

GOEMETRIC MODELING OF GAS HYDRATE STRUCTURAL PROPERTIES AND GUEST-HOST INTERACTIONS

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Abstract. Gas hydrates are inclusion compounds that form in conditions of low temperature and high-pressure systems with water and gaseous molecules. Their potential use in carbon capture and storage, energy exploitation, and flue gas extraction makes them prime candidates for various engineering applications and climate change mitigation technologies. However, their nucleation is poorly understood and the effect of guest molecule interactions with the host on macroscale properties has yet to be elucidated. Herein we study the optimal positions of a point mass, linear molecule, and planar triangular guest molecule using a distance minimization technique that can replicate preliminary density functional theory results. The linear molecule shows strong alignment to hexagonal phases of cages, while the triangular guest molecule shows very distinct positions. These positions indicate a lower number of degrees of freedom, which in turn affect the molecules' ability to move and vibrate in heat absorption, for example. Additionally, it shows that hydrate formation may only be possible when the guest is oriented a certain way, providing an avenue to control nucleation by adjusting guest molecule position with external fields.

1 INTRODUCTION

Gas hydrates (GH) are inclusion compounds comprising a backbone of water molecules that enclose guest molecules in separate cages. Each volume of hydrate contains 160 volume equivalents of gas. Initially, large scale gas hydrate research was centered around the flow assurance problems they cause in the extraction and transportation of petroleum and its

derivatives. Naturally occurring gas hydrates are also studied to satisfy global energy demand. Their potential use in the removal of carbon from the atmosphere, carbon capture and storage, and for energy exploitation makes gas hydrates a prime candidate for climate change mitigation research. [1,2]

The formation and stability of GH are governed by the Van der Waals forces established between the guest and host molecules. Without gas molecules, the lattice structure of GH may collapse and form ice or liquid water. The empty lattice may remain in a metastable state. Methane and carbon dioxide are the most common gas molecules encapsulated in these structures. Methane is estimated to constitute about 80% of gas hydrate occurrence. [3]

The possible hydrates that can be formed by specific guest molecules are separated into three main structures: structure I (sI), structure II (sII), and structure H (sH). The structures are composed of large and small cages, with one cage type being common to all three hydrate types. The other cage types differentiate the structures and determine what gas molecules form what hydrate. The sI unit cell is cubic and is composed of 46 water molecules arranged into eight cages. There are two small cages, in the shape of pentagonal dodecahedrons (5^{12}), and six large cages, in the shape of tetrakaidecahedrons ($5^{12}6^2$). Carbon dioxide, methane, ethane, and hydrogen sulfide are some sI hydrate formers, both as the only guest and in specific combinations of two guests. The sII unit cell is also cubic and is composed of 136 water molecules arranged into 24 cages. There are 16 small cages, in the shape of pentagonal dodecahedrons (5^{12}), and eight large cages in the shape of hexakaidecahedrons ($5^{12}6^4$). Propane, iso-butane, and natural gas mixtures are formers of sII hydrates, although the occupancy is more complex than for sI hydrates because of the size difference between the large and small cages. The sH unit cell is hexagonal and is composed of 34 water molecules arranged into six cages. There are five small cages, three in the shape of pentagonal dodecahedrons (5^{12}) and two in the shape of irregular dodecahedrons ($4^35^66^3$), and one huge cage in the shape of icosahedrons ($5^{12}6^8$). The sH hydrates must always form with two different guests, one for the small cages and one for the huge cages. [4] Combinations of small and large formers of sH hydrates are methane for small cages and neohexene, methylcyclohexane, and pinacolone for large cages. [5] Schematic representations of the five cage types are displayed in figure 1.

The formation of GH is a sophisticated crystallization process controlled by heat and mass transfer. It can be characterized as two steps: hydrate nucleation and hydrate growth. Hydrate nucleation is a microscopic process to reach the critical size required for sustained growth. [2] Vast amounts of water and gas initially form small clusters, further growing and dispersing into hydrate nuclei. However, the mechanism of the nucleation process still needs to be clarified. The nucleating at interface hypothesis, the liable cluster nucleation hypothesis, and the local structuring hypothesis are briefly introduced here.

