# Gümüşhane University Journal of Science

GUFBD / GUJS (2025) 15(2): 451-462 doi: 10.17714/gumusfenbil.1627107

# Theoretical investigation of the effects of large cage guest CF<sub>3</sub>Br and small cage guests CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S on the stability of double clathrate hydrates

Büyük kafes konuğu  $CF_3Br$  ve küçük kafes konukları  $CH_4$ ,  $CO_2$  ve  $H_2S$ 'in çift klatrat hidratların kararlılığı üzerindeki etkilerinin teorik incelenmesi

# Zafer MAŞLAKCI\* 问

Bandirma Onyedi Eylul University, Susurluk Agriculture and Forestry Vocational School, Department of Chemical and Chemical Processing Technologies, 10600, Balikesir, Türkiye

#### Abstract

Guest-host interactions in double clathrate hydrates were investigated through computational molecular-level simulations. This approach focuses on important molecular properties of CF<sub>3</sub>Br clathrate hydrates that were not previously well-characterized. The aim of this study is to investigate the characteristics of guest-host interactions of the CF<sub>3</sub>Br molecule in clathrate hydrate structures using quantum mechanical calculations. In the present study, a water cluster comprising small and large cages, referred to as the cluster, was used to mimic s-II clathrate hydrates. The s-II cluster was filled with CF<sub>3</sub>Br as the large cage (l-c) molecule and H<sub>2</sub>S, CO<sub>2</sub>, CH<sub>4</sub> as the small cage (s-c) molecules. The  $5^{12}+5^{12}6^4$  cluster, containing a combination of l-c and s-c molecules, underwent energy optimization at the BLYP/6-31++G(d,p) level using Gaussian 16. As the molecular weight of the guest increased, the interaction between the guest and host molecules also increased for the  $5^{12}+5^{12}6^4$  cluster. The incorporation of CF<sub>3</sub>Br into the large cage (l-c) strengthened the guest-host interactions, leading to greater structural stability. This highlights the potential of clathrate hydrates for applications in energy storage systems. The guest-host interactions of CF<sub>3</sub>Br-containing double clathrate hydrates have been investigated at the molecular level for the first time, contributing to the development of the thermodynamic and kinetic properties of clathrate hydrates.

Keywords: CF<sub>3</sub>Br, Clathrate hydrates, DFT, Double cage

# Öz

Çift klatrat hidratlardaki konuk-konak etkileşimleri, hesaplamalı moleküler düzeyde simülasyonlar aracılığıyla incelenmiştir. Bu yaklaşım, daha önce iyi karakterize edilmemiş olan CF<sub>3</sub>Br klatrat hidratların önemli moleküler özelliklerine odaklanmaktadır. Bu çalışmanın amacı CF<sub>3</sub>Br molekülünün klatrat hidrat yapılarındaki konuk-konak etkileşimlerinin kuantum mekanik hesaplamalar ile özelliklerini incelemektir. Bu çalışmada, s-II klatrat hidratları taklit etmek için küçük ve büyük kafeslerden oluşan bir su kümesi, küme olarak adlandırılmıştır. S-II kümesi, büyük kafes (l-c) molekülü olarak CF<sub>3</sub>Br ve küçük kafes (s-c) molekülleri olarak H<sub>2</sub>S, CO<sub>2</sub>, CH<sub>4</sub> ile doldurulmuştur. l-c ve s-c moleküllerinin bir kombinasyonunu içeren 5<sup>12</sup>+5<sup>12</sup>6<sup>4</sup> kümesi, Gaussian 16 kullanılarak BLYP/6-31++G(d,p) seviyesinde enerji optimizasyonuna tabi tutulmuştur. 5<sup>12</sup>+5<sup>12</sup>6<sup>4</sup> kümesi için konuk molekülün moleküler ağırlığı arttıkça, konuk ve konak moleküller arasındaki etkileşim de artmıştır. CF<sub>3</sub>Br'nin büyük kafese (l-c) dahil edilmesi, konuk-konak etkileşimlerini güçlendirerek yapısal stabilitenin artmasına yol açmıştır. Bu durum, klatrat hidratların enerji depolama sistemlerindeki potansiyel uygulamalarını vurgulamaktadır. CF<sub>3</sub>Br içeren çift klatrat hidratların konuk-konak etkileşimlerini moleküler seviyede ilk kez incelenmiş olup klatrat hidratların termodinamik ve kinetik özelliklerinin geliştirilmesine katkı sağlayacaktır.

Anahtar kelimeler: CF<sub>3</sub>Br, Klatrat hidratlar, DFT, Çift kafes

\*Zafer MAŞLAKCI; zmaslakci@bandirma.edu.tr

# 1. Introduction

Clathrate hydrates (also known as gas hydrates) are solid inclusion compounds comprising an ice-like network of host water molecules linked through hydrogen bonding. Unlike the ice structure, the arrangements of water molecules create cavities (host lattice) that can enclose a wide variety of small gas molecules (<10 Å, guests). Clathrate hydrates are known to have three distinct crystalline structures under appropriate thermodynamic conditions: structure I (sI), structure II (sII), and structure H (sH) (Sloan & Koh, 2008; Sloan, 2023). In clathrate hydrate structures, van der Waals interactions between water molecules and enclosed guest molecules stabilize the host lattice. However, recent studies have experimentally detected long-lived host-guest interactions. These interactions vary depending on the type of small and large cage guests and temperature; however, no consistent trend has been reported (Devlin & Monreal 2010a; Uras-Aytemiz et al., 2011). Similarly, the "all vapor method" has highlighted the significance of host-guest interactions in determining which guests occupy small cages and which species dominate (e.g., small cage guests like CO<sub>2</sub> and CH<sub>4</sub>) (Uras-Aytemiz et al., 2011; Uras-Aytemiz et al., 2012). The term expressed as "equilibrium ratios" is used to determine the amount of competing molecules. The term "equilibrium ratios" refers to systems where molecules spend the majority of their time at the center of the cage, ensuring that the conditions for such behavior are met. Under these conditions, the molecules do not form hydrogen bonds. In the experimental study conducted entirely using the vapor method, the stability of small cage guests relative to each other while inside the small cage was investigated. The term "equivalency ratios" reflects the effect of guest-host interactions and is the main subject of this study.

