



Polarization response of methane encapsulated in water cages



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ABSTRACT

The polarization effect of methane hydrates was investigated with first-principles calculations. The performances of various exchange-correlation functionals and basis sets used in the polarizability calculations for these non-bonded systems were carefully examined. M06-2X and CAM-B3LYP produce results similar with those at MP2 level. The total polarizability of methane hydrates is about the sum of those of methane and empty water cages. However, this does not mean a simple summation rule for the polarizability of methane hydrates. Further analysis reveals a reduced polarizability of encapsulated CH₄ and an enhanced polarizability of water cage.

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1. Introduction

When methane meets water under low temperature and high pressure, it may form methane hydrates that exist widely on the seabed. The estimated amount of energy in methane hydrates around the world is massive, nearly twice the amount of conventional fossil energy supply [1,2]. These natural gas hydrates are therefore regarded as an important energy resource in the future when the oil and coal reserves run out. But this new energy resource is facing drilling challenges such as technical, environmental, and economical limitations. Nowadays the extraction of methane hydrates from seabed remains a difficult task. Depressurization and thermal stimulation are two main approaches under consideration [3,4]. Other approaches including electric field induction, chemical flooding, manipulating robots, etc. were also proposed [5]. All these strategies aim to destabilize the hydrate structures and then collect the released natural gas. Neither fundamental theory nor applied techniques, however, have been well established so far for all these approaches. In this study, we focus on the basics of methane hydrates under an external field by means of density functional theory (DFT) calculations. To our knowledge, the polarization response of methane hydrates has not been addressed yet in previous studies.

Three main structural types of gas hydrates, namely sI, sII, and sH, have been characterized in their single crystals using neutron or X-ray diffraction techniques [6–11]. Since sH exists only in anecdotal occurrence, most studies and applications focused on the gas hydrates of sI and sII [12–14]. Both sI and sII consist of 20-molecule water cages, which are in the shape of pentagonal dodecahedra, namely 5¹². These 5¹² building blocks assemble with each other and form large cages of 5¹²6² (sI) and 5¹²6⁴ (sII) between the 5¹² interstices depending on their combination patterns. The large volume of the water cages allows guest molecules to be encapsulated. It has been revealed that the guest molecules, temperature and pressure directly influence the hydrate structures [15–18]. Both sI and sII structures are formed for methane hydrates. The structural models of sI and sII are therefore used in this work.

Some classical molecular dynamics simulations have been performed to study the structures and properties [8,19–28] of methane hydrates. A number of ab initio studies [29–36] have been carried out to investigate the electronic structures, stability, guest diffusions, etc. in recent years. In an earlier study [37], we calculated the structures of methane and ethane hydrates in the presence of tetrahydrofuran (THF) in order to understand the structural basis of the THF-aided methane and ethane separation in their hydrates. In this work, we extend our study to the polarization response of the sI and sII methane hydrates by computing their linear polarizability, which is a measure of electronic response against an external electric field. Insight to the molecular polarizability is crucial for understanding their behaviors induced by electric fields.

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2. Methodology

First we extracted model molecules s1 and s2 from sI and sII crystalline structures, respectively, as shown in Fig. 1. Both s1 and s2 have a small 5^{12} cage and a large $5^{12}6^2$ (s1) or $5^{12}6^4$ (s2) cage. Methane can occupy either of the cages or both. The CH_4 was placed at the cage center in the initial structures. Then the structures of empty and occupied s1 and s2 were optimized at DFT level using B97-D [38] functional and 6-31G(d,p) basis set, followed by polarizability calculations. Dispersion correction to exchange–correlation (XC) functionals is essential for properly describing these weakly bonded systems. The reliability of B97-D for non-bonded systems has been assessed by several authors [39–42]. In our previous study [37], we compared the performances of four functionals, B97-D [38], BLYP-D [43], B3LYP-D [43] and PBE-D [43], as well as MP2 [44], and found B97-D produced reliable results for the methane hydrate structures.

Molecular polarizability can be deduced from the energy expression of a molecule under an external static field

$$E(F_i) = E(0) - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \dots \quad (1)$$

where i and j run over x , y and z . $E(0)$ is the field-free energy, μ_i and α_{ij} are dipole moment and polarizability components, respectively. The α components can be computed with the finite-field (FF) method [45]. From Eq. (1), one has

$$\alpha_{ii} F_i^2 = E(F_i) + E(-F_i) - 2E(0). \quad (2)$$

In the FF calculations, the applied field strength was set to 0.001 au and the SCF convergence criteria were set to 10^{-6} au in density, which are sufficient to ensure both the computational precision and numerical stability in the polarizability calculations. Various exchange–correlation functionals, B97-D [38], B3LYP [46,47], M06-2X [48], X3LYP [49], TPSSh [50], BLYP [46,47] and long-range corrected LC-BLYP [51] and CAM-B3LYP [52] with 6-31++G(d,p) [53] and 6-311++G(d,p) [54], aug-cc-pVDZ and aug-cc-pVTZ [55] basis sets were employed in the FF calculations. A comparison with MP2 [44] calculations was carried out for the model $\text{CH}_4@5^{12}$ system.