According to the nucleating at interface hypothesis, nucleation occurs on the vapor side of the interface. [2] Gas molecules are initially transported to the water-gas interface, where they are adsorbed on aqueous surface. Subsequently, these adsorbed gas molecules migrate to a stable location by diffusion. When the adsorbed molecules reach this location, water molecules form first partial, and then complete cages around the adsorbed molecules. [2] The growth of these cages can occur by adding of water and gas molecules to existing cavities, aggregation mechanisms, or a combination of both. The formation of a hydrate film at the interface could support this hypothesis. Nevertheless, this hypothesis is not valid for hydrates with higher density than water. [6]

The labile cluster nucleation hypothesis has a higher degree of generality. It can be applied to scenarios of hydrate nucleation regardless of the presence or absence of free gas or liquid phase guest molecules. [6] Initially, labile ring structures of pentamers and hexamers formed in the pure liquid water phase. As the gas dissolved in water, labile clusters formed immediately. The size of the guest molecules dictates the number of water molecules in each cluster shell. [2] The clusters of the dissolved species combine to form the unit cell. Nucleation is hindered until the clusters can transform to the other geometry if only one cavity type is present in the liquid phase. Nucleation kinetics are affected by the cluster transformation process, where an activation barrier is involved. Furthermore, alternative structures emerge during the transformation process, providing parallel formation pathways and decelerating the nucleation kinetics. [2]

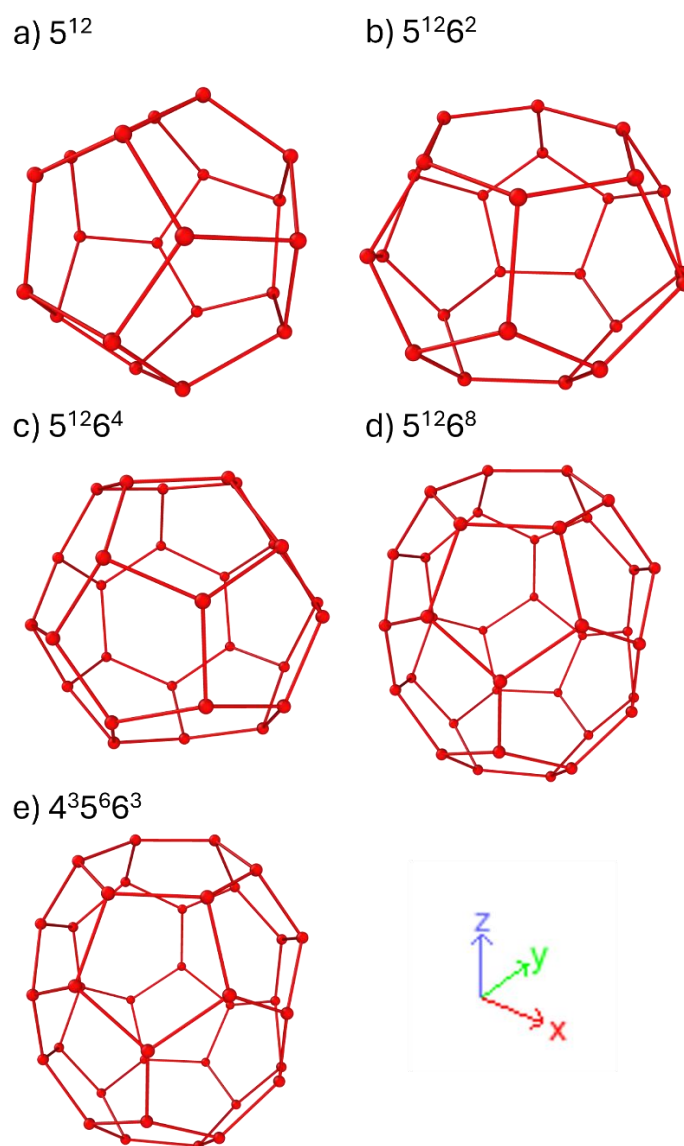


Figure 1: Different cages for sI, sII, and sH gas hydrates

Based on the Landau free energy calculations, the local structuring nucleation hypothesis is used to analyze the nucleation mechanism of carbon dioxide hydrate at the liquid water-liquid carbon dioxide interface. [2] According to the free energy calculations, the labile cluster hypothesis is unlikely responsible for carbon dioxide hydrate nucleation, as labile clusters tend to disintegrate instead of agglomerating. According to the structuring nucleation hypothesis, a group of guest molecules (CO_2) is arranged like that of clathrate hydrate phase. This leads to a local order of the surrounding water molecules that differs from that in the bulk water phase. Hydrate nucleation begins when the number of carbon dioxide molecules in this arrangement with a local order exceeds the threshold for a critical hydrate nucleus. [6]

