Computational density-functional approaches on finite-size and guest-lattice effects in CO₂@sII clathrate hydrate

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ABSTRACT

We performed first-principles computations to investigate guest–host/host–host effects on the encapsulation of the CO₂ molecule in sII clathrate hydrates from finite-size clusters up to periodic 3D crystal lattice systems. Structural and energetic properties were first computed for the individual and first-neighbors clathrate-like sII cages, where highly accurate *ab initio* quantum chemical methods are available nowadays, allowing in this way the assessment of the density functional (DFT) theoretical approaches employed. The performance of exchange–correlation functionals together with recently developed dispersion-corrected schemes was evaluated in describing interactions in both short-range and long-range regions of the potential. On this basis, structural relaxations of the CO₂-filled and empty sII unit cells yield lattice and compressibility parameters comparable to experimental and previous theoretical values available for sII hydrates. According to these data, the CO₂ enclathration in the sII clathrate cages is a stabilizing process, either by considering both guest–host and host–host interactions in the complete unit cell or only the guest–water energies for the individual clathrate-like sII cages. CO₂@sII clathrates are predicted to be stable whatever the dispersion correction applied and in the case of single cage occupancy are found to be more stable than the CO₂@sI structures. Our results reveal that DFT approaches could provide a good reasonable description of the underlying interactions, enabling the investigation of formation and transformation processes as a function of temperature and pressure.

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I. INTRODUCTION

Gas hydrates or clathrates are complex crystalline structures, made up of H-bonded water molecules forming a network with cages of different shapes and sizes, where guest molecules can get trapped under appropriate thermodynamic (temperature and pressure) conditions.^{1,2} These compounds are naturally abundant in Earth's permafrost regions and deep sea sediments and are also likely to occur in other planetary bodies.^{3,4} On a more general perspective, they are considered as potential energy sources (e.g., CH₄ and H₂ clathrates) or promising materials for gas storage (e.g., CO₂ clathrates) with outstanding importance for gas-control technologies.^{5–16}

Understanding fundamental properties of such gas hydrates is crucial for their future exploitation and applications. Therefore, numerous experimental and theoretical efforts have been devoted to

investigating the structure and stability, formation and dissociation mechanisms, and physical properties of a variety of gas hydrates.^{17–33}

The most common types of crystalline structures for the gas hydrates are as follows: sI (structure I), sII (structure II), and sH (structure H). The specific structure depends on the size of the guest molecule, as well as the temperature–pressure conditions. Furthermore, as temperature and/or pressure increases, structural transformation from one structure to another may occur, as well as the possible coexistence of structures, or even stabilization of one structure can be triggered by adding more guest molecules.

For example, CO₂ clathrates have been mainly found in the sI crystal structure, and binary CO₂@sH clathrate hydrates have also been reported, while there are some evidence of metastable sII-type ones.^{34–36} As they can be synthesized in the laboratory under specific conditions, various structural and spectroscopic measurements, through x-ray, powder x-ray, and neutron diffraction,

solid-state nuclear magnetic resonance (NMR), Raman, and infrared spectroscopy investigations have been reported.^{37–41} From a theoretical point of view, there are several molecular dynamics simulations using semiempirical potentials to study the occupancy of sI and sH clathrates,^{42–55} some of them supporting the single occupation of the sI cages⁵¹ through a comparison with trends observed in IR vibrational CO₂ stretching frequency shifts in solid hydrates,⁴⁰ as well as *ab initio* electronic structure studies focused on the interaction between a cage (host) and a guest (CO₂ molecules), the stability of clathrate hydrates cages,^{56–63} and the evaluation of the molecular vibrations of the guest molecule/s.^{64–66} More recently, the performance of 45 density functional theory including dispersion corrections (DFT-D) functionals has been systematically evaluated for describing intermolecular interactions of CO₂ in all sI, sII, and sH isolated cavities,⁶² concluding on the rotational ability and orientational preference of CO₂ in the large sI and sH clathrate cages in accord with previous experimental and theoretical studies.^{39–41,51,55,60,61,63} Earlier *ab initio* and first-principles studies were only limited to the cluster models, and more recently, DFT-D calculations for the CO₂@sI and CO₂@sH crystal lattices^{60,67–69} investigating their structural stability and storage capacity of the cavities have been reported.

