-\frac{\Delta U}{k_B T}\right) \quad (19)$$

The Gibbs free energy as a function of concentration of guest molecules can be estimated, if we evaluate the integrals in Eq. (16). The integrands, i.e., the occupancies of the large and small cages versus the guest molecule chemical potentials, in the Eq. (16) can be obtained with isobaric

SGMC simulations conducted in the ranges of  $\mu_p$  and  $\mu_h$  specifying the integration path from an empty hydrate to a completely occupied one. By allowing trial insertions and deletions in the large cavities only, we change the promoter molecule chemical potential in the range  $(\mu_p^{(0)}, \mu_p)$  and fill all the large cages of an empty hydrate with promoter molecules; then by permitting occupancy changes of the small cavities only, all the small cages get occupied with hydrogen molecules by changing the hydrogen chemical potential in  $(\mu_h^{(0)}, \mu_h)$ . In other words, in order to obtain completely filled hydrate, we start filling the large cages of an empty hydrate with promoters and then, when the large cages are fully occupied, we begin filling the small cages with H<sub>2</sub>. This method of forming a hydrate with guest molecules corresponds to the experimental procedure<sup>44,45</sup>. In an experiment, a sample of aqueous solution of a compound is prepared first and then the content is pressurized up to desired pressure by supplying H<sub>2</sub> to form a hydrogen hydrate.

### III. CHOICE OF PROMOTER MOLECULES

The list of various molecules studied as promoters for sII hydrogen clathrate is given in Table 1. Almost all of these molecules are experimentally known as good promoters for clathrate hydrates. Although it has only been found experimentally that 1-propanol (1PROP) and 2-propanol (2PROP) can form stable sII clathrate hydrates in the presence of help gas such as methane, we considered these compounds as potential promoter molecules for sII hydrogen clathrate formation to study whether the difference in molecular geometry of chemically similar guests can affect the stability of sII hydrogen clathrate. Similarly, promoters 1DCFE and 2DCFE are also studied to find out whether the geometry of guests can influence hydrogen clathrate stability. The dipole moment and the van der Waals volume of the promoters are provided in the same Table 1 as well. The dipole moment is computed using Gaussian 03<sup>35</sup> and van der Waals volumes are obtained according to Ref. 46. To determine the correlation of clathrate hydrate stability with the dipole moment of promoter, the molecules with the same van der Waals volumes are considered, namely 1DCFE and 2DCFE, CONE and DHF, 1PROP and 2PROP. Moreover, two groups of molecules (THF, DHF, FUR) and (CP, CENE) with different number of chemically bonded hydrogen atoms are tested.



## IV. RESULTS AND DISCUSSION

### A. Occupancy dependence

Monte Carlo calculations in the isobaric semigrand ensemble were conducted to simulate occupancy fluctuations of guest molecules, i.e., composition of the sII clathrate hydrate. To study the dependence the Gibbs free energy of the hydrate on concentration of guest molecules (promoters and H<sub>2</sub>), the SR and isobaric SGMC simulations were carried out using THF as a promoter molecule at 253 K and 1000 atm. THF molecule has roughly mean van der Waals volume in the list of studied promoter molecules (Table 1). When promoter molecules are big and have complex geometry, trial insertions in SGMC simulation become rather inefficient. The SR method is employed to calculate the free energy of zero-occupancy and fully occupied sII hydrate. The ensemble averages of number of guest molecules, i.e. occupancies, of the large and small cages are obtained using SGMC simulations. The occupancies as a function of the guest chemical potentials are required to evaluate the Gibbs free energy of partially/fully filled hydrate with Eq. 16. Fractional occupancies of the large and small cages as a function of guest chemical potential are shown in Figures 1 and 2, respectively. Low acceptance rate of trial insertions of big molecules and small number of the large cavities in sII hydrate compared to the amount of the small cavities result are reasons preventing to obtain reliable occupancy curve in the large cages for such big molecules as tetrahydropydan, cyclopentane, and cyclopentane. Figure 1 shows the fractional occupancies of the large cages filled with THF, starting from an empty sII clathrate hydrate. The results of our isobaric SGMC simulations demonstrate that when all the large cavities are occupied by promoter molecules, the small cavities accommodate only one H<sub>2</sub> molecule, i.e., multiple H<sub>2</sub> occupancy of the small cages is not observed. These results are in agreement with reported experimental<sup>45,47</sup> and simulation<sup>48</sup> studies. A thermodynamic consistency check is performed by comparing the Gibbs free energy of a sII fully filled hydrate calculated using two methodologies: semigrand Monte Carlo and the self-referential Monte Carlo simulations. The sII clathrate hydrate fully occupied with THF and H<sub>2</sub> guests is simulated at 253 K and 1000 atm. The value of the Gibbs free energy calculated with SGMC simulations is  $-8.40 \pm 0.04$  kcal/mol. The Gibbs