Upon examining the entire formation process, we observe that the unit cell of the GH is made up of distinct cavities. Therefore, using some geometric tools, we can ascertain some information about the interaction with guest molecules and lead to examinations of macroscale manifestations of atomic scale geometries.

GHs have several potential technological applications. They could be used for transportation and storage, as it can store and release about 180 m^3 of gas per 1 m^3 of hydrate at standard conditions. [7] This works for small hydrocarbon guest molecules, typically one molecule per cavity. The guest molecules are separated by the water cages by about 0.5 nm , which means that the energy density in hydrates is comparable to that of a highly compressed gas. In addition, a significant fraction of fossil fuels is stored in clathrate hydrate in marine sediments. The amount of energy in hydrates is equivalent to twice that of all other fossil fuels combined, making it a potential fuel source to meet the ever-growing demand. [1] However, existing extraction methods are expensive and not practical. Gas hydrate also has the potential to store carbon dioxide, providing a new carbon dioxide capture mechanism. The main idea is to ensure carbon dioxide prefers to partition in hydrate phase when mixed with other gases. [8] Hydrate-based gas separation or capture technologies have attracted wide attention due to their excellent characteristics such as moderate operation conditions, low energy penalty, and being environmentally friendly. However, the slow natural hydrate formation rate dramatically limits the application of hydrate-based technology. In order to improve the formation rate, several methods have been developed: (1) using mechanical methods such as stirring, spraying, and bubbling to decrease the induction time; (2) using chemical additives to promote mass and heat transfer; (3) combining two or more surfactants or materials to increase the solubility of the guest molecule by lowering the surface tension; (4) applying external fields such as electromagnetic field and electric field to generate force on microparticles and provide energy for hydrate nucleation and growth. [7]

To establish a basic understanding of natural gas hydrates, we will provide an overview of geometric optimization procedures used to minimize the guest-host distance in the hydrate cavity to find a method to help reduce the potential energy but also provides a good initial guess for future projects (e.g., in density functional theory). This information will also explain some anomalous trends in thermal properties of gas hydrates, as the ability of a structure to store energy is controlled by its ability to vibrate and move with its available degrees of freedom. We elaborate on the methods employed for simple atom, linear molecules, and triangular molecules, including tests on all give water cavities to improve understanding and effects of geometric interactions in the proposed nucleation pathways.

2 METHODOLOGY

The primary objective is to verify the minimum distance of a given guest geometry from all vertices in the cage, with the relevant backbone coordinates taken from literature. [9] We first verify that the method correctly estimates the center of the cage from these coordinates to validate the methods. Then, degrees of freedom are introduced to allow for molecule rotation along multiple axes. Heat maps are constructed where appropriate to assess the distance landscape and use it as a pseudo-energy landscape to suggest possible ground state configurations without requiring computationally intensive density functional theory calculations.

The single atom calculations require only variation of the placement in the cage structure. The linear molecule has some more complexities. Following our previous work with carbon dioxide sI hydrates, determining the root of the alignment of the linear molecule with the hexagonal faces of the $5^{12}6^2$, we seek to allow for the constrained rotation of a linear molecule in the different cage types to determine if there are other locations of distances minimums. [10] Using a bond angle of π radians and a bond length of 1.16 Angstroms between the center atom and the two end atoms, we can determine the positions by varying only that of the central atom. The bond length used reflects that of carbon dioxide. Then, we employed spherical coordinates to allow for the rotation of the molecule. The coordinates of the one of the two oxygen atoms can be express in terms of radius, elevation (θ), and azimuth (ϕ) relative to the central carbon atom. Then, the other oxygen atom’s position can be directly determined along the same axis. Transformations from spherical to cartesian coordinates are shown in table 1. The elevation is taken relative to the vertical, z axis and the radius of the sphere is defined as the bond length of the representative molecule being modeled. The azimuth is taken relative to the positive x axis.