Despite the above-mentioned efforts and some experimental evidence of metastable CO₂@sII clathrates, to the best of our knowledge, there is no any theoretical study for the CO₂ molecule/s encapsulated in the crystalline sII hydrate structure. The whole set of previous studies available outlines the importance of guest–water (host) interactions in the stability of the gas hydrates, while crystal lattice (host–host) effects should also be taken into account for their full description. Nowadays, first-principles calculations within the DFT-D formalism are commonly used for studying molecular interaction in the condensed phase.⁷⁰ Although dealing with clathrates represents a challenging task, as one should correctly describe, within the same methodology, both the intramolecular hydrogen-bond interactions between water molecules in the host lattice, as well as the van der Waals (vdW) interactions between the trapped molecule and host water cages.^{71–75} Thus, in the framework of the CO₂ clathrates, we performed DFT-D calculations on the structural properties and stability of the sII structure by considering the guest–host (cage/s) interactions in finite-size clathrate-like cages, where valuable additional information can also be obtained from *ab initio* wavefunction (WF) based calculations, as well as guest–host

(lattice) effects in the complete sII unit cell. On the basis of previous investigations on CO₂@sI clathrates,^{60,62,63,67–69} specific exchange–correlation functionals were employed in the CO₂@sII case, including dispersion corrections, in order to fully represent the underlying interactions.

II. COMPUTATIONAL DETAILS

The sII host-lattice contains individual dodecahedral (5¹² or D) and hexadecahedron (5¹²6⁴ or H) cages (see the left panel of Fig. 1), while combinations of them, present in the sII crystal, are displayed in the middle panel of Fig. 1. Individual cages are chosen to explore guest–cage interactions, while such two-adjacent cage systems were selected to study any further inter-cage first-neighbors effects. The two-adjacent cages correspond to the small–small (namely, CO₂@DD) cages with 35 water molecules, small–large (namely, CO₂@DH) cages with 43 water molecules sharing a pentagonal face, and large–large (namely, CO₂@HH) cages with 50 water molecules sharing a hexagonal face (see the middle panel of Fig. 1). The bulk CO₂@sII clathrate hydrate crystal structure is shown in the right panel of Fig. 1, together with its unit cell (see the black colored box). The cubic unit cell (with space group Fd3m) has 136 water molecules forming in total 24 cavities: 16 5¹² cages with 20 water molecules each and eight 5¹²6⁴ cages with 28 water molecules each. The empty sII clathrate crystal structure is taken from the 3D crystalline framework given in Ref. 76, with the oxygen atoms' positions extracted from the x-ray diffraction experiments, while the hydrogen atoms' orientations have been determined from TIP4P water model optimizations, satisfying both zero dipole moment and ice rules for the unit cell configuration.⁷⁶ Individual and two-adjacent cage systems were obtained from the empty 3D sII crystal using the DENEb software package,⁷⁷ choosing the specific proton distributions (see Fig. 1), as all different distributions of them show similar potential energies.

Electronic structure DFT calculations were performed for both periodic cubic CO₂@sII and sII unit shells, as well as for aperiodic clusters using the Quantum Espresso (QE) code^{78,79} and Gaussian⁸⁰ package, while WF-based computations were carried out for the empty and CO₂-filled clathrate-like D, H, DD, DH, and HH cages with Molpro⁸¹ and ORCA⁸² packages. In particular, reference interaction energies for such cages were obtained from

FIG. 1. Left panel: CO₂@5¹² (D) and CO₂@5¹²6⁴ (H) individual clathrate cages. Middle panel: Two-adjacent DD, DH, and HH CO₂@sII cages. Right panel: Bulk CO₂@sII clathrate hydrate crystal structure, with the black box indicating its unit cell. The red color corresponds to the oxygen atoms, the gray color corresponds to hydrogens, and the turquoise color corresponds to carbons.