free energy obtained using the SR calculations in NVT ensemble is  $-8.39 \pm 0.03$  kcal/mol. One can see the excellent agreement between the values of free energy calculated with different techniques. The SR method is employed to obtain the Gibbs free energy of the empty hydrate ( $-8.56 \pm 0.04$  kcal/mol) used as a reference state for SGMC simulations.

Figure 3 shows the Gibbs free energy of the unit cell of sII clathrate hydrate as a function of THF content in the large cages at five different concentrations of  $H_2$  in the small cages. Since the Gibbs free energy of fully filled sII hydrogen hydrate is the lowest, as Figure 3 demonstrates, the relative stability of sII clathrate hydrates in the remainder of the paper is studied under the assumption of full occupancy. In this case we can use the self-referential technique to determine the free energy. The SR method enables us to calculate the free energy of hydrate filled with promoter molecules bigger than THF. One can note that for all occupancies of hydrogen in small cages, the Gibbs free energy decreases linearly and proportionally to the THF content. A similar behaviour of the configurational energy of sII at different THF and  $H_2$  occupancies was observed using molecular dynamics simulations<sup>25</sup>. The linear dependence of the Gibbs free energy on the THF content indicates that these promoter molecules do not distort water host lattice significantly.

## B. Comparison of promoter molecules

To determine the relative stability of sII clathrate hydrates with various promoter molecules the Helmholtz free energy calculations of the completely occupied hydrates were performed at four temperatures 233 K, 253 K, 273 K and 293 K. One hydrogen molecule is placed in each small sII cage and a single promoter molecule in each large cage.

The configurational energies per mole of sII hydrogen clathrates with the large cages occupied by different promoter molecules at various temperatures are shown in Figure 4. The configurational energy is calculated with Eq. (1). From the figure it can be noticed that in terms of configurational energy, the five most promising promoters at 233 K are 1,3-dioxolane (DIO), tetrahydrofuran (THF), cyclobutanone (CONE), tetrahydropyran (THP), and cyclopentane (CP). In the same Figure 4, the Gibbs free energies of the sII hydrogen clathrates are compared. The Gibbs free

energy per mole is computed according to Eq. (2). Based on the Gibbs free energy, the five best promoter molecules forming most stable the hydrate clathrates at 233 K are cyclobutanone (CONE), tetrahydrofuran (THF), 2,5-dihydrofuran (DHF), acetone (ACET), and tetrahydropyran (THP). It is observed experimentally that all these organic compounds are efficient promoter molecules for clathrate hydrates formation<sup>49,44,50,51,52</sup>.

Given the Gibbs free energy and the enthalpy  $H = U + PV$  of a clathrate, one can deduce an entropic ( $TS$ ) contribution from the thermodynamic relation

$$G = U + PV - TS \quad (20)$$

Figure 5 shows the  $TS$  contribution to the Gibbs free energy of sII hydrogen clathrate filled with different promoter molecules at various temperatures. Since the correlations among quantities  $G$ ,  $U$ , and  $PV$  in Eq. (20) are not known explicitly, the standard errors of in  $TS$  are not shown. Notice that the  $TS$ -contribution is always negative. Figure 5 indicates at 233 K that, although the clathrate filled with 1,3-dioxolane (DIO) promoter molecules is the first in the list of clathrates with lowest configurational energy, it is the sixth system in terms of the Gibbs free energy due to a large  $TS$  contribution. One can also conclude that sII with 2,5-dihydrofuran (DHF) molecules has a low Gibbs free energy due to a relatively small  $TS$  contribution. At temperature 253 K as well as at 233K the clathrates filled with tetrahydrofuran (THF), cyclobutanone (CONE), tetrahydropyran (THP), 1,3-dioxolane (DIO), and cyclopentane (CP) promoter molecules have the lowest configurational energy (Figure 4). The Gibbs free energies shown in Figure 4 indicate that sII clathrates with tetrahydrofuran (THF), 1,3-dioxolane (DIO), 2,5-dihydrofuran (DHF), cyclobutanone (CONE), and 1,1-dichlorofluoroethane (1DCFE) molecules are the most stable. Figure 5 shows that the Gibbs free energy of sII with tetrahydropyran (THP) is relatively high due to a large  $TS$  contribution, whereas sII with 1,1-dichlorofluoroethane (1DCFE) has a smaller  $TS$  contribution, which puts 1DCFE in the list of five best promoters at 253 K.