Table 1: Spherical coordinate transformations for a representative carbon dioxide molecule

Atom	X [\AA]	Y [\AA]	Z [\AA]
C	x	y	z
O ₁	$x + r \sin \theta \cos \phi$	$x + r \sin \theta \sin \phi$	$z + r \cos \theta$
O ₂	$x - r \sin \theta \cos \phi$	$x - r \sin \theta \sin \phi$	$z - r \cos \theta$

Finally, we calculate the sum of the distances between each atom and the vertices of the cage. By varying the elevation and azimuth, one can examine the effect of different rotations in the cage. We employed this procedure for all five cage types present in sI, sII, and sH hydrates.

Examining a triangular molecules like ethylene oxide provides an excellent way to examine the effect of a small, planar molecule in the cage. In this case, we mimic ethylene oxide. The distances calculate is the same as for the linear molecule, but the construction of a randomly orientation triangular molecule has some complexities. While the elevation and azimuth allow for the determination of two atoms of the molecule, they do not fix the third atom due to possible rotations. Therefore, we extended the method by employing the well-known Rodrigues’ Rotation Formula to rotate a vector representing the missing atom in space, given a specific axis and rotation angle. This allowed for the construction of the triangle for any number of rotation angles, adding a degree of freedom.

4 RESULTS

4.1 Single Atom

Following the general procedure for the single atom, we correctly reproduced the cage centers for all cage types by minimizing the distance between the atom and the vertices of the cages. The calculated coordinates are presented in table 2. While these are results for single atoms, small, spherical guest molecules will follow these results. X-ray diffraction experiments confirm the positions of the cage centers and the fact that methane molecules will not be constrained rotationally and may occupy various configurations that match the lowest energy and net dipole states. [9]

Table 2: Cage centers for single atom guests

Cavity	X [Å]	Y [Å]	Z [Å]
5^{12}	0.000	6.015	0.000
$5^{12}6^2$	3.008	0.000	0.000
$5^{12}6^4$	8.655	8.655	8.655
$4^35^66^3$	6.110	3.576	5.108
$5^{12}6^8$	6.110	10.617	5.069

The replication of results with simple geometric optimization lends accuracy to the proposed geometric optimization methods. In cases where the guest molecule is not small and spherical, we continue with more complex geometries like the carbon dioxide linear molecules that present more nuanced results.

4.2 Linear Molecule

Following the general procedure for the linear molecule, we correctly found that the center of the cage, for all cage types, was the optimal placement of the central atom (carbon for carbon dioxide) regardless of the rotation of the molecule. However, the significant analysis came in examining the elevation and azimuth angles which showed certain analysis in the linear molecules. The simple shape of this molecule showed that these two parameters were the only degrees of freedom available to fully define the system and therefore can be summarized well with a heat map of the orientations, shown in figure 2.