Surfaces play a critical role in gas-hydrate interactions, particularly in the uptake and release of guest molecules and adsorbates. Despite their clear importance in clathrate hydrate formation, little is known about the molecular-level structure of the outermost surface of clathrate hydrates (Uras-Aytemiz et al., 2011; Uras-Aytemiz et al., 2012) or how interior structures and their transformations are influenced by adsorbates. Using advanced experimental methods with ice nanoparticles, significant progress has been made in understanding bare hydrate surfaces (Richardson et al., 1985; Fleyfel & Devlin 1988; Fleyfel et al., 1990; Hernandez et al., 1998; Gulluru & Devlin 2006; Devlin & Monreal 2010a; Devlin & Monreal 2010b; Uras-Aytemiz et al., 2011; Uras-Aytemiz et al., 2012). Generating bare clathrate hydrate surfaces without losing interior guests was identified as an essential first step, and this objective has now been achieved. It is crucial that guest molecules bind only weakly to the hydrate surface while maintaining a stable presence within the hydrate cages. Theoretical studies like this one investigate how guest molecules (CF<sub>3</sub>Br in large cages and CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S in small cages) influence the stability of the hydrate lattice. Crystal surfaces in clathrate hydrates are important because they can undergo structural relaxation, adsorption, or potential rearrangements due to guest-host interactions. If guest molecules contribute to stronger hydrogen bonding or alter the lattice parameters, these effects could extend to surface stability, impacting nucleation and growth processes. Some studies have shown that guest molecule size and polarity affect surface adsorption and the dissolution behavior of clathrate hydrates. For instance, studies on CH<sub>4</sub> or CO<sub>2</sub> hydrates (Kvamme et al., 2007; Falenty et al., 2014) suggest that guest molecules contribute to lattice distortions. The study examined the surface stability and decomposition processes of CO<sub>2</sub> hydrates, demonstrating that guest molecules exhibit different behaviors on the crystal surface. Specifically, it was reported that CO<sub>2</sub> is more stable on the surface, whereas CH<sub>4</sub> can escape from the hydrate surface more easily (Falenty and Kuhs, 2009). The interactions of CO<sub>2</sub> and CH4 on hydrate surfaces have been experimentally investigated, and it has been shown that CO2 can adsorb onto CH<sub>4</sub> hydrate surfaces (Uchida et al., 2002). The analysis of the surface decomposition mechanisms of natural gas hydrates has determined that surface stability varies depending on the composition of the guest molecules (Staykova et al., 2003). Molecular dynamics studies on the stability of hydrate surfaces containing CH<sub>4</sub> and CO<sub>2</sub> have shown that CO<sub>2</sub> is more stable than CH<sub>4</sub> due to its surface interactions (Jacobson et al., 2010). Previous studies have reported that hydrogen bonding occurs between the guest and host molecules. In this context, Alavi and his group conducted a series of calculations: they examined alcohols (ethanol, 1propanol, 2-propanol) in the sII structure, along with propane and butane molecules (large cage guests) and CH4 molecules (small cage guests) (Alavi et al., 2010). In another study, they investigated ether molecules (such as THF and THP) as simple hydrates in the sII structure. These studies reported that ethers and alcohols form hydrogen bonds with host water molecules. A bulk study examining the hydrogen bonding between various guest molecules and host water molecules, as observed in experimental data, has been reported (Alavi and Ripmeester, 2012). What distinguishes this study from others is its investigation of the contribution of hydrogen bonding between small and large cage guest molecules and host water molecules. For this purpose, CO<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, and Xe were selected as small cage guests, and it was stated that CO<sub>2</sub> stabilizes the hydrogen bonding between THF molecules and water. Therefore, determining the characteristics of double-cage structures will enable a better understanding of interactions in crystal structures.

Starting with arrays of cold ice nanocrystals, a pair of hydrates was successfully prepared that met these criteria: specifically, a structure-II hydrate with large cage CF<sub>3</sub>Br and small cage H<sub>2</sub>S (Buch et al., 2009). FTIR spectra have been obtained for the 3-coordinated water molecules at dangling-oxygen and dangling-hydrogen surface sites in arrays of clathrate hydrate nanocrystals. In contrast to ice nanocrystals, studies have investigated whether a "regular" hydrate lattice structure extends to the outermost surface (Buch et al., 2009). This knowledge of gas hydrates has guided efforts to identify optimal guest mixtures for catalyzing all-vapor clathrate hydrate formation. The transformation of solids due to external factors is often strongly influenced by the intrinsic properties of surfaces. Similar to ice nanocrystals, numerous CH nanocrystalline particles are now easily accessible, and various studies on this subject are available in the literature (Davidson, 1973; Buch et al., 2004). For example, dangling group frequencies of CF<sub>3</sub>Br-H<sub>2</sub>S double clathrate hydrates can be observed even at 170 K, suggesting that clathrate hydrate nanoparticles are retained at higher temperatures than ice (Buch et al., 2009). Simple s-I H<sub>2</sub>S clathrate hydrate or double s-II CF<sub>3</sub>Br-H<sub>2</sub>S can form at temperatures as low as 120 K within a one-hour time frame, with H<sub>2</sub>S acting as one of the guests promoting low-temperature clathrate hydrate formation.