the domain-based local pair natural orbital coupled cluster theory with single, double, and perturbative triple excitations (DLPNO-CCSD(T)) approach and Möller–Plesset perturbation theory, such as density fitting DF-MP2, as implemented in the ORCA^{82,83} and Molpro⁸¹ packages of codes, respectively. The correlation-consistent aug-cc-pVXZ (AVXZ) basis sets (with X = T, Q, 5)⁸⁴ were employed in the conventional methods for orbital expansion, auxiliary basis sets were employed for the resolution of the identity (OptRI), and density fitting of the Fock, exchange, and two-electron integrals (JKfit, MP2fit/CCSDfit) was employed for the DLPNO and DF variants.^{81,82} Furthermore, as part of the DLPNO scheme, the correlation fitting basis set aug-cc-pVTZ/C was used for the resolution of identity approximation, and tight threshold for both SCF and PNO settings was chosen to ensure convergence and reduce numerical noise, respectively. The counterpoise (CP) corrections,⁸⁵ E_{CP} , were applied to energies to reduce the basis set superposition error (BSSE) effects in the present calculations. On the basis of previous studies,^{60–63,67–69} we choose to employ the revPBE, PW86PBE, and B3LYP functionals in the DFT calculations using the standard implementation in the LIBXC library.⁸⁶ The additional dispersion corrections are included using the exchange dipole moment (XDM), D3, and D4 many-body schemes,^{87–91} as implemented in the POSTG code⁹² and DFTD3/DFTD4 programs,^{93,94} respectively.

The DFT calculations for the isolated cage/s were performed at the Γ -point only, in a cubic simulation cell of volume $30 \times 30 \times 30 \text{ \AA}^3$. The Makov–Payne method of electrostatic interaction correction was considered for these aperiodic systems, where the convergence of the energy is determined by the longest-ranged forces, which usually are electrostatic interactions, evaluated in the limit of large supercells.⁹⁵ Regarding the DFT computations for the periodic $\text{CO}_2@s\text{II}$ and empty $s\text{II}$ unit cells, the plane wave/pseudopotential approach within the projector-augmented-waves (PAW) method⁹⁶ was employed using the standard PAW pseudopotentials, such as the PBE (Perdew–Burke–Ernzerhof)- and BLYP (Becke’s exchange functional with the correlation functional by Lee, Yang, and Parr) based pseudopotential supplied within the QE code. The energy cut-off for the plane wave expansion of the wavefunctions, $E_{\text{cut}}(\text{wfc})$, was chosen at 60 Ry (816 eV) and charge density, $E_{\text{cut}}(\rho)$, at 300 Ry (4081 eV) (see the convergence of total energies for few selected functionals in Fig. S1 of the [supplementary material](#)). A Monkhorst–Pack $2 \times 2 \times 2$ k -point grid⁹⁷ in the reciprocal space was used per unit cell. Full and partial geometry optimizations were performed by relaxing all atomic positions or only those of the CO_2 keeping fixed the water cage framework, respectively. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newton algorithm was employed until components of forces are smaller than $0.05 \text{ eV/\AA}$.

The cohesive energies per water molecule for the fully occupied $\text{CO}_2@s\text{II}$ and the empty $s\text{II}$ hydrates were computed as $\Delta E_{\text{coh}}^{\text{CO}_2@s\text{II}}(a) = \frac{E_{\text{CO}_2@s\text{II}}(a) - 136E_{\text{H}_2\text{O}} - 24E_{\text{CO}_2}}{136}$ and $\Delta E_{\text{coh}}^{\text{empty}(s\text{II})} = \frac{E_{\text{empty}(s\text{II})}(a_0) - 136E_{\text{H}_2\text{O}}}{136}$, respectively, where $E_{\text{CO}_2@s\text{II}}(a)$ and $E_{\text{H}_2\text{O}}/E_{\text{CO}_2}$ are the total energies of the fully occupied $\text{CO}_2@s\text{II}$ hydrate unit cell with a lattice constant a and the isolated ground-state $\text{H}_2\text{O}/\text{CO}_2$ molecules, respectively, while $E_{\text{empty}(s\text{II})}(a_0)$ is the total energy of the empty $s\text{II}$ hydrate unit cell at the equilibrium lattice constant a_0 . Thus, the binding energy per CO_2 molecule encaged in the empty $s\text{II}$ crystal unit cell is given by

$$\Delta E^{\text{CO}_2@s\text{II}} = \frac{E_{\text{CO}_2@s\text{II}}(a_0) - E_{\text{empty}(s\text{II})}(a_0) - 24E_{\text{CO}_2}}{24}. \quad (1)$$

In turn, the binding energies of CO_2 molecules trapped in isolated (D, H, DD, DH, HH) $s\text{II}$ cages are computed as the difference of the total energy of the CO_2 -occupied cage/s and the energies of the empty cage/s and the CO_2 molecules, $\Delta E = E_{\text{CO}_2@s\text{II cage}}^{\text{opt}} - E_{s\text{II cage}}^{\text{opt}} - nE_{\text{CO}_2}^{\text{opt}}$, at the corresponding full or partial geometry-optimized configuration, as described above, of $\text{CO}_2@D/H/DD/DD/HH$, with n being maximum one CO_2 molecule per cage. In addition, the cohesive energies for each N water cage (empty) system are obtained as the difference of the cluster energy and the energies of the geometry-relaxed water monomers, $\Delta E_{\text{coh}} = E(s\text{II cage})_{N=20,28,35,43,50} - N \cdot E_{\text{H}_2\text{O}}$.