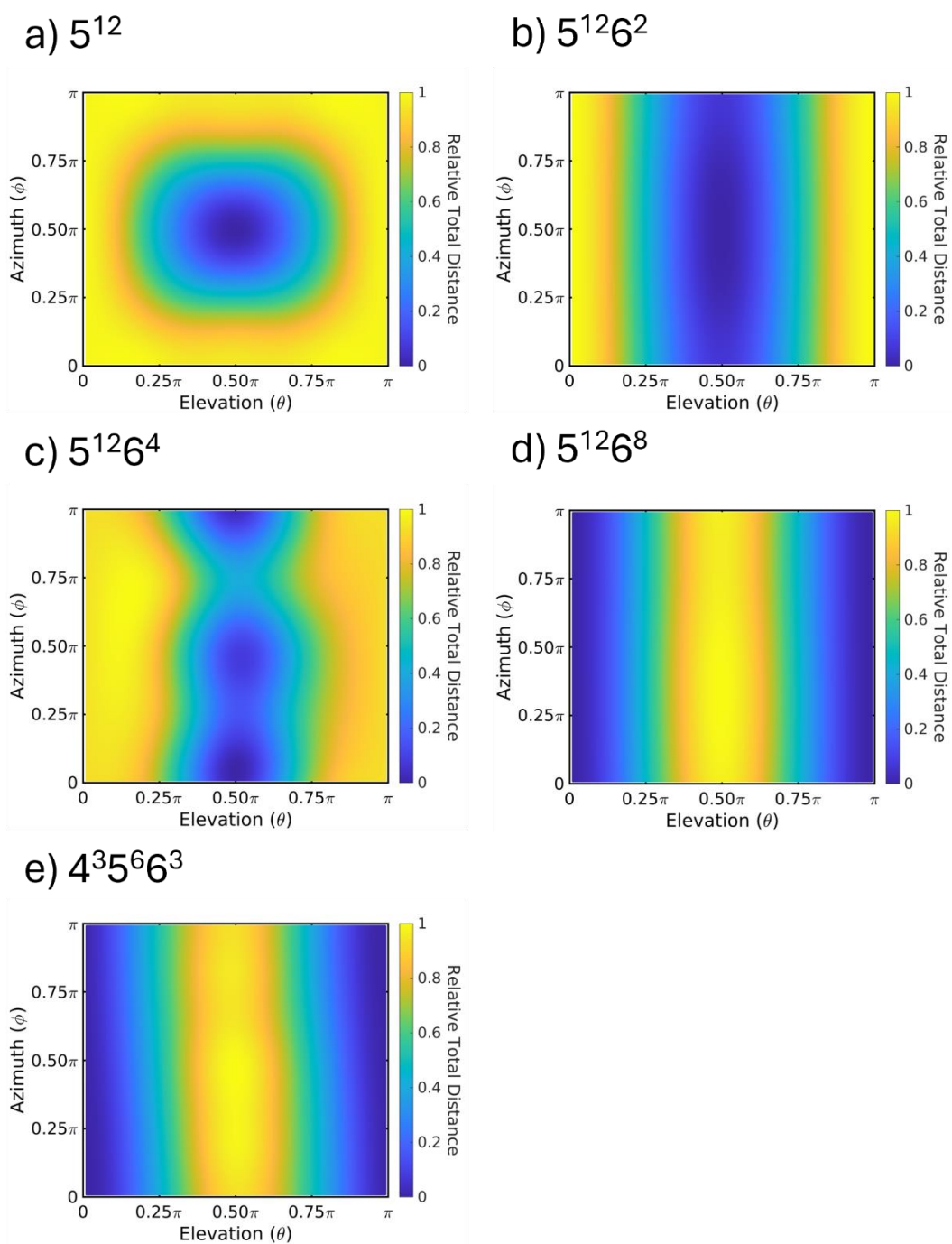


Figure 2: Heat map of the relative distance as a function of elevation and azimuth angle

Figure 2 shows heat maps for the linear molecule, with the relative total distance from all vertices as a function of the elevation and azimuth angles. Plot a) shows the minimum distance at both an elevation and azimuthal angle around $\pi/2$ radians, corresponding to a minimum distance line. However, density functional theory studies show that usually, in the 5^{12} cage, there is little restriction on rotational behaviors. [10] Plot b) shows that the minimum distance

is insensitive to the azimuth angle but strongly sensitive to the elevation angle. The minimum distance corresponding to the $\pi/2$ elevation corresponds to the molecule sitting on a plane that is parallel to the two hexagonal faces of the $5^{12}6^2$, a finding sparingly mentioned in literature but significant with its interactions with the backbone. [10,11] Plot c), corresponding to the $5^{12}6^4$ cage shows a similar heat map. This is because the location of the hexagons is also located on the top and bottom of the cage, but not directly at in the $5^{12}6^2$ cages, hence the split into roughly three stable regions. The differences between these two cage types may be removed once DFT can be performed and the effect of protons can be resolved.

Plot d) shows the heat map for $5^{12}6^8$ cage types, with the minimum distance location at 0 radians or π radians. These two points are equivalent for the linear molecule and suggest that it is preferably location aligned vertically in this cage. Much like the $5^{12}6^2$ and $5^{12}6^4$ cages, this yields an alignment that is parallel to the hexagonal phases, as in the $5^{12}6^8$ cages, the hexagons form a ring around the cage in the waist region, where the faces are along the z axis. If unrolled, all 8 hexagons would be in line and sharing one edge for each adjacent hexagon, a linear chain of hexagons. The DFT results for the $5^{12}6^2$ cages suggest that the minimum distance criteria mask the minimum energy configuration and therefore that the carbon dioxide guest molecules would align in this fashion. The heatmap for the $4^35^66^3$ is displayed in plot e). The results are very similar to d), and for the same reasons. In this case, the squares and hexagons form a ring with the faces along the z axis, yielding a molecule that prefers to be aligned vertically in the system. The results from these heat maps explain that linear guest molecules will tend to align themselves parallel to the hexagons, which in turn yields information about rotational degrees of freedom.