 $H_2S$  catalysis can facilitate the incorporation of relatively large guests into large clathrate hydrate cages under conditions where the same guests would not react with ice. It is known that  $H_2S$  not only forms the s-I clathrate hydrate structure but also contributes to the formation of many double clathrate hydrates, where it serves as the small cage guest (Buch et al., 2009). In order to examine the effect of methane and carbon dioxide on cage structures, sI and sII double cage structures were initially studied with small cages containing methane, while the large cages remained empty. Subsequently, methane was added to the center of the small cages of the sI and sII double cage structures, leaving the large cages empty. The effect of methane has been analyzed quantum mechanically using different basis sets (Fan et al., 2013; An et al., 2018).

DFT calculations have been conducted using a double-cage structure, which is a combination of  $5^{12}$  and  $5^{12}6^4$ cages. It has been shown that certain substances significantly increase the rate of formation and the final amount of hydrate formed in a catalytic manner when included in an all-vapor pre-mixture. This catalytic effect can largely be attributed to the ability of a guest molecule to create ice-like defects, as described by the Trout-Buch model (Davidson, 1973; Demurov et al., 2002; Buch et al., 2004; Buch et al., 2009; Fan et al., 2013; An et al., 2018). These defects facilitate the accelerated movement of guest molecules. Recent studies have reported clathrate hydrate formation results obtained at very low temperatures and pressures (Ghosh et al., 2019a; Ghosh et al., 2019b). Compared to several known hydrogen-bonding catalysts, the catalytic activity of CF<sub>3</sub>Br must originate from a different mechanism. Bromine's effectiveness in catalyzing the formation of clathrate hydrates via defects associated with halogen bonds could enhance our general understanding of defect-based processes and potentially lead to the development of more powerful halogenbond-based catalysts. For this purpose, the interactions of guest molecules in small cage structures (CH<sub>4</sub>,  $CO_2$ , and  $H_2S$ ) and the guest molecule in large cage structures (CF<sub>3</sub>Br) were studied systematically. In this context, the stability of the CF<sub>3</sub>Br molecule in the large cage and how the stability of the specified clathrate hydrates changes in the presence of small guest molecules placed in the small cage (equivalency ratios) were investigated.

# 2. Calculation method

In order to evaluate the stability of the small and large caged guest molecules, this study focuses on the interactions of guest molecules within the cages. A model is presented here, comprising a combination of  $5^{12}$  and  $5^{12}6^4$  cages for s-II clathrate hydrates, based on known structures from diffraction data. The effect of alternating the small-cage molecule while retaining the same large-cage guest on stability is determined. In this study, all structures have been subjected to an optimization procedure without fixing the water molecules ( $5^{12}$  refers to 12 pentagonal cage walls). In order to understand the catalytic ability of the CF<sub>3</sub>Br molecule in clathrate hydrate structures, systematic quantum mechanical calculations at the DFT level were performed. In these calculations, the BLYP functional (Becke exchange functional combined with the Lee-Yang-Parr correlation functional) (Becke, 1988; Lee, Yang & Parr, 1988) was used along with the 6-31++G(d,p) basis

set. The 6-31++G(d,p) basis set includes polarization (d,p) and diffuse (++) functions, which enhance the accuracy of describing electron distribution, particularly in weak interactions such as hydrogen bonding and van der Waals forces, making it suitable for investigating guest-host interactions in clathrate hydrates (Alavi & Ripmeester 2010;2012; Buch et al., 2004;2009; Takeuchi et al., 2013; Jacobson et al., 2010; Yang et al., 2015). In the present study, a water cluster comprising a combination of small (5<sup>12</sup>) and large (5<sup>12</sup>6<sup>4</sup>) cages, referred to hereafter as the  $5^{12+}5^{12}6^4$  cluster, was used as a model to mimic the s-II clathrate hydrate. The  $5^{12+}5^{12}6^4$  cluster was isolated from the s-II unit cell, as described in (Takeuchi et al., 2013), and is shown in Figure 1.



**Figure 1.** The  $5^{12} + 5^{12}6^4$  cluster used as model for s-II clathrate hydrate.

The  $5^{12}+5^{12}6^4$  cluster was filled with CF<sub>3</sub>Br as the l-c (large cage) molecule and H<sub>2</sub>S, CO<sub>2</sub>, and CH<sub>4</sub> as the s-c (small cage) molecules. Each combination of l-c and s-c molecules within the  $5^{12}+5^{12}6^4$  cluster was subjected to an energy optimization procedure at the BLYP/6-31++G(d,p) level using Gaussian 16 (Frisch et al., 2016). The initial orientation of all s-c and l-c molecules was kept consistent across combinations and used as the input geometry. As a result of the DFT calculations, the total charge of the studied structure was determined to be 0, and its multiplicity was found to be 1. This indicates that the structure is a neutral and singlet-state system.