III. RESULTS AND DISCUSSION

A. Clathrate-like clusters: Individual and two-adjacent $\text{CO}_2@s\text{II}$ cages

We first considered the D and H individual cages (see the left panel of Fig. 1) in the $s\text{II}$ cubic unit cell, and we computed

FIG. 2. Interaction and cohesive energies (per water molecule in kcal/mol) for the individual CO_2 -filled and empty D and H cages, respectively, obtained from the indicated DFT-D and DLPNO-CCSD(T)/AVTZ (dashed lines) calculations. Solid lines correspond to the DF-MP2/CBS(TQ) (binding energies for $\text{CO}_2@D/H$) and DF-MP2/CBS(Q5) (cohesive energies for D/H) data from Refs. 62 and 98, respectively.

interaction and cohesive energies of the CO₂-filled and empty sII cages, respectively. In Fig. 2, we display the energy values obtained using the PW86PBE, revPBE, and B3LYP functionals together with specific dispersion corrections, as they have been previously found to have better performed in CO₂@sI clathrates,^{60,62,63} together with the cohesive energies of the empty H and D cages (see Table S1 of the supplementary material). For both CO₂-filled and empty D and H individual sII cages, we also carried out DLPNO-CCSD(T) calculations at the same configurations, and the obtained interaction energies are displayed in Fig. 2 (see vertical dashed lines). Furthermore, reference DF-MP2/CBS binding energy values are available in the literature⁶² for the optimized geometries of each CO₂@D and CO₂@H cage, as well as cohesive energies for the empty D and H cages⁹⁸ (see vertical solid lines in Fig. 2). In the case of the CO₂@D/H cages, such DF-MP2 values serve as an upper limit of the corresponding DLPNO-CCSD(T) or DFT-D interaction energies.

By comparing the DFT-D functionals with these reference data from WF-based methods, one can see that the estimates of the PW86PBE functional with D4 and XDM dispersions are close to the DLPNO-CCSD(T)/AVTZ data for both CO₂@D and CO₂@H cages, while the same functional with D3(BJ) corrections underestimates such energy with respect the DLPNO references, as well as revPBE-D3(0) and B3LYP with D3(BJ) and D4 schemes. revPBE-D3(BJ) also underestimates interaction energy for the CO₂@D cage, although it produces a close value for the CO₂@H, considering the DLPNO-CCSD(T) data. With respect to the cohesive energy of the empty D and H cages, the PW86PBE functional with D3(BJ), D4, and XDM corrections overestimates these energies compared to the DF-MP2 and DLPNO reference data, while

all remaining functionals underestimate them, with B3LYP-D3(BJ) and D4 yielding the closest values to the DF-MP2/CBS calculations. All functionals studied here predict that CO₂@5¹² configurations are more stable than the CO₂@5¹²6⁴ ones, while empty D and H cages show similar values of cohesive energies.

Furthermore, we also checked the performance of these functionals at selected representative configurations, aiming to extract further information on a well-balanced description of the guest-host interaction in the CO₂@D/H sII cages. In Fig. 3, we display the interaction energy as CO₂ moves along the the Z axis with its orientation fixed at $(\theta, \phi) = (60^\circ, 90^\circ)$ and $(90^\circ, 180^\circ)$ in the D and H cages, respectively, where θ and ϕ are the polar and azimuthal angles, respectively. One can see certain differences in the potential curves, corresponding to their well-depths, as well as in the repulsive part of them close to potential barriers. Potential curves show very similar behavior around the equilibrium configurations for all functionals studied, as well as for the DF-MP2/CBS and DLPNO-CCSD(T) calculations. The D cage is formed by 12 pentagons, while the H cage is anisotropic, consisting of four six-membered and twelve five-membered water rings. Thus, for the CO₂@D cage, the curves are symmetric to the Z axis directions, with barriers corresponding to CO₂ at the center of a pentagon face of the D cage, while for the CO₂@H cage system, the curves are different in the +Z and -Z directions, influenced by the asymmetry of the H cage, as CO₂ is approaching different faces of this cage along the Z axis, such as the center of a hexagon along the -Z direction or a water molecule shared by three pentagons in the +Z direction. In general, the DFT-D calculated curves show similar behavior, with the PW86PBE-XDM energies being lower than the DLPNO-CCSD(T) results for both CO₂@D and CO₂@H cages,

FIG. 3. Scans along the z axis keeping fixed the CO₂ orientation inside the individual D and H sII cages (see the text).

while PW86PBE-D4 are even lower and closer to the DF-MP2/CBS energies.