4.3 Triangular Molecule

As the triangular molecule placement account to the geometric distance minimization involves the additional degree of freedom of rotation, it is less suitable to the two-dimensional representation of a heat map. Additionally, the optimized positions are more discrete and more complex. Figure 3 shows the eight possible minimum distance configurations available to the triangular guest molecule, modelled here with ethylene oxide (without protons), in the 5^{12} cages. In the $5^{12}6^2$ cages, the triangular guest shows four optimum positions that are neither parallel nor perpendicular to the hexagonal faces, as in the linear case. This result is shown in figure 4.

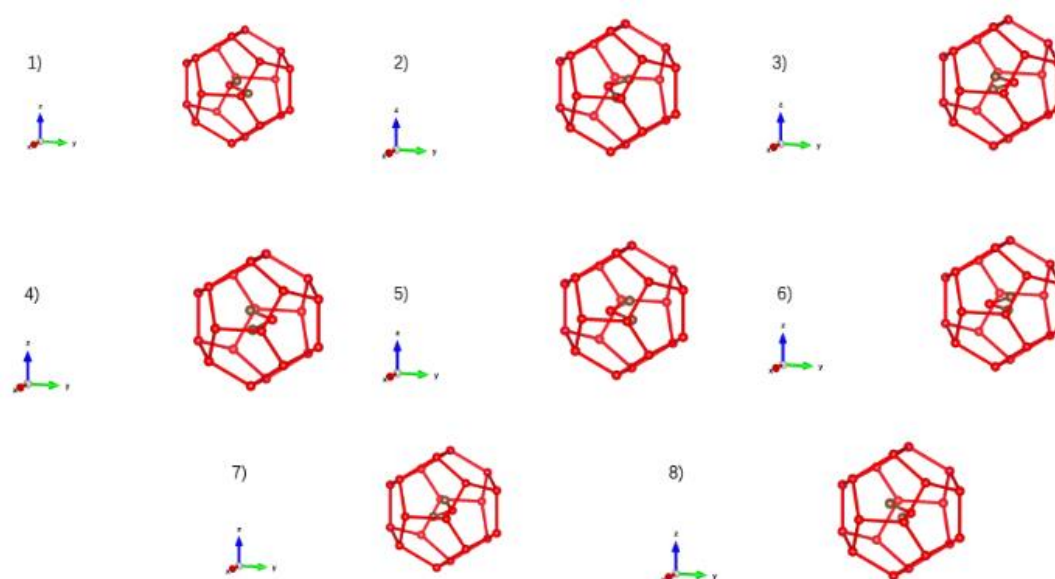


Figure 3: Optimized positions of the triangular molecule in the 5^{12} cage

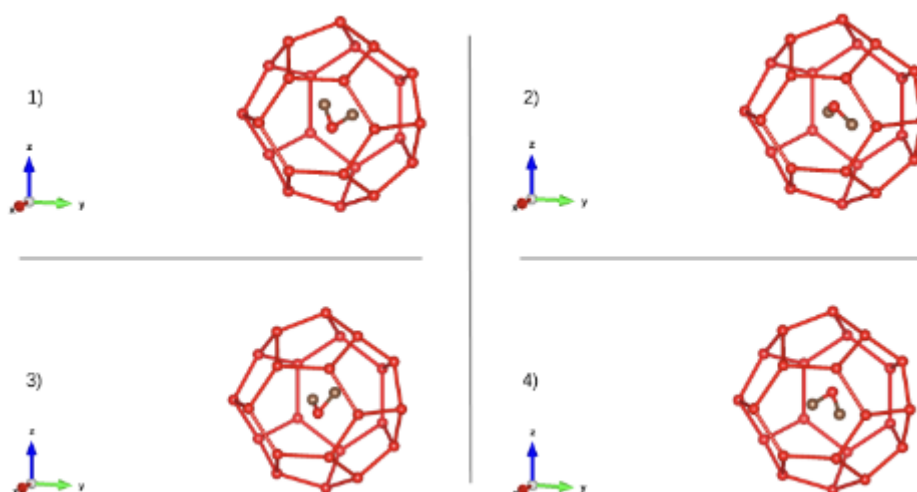


Figure 4: Optimized positions of the triangular molecule in the $5^{12}6^2$ cage

In the cases of the $5^{12}6^4$, $5^{12}6^8$, and $4^35^66^3$ cages, the triangular molecule can exist in only one minimum distance configuration. In the $5^{12}6^4$ cage, the molecule will be aligned normal to the x - y plane, which is displayed in figure 5. The same is the case for the $5^{12}6^8$ cage, displayed in figure 6. In the case of the $4^35^66^3$ cage, the triangular molecule is aligned parallel to the hexagonal and square phases, seen in figure 7, the same behavior as the linear guest molecule.