The interaction energies of the  $5^{12}+5^{12}6^4$  cluster filled by CF<sub>3</sub>Br as the l-c molecules, and H<sub>2</sub>S, CO<sub>2</sub>, CH<sub>4</sub> as the s-c molecules are calculated from the following equations;

 $\Delta E_1 = E (5^{12}+5^{12}6^4 \text{ cluster contains only s-c molecules}) - E (l-c and s-c empty 5^{12}+5^{12}6^4 \text{ cluster}) - E (s-c molecule monomer)$ 

 $\Delta E_2 = E (5^{12}+5^{12}6^4 \text{ cluster contains only l-c molecules}) - E (l-c and s-c empty 5^{12}+5^{12}6^4 \text{ cluster}) - E (l-c molecule monomer)$ 

 $\Delta E_3 = E (5^{12}+5^{12}6^4 \text{ cluster contains l-c and s-c molecules}) - E (l-c and s-c empty 5^{12}+5^{12}6^4 \text{ cluster}) - E (l-c molecule monomer) - E (s-c molecule monomer)$ 

#### 3. Results and discussion

#### **3.1. Dimer structures**

The optimized structures of the CF<sub>3</sub>Br····H<sub>2</sub>O, H<sub>2</sub>S····H<sub>2</sub>O, CO<sub>2</sub>····H<sub>2</sub>O, and CH<sub>4</sub>····H<sub>2</sub>O dimers are presented in Figure 2. In Table 1 presents the interaction energies, along with selected distances and angles, for the dimer molecules.

In the dimer structures presented in Figure 2, which were optimized, there is a weak van der Waals interaction between the  $CF_3Br$  molecule and the water molecule. Since  $CF_3Br$  is a polar molecule, it can interact strongly with the water molecule. This causes the oxygen atom of the water molecule to orient toward the  $CF_3Br$  molecule. The interaction between the  $H_2S$  molecule and the water molecule forms a structure where the sulfur atom (proton acceptor) interacts with the hydrogen atom of the water molecule

 $\begin{array}{c} & & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$ 

(proton donor). H<sub>2</sub>S, being a partially polar molecule, can form hydrogen bonds with the water molecule. These bonds are strong in terms of interaction energy.

Figure 2. Optimized structures of dimer structures at the BLYP/6-31++G(d,p).

**Table 1.** The interaction energies and some structural parameters for the the dimers of both s-c and l-c guests with the water molecule calculated at the BLYP method 6-31++G(d,p) level.

	Energy	Mean	Shor	test	Diameter	Distances (Å)	
System	(kcal/mol)	$\mathbf{O}_w \cdots \mathbf{O}_w$	Guest…O <sub>w</sub> (Å)		of cage (Å)	and angles (deg)	
		(Å)					
CF <sub>3</sub> Br···H <sub>2</sub> O	-4.2	-	$Br \cdots O_w$	2.95	-	Br-C	1.96
						C-F	1.36
						O-H	0.98
						H-O-H	105.1
						C- $Br$ ···O <sub>w</sub>	179.2
CH4····H2O	-0.1	-	$H \cdots O_w$	2.67	-	C-H	1.09
						O-H	0.97
						H-O-H	105.0
						H-C-H	109.7
						$C\text{-}H\text{-}\text{-}O_w$	178.9
CO <sub>2</sub> ···H <sub>2</sub> O	-3.4	-	$C \cdots O_w$	2.86	-	C-O	1.18
						O-H	0.97
						H-O-H	105.5
						0-C-0	177.8
						$C \cdots H_w - O_w$	127.3
H <sub>2</sub> S····H <sub>2</sub> O	-5.9	-	$S \cdots O_w$	2.55	-	H-S	1.35
						O-H	0.98
						H-O-H	105.1
						H-S-H	92.54
						$S \cdots H_w - O_w$	166.5

In the CH<sub>4</sub>···H<sub>2</sub>O interaction, the geometry of the structure illustrates the behavior between the hydrogen atom of the CH<sub>4</sub> molecule (proton donor) and the oxygen atom of the water molecule (electron acceptor). In the interaction between CO<sub>2</sub> and the water molecule, the carbon atom acts as an electron-accepting Lewis acid, while the water molecule acts as an electron-donating Lewis base. Despite being a linear molecule, CO<sub>2</sub> contains partially polar regions. These polar regions interact with the oxygen atom of the water molecule. The CF<sub>3</sub>Br, H<sub>2</sub>S, and CO<sub>2</sub> molecules exhibit stronger interactions with the water molecule compared to other molecules. This makes them more stable within clathrate hydrate structures. CH<sub>4</sub>, due to its apolar nature, exhibits weak interactions with water, which results in lower stability.

# 3.2. Double clathrate hydrates

The optimized structures of the  $5^{12}+5^{12}6^4$  cluster filled with CF<sub>3</sub>Br as the l-c molecule and H<sub>2</sub>S, CO<sub>2</sub>, and CH<sub>4</sub> as the s-c molecules are shown in Figures 3 and 4. In the present study, the primary contribution to the guest-host interactions arises from van der Waals interactions.

In Table 2 presents the interaction energies, along with selected distances and angles, for the  $5^{12}+5^{12}6^4$  cluster filled with CF<sub>3</sub>Br as the l-c molecule and H<sub>2</sub>S, CO<sub>2</sub>, and CH<sub>4</sub> as the s-c molecules. For comparison, the dimers of both the s-c and l-c guest molecules with a water molecule are also included (Table 1). It denotes the average oxygen-oxygen distance among all water molecules in the hydrate cage. The Ow symbol represents the oxygen atoms in the water molecules present in hydrate structures. The stability of clathrate hydrates and the properties of the cage structure vary depending on the Ow…Ow distance. The Ow…Ow distance indicates the width, compactness, and relationship of the hydrate structure with hydrogen bonds. While small guest molecules (e.g., CH<sub>4</sub>, CO<sub>2</sub>) do not significantly expand the cage, larger guest molecules (e.g., CF<sub>3</sub>Br) can increase the Ow…Ow distance.



