Exploring CO₂@sI Clathrate Hydrates as CO₂ Storage Agents by Computational Density Functional Approaches

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1 Abstract

The formation of specific clathrate hydrates and their transformation at given thermodynamic conditions depends on the interactions between the guest molecule/s and the host water lattice. Understanding their structural stability is essential to control structure-property relations involved in different technological applications. Thus, the energetic aspects relative to CO₂@sI clathrate hydrate are investigated through the computation of the underlying interactions, dominated by hydrogen bonds and van der Waals forces, from first-principles electronic structure approaches. The stability of the CO₂@sI clathrate is evaluated by combining bottom-up and top-down approaches. Guest-free and CO₂ guest-filled aperiodic cages, up to the gradually CO₂ occupation of the entire sI periodic unit cells were considered. Saturation, cohesive and binding energies for the systems are determined by employing a variety of density functionals and their performance is assessed. The dispersion corrections on the non-covalent interactions are found to be important in the stabilization of the CO₂@sI energies, with the encapsulation of the CO₂ into guest-free/empty cage/lattice being always an energetically favorable process for most of the functionals studied. The PW86PBE functional with XDM or D3(BJ) dispersion corrections predicts a lattice constant in accord to the experimental values available, and simultaneously provides a reliable description for the guest-host interactions in the periodic CO₂@sI crystal, as well as the energetics of its progressive single

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cage occupancy process. It has been found that the preferential orientation of the single CO₂ in the large sI crystal cages has a stabilizing effect on the hydrate, concluding that the CO₂@sI structure is favored either by considering the individual building block cages or the complete sI unit cell crystal. Such benchmark and methodology cross-check studies benefit new data-driven model research by providing high-quality training information, with new insights that indicate the underlying factors governing their structure-driven stability, and triggering further investigations for controlling the stabilization of these promising long-term CO₂ storage materials.

2 Introduction

CO₂ clathrate hydrates are involved in current potential applications in sustainable industries, such as CO₂ capture technologies, that are necessary to be developed to store this greenhouse gas. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12] Thus, both scientific and technological communities, from different fields of chemistry, physics, geology, engineering, etc., have devoted numerous collaborative research efforts, involving investigations at microscopic level using molecular simulation tools, as several processes (hydrate nucleation or growth or cage occupancy) could get hardly accessible though experimentation [13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 12]. However, a key point for any of such computational approaches to be useful in hydrate science is the proper modeling of the underlying interactions, to build up predictive models providing detailed knowledge on energetics and structural properties under various thermodynamic conditions. [24, 25, 26, 27, 28, 29]

Clathrate hydrates are crystalline water-based compounds, in which enclathrated guest (typically gases) molecules are trapped inside the cavities of the their lattice structure. CO₂ clathrates are normally of sI type (crystallographic cubic structure type I), however, there has been some experimental evidence for the formation of a metastable sII type (cubic structure type II), while only binary forms of the sH type (hexagonal structure) have been reported under high pressure. [1, 30, 31, 32, 33, 34] Recent investigations by X-ray, powder X-ray, and neutron diffraction techniques, [35, 36, 37, 38] as well as via Raman, solid-state NMR and the infrared (IR and FTIR) spectroscopy have been reported on the spectroscopic characterization of the sI and sII CO₂ clathrates, [34, 39, 31, 40, 41] while molecular dynamics simulations have been carried out to study the occupancy of the sI and sH types [42, 43]. More recent studies have also reported on the structural and mechanical properties of the CO₂ clathrates, providing information about the stability, cage deformations, vibrational frequencies and guest saturation process with relevance for storage purposes [30, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54]. Further, several laboratory-scale studies have investigated the possibility of CH₄-CO₂ replacement in hydrates [55, 56, 57], as an attractive approach to produce new CH₄ energy resources and at the same time sequestration media.

Most of the computer molecular simulations have relied