It can be seen from Figure 4 that at 273 K the sII clathrates with the lowest configurational energy are those filled with 1,3-dioxolane (DIO), tetrahydrofuran (THF), cyclobutanone (CONE), tetrahydropyran (THP), cyclopentane (CP). Comparison of the Gibbs free energies in Figure 5 suggests that the most efficient promoters at 273 K are tetrahydrofuran (THF), 2-propanol (2PROP),

1,3-dioxolane (DIO), cyclobutanone (CONE), and acetone (ACET). From Figure 5 it can be seen that relatively low Gibbs energy of sII filled with 2-propanol (2PROP) is due to a small *TS* contribution of the sII hydrogen clathrate. Although the sII with cyclopentane (CP) and tetrahydropyran (THP) have low configurational energy, their Gibbs energy is relatively high due to a large *TS* contribution (Figure 5).

The list of the five best promoter molecules forming sII hydrogen clathrates with the lowest configurational energy at 293 K is the same within the uncertainty as at the lower temperatures considered, namely: tetrahydrofuran (THF), tetrahydropyran (THP), cyclobutanone (CONE), 1,3-dioxolane (DIO), and cyclopentane (CP), see Figure 4. In terms of the Gibbs free energy (Figure 4) the five most promising promoter molecules for sII hydrogen clathrate at 293 K are cyclobutanone (CONE), cyclopentane (CP), dichlorofluoromethane (DCFM), tetrahydrofuran (THF), 2,5-dihydrofuran (DHF). From Figure 5 it can be seen that the relatively low Gibbs free energy of sII+H<sub>2</sub>+DCFM is due to a small *TS* contribution.

For the promoter molecules THF, DHF, and FUR which have different number of hydrogen atoms bonded to carbon atoms of a five-membered ring hydrogen atoms, the stability of the hydrogen clathrate increases in the order: furan (FUR) < dihydrofuran (DHF) < tetrahydrofuran (THF). For compounds CP and CENE having different number of chemically bonded hydrogen molecules as well, the stability increases in the way: cyclopentene (CENE) < cyclopentane (CP).

### C. Temperature dependence

It is worth noting that the stabilizing effect of promoter molecules is temperature dependent. This can be explained by the thermodynamic equation

$$G(T) = G(T_0) - \int_{T_0}^T S(T') dT' \quad (21)$$

showing that the entropy contribution can change the relative order of the stability with temperature. It has been found that the entropy makes a considerable contribution to the free energy of binary sII hydrogen clathrates, so that the stabilization of the structure cannot be determined from configurational energy considerations alone. This is supported, for instance, by the Gibbs free energy

of hydrogen sII with 2,5-dihydrofuran (DHF) molecules. Although such a system has moderate configurational energy, due to small  $TS$  contribution at all studied temperatures except 293 K, its rather low Gibbs free energy indicates that 2,5-dihydrofuran is among six best promoters.

In Figure 6, the Gibbs free energy per mole of sII hydrogen clathrates with the large cavities filled with the most efficient promoters tetrahydrofuran (THF) and 2,5-dihydrofuran (DHF), an intermediate promoter acetone (ACET), and the least efficient promoter 1,2-dichlorofluoroethane (2DCFE) for temperatures in the range of 233 K – 293 K is shown. The Gibbs free energy increases roughly linearly as the temperature increases. At constant pressure the change in Gibbs free energy with temperature can be expressed by

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (22)$$

Since the entropies of binary hydrogen sII show very little dependence on the type of promoter molecule and temperature, according to Eq. (22) the slopes of the Gibbs free energy versus temperature in Figure 6 should be approximately similar. Nevertheless, changes in entropy for some specific molecules may alter the order of stabilization.

#### D. Size, geometry and dipole moment dependence

The results presented in Figures 7 and 8 indicate clearly that at 233 K there is no correlation of the free energy either with the dipole moment or with the van der Waals volume of promoter molecule. No such correlation was observed at 253 K, 273 K, and 293 K either. It is interesting to note in Figure 9 that at 233 K there is some correlation between the unit cell volume of sII hydrogen clathrate and the van der Waals volume of promoter molecule, although this trend is not fully regular. This relationship is in line with the experimental observations of binary sII clathrates<sup>53</sup>. The trend is more distinctive for the cyclic promoter molecules. A similar relationship is also found at 253 K, 273 K, and 293 K. The observed difference in the free energy of the sII filled with chemically similar 1PROP and 2PROP is most likely due to differences in molecular geometry of the alcohols. Similarly, at all temperatures 1DCFE is a better promoter than 2DCFE probably due to different geometries of these compounds.