Previous studies have shown that the orientation of CO₂ in the sI cages, especially in 5¹²6² (or T cage), has a stabilizing effect on the clathrate. Thus, here, the orientation of a single CO₂ molecule in the D and H sII cages is also investigated, and in Fig. 4, we display contour plots of how the potential varies as a function of θ and

ϕ angles in each of the rigid D (upper panel) and H (lower panel) cages from the PW86PBE-D4 calculations. The dark colored regions correspond to the potential minima, while light colored ones correspond to higher energy values. One can see that in the H cage for small θ angles, around 0°, CO₂ can freely rotate in ϕ , while in the D cage, such rotation of the guest molecule is pretty much hindered with high potential barriers nearby, in accord with previous

FIG. 4. Contour plots of the potential energy in the (ϕ, θ) -plane for the CO₂@D (upper panel) and CO₂@H (lower panel) cages. The equipotentials are plotted from -5.2 kcal/mol to 0.3 kcal/mol and from -5.0 kcal/mol to -3.2 kcal/mol with intervals of 0.5 kcal/mol and 0.3 kcal/mol for the D and H cases, respectively.

results^{61–63} on CO₂@sII cages. In particular, CO₂ is located at the center of the D sII cage with $\theta = 60^\circ$ and $\phi = 90^\circ$ (see the corresponding coordinate system in the inset of Fig. 3), while for the H cage, values of $\theta \sim 0^\circ$ and $0^\circ < \phi < 360^\circ$ (see the coordinate system in the inset of Fig. 3) were obtained, with CO₂ being almost ($r = 0.002$ Å) at the center of the H cage. Taking into account the orientational anisotropy in the PW86PBE-D4 calculations, the above minimum energy configurations for CO₂@D and CO₂@H were found at energies of -5.24 kcal/mol and -5.03 kcal/mol, respectively. Such estimates are comparable to -6.148 kcal/mol and -5.083 kcal/mol binding energies reported in DF-MP2/CBS calculations for the CO₂@D and CO₂@H cages, although the PW86PBE-D4 results show that there is no significant preference of CO₂ for the D or H cages.

Once the guest–cage interactions were checked, we further explored the inter-cage effects by carrying out the same level of computations for larger-size consisting of two-adjacent sII cages, in order to evaluate any influence on the interaction of the nearest neighbors. Thus, the two-adjacent DD, DH, and HH sII cages (see the middle panel of Fig. 1) of 35, 43, and 50 water molecules, respectively, are also examined. We first performed partial optimizations employing the PW86PBE-D4 functional and then single-point energy DF-MP2, DLPNO-CCSD(T) and PW86PBE-XDM calculations. The interaction energies (including CP corrections) for both fully and partially CO₂-occupied cage systems were obtained. For all two-adjacent cages studied, we considered full (1 + 1) and the configurations when only one of the two cages is occupied, namely, (1 + 0) and (0 + 1), respectively. In Fig. 5, we show the computed energies for the DD, DH, and HH systems considering the CO₂ configurations previously described (see insets). The dashed lines correspond to the DLPNO-CCSD(T) energies, while solid lines correspond to those from the DF-MP2/AVTZ calculations for each of these systems (see Table S2 of the [supplementary material](#)). The values obtained from the PW86PBE-XDM and PW86PBE-D4 computations are very similar and comparable to the DF-MP2 and DLPNO-CCSD(T) estimates, with energy differences of less than 0.5 kcal/mol in the case of (1 + 1) CO₂@DD, 0.3 kcal/mol for CO₂@DH, and less than 0.1 kcal/mol in the CO₂@HH cages. One can see that similar behavior was also found when such comparisons were made for the individual D and H cages (see Figs. 2 and 3) with differences of 0.03 kcal/mol and 0.01 kcal/mol, respectively, in the PW86PBE-D4 calculations. This indicates that PW86PBE-D4 provides relatively good predictions of the guest–cage and inter-cage interactions.

