



Energy and spectral characteristics of hydrogen occupied pure and tetrahydrofuran doped water cages



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ABSTRACT

Hydrogen clathrate hydrates consist of hydrogen molecules which can be encapsulated in several polyhedral water cages. In this work, we apply quantum chemistry methods to calculate interaction energy, cage deformation energy and spectral properties with multiple occupancy of hydrogen in $(\text{H}_2\text{O})_{20}$, and pure and tetrahydrofuran doped $(\text{H}_2\text{O})_{28}$ water cages. The interaction energies and cage deformation energy show that $\text{H}_2@(\text{H}_2\text{O})_{20}$, $4\text{H}_2@(\text{H}_2\text{O})_{28}$ and $\text{H}_2 + \text{THF}@(\text{H}_2\text{O})_{28}$ cages are more preferred compared to other occupancies. The vibrational modes of water molecules of the $\text{H}_2@(\text{H}_2\text{O})_{20}$, $4\text{H}_2@(\text{H}_2\text{O})_{28}$ and $\text{H}_2 + \text{THF}@(\text{H}_2\text{O})_{28}$ cages show a red-shift relative to the $2\text{H}_2@(\text{H}_2\text{O})_{20}$, $(n\text{H}_2)_{n=1-3}@(\text{H}_2\text{O})_{28}$ and $2\text{H}_2 + \text{THF}@(\text{H}_2\text{O})_{28}$ cages. The interaction energies and spectral trends validate experimental findings on maximum occupancy of hydrogen in various water cages.

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1. Introduction

Clathrate hydrates are crystalline solids made up of polyhedral water cages where gas molecules like hydrogen, methane etc., can be encapsulated. These hydrates have potential applications for energy storage or as a hydrogen storage material [1–3]. Hydrogen clathrate hydrates consist of sixteen $(\text{H}_2\text{O})_{20}$ cages (a dodecahedron structure formed from 20 water molecules) and eight $(\text{H}_2\text{O})_{28}$ cages (a hexakaidecahedron structure formed from 28 water molecules), where hydrogen molecules can be encapsulated in each cage to form a sII hydrate lattice. The resultant sII hydrate lattice consists of 136 water molecules [3] per unit cell. The characterization of hydrogen occupancy has attracted several experimental investigations. For example, a first study performed by Mao et al. [4,5] showed a double occupancy of H_2 in the $(\text{H}_2\text{O})_{20}$ cage and a quadruple occupancy of H_2 in the $(\text{H}_2\text{O})_{28}$ cage. Lokshin et al. [6] synthesized hydrogen clathrate hydrates and characterized its stability using high pressure neutron diffraction techniques. The authors observed a single occupancy of H_2 in the $(\text{H}_2\text{O})_{20}$ cage and a quadruple occupancy of H_2 in the $(\text{H}_2\text{O})_{28}$ cage at 220 MPa and 200 K. While, the formation of pure hydrogen clathrate hydrates requires conditions of very high pressure, the addition of molecules like Tetrahydrofuran (THF) [7–9] was shown to reduce the pressure in which these clathrate hydrates can be

formed. The general conclusions obtained from various experiments [10–16] show that depending on the concentration of THF, either a single or double occupancy of H_2 in the $(\text{H}_2\text{O})_{20}$ cage can be achieved. While, a maximum of quadruple occupancy of H_2 in the $(\text{H}_2\text{O})_{28}$ cage was possible, the occupancy was found to decrease with increasing concentration of THF.

Computational methods based on MP2 and Density Functional Theory (DFT) have largely focused on the characterization of H_2 occupancy in the $(\text{H}_2\text{O})_{20}$ and $(\text{H}_2\text{O})_{28}$ cages. For example, the interaction energies reported from the *ab initio* calculations of Patchkovskii and Tse [17], Yedlapalli et al. [18], Chattaraj et al. [19] and Willow and Xantheas [20] revealed a maximum of double occupancy in the $(\text{H}_2\text{O})_{20}$ cage and quadruple occupancy in the $(\text{H}_2\text{O})_{28}$ cage. Kumar et al. [21,22] employed dispersion corrected functionals in DFT and MP2 methods to calculate the interaction energy of single occupancy of H_2 in the $(\text{H}_2\text{O})_{20}$ cage. The authors concluded that interaction energies obtained using the BLYP-D3 functional was in agreement with MP2 method. Basic and co-workers [23] employed Diffusion Monte Carlo (DMC) simulations to study the quantum dynamics of H_2 in the $(\text{H}_2\text{O})_{28}$ cages of the sII clathrate hydrate. The authors considered a rigid water cage framework and observed that Zero Point Energy increase with increasing hydrogen occupancy in the cages. The authors characterized the translational and rotational (T–R) motions of H_2 molecules and concluded that a quadruple occupancy of H_2 in the $(\text{H}_2\text{O})_{28}$ cage to be the most stable. Wang et al. [24] performed DFT calculations using a B3LYP functional coupled with an ONIOM