## V. CONCLUSIONS

The Gibbs free energy of sII clathrate hydrate is calculated as a function of hydrogen and THF contents using isobaric semigrand Monte Carlo simulations at 253 K and 1000 atm. The results indicate that the Gibbs free energy decreases linearly in proportion to the THF content for all occupancies of hydrogen in small cages. It was determined that the Gibbs free energy of the unit cell of fully filled sII hydrogen hydrate has the lowest value compared to the free energy at different contents of guest molecules. Therefore, the relative stability of sII clathrate hydrates was studied for completely filled hydrates.

Binary sII fully occupied hydrogen clathrates formed by various promoter molecules (Table 1) are studied by means of the SR Monte Carlo simulations at 1000 atm and in a temperature range of 233 K to 293 K. Molecular dynamics (MD) simulations<sup>9,10,11</sup> showed that in binary sII structure some promoter molecules can form hydrogen bonds with the host water molecules. The hydrogen bonds affect the clathrate hydrate structure and the dynamics of guest and host water molecules. It was observed in the study<sup>9</sup> that the oxygen atoms of 1,3-dioxolane (DIO) does not form hydrogen bonds with the large cage water molecules. As temperature increases, the probability of hydrogen bonds between the guest and the host water molecules can either decrease or increase depending on the guest<sup>11</sup>, whereas it is expected that the stability of clathrate decreases. Moreover, the probabilities of hydrogen bond formation in binary 1-propanol and 2-propanol + methane structure II are very similar in a temperature range of 100 K to 250 K.<sup>10</sup> Besides, many molecules listed in Table 1 do not have an electronegative hydrogen bond accepting atom. It means that hydrogen bonding between promoter guest with the large cage water molecules is an ambiguous measure of stability of sII clathrate hydrates and free energy studies are needed.

In the experimental study Ref. 44 the stability of fully occupied sII hydrogen clathrate increases in the order 1,3-dioxolane (DIO) < 2,5-dihydrofuran (DHF) < tetrahydropyran (THP) < furan (FUR) < tetrahydrofuran (THF) < cyclopentane (CP). In this study all measurements have been conducted on the dissociation curve of the clathrate hydrates. The stability has been related to the

maximum temperature at which the clathrate phase disappears for a given pressure, i.e., the experimental data have to be described by the formation free energy of the hydrogen clathrate which equals to the sum of free energies of its components. The Gibbs free energy calculations obtained with the SR method indicate another order of stability. Our calculations are not carried out on the dissociation curve of the clathrate hydrates and we obtain the stabilization free energy from our simulations which is different from the formation free energy corresponding to the experimental conditions<sup>44</sup>. Among tested promoter molecules there are five molecules with five-membered rings, namely cyclopentane (CP), tetrahydrofuran (THF), 2,5-dihydrofuran (DHF), 1,3-dioxolane (DIO), and furan (FUR). The Gibbs free energy demonstrates that all these molecules are relatively efficient promoters. On the other hand, it is determined that some molecules which do not have such a ring, for example, cyclobutanone (CONE) and acetone (ACET) are good stabilizers of sII hydrogen clathrates as well. At all temperatures, for the two groups of molecules (THF, DHF, FUR) and (CP, CENE), the more hydrogen atoms bonded to carbon atoms of a five-membered ring a molecule has, the more efficient promoter this compound is. There is a rough correlation between the unit cell volume of sII hydrogen clathrate and the van der Waals volume of promoter molecule. The Gibbs free energy of sII hydrogen clathrate increases roughly linearly as the temperature increases. No direct correlation of the free energy or configurational energy with either van der Waals volume or dipole moment, or the shape of promoter molecule is unveiled. It is clearly that stability of hydrogen clathrate is an interplay of the size, van der Waals volume, dipole moment and probably most importantly molecular geometry of promoter molecule. The absence of any concrete guidelines complicates the search for an efficient promoter. Therefore, full free energy calculations are required to assess the stability of clathrate hydrates filled with different promoter molecules.