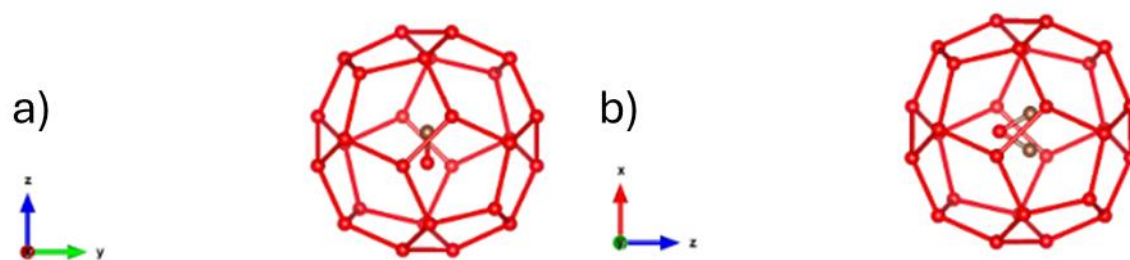


Figure 5: Optimized position for the triangular molecule in the $5^{12}6^4$ viewed from a) x-axis, b) y-axis

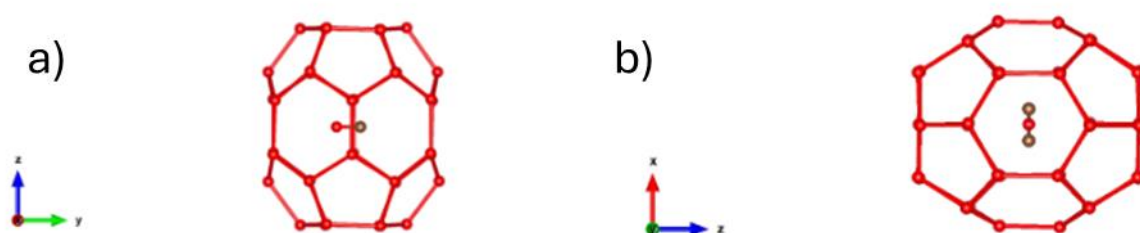


Figure 6: Optimized position for the triangular molecule in the $5^{12}6^8$ cage viewed from a) x-axis, b) y-axis

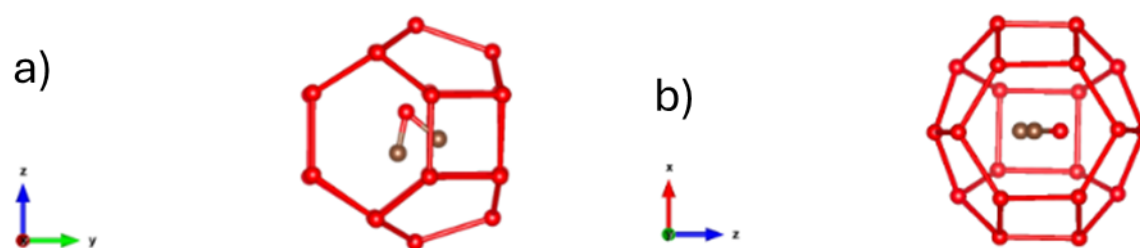


Figure 7: Optimized position for the triangular molecule in the $4^35^66^3$ cage viewed from a) x-axis, b) y-axis

The triangular guest molecule shows more nuanced orientational behaviors due to its additional degree of freedom in comparison to the linear guest molecule. The distinct distance minimums, which coincide with energy minimums from certain DFT studies for linear molecules, may be cancelled out during material changes to the structure, particularly expansion. Additionally, the effect of temperature, the presence of protons and the full consideration of the electron effects may change the positions and depth of the energy wells. However, the methodology presented herein provides accurate estimates for starting points of future orientational studies or costly simulations where there would be a material benefit to starting near a point that is already considered quasi-minimized.