**Figure 3.** Optimized structures for the  $5^{12}$  cluster filled by CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S as the s-c molecules. All calculations were done at the BLYP/6-31++G(d,p).

It is interesting to note that the shortest distances between the oxygen atoms of the cage water molecules and the guest molecules CF<sub>3</sub>Br, CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>S within the 5<sup>12</sup>6<sup>4</sup> cages are very similar to those observed in their respective dimers with water (shortest Guest…Ow distances). However, the angles (X…Yw, where Y = O or H) measured for the encaged molecules in the 5<sup>12</sup>6<sup>4</sup> cluster deviate from their respective dimer values. Specifically, the angles are as follows: 152–163° for encaged CF<sub>3</sub>Br compared to 179° for the CF<sub>3</sub>Br…H<sub>2</sub>O dimer; 159–163° for encaged CH<sub>4</sub> compared to 178° for the CH<sub>4</sub>…H<sub>2</sub>O dimer; 134–143° for encaged CO<sub>2</sub> compared to 127° for the CO<sub>2</sub>…H<sub>2</sub>O dimer; and 152–168° for encaged H<sub>2</sub>S compared to 166° for the H<sub>2</sub>S…H<sub>2</sub>O dimer.



**Figure 4.** Optimized structures for the  $5^{12}+5^{12}6^4$  cluster filled by CF<sub>3</sub>Br as the l-c molecule and CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S as the s-c molecules. All calculations were done at the BLYP/6-31++G(d,p).

The interaction energies of different cage structures obtained as a result of geometric optimizations are given in Figure 5. In Table 2, the interaction energies of the l-c molecules ( $\Delta E_1$ ) when the s-c is empty and those of the s-c molecules ( $\Delta E_2$ ) when the l-c is empty are provided. It is well established that host-guest interactions determine the stability of clathrate hydrate structures. Previous studies have shown that s-c molecules contribute to the catalytic activity of large-cage molecules. In other words, certain s-c molecules enhance the hydrogen bonding behavior of l-c molecules. (Davidson, 1973; Demurov et al., 2002; Buch et al., 2004; Buch et al., 2009; Alavi & Ripmeester, 2012; Fan et al., 2013; Takeuchi et al., 2013; An et al., 2018; Ghosh et al., 2019a; Ghosh et al., 2019b). According to the values given in Figure 5, negative interaction energy indicates that the configuration is energetically favorable and stable. This means that guest molecules (such as H<sub>2</sub>S, CO<sub>2</sub>, CH<sub>4</sub>, etc.) form a stable interaction with the cage structure. The cage structures containing CF<sub>3</sub>Br generally have more negative energy values, meaning they are more stable. When small cages are filled while large cages remain empty, the structures have positive interaction energies, indicating that they are less stable without guest molecules.

The interaction energies of both 1-c and s-c molecules ( $\Delta E_3$ ) when they are present together are also given in Table 2. The results indicate that the interaction energy of CH<sub>4</sub>@5<sup>12</sup> with an empty 5<sup>12</sup>6<sup>4</sup> cage (4.84 kcal/mol) is lower than that of CO<sub>2</sub>@5<sup>12</sup> with an empty 5<sup>12</sup>6<sup>4</sup> cage (3.36 kcal/mol). For 5<sup>12</sup>/(guest)@5<sup>12</sup>6<sup>2</sup> clusters, the interaction energy increases with the molecular size of the guest molecule encapsulated in the 5<sup>12</sup>6<sup>2</sup> cavity. Similarly, for CH<sub>4</sub>@5<sup>12</sup> with an empty 5<sup>12</sup>6<sup>4</sup> cage, when the 5<sup>12</sup>6<sup>4</sup> cavity is filled with a CF<sub>3</sub>Br molecule, the interaction energy reaches -8.65 kcal/mol. The same trend is observed when CO<sub>2</sub> is in the small cage and CF<sub>3</sub>Br is in the large cage. For CO<sub>2</sub>@5<sup>12</sup> with an empty 5<sup>12</sup>6<sup>4</sup> cage and H<sub>2</sub>S@5<sup>12</sup> with an empty 5<sup>12</sup>6<sup>4</sup> cage, when the 5<sup>12</sup>6<sup>4</sup> cavity is filled with a CF<sub>3</sub>Br molecule, the interaction energies are -10.1 kcal/mol and -11.5 kcal/mol, respectively. The stability of the guest molecules relative to one another was analyzed under the condition referred to as equivalency ratios. The stability of the guest molecules relative to one another was analyzed using equivalency ratios, which compare the interaction energies are empty or occupied by

 $CF_3Br$ , the interaction energies of small-cage guests follow the order  $H_2S > CO_2 > CH_4$ . This indicates that  $H_2S$  exhibits the strongest interaction with the hydrate framework, followed by  $CO_2$  and  $CH_4$ . The equivalency ratio approach allows for a systematic comparison of the relative stability of guest molecules based on their binding strengths and preferred occupancy within the hydrate structure.



**Figure 5.** The optimized interaction energies for the  $5^{12}+5^{12}6^4$  cluster filled with CF<sub>3</sub>Br as the large-cage (l-c) molecule and HCN, CO<sub>2</sub>, and H<sub>2</sub>S as the small-cage (s-c) molecules, calculated at the BLYP method and 6-31++G(d,p) level.