In particular, according to the present PW86PBE-D4 computations, CO₂@D is by 0.2 kcal/mol more stable than the CO₂@H cage. In the case of the two-adjacent cage systems, the most energetically efficient filling process is found when CO₂ molecules occupy the HH cages with an energy of -10.36 kcal/mol, while close energy values of -9.22 kcal/mol and -9.05 kcal/mol are obtained for the (1 + 1) CO₂@DH, and CO₂@DD cages, respectively, from the PW86PBE-D4 calculations. Among the cases studied, we found that the presence of the neighbor empty or CO₂-filled cage clearly affects the energetics, as well as the position/orientation of the CO₂ molecules inside all DD, DH, and HH cages, with the CO₂ molecules shifted from the center of the cages. In particular, values ranging between 0.296 Å and 0.101 Å are obtained (see Table S3 of the [supplementary material](#)), which correspond to the (1 + 0) and (0 + 1) DD cases, respectively,

FIG. 5. Interaction energies for the (1 + 1), (1 + 0), and (0 + 1) full/partially CO₂-occupied two-adjacent DD, DH, and HH sII cages from the PW86PBE-XDM/D4 calculations and their comparison with the corresponding DF-MP2/AVTZ (solid lines) and DLPNO-CCSD(T) (dashed lines) values.

with both position and orientation mainly marked by the occupation of one of the cages, while the guest–guest interactions are almost negligible.

B. CO₂@sII clathrate unit cell crystal: Structural stability

In order to evaluate guest-lattice effects on the interaction, we continue by carrying out geometry optimizations of the fully occupied CO₂@sII and the empty sII unit cell volumes (see the right panel of Fig. 1). In Fig. 6 (see the left panel), we plot the computed cohesive energies as a function of the lattice constant α , using the PW86PBE functional, as implemented in the QE code, including both XDM and D4 dispersion corrections, and their values are listed in Table S4 of the [supplementary material](#). The equilibrium lattice constants, α_0 , and the corresponding $\Delta E_{coh}^{CO_2@sII}$ and $\Delta E_{coh}^{empty(sII)}$ energies were determined by fitting the values of the total $E_{CO_2@sII}(\alpha)$ and $E_{empty(sII)}(\alpha)$ energies, at several α values with a step of 0.2 Å, to Murnaghan's equation of state (MEOS).⁹⁹ The experimental lattice parameter values available in the literature from neutron diffraction studies¹⁰⁰ were considered here as the reference data to compare with the empty equilibrium sII lattice parameters predicted by each of the DFT-D approaches, while for the CO₂@sII case,

FIG. 6. Cohesive energies of the fully occupied $\text{CO}_2@\text{sII}$ clathrate unit cell and empty sII hydrate as a function of the lattice constant α (left panel) and pressure effects on both hydrates (right panel). Dashed lines correspond to the experimental α_0 value reported in Refs. 32 and 100. Symbols indicate the computed values from the DFT-D calculations, while solid lines show their corresponding MEOS fits.

comparisons were made with the corresponding thermal expansion parameter of the experimental unit cell of the $\text{CO}@\text{sII}$ hydrate available in the literature³² (see vertical dashed lines in the left panel of Fig. 6).

For the equilibrium lattice constant of the empty sII hydrate, values, such as $\alpha = 17.12471 \text{ Å}$ at $T = 10 \text{ K}$, 17.13041 Å at $T = 100 \text{ K}$, and 17.14611 Å at $T = 140 \text{ K}$, have been reported in neutron diffraction experiments, and the thermal expansivity of the sII lattice has been investigated.¹⁰⁰ In the present DFT calculations, the α_0 values are obtained through potential energy optimizations for the empty sII and $\text{CO}_2@\text{sII}$ crystal cells, so both thermal and vibrational zero-point effects are not taken into account. Thus, if we want to compare them with experimental data, we should consider the reported values at zero pressure and temperature. In the literature, the extrapolation to the temperature of 0 K through polynomial fits to the experimentally measured T-dependent lattice constants has been investigated and a value of 17.1251 Å has been reported¹⁰⁰ for the sII hydrate. Regarding the increase in pressure, the composition of the samples will tend to 100% filling of the cages, and in Fig. 6 (see the right panel), we plotted the pressure-lattice constant diagrams for both $\text{CO}_2@\text{sII}$ and sII hydrates computed from the PW86PBE-D4 and PW86PBE-XDM calculations together with their MEOS fits. As expected, one can see the compression of the sII and $\text{CO}_2@\text{sII}$ lattices under pressure.