3. Results and discussion

Both s1 and s2 have two cages. The small one is 5^{12} , and the big one is $5^{12}6^2$ for s1 and $5^{12}6^4$ for s2. The water molecules are linked via hydrogen bonds (HBs). Molecular CH_4 may occupy either cage or both. In all cases, single or double occupations, the CH_4 is located about the cage center. The encapsulation of CH_4 leads to very small changes to the HB network and volume of the host cage. The structural details of methane and ethane hydrates have been addressed in our previous study [37].

Methane hydrates are characterized by their non-bonded interaction among CH_4 and water molecules. It is necessary to validate

the polarizability computation strategy for these specific systems. The $\text{CH}_4@5^{12}$ cage was selected for the polarizability calculations with various XC functionals and basis sets. The $\text{CH}_4@5^{12}$ structure was optimized with B97-D/6-31G(d,p) and the obtained structure is similar with those in s1 and s2. The computed $\langle \alpha \rangle$ values are in three groups, as shown in Table 1. B97-D and BLYP produce large values, followed by B3LYP, X3LYP and TPSSh, while M06-2X, LC-BLYP, and CAM-B3LYP give small values. The $\langle \alpha \rangle$ values of the third group are similar with the MP2 results with the same basis set. It is clear that the long-range correction to the exchange functionals in LC-BLYP and CAM-B3LYP has considerable effect on the computed $\langle \alpha \rangle$ of the methane hydrates. The M06-2X is known to its good performance in describing non-covalent interactions. Under the same XC functional, the basis sets 6-31++G(d,p) and 6-311++G(d,p) produce similar results, which increase by about 8% with aug-cc-pVDZ, while further augmentation in aug-cc-pVTZ leads to very small improvements (<3%). The MP2/aug-cc-pVDZ calculations are too demanding to be practical, but one can deduce that comparable results can be obtained by the DFT calculations with selected functionals. Therefore, the M06-2X and CAM-B3LYP were used in the subsequent polarizability calculations for the s1 and s2 structures.

Table 2 lists the $\langle \alpha \rangle$ values of empty, singly and doubly occupied s1 and s2 structures. The two functionals, M06-2X and CAM-B3LYP, produce similar results with their differences less than 3% under the same basis set aug-cc-pVDZ. For the empty water cages, their $\langle \alpha \rangle$ (379.55 au with M06-2X) are larger than the $\langle \alpha \rangle$ sum of individual water molecules (349.83 au with M06-2X), resulting from the intermolecular charge transfer effect through the HB network in the presence of an external field, as revealed in our previous studies [56–58]. However, no enhancement in $\langle \alpha \rangle$ is noted for the encapsulation of CH_4 . First, for the singly occupied s1 and s2 structures, their $\langle \alpha \rangle$ values are nearly the $\langle \alpha \rangle$ sum of empty cages and single CH_4 molecule. Next, the $\langle \alpha \rangle$ values of CH_4 in the large cages are nearly the same with those of CH_4 in the small cage, implying that the locations of CH_4 have little effect on $\langle \alpha \rangle$. Finally, for the doubly occupied s1 and s2, their $\langle \alpha \rangle$ values are about the $\langle \alpha \rangle$ sum of empty cages and two individual CH_4 molecules. Our calculations reveal that a simple summation rule holds for the $\langle \alpha \rangle$ of methane hydrates. This is quite different from the polarization response in carbon cages. In previous study [59], we have found that the polarizability of a noble gas atom encapsulated by fullerene is remarkably smaller than the summation of the free noble gas atom and the empty fullerene.

What does this summation rule imply for the polarization behaviors of methane hydrates? The interaction between CH_4 and the water cages is mainly contributed by weak van der Waals forces. The distances between the H atoms of CH_4 and the O atoms of H_2O are larger than 2.5 Å [37]. However, the weak CH_4 –water interaction is not the reason responsible for the $\langle \alpha \rangle$ independence of methane. In the noble-gas encapsulated fullerenes, the interaction between the noble gas atoms and the carbon cages is also weak,

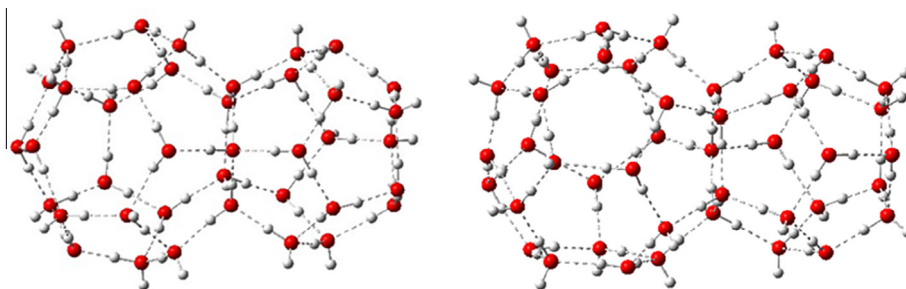


Fig. 1. Two prototypical structures, s1 (left) and s2 (right) of methane hydrates. Methane occupies either or both cages.

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