When the small cages are filled with CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>S molecules while the large cages remain empty, the interaction energies follow the order H<sub>2</sub>S > CO<sub>2</sub> > CH<sub>4</sub>. When the large cages are filled with CF<sub>3</sub>Br molecules, the order remains the same: H<sub>2</sub>S > CO<sub>2</sub> > CH<sub>4</sub>. The results indicate that the CF<sub>3</sub>Br molecule interacts more strongly with the cage compared to the others. Among the small cage molecules, H<sub>2</sub>S contributes the most to the stability of the CF<sub>3</sub>Br molecule, with an interaction energy of -11.5 kcal/mol, while CH<sub>4</sub> contributes the least, with -8.65 kcal/mol. When compared individually, the energy values of the guest gas molecules vary depending on their positions and orientations within the cages. The polarization effects of water in these rings also influence the stability of the cage, along with the molecules in the small cage. The analysis of energy values for dimer structures formed by small and large cage guests with water reveals that the interaction energy follows the order H<sub>2</sub>S > CO<sub>2</sub> > CH<sub>4</sub>. These findings suggest that the interactions observed in dimers are also present within cage structures. Similar to the results of previous studies (Uras-Aytemiz et al., 2012), it demonstrates that these interactions play a critical role in determining the stability of the cage.

In the presence of guest molecules in the small cage, it was observed that the interaction strength increased when the CF<sub>3</sub>Br molecule was introduced into the large cage, compared to the case where the large cage was empty. Furthermore, the stability of the hydrates increases with the molecular size of the guest molecules in the cages, as well as with the interaction between the guest molecules and the water molecules (An et al., 2018).

**Table 2.** The interaction energies and some structural parameters for the  $5^{12}+5^{12}6^4$  cluster filled by CF<sub>3</sub>Br as the l-c molecules, and HCN, CO<sub>2</sub> and H<sub>2</sub>S as the s-c molecules calculated at the BLYP/6-31++G(d,p).

System	Energy (kcal/mol)	Mean O <sub>w</sub> …O <sub>w</sub> (Å)		Shortest GuestO <sub>w</sub> (Å)		Diameter of cage (Å)		Distances (Å) and angles (deg)	
empty $5^{12}$ + empty $5^{12}6^4$		S-C	2 75		,	8-C	7 75		
chipty of a chipty of t		1-c	2.75	_		1-c	8 85	_	
empty 5 <sup>12</sup> + CF <sub>3</sub> Br@5 <sup>12</sup> 6 <sup>4</sup>		s-c	2.75	Br···O	3.54	s-c	7.95	Br-C	1.95
····· <b>p</b> ·· <b>j</b> ···························	$\Delta E_2 = -12.6$			21 0 w	010 .			C-F	1.36
								F-C-Br	111.0
								$C\text{-}Br \cdots O_w$	163.4
		l-c	2.75	-		l-c	8.85	-	
$CH_4@5^{12} + empty 5^{12}6^4$		S-C	2.75	$H \cdots O_w$	2.81	s-c	7.75	C-H	1.09
	$\Delta E_1 = 4.84$							н-с-н	109.8
		1.0	2 75			1.0	0 05	C-H···O <sub>w</sub>	159.6
		1-0	2.75	-		1-0	0.05	-	
$CO_2@5^{12} + empty 5^{12}6^4$	AE 2.26	S-C	2.75	$C \cdots O_w$	3.07	s-c	8.05	C-0	1.18
	$\Delta E_1 = 3.36$							0-C-0	1/9.3
		l-c	2 75	_		1-c	8 85	С-0…п <sub>w</sub>	134.4
$11 S @ 5^{12} + compty 5^{12} c^4$		10	2.15	U. O	0.21	10	7.75	ПС	1.26
$H_2S@S + empty 5 6$	AE = 1.53	s-c	2.05	H···O <sub>w</sub>	2.31	s-c	1.15	н-5 иси	1.30
	$\Delta E_{1} = 1.55$							S-H···O	167.7
		l-c	2.75	-		1-c	8 85	-	10,11,
CH4@5 <sup>12</sup> + CF3Br @5 <sup>12</sup> 6 <sup>4</sup>		s-c	2.75	H···Ow	2.77	s-c	7.65	C-H	1.09
	$\Delta E_3 = -8.65$					~ -		Н-С-Н	109.2
								$C-H\cdots O_w$	163.5
		l-c	2.65	$Br{\cdots}O_w$	3.58	l-c	8.85	Br-C	1.95
								C-F	1.36
								F-C-Br	111.3
$\overline{(0,0,0,0)}$			0.75	0.0	2.00		7.05	$C-Br\cdots O_w$	152.1
$CO_2 @ 5^{-2} + CF_3 Br @ 5^{-2} 6^{-2}$	AE = 10.1	S-C	2.75	$C \cdots O_w$	2.99	s-c	7.85	C-O	1.18
	$\Delta L_3 = -10.1$							C-OH	1/9.4
		l-c	2.65	Br···O	3.45	1-c	8.85	Br-C	1.95
				~ ~ w				C-F	1.36
								F-C-Br	111.1
								$C\text{-}Br {\cdots} O_w$	154.8
$H_2S@5^{12} + CF_3Br @5^{12}6^4$		s-c	2.75	$H{\cdots}O_w$	2.25	s-c	7.75	H-S	1.36
								H-S-H	91.8
	$\Delta E_3 = -11.5$	1.	275	D., O	264	1.	0.05	S-H···O	166.1
		1-C	2.15	BLO <sup>w</sup>	3.04	1-C	8.85	BI-U C-F	1.95
								E-C-Br	111 1
								$C-Br\cdots O_w$	152.5

# 4. Discussion and conclusions

The results were discussed in terms of the stability of the  $CF_3Br$  molecule in the large cage and how the stability of the specified clathrate hydrates changes in the presence of small guest molecules (H<sub>2</sub>S, CO<sub>2</sub>, CH<sub>4</sub>) placed in the small cage. The structure of an empty cage in the double cage system was found to be less stable than the double cage structure in which both cages were occupied by guest molecules. Compared to empty cages, the cages containing guest molecules were more stable.