5 CONCLUSIONS

Gas hydrates are crystalline, ice-like compounds composed of water and gas molecules that form under specific conditions of low temperature and high pressure, typically in deep-sea

sediments and permafrost regions. Gas hydrates have obtained considerable interest due to their potential applications in energy transportation, storage, and carbon dioxide capture. Their nucleation process needs to be clarified. Orientational studies of guest molecules in cages based on geometric distance minimization proves to be a worthwhile pursuit in generating quasi-minimized structures to be fine-tuned with density functional theory. The results obtained in this report are based on minimizing the distance of the guest to the vertices of the host structure by varying the available degrees of freedom. However, it is difficult to formulate a function that encapsulates all cavity vertices. Furthermore, it becomes essential to incorporate techniques from the field of packing problems, accounting for the volume occupied in 3-dimensional space. This represents a significant departure from our current approach, where atoms are simplified as a point mass. However, the findings presented herein show remarkable orientational behaviors, with restricted degrees of freedom that may have significant impact in current understanding of nucleation and growth studies, as well as in explaining the anomalous thermal behaviors of gas hydrates.

REFERENCES

- [1] E. D. Sloan, *Fundamental Principles and Applications of Natural Gas Hydrates*, Nature **426**, 353 (2003).
- [2] E. D. Sloan and C. A. (Carolyn A. Koh, *Clathrate Hydrates of Natural Gases*, 3rd ed. / (CRC Press, Boca Raton, FL, 2008).
- [3] X. Zhu, A. D. Rey, and P. Servio, *Multiscale Piezoelasticity of Methane Gas Hydrates: From Bonds to Cages to Lattices*, Energy Fuels (2022).
- [4] J. Carroll, *Natural Gas Hydrates: A Guide for Engineers*, 3rd ed. (Gulf Professional Publishing, 2014).
- [5] S. M. Daghash, P. Servio, and A. D. Rey, *Structural Properties of sH Hydrate: A DFT Study of Anisotropy and Equation of State*, Mol. Simul. **45**, 1524 (2019).
- [6] J. M. Schicks, *Gas Hydrates in Nature and in the Laboratory: Necessary Requirements for Formation and Properties of the Resulting Hydrate Phase*, ChemTexts **8**, 13 (2022).
- [7] Z. Xia, Q. Zhao, Z. Chen, X. Li, Y. Zhang, C. Xu, and K. Yan, *Review of Methods and Applications for Promoting Gas Hydrate Formation Process*, J. Nat. Gas Sci. Eng. **101**, 104528 (2022).
- [8] P. Linga, R. Kumar, and P. Englezos, *The Clathrate Hydrate Process for Post and Pre-Combustion Capture of Carbon Dioxide*, J. Hazard. Mater. **149**, 625 (2007).
- [9] F. Takeuchi, M. Hiratsuka, R. Ohmura, S. Alavi, A. K. Sum, and K. Yasuoka, *Water Proton Configurations in Structures I, II, and H Clathrate Hydrate Unit Cells*, J. Chem. Phys. **138**, 124504 (2013).
- [10] S. L. Mathews, P. D. Servio, and A. D. Rey, *Heat Capacity, Thermal Expansion Coefficient, and Grüneisen Parameter of CH₄, CO₂, and C₂H₆ Hydrates and Ice I_h via Density Functional Theory and Phonon Calculations*, Cryst. Growth Des. **20**, 5947 (2020).
- [11] F. Izquierdo-Ruiz, A. Otero-de-la-Roza, J. Contreras-García, O. Prieto-Ballesteros, and J. M. Recio, *Effects of the CO₂ Guest Molecule on the sI Clathrate Hydrate Structure*, Materials **9**, (2016).