The calculated α_0 and the corresponding values of bulk moduli B_0 and bulk modulus pressure derivative, B'_0 , at zero pressure were

estimated from the corresponding MEOS fits, for both the $\text{CO}_2@\text{sII}$ clathrate and the empty sII hydrate, assuming linear dependence of the bulk modulus with pressure, $B = B_0 + B'_0 \times P$, with B_0 being constant, and valid for $0 < P < B'_0/2$. From the PW86PBE-XDM/D4 calculations, we obtained $\alpha_0 = 17.031/17.103 \text{ Å}$, $B_0 = 17.149/16.053 \text{ GPa}$, and $B'_0 = 6.035/7.680$ for the bulk $\text{CO}_2@\text{sII}$ clathrate and $\alpha_0 = 16.940/16.974 \text{ Å}$, $B_0 = 15.644/15.260 \text{ GPa}$, and $B'_0 = 7.887/8.649$ in the case of the empty sII hydrate. Both functionals predict larger B_0 values for $\text{CO}_2@\text{sII}$ than the empty sII hydrate, and they are also larger compared to the bulk $\text{CO}_2@\text{sI}$ and sI ,^{27,32,60,68} indicating a higher compressibility of the sII lattices. Regarding the α_0 sII lattice constants, one can see that values of $16.940/16.974 \text{ Å}$ are between experimentally reported 17.1251 Å ¹⁰⁰ and a theoretical estimate in recent revPBE calculations of 16.86 Å .^{101,102} Unfortunately, no experimental data are available for $\text{CO}_2@\text{sII}$, so both $17.031/17.103 \text{ Å}$ values obtained from the present PW86PBE-XDM/D4 calculations are found close to experimentally measured α_0 values of 17.063 Å and 17.083 Å for $\text{CO}@\text{sII}$ and $\text{N}_2@\text{sII}$ hydrates, respectively.^{32,100}

In Fig. 7 (see the left panel), we present the binding of CO_2 to the empty sII hydrate and the formation energy of empty sII, at their corresponding equilibrium lattice constant α_0 , obtained from the present DFT-D computations. We found that for the empty sII hydrate, both PW86PBE-XDM and D4 calculations predict close cohesive energy values of $-13.594 \text{ (kcal/mol)/H}_2\text{O}$ and $-13.194 \text{ (kcal/mol)/H}_2\text{O}$, while in the case of the $\text{CO}_2@\text{sII}$ clathrate, the

FIG. 7. Binding energies of the fully occupied CO₂@sII clathrate unit cell and empty sII hydrate as obtained from the indicated DFT-D calculations and their comparison with the corresponding DF-MP2/CBS and DLPNO-CCSD(T) energies of the individual D and H sII cages (left panel). Orientation of the CO₂ molecules in the fully occupied sII crystal unit cell (see also Table S3 of the [supplementary material](#)) from the PW86PBE-D4 geometry relaxation calculations (left panel).

PW86PBE-XDM dispersion-corrected functional predicts a stronger binding of CO₂ compared to the PW86PBE-D4, with energies of -17.986 (kcal/mol)/CO₂ and -13.704 (kcal/mol)/CO₂, respectively. Both energies are found to be lower than the corresponding reference values from the DF-MP2/CBS and DLPNO-CCSD(T) calculations (see vertical solid and dashed lines in Fig. 7) of the individual D and H sII cages. Furthermore, by comparing with the binding energies predicted for the individual CO₂@D and CO₂@H cages using the same DFT-D functional, such as PW86PBE-D4, we may conclude that host–host interactions have an important stabilizing effect on CO₂@sII. In order to complete the stability analysis of the CO₂@sII clathrate and in comparison with the CO₂@sI structure, we also computed the release of energy with respect to the empty sII and the free CO₂ molecules considering single full cages occupancy. A total energy difference of -107.311 kcal/mol and -53.695 kcal/mol is obtained from the PW86PBE-XDM and D4 calculations, with a mean energy of occupation of -4.471 (kcal/mol)/CO₂ and -2.237 (kcal/mol)/CO₂, respectively. Although both XDM and D4 dispersion schemes exhibit similar behavior on the energetics of the CO₂@sII clathrates, which are predicted to be more stable than the CO₂@sI ones, compared to their release energy of -46.09 kcal/mol reported in previous PW86PBE-XDM calculations.^{60,69} Thus, in Fig. 7 (see the right panel) and Table S4 (see the [supplementary material](#)), we present the results obtained on structural properties of the CO₂ molecules in the fully occupied sII clathrate from all atoms geometry relaxations at the corresponding $\alpha_0 = 17.031$ Å and 17.103 Å values in the PW86PBE-XDM and PW86PBE-D4 calculations, respectively. The CO₂ molecules trapped in the eight H cages are indicated by blue color, while those inside the 16 D sII cages are indicated by orange. As it can be seen, θ angles are between 70° and 110° for the D cages and around 90° for the H cages with ϕ around 0° in most cases, with the CO₂ molecules located at the center