In the presence of guest molecules in the small cage, it was observed that the interaction increased when the CF<sub>3</sub>Br molecule was introduced into the large cage, compared to when the large cage was empty. This interaction was particularly stronger when an H<sub>2</sub>S molecule was present in the small cage, compared to other small cage guest molecules such as CH<sub>4</sub> and CO<sub>2</sub>. Here, the first steps were taken using the strong catalyst

CF<sub>3</sub>Br, providing further insights into enhancing catalytic power and versatility through the combination of catalysts. The placement of CF<sub>3</sub>Br in the large cage (l-c) enhanced the guest-host interactions, thereby increasing the stability of the structure. This demonstrated the potential applicability of clathrate hydrates in energy storage systems. It was observed that as the molecular weight of the guest molecule increases (e.g., H<sub>2</sub>S, CO<sub>2</sub>), the guest-host interactions become even stronger. This indicates the potential for achieving higher energy density and greater energy storage capacity.

From the results obtained by examining the stability of guest molecules in double cages, it has been observed that the presence of guest molecules in the cages influences each other. The effect of other alkanes on the stability of the double cage will also be explored in future studies. In addition to contributing to basic science, the findings of this study will advance hydrate research. In particular, these results are significant in providing a molecular perspective to recent and ongoing experimental studies (at low temperatures in crystal structures) on clathrate hydrates. Overall, understanding the physical chemistry of gas hydrates is valuable not only for the science of hydrogen-bonded systems but also for future technological advancements.

#### Acknowledgement

The numerical calculations in this article were partially performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources).

# Author contribution

The entire article was written by the primary author.

# **Declaration of ethical code**

The author of this article declares that the materials and methods used in this study do not require ethical committee approval and/or legal-specific permissions.

#### **Conflicts of interest**

The author declares that there is no conflict of interest.

#### References

- Alavi, S., Udachin, K., & Ripmeester, J. A. (2010). Effect of guest-host hydrogen bonding on the structures and properties of clathrate hydrates. *Chemistry A European Journal*, 16(3), 1017–1025. https://doi.org/10.1002/chem.200902351
- Alavi, S., & Ripmeester, J. A. (2012). Effect of small cage guests on hydrogen bonding of tetrahydrofuran in binary structure II clathrate hydrates. *The Journal of Chemical Physics*, 137(5), 054712. https://doi.org/10.1063/1.4739928
- An, T., Zhang, H., Zhang, Q., Wang, Y., & Shi, P. (2018). Influence of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> molecules on stability of doublecage of sI clathrate hydrate. *Computational and Theoretical Chemistry*, 1123, 128-134. https://doi.org/10.1016/j.comptc.2017.11.019
- Buch, V., Bauerecker, S., Devlin, J. P., Buck, U., & Kazimirski, J. K. (2004). Solid water clusters in the size range of tens-thousands of H<sub>2</sub>O: A combined computational/spectroscopic outlook. *International Reviews in Physical Chemistry*, 23(3), 375-433. https://doi.org/10.1080/01442350412331316124
- Buch, V., Devlin, J. P., Monreal, I. A., Jagoda-Cwiklik, B., Uras-Aytemiz, N., & Cwiklik, L. (2009). Clathrate hydrates with hydrogen-bonding guests. *Physical Chemistry Chemical Physics*, 11(44), 10245-10265. https://doi.org/10.1039/B911600C

Davidson, D. W. (1973). Water: A Comprehensive Treatise. In F. Franks (Ed.), Plenum, New York.