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model to characterize spectral properties and cage occupancy in pure hydrogen clathrate hydrates. The authors observed that the calculated frequencies deviate significantly from experiments due to the limitations of the B3LYP functional in describing the weak inter-molecular interactions which exist in these cages.

The limitations of the B3LYP functional and dispersion excluded functionals have been discussed in the work of Ramya et al. [25–27]. For example, the authors demonstrated the effect of dispersion on spectral properties using the B97-1 [28] functional (which excludes dispersion from B97-D [29] functional) and a B97-D exchange correlation functional. The authors found that the spectral properties calculated using the B97-D functional are in excellent agreement with experimental data [27]. However, the authors confined their investigation only to a single occupancy of H₂ in (H₂O)₂₀, and pure and THF doped (H₂O)₂₈ cages. While the single occupancy of H₂ does serve as a benchmark, experimental studies have focused on multiple occupancy of H₂ in various cages. Hence, the objective of the present study is to apply DFT to calculate interaction energy, cage deformation energy and spectral properties of several possible occupancies of H₂ in (H₂O)₂₀, and pure and THF doped (H₂O)₂₈ cages. The success of the B97-D functional for accurate prediction of spectral properties coupled with the limitations of B3LYP functional used in previous work [17–19] have motivated us to employ the B97-D functional in the present study. The computational details are described in Section 2. The energy and spectral properties are presented in Section 3. A summary of important results concludes this paper.

2. Computational details

The calculations performed in this work employed the Gaussian 09 [30] program with a cc-pVTZ basis set. In this present study, we have chosen configurations for each water cage as follows: Four configurations of (H₂O)₂₀ cages which differ in symmetry C_i (Structure S1), C₅ (Structure S2), S₁₀ (Structure S3) and dodecahedral min (Structure S4) were employed using the cage coordinates of Ojamae and co-workers [31,32]. The fifth configuration (Structure S5) was created by a random orientation of non-hydrogen bonded protons of the (H₂O)₂₀ cage. In the (H₂O)₂₈ cages (since symmetry information is unknown), we created five structures (S1–S5) which differ in proton orientation using the cage coordinates of Sloan and Koh [3]. A schematic representation of (H₂O)₂₀ and (H₂O)₂₈ cages are shown in Fig. 1. For each structure, the input geometry of multiple occupancy of H₂ in (H₂O)₂₀ and (H₂O)₂₈ cages (pure and THF doped) was created as follows: The input geometry of the (nH₂)_{n=1,2}@(H₂O)₂₀ cages were generated by an inclusion of a single H₂ molecule in the optimized (nH₂)_{n=0,1}@(H₂O)₂₀ cages respectively. The input geometry of the H₂@(H₂O)₂₈ cage was obtained by an inclusion of a single H₂ molecule in the optimized (H₂O)₂₈ cage. The input geometry of the (nH₂)_{n=2–4}@(H₂O)₂₈ cages were

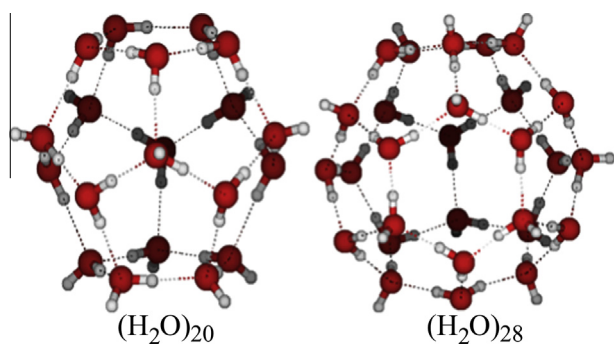


Fig. 1. A schematic representation of (H₂O)₂₀ and (H₂O)₂₈ cages.