## **ASSOCIATED CONTENT**

### **Supporting Information.**

The calculated atomic positions, fitted charges and the LJ parameters of the promoter molecules are provided as Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**Table 1.** List of promoters tested with their acronyms, dipole moments and van der Waals volumes.

Acronym	Promoter name	Molecular formula	Dipole moment, D	$V_{\text{vdW}}, \text{\AA}^3$
THP	tetrahydropyran	$\text{C}_5\text{H}_{10}\text{O}$	1.5501	91.47
CP	cyclopentane	$\text{C}_5\text{H}_{10}$	0.0248	82.68
CENE	cyclopentene	$\text{C}_5\text{H}_8$	0.2325	80.04
1DCFE	1,1-dichlorofluoroethane	$\text{C}_2\text{H}_3\text{Cl}_2\text{F}$	1.9723	79.64
2DCFE	1,2-dichlorofluoroethane	$\text{C}_2\text{H}_3\text{Cl}_2\text{F}$	1.5004	79.64
FCP	fluorocyclopentane	$\text{C}_5\text{H}_9\text{F}$	2.0783	88.75
THF	tetrahydrofuran	$\text{C}_4\text{H}_8\text{O}$	1.6652	74.17
CONE	cyclobutanone	$\text{C}_4\text{H}_6\text{O}$	2.9724	71.54
DHF	2,5-dihydrofuran	$\text{C}_4\text{H}_6\text{O}$	1.6512	71.54
1PROP	propanol	$\text{C}_3\text{H}_8\text{O}$	1.7909	69.23
2PROP	2-propanol	$\text{C}_3\text{H}_8\text{O}$	1.7096	69.23
TFE	1,1,1,2-tetrafluoroethane	$\text{C}_2\text{H}_2\text{F}_4$	2.0575	67.42
ACET	acetone	$\text{C}_3\text{H}_6\text{O}$	2.9820	66.60
DIO	1,3-dioxolane	$\text{C}_3\text{H}_6\text{O}_2$	1.5121	65.67
BTFM	bromotrifluoromethane	$\text{CBrF}_3$	0.6150	63.34
DCFM	dichlorofluoromethane	$\text{CHCl}_2\text{F}$	1.2740	62.34
FUR	furan	$\text{C}_4\text{H}_4\text{O}$	0.6251	58.00
1DFE	1,1-difluoroethane	$\text{C}_2\text{H}_4\text{F}_2$	2.2971	55.28
DME	dimethylether	$\text{C}_2\text{H}_6\text{O}$	1.3535	51.94

**Figure 1.** Fractional occupancies of the large cages filled with THF molecules versus the promoter chemical potential in the sII clathrate hydrate at  $T = 253$  K and  $P = 1000$  atm.

**Figure 2.** Fractional occupancies of the small cages filled with  $H_2$  molecules versus the hydrogen chemical potential in the sII clathrate at  $T = 253$  K and  $P = 1000$  atm.

**Figure 3.** Dependence of the Gibbs free energy of the unit cell on the concentration of THF in the large cages  $x_p$  at five different concentrations of  $H_2$  in the small cages  $x_h$ . Error bars are smaller than symbol sizes.

**Figure 4.** The configurational energy per mole (columns mapped to the primary (left) axis and filled with wide downward diagonal lines) and the Gibbs free energy per mole (empty columns mapped to the secondary (right) axis) of sII hydrogen clathrates with different promoters studied at various temperatures. Standard errors are to two standard deviations.

**Figure 5.** The configurational energy per mole (columns mapped to the primary (left) axis and filled with wide downward diagonal lines) and the  $TS$  contribution to the Gibbs free energy (solid filled columns mapped to the secondary (right) axis) of sII hydrogen clathrates with different promoters studied at various temperatures. Standard errors of  $U$  are to two standard deviations.

**Figure 6.** The temperature dependence of the Gibbs free energy of sII hydrogen clathrate for four different promoter molecules. Standard errors of are to two standard deviations.

**Figure 7.** The dipole moment of promoter versus and the Gibbs free energy per mole of sII hydrogen clathrates with different promoters studied at 233 K.

**Figure 8.** The van der Waals volume of promoter versus and the Gibbs free energy per mole of sII hydrogen clathrates with different promoters studied at 233 K.

**Figure 9.** The unit cell volume of sII hydrogen clathrates with the different promoters studied versus the van der Waals volume of the promoter molecules at 233 K. Standard errors of  $V$  are to two standard deviations. Labels, standard deviations, and trend line are provided only for the cyclic promoter molecules (solid circles). The rest of promoters are marked with open circles.













