



# Characterization of interaction energy and vibrational Raman spectra of nitrogen clathrate hydrates



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## ABSTRACT

Nitrogen clathrate hydrates are caged compounds where nitrogen molecules are encapsulated in dodecahedron ( $5^{12}$ ) and hexakaidecahedron ( $5^{12}6^4$ ) water cages. In the present work, we characterize the interaction energy and vibrational Raman spectra of multiple occupancy of  $N_2$  in  $5^{12}$  and  $5^{12}6^4$  water cages using Density Functional Theory. The interaction energies shows that  $5^{12}(N_2)$  and  $5^{12}6^4(N_2)_2$  cages to be the most stable, which is consistent with experimental observations. The spectral shifts suggest the  $5^{12}(N_2)$  and  $5^{12}6^4(N_2)_2$  cages are more stable compared to the  $5^{12}(N_2)_2$  and  $5^{12}6^4(N_2)_{n=1,3}$  cages respectively which corroborate the trends seen from interaction energies.

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## 1. Introduction

Nitrogen clathrate hydrates [1] are cage compounds where nitrogen gas molecules are encapsulated in various polyhedral water cages of a sII hydrate lattice. The sII hydrate lattice consist of sixteen  $5^{12}$  cages (a dodecahedron cage of 20 water molecules) and eight  $5^{12}6^4$  cages (a hexakaidecahedron cage of 28 water molecules). These hydrates exist in abundance in the solar system and in interstellar space [2,3]. Recently, an inclusion of hydrogen molecules in the cages of nitrogen clathrate hydrates was explored as potential candidates for hydrogen storage at moderate pressure [4]. Experimental techniques like Raman spectroscopy has been used to characterize occupancy and probe vibrational modes in clathrate hydrates [5]. Dyadin et al. [6] synthesized  $N_2$  clathrate hydrates and found that extremely high pressures (1500 MPa) were required for the formation of these clathrate hydrates. Similarly, Sugahara et al. [7] observed the spontaneous formation of  $N_2$  clathrate hydrates at high pressure (440 MPa). Sasaki et al. [8] employed Raman spectroscopy to determine the phase transformation of  $N_2$  clathrate hydrates and observed a spontaneous formation at high pressure (6000 MPa) at  $T = 296$  K. The Raman spectroscopy measurements of Champagnon et al. [9], neutron diffraction studies of Chazallon and Kuhs [10] and Molecular Dynamics (MD) simulations of Horikawa et al. [11], and van Klaveren et al. [12,13] revealed the  $5^{12}(N_2)$  and  $5^{12}6^4(N_2)_2$  cages to be the most stable. van Hinsberg et al. [14] employed high pressure Raman spectroscopy and observed that the encapsulation of

$N_2$  in the cages of clathrate hydrates leads to a shift of vibrational modes to lower wave-numbers compared to free nitrogen molecule.

While, experiments and MD simulations have provided some insights into the cage occupancy of nitrogen clathrate hydrates, an *ab initio* study of stability and spectral properties can enhance the present understanding of the cage occupancy of  $N_2$  clathrate hydrates. The objective of this work is to investigate the cage occupancy via characterization of interaction energy and vibrational Raman spectra associated with an encapsulation of  $N_2$  in the  $5^{12}$  and  $5^{12}6^4$  cages using Density Functional Theory (DFT). The B97-D [15] functional has been chosen for the present study based on a previous work [16,17] which demonstrated that the calculated spectral properties on the cages were in agreement with spectroscopic studies on the hydrate lattice. The computational details are described in Section 2. The calculated interaction energy and vibrational Raman spectra are discussed in Section 3. A summary of key results concludes this paper.

## 2. Methodology

Calculations were performed using the Gaussian 09 [18] program with a 6-311++G(d,p) basis set. The input configurations of  $5^{12}$  and  $5^{12}6^4$  cages were taken from X-ray diffraction data of McMullan et al. [19] The input configurations of the  $5^{12}(N_2)_{n=1,2}$  cages was derived by an encapsulation of a single  $N_2$  molecule in the optimized  $5^{12}(N_2)_{n=0,1}$  cages respectively. Similarly, the input configuration of the  $5^{12}6^4(N_2)_{n=1-3}$  cages was derived by an encapsulation of a single  $N_2$  molecule in the optimized  $5^{12}(N_2)_{n=0-2}$  cages

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respectively. Geometry optimization has been performed on each cage using a Beryn [20,21] algorithm. The optimization was achieved by an opt=tight keyword (Root Mean Square (RMS) force =  $10^{-5}$  a.u., Maximum force =  $1.5 \times 10^{-5}$  a.u., RMS displacement =  $4 \times 10^{-5}$  a.u., Maximum displacement =  $6 \times 10^{-5}$  a.u.). An ultrafine grid was used for evaluation of two electron integrals. The optimized configurations of multiple occupancy of  $N_2$  in  $5^{12}$  and  $5^{12}6^4$  cages are shown in Fig. 1 respectively. The total energy was calculated at the optimized geometry and further corrected for Basis Set Superposition Error (BSSE) [22] and Zero Point Vibrational Energy (ZPVE). The interaction energy is calculated as:

$$\text{Interaction energy} = E[\text{cage} \cdot (N_2)_n] - E[\text{cage}] - n * E(N_2) \quad (1)$$

where  $n$  is the number of nitrogen molecules,  $E(N_2)$  is the total energy of an isolated nitrogen molecule.  $E[\text{cage} \cdot (N_2)_n]$  is the total energy of  $5^{12}$  or  $5^{12}6^4$  cage containing the encapsulated nitrogen molecule(s).  $E[\text{cage}]$  is the total energy of  $5^{12}$  or  $5^{12}6^4$  cage. To examine the structural integrity of the cages, we have calculated the deformation energy of the water cage associated with encapsulation of  $N_2$  in the  $5^{12}$  or  $5^{12}6^4$  cages. The deformation energy is calculated as:

$$\text{Deformation energy} = E[\text{cage}] - E[\text{cage}]^{\text{enc}} \quad (2)$$