obtained by an inclusion of a single H₂ molecule in the optimized (nH₂)_{n=1–3}@(H₂O)₂₈ cages respectively. The input geometry of the THF@(H₂O)₂₈ cage was created by an inclusion of THF in the (H₂O)₂₈ cage and re-optimized. The input geometry of the (nH₂)_{n=1,2} + THF@(H₂O)₂₈ cages were obtained by an inclusion of a single H₂ molecule in optimized (nH₂)_{n=0,1} + THF@(H₂O)₂₈ cages, respectively. Further, increasing H₂ occupancy in pure and THF doped (H₂O)₂₀ and (H₂O)₂₈ cages leads to a disintegration of the cage structure. The complete details of optimization are described in Ref. [27]. The total energy is calculated at the optimized geometry of each cage. The total energy for each cage is shown in Table S1 (Supporting information). The total energy is further corrected for Basis set Superposition Error (obtained using the counterpoise method [33,34]) and Zero Point Vibrational Energy (ZPVE). The interaction energy is calculated as:

Hydrogen occupied (H₂O)₂₀ or (H₂O)₂₈ cages

$$: E[(n\text{H}_2)_n @ (\text{H}_2\text{O})_m] - E[(\text{H}_2\text{O})_m] - n * E[\text{H}_2] \quad (m = 20, 28) \quad (1)$$

Hydrogen occupied THF doped (H₂O)₂₈ cages

$$: E[(n\text{H}_2)_n + \text{THF} @ (\text{H}_2\text{O})_{28}] - E[\text{THF} @ (\text{H}_2\text{O})_{28}] - n * E[\text{H}_2] \quad (2)$$

where n is the number of hydrogen molecules, $E[\text{H}_2]$ is the total energy of an isolated hydrogen molecule. $E[(n\text{H}_2)_n @ (\text{H}_2\text{O})_m]$ is the total energy of (H₂O)₂₀ or (H₂O)₂₈ cage containing the encapsulated hydrogen molecule(s). $E[(\text{H}_2\text{O})_m]$ is the total energy of (H₂O)₂₀ or (H₂O)₂₈ cage. $E[\text{THF} @ (\text{H}_2\text{O})_{28}]$ is the total energy of the THF@(H₂O)₂₈ cage respectively. $E[(n\text{H}_2)_n + \text{THF} @ (\text{H}_2\text{O})_{28}]$ is the total energy of the THF@(H₂O)₂₈ cage containing the encapsulated hydrogen molecule(s). The structural integrity of the water cage is defined by a cage deformation energy (E_{def}) calculated as [35]:

$$E_{\text{def}} = E_{\text{cage}} - E_{\text{cage} \dots \text{complex}} \quad (3)$$

E_{cage} is the total energy of the optimized geometry of free (H₂O)₂₀ or (H₂O)₂₈ cage. $E_{\text{cage} \dots \text{complex}}$ is the total energy of the (H₂O)₂₀ or (H₂O)₂₈ cage (the optimized cage obtained by inclusion of H₂ or THF molecules). The spectral properties are characterized using Raman Frequency calculations [36] performed at the optimized geometry of each cage.

3. Results and discussion

3.1. Interaction energy

For each cage and structure (S1–S5), the calculated interaction energy with the corresponding ZPVE contributions are shown in Table S2 (Supporting information). The average interaction energy and the average ZPVE contributions shown in Table 1 are used for further analysis. A increasing negative value of interaction energy indicates more stability of the hydrogen encapsulated cage. For example, the interaction energy of the H₂@(H₂O)₂₀ cage is –2.09 kcal/mol, and the 2H₂@(H₂O)₂₀ cage is 0.35 kcal/mol, which show that the H₂@(H₂O)₂₀ cage is more stable compared to the 2H₂@(H₂O)₂₀ cage. The interaction energy (calculated from this study) for the H₂@(H₂O)₂₀ cage is in close agreement with the results reported by Kumar et al. [21,22] using DFT/BLYP-D3 functional and MP2 methods. Further, as seen from Table 1, the trends in our calculated interaction energy are in qualitative agreement with the DFT calculations of Patchkovskii and Tse [17], Chattaraj et al. [19]. The quantitative differences arise due to the dispersion corrected B97-D functional employed in this study. A triple occupancy of H₂ in the (H₂O)₂₀ cage could not be achieved due to disintegration of the water cages.

In the (H₂O)₂₈ cage, interaction energy increases with occupancy of H₂, where the 4H₂@(H₂O)₂₈ cage (–4.35 kcal/mol) is the

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