of the D cage, or shifted by around 0.1 Å– 0.2 Å from the center of the H cage, as it was found in the case of the two-adjacent cages studied here. Our results show that CO₂ molecules have specific positions and orientations inside the sII cages, clearly depending on the cage's type in the unit cell.

IV. SUMMARY AND CONCLUSIONS

In this work, guest–host and host–host effects on the encapsulation of the CO₂ molecule in sII clathrate hydrates were investigated using both finite-size clathrate-like clusters and periodic 3D crystal lattice systems. Building blocks of the CO₂@sII crystal, such as the individual D and H cages, as well as two-adjacent DD, DH, and HH cage systems, were first considered to ensure an overall description of the CO₂-cage and inter-cages interactions at various representative (equilibrium and nonequilibrium) configurations from DLPNO-CCSD(T) and DF-MP2 methods, as well as selected DFT-D computational approaches.

Interaction energies were first computed for such clathrate-like sII cages, and the performance of selected exchange–correlation functionals including dispersion corrections was assessed. Most of these DFT-D approaches yield an overall well-balanced performance, with the dispersion-corrected PW86PBE-D4/XDM functionals showing a good prediction of the energetics for both CO₂-filled and empty cage systems. Such satisfactory results rely mainly on a reliable description of both the water–water hydrogen-bond network and CO₂–water vdW interactions and can serve to investigate the stability of the CO₂ clathrate hydrates by also considering the host–host interactions in the complete sII unit cell crystal. In all cases studied, the inclusion of CO₂ either in the D/H cage or in the DD/DH/HH cages is an energetically favorable process.

By analyzing the guest–cage interactions, no significant preference of the encapsulated CO₂ for one or the other sII cages was found, with the CO₂ molecules located at the center of each individual D and H cage, while in the case of the two-adjacent cages, some preference was observed in the partially occupied (1 + 0) and (0 + 1) cages in the DD system, with the CO₂ positions being shifted by around 0.2 Å from the center of all DD, DH, and HH cages.

In turn, cohesive and binding energies through structural geometry relaxation DFT-D calculations of the full CO₂-filled and empty sII unit cells were determined, and their structural properties and stability were discussed. Our results show the importance of dispersive forces in the stabilization of the bulk CO₂@sII, and we found that their stability could be properly determined by taking into account dispersion corrected schemes such as D4 or XDM ones. Thus, the present PW86PBE-D4/XDM computations yield lattice constants and compressibility parameters comparable to experimental and previous theoretical values available for the sII and similar gas sII hydrates due to the lack of available data for the CO₂@sII ones.

Their stability is evaluated for the single CO₂ cage occupation, and on the basis of the present results, the CO₂ enclathration in the sII clathrate cages is a stabilizing process, by considering either both guest–host and host–host interactions in the complete unit cell or only the guest–water energies for the individual D or H clathrate-like sII cages. The CO₂@sII clathrates are predicted to be stable when D4 or XDM dispersion correction is included. Moreover, in this case, single cage occupancy was found to be more stable than the CO₂@sI structures. However, in predicting the CO₂-formed clathrate structures, further investigations are required, taking into account thermodynamic factors to reach a complete description as a function of temperature and pressure. Indeed, there are a number of obvious extensions to the current work, such as the consideration of multiple cage occupancy and other type of CO₂ clathrate structures (e.g., CO₂@sI and CO₂@sH), as well as the incorporation of enthalpic and entropic effects to determine whether the calculated stabilization energies are related to observed phase diagram transformations, which may be addressed in future studies.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for convergence checks, interaction, and cohesive energies of the systems under study, as well as CO₂ orientation inside clathrate-like clusters and bulk sII CO₂ hydrate crystal structure.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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