For example, the deformation energy on single occupancy of  $N_2$  in  $5^{12}$  cage is calculated as follows:  $E[\text{cage}]$  is the total energy of the optimized  $5^{12}$  cage,  $E[\text{cage}]^{\text{enc}}$  is obtained by removal of the  $N_2$  molecule from the optimized geometry of the  $5^{12}N_2$  cage followed by a single point energy calculation. Raman intensities were calculated using a harmonic approximation and can be written as: [23,24]

$$\text{Raman intensity} \propto \left( \frac{\partial \alpha}{\partial q} \right)^2 \quad (3)$$

where  $\alpha$  is the polarizability and  $q$  is the normal coordinate. Frequencies calculated (using analytical second derivatives) at the optimized geometry did not show any imaginary frequencies which illustrates these cages to be minimum energy structures.

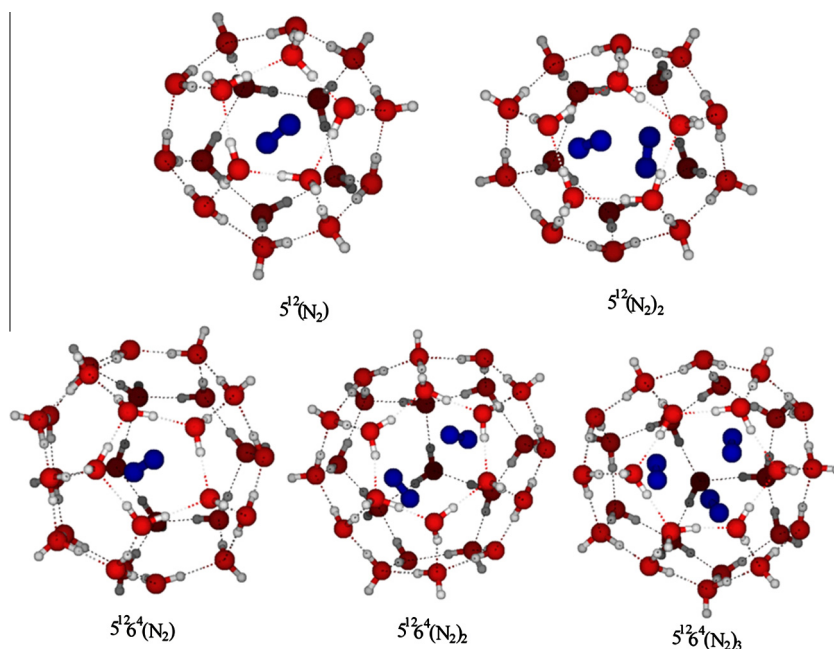
## 2.1. Interaction energy

The interaction energies, ZPVE contributions and deformation energy are shown in Table 1. The increasing negative value of interaction energy illustrates more stability, and a positive value of interaction energy suggests meta-stability. The interaction energy shows that the  $5^{12}(N_2)$  cage ( $-3.27$  kcal/mol) is more stable compared to the  $5^{12}(N_2)_2$  cage ( $7.59$  kcal/mol). The interaction energy in the  $5^{12}(N_2)$  cage (in our study) show more stability compared to the interaction energy ( $-2.59$  kcal/mol) reported by Kumar et al. [25] This difference is due to the choice of method between these calculations. The interaction energy in the  $5^{12}6^4(N_2)$  and  $5^{12}6^4(N_2)_2$  cages are  $-3.00$  kcal/mol and  $-3.76$  kcal/mol, respectively, which illustrates that both cages are stable. The interaction energy in the  $5^{12}6^4(N_2)_3$  cage is  $-0.43$  kcal/mol which show less stability compared to the  $5^{12}6^4(N_2)_{n=1,2}$  cages. Further, attempts to obtain triple and quadruple occupancy of  $N_2$  in  $5^{12}$  and  $5^{12}6^4$  cages respectively, leads to a disintegration of the water cages. The maximum stability of the  $5^{12}(N_2)$  and  $5^{12}6^4(N_2)_2$  cages seen from the interaction energies validate the experimental observations of Champagnon et al. [9] and Chazallon and Kuhs [10] and MD simulations of Horikawa et al. [11] and van Klaveren et al. [13] The large ZPVE contributions to the interaction energy in the  $5^{12}(N_2)_2$  and  $5^{12}6^4(N_2)_3$  cages leads to meta-stability or less stability of these cages. The large ZPVEs with increasing occupancy is also consistent with the observations of Bacic and co-workers [26]. An examination of the deformation energy shows the following trends: The deformation energy in the  $5^{12}(N_2)$  and  $5^{12}(N_2)_2$

**Table 1**

Interaction energy and deformation energy. Contributions from ZPVE to interaction energy in parenthesis.

Cage	Cage radii (Å)	Interaction energy (kcal/mol)	Deformation energy (kcal/mol)
$5^{12}(N_2)$	3.9	$-3.27$ (0.49)	0.4
$5^{12}(N_2)_2$	4.2	$7.59$ (10.24)	4.9
$5^{12}6^4(N_2)$	4.6	$-3.00$ (0.52)	0.5
$5^{12}6^4(N_2)_2$	4.6	$-3.76$ (0.54)	0.7
$5^{12}6^4(N_2)_3$	4.7	$-0.43$ (5.40)	1.6



**Fig. 1.** Structure of  $5^{12}(N_2)_{n=1,2}$  and  $5^{12}6^4(N_2)_{n=1-3}$  cages.

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