- Demurov, A., Radhakrishnan, R., & Trout, B. L. (2002). Computations of diffusivities in ice and CO<sub>2</sub> clathrate hydrates via molecular dynamics and Monte Carlo simulations. *The Journal of Chemical Physics*, 116(2), 702-709. https://doi.org/10.1063/1.1425821
- Devlin, J. P., & Monreal, I. A. (2010a). Instant Conversion of Air to a Clathrate Hydrate: CO<sub>2</sub> Hydrates Directly from Moist Air and Moist CO<sub>2</sub>(g). *The Journal of Physical Chemistry A*, 114(50), 13129-13133. https://doi.org/10.1021/jp110614e
- Devlin, J. P., & Monreal, I. A. (2010b). Clathrate-hydrate ultrafast nucleation and crystallization from supercooled aqueous nanodroplets. *Chemical Physics Letters*, 492(1-3), 1-8. https://doi.org/10.1016/j.cplett.2010.03.072
- Falenty, A., & Kuhs, W. F. (2009). "Self-preservation" of CO<sub>2</sub> gas hydrates: Surface microstructure and ice perfection. *The Journal of Physical Chemistry B*, 113(49), 15975–15988. https://doi.org/10.1021/jp906859a
- Falenty, A., Hansen, T. C., & Kuhs, W. F. (2014). Formation and properties of ice XVI obtained by emptying a type sII clathrate hydrate. *Nature*, *516*(7530), 231–233. https://doi.org/10.1038/nature14014
- Fan, X., Xu, L., Liu, L., Minghui, Y., Qun, Z., & Mingli, Y. (2013). Polarization response of methane encapsulated in water cages. *Computational and Theoretical Chemistry*, 1013, 52-56. https://doi.org/10.1016/j.comptc.2013.03.013
- Fleyfel, F., & Devlin, J. P. (1988). FT-IR spectra of 90 K films of simple, mixed, and double clathrate hydrates of trimethylene oxide, methyl chloride, carbon dioxide, tetrahydrofuran, and ethylene oxide containing decoupled water-d2. *The Journal of Physical Chemistry*, 92(3), 631-635. https://doi.org/10.1021/j100314a013
- Fleyfel, F., Richardson, H. H., & Devlin, J. P. (1990). Comparative sulfur dioxide infrared spectra: Type I and II clathrate hydrate films, large gas-phase clusters, and anhydrous crystalline films. *The Journal of Physical Chemistry*, 94(18), 7032-7037. https://doi.org/10.1021/j100381a021
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., et al. (2016). Gaussian 16, Revision C.01. Gaussian Inc., Wallingford CT.
- Ghosh, J., Bhuin, R. G., Ragupathy, G., & Pradeep, T. (2019a). Spontaneous Formation of Tetrahydrofuran Hydrate in Ultrahigh Vacuum. *The Journal of Physical Chemistry C*, 123, 16300-16307. https://doi.org/10.1021/acs.jpcc.9b04370
- Ghosh, J., Methikkalama, R. R. J., Bhuin, R. G., Ragupathy, G., Choudhary, N., Kumar, R., & Pradeep, T. (2019b). Clathrate hydrates in interstellar environment. *Proceedings of the National Academy of Sciences of the United States of America*, 116, 1526-1531. https://doi.org/10.1073/pnas.1814293116
- Gulluru, D. B., & Devlin, J. P. (2006). Rates and Mechanisms of Conversion of Ice Nanocrystals to Ether Clathrate Hydrates: Guest-Molecule Catalytic Effects at ~120 K. *The Journal of Physical Chemistry A*, 110(5), 1901-1906. https://doi.org/10.1021/jp056254u
- Hernandez, J., Uras, N., & Devlin, J. P. (1998). Coated Ice Nanocrystals from Water–Adsorbate Vapor Mixtures: Formation of Ether–CO<sub>2</sub> Clathrate Hydrate Nanocrystals at 120 K. *The Journal of Physical Chemistry B*, 102(23), 4526-4535. https://doi.org/10.1021/jp9811474
- Jacobson, L. D., & Herbert, J. M. (2010). An efficient, fragment-based electronic structure method for molecular systems: Self-consistent polarization with perturbative two-body exchange and dispersion. *Journal of Chemical Physics*, 133(15), 154108. https://doi.org/10.1063/1.3490188
- Kvamme, B., Graue, A., Buanes, T., Kuznetsova, T., & Ersland, G. (2007). Storage of CO<sub>2</sub> in natural gas hydrate reservoirs and the effect of hydrate as an extra sealing in cold aquifers. *International Journal of Greenhouse Gas Control*, 1(2), 236–246. https://doi.org/10.1016/S1750-5836(06)00002-8
- Richardson, H. H., Wooldridge, P. J., & Devlin, J. P. (1985). FT-IR spectra of vacuum deposited clathrate hydrates of oxirane, H<sub>2</sub>S, THF, and ethane. *The Journal of Chemical Physics*, 83(9), 4387-4394. https://doi.org/10.1063/1.449055
- Sloan, E. D. (2023). Fundamental principles and applications of natural gas hydrates. *Nature*, 426(6964), 353-359. https://doi.org/10.1038/nature02135

Sloan, E. D., & Koh, C. A. (2008). Clathrate Hydrates of Natural Gases. 3rd ed. Taylor & Francis, New York.

- Staykova, D. K., Kuhs, W. F., Salamatin, A. N., & Hansen, T. (2003). Formation of porous gas hydrates from ice powders: Diffraction experiments and multistage model. *The Journal of Physical Chemistry B*, 107(37), 10299-10311. https://doi.org/10.1021/jp027787v
- Takeuchi, F., Hiratsuka, M., Ohmura, R., Alavi, S., Sum, A. K., & Yasuoka, K. (2013). Water proton configurations in structures I, II, and H clathrate hydrate unit cells. *The Journal of Chemical Physics*, 138(12), 124504. https://doi.org/10.1063/1.4795499
- Uchida, T., Takeya, S., Kamata, Y., Ikeda, I. Y., Nagao, J., Ebinuma, T., Narita, H., Zatsepina, O., & Buffett, B. A. (2002). Spectroscopic observations and thermodynamic calculations on clathrate hydrates of mixed gas containing methane and ethane: Determination of structure, composition, and cage occupancy. *The Journal of Physical Chemistry B*, 106(48), 12426-12431. https://doi.org/10.1021/jp025884i
- Uras-Aytemiz, N., Cwiklik, L., & Devlin, J. P. (2012). Tracking all-vapor instant gas-hydrate formation and guest molecule populations: A possible probe for molecules trapped in water nanodroplets. *The Journal of Chemical Physics*, 137(20), 204501. https://doi.org/10.1063/1.4767370
- Uras-Aytemiz, N., Monreal, I. A., & Devlin, J. P. (2011). Communication: Quantitative Fourier-transform infrared data for competitive loading of small cages during all-vapor instantaneous formation of gas-hydrate aerosols. *The Journal of Chemical Physics*, 135(14), 141103. https://doi.org/10.1063/1.3652756
- Yang, Y., Yu, H., York, D., Cui, Q., & Elstner, M. (2015). Extension of the Self-Consistent-Charge Density-Functional Tight-Binding Method: Third-Order Expansion of the Density Functional Theory Total Energy and Introduction of a Modified Effective Coulomb Interaction. *Journal of Physical Chemistry A*, 119(3), 620–632. https://doi.org/10.1021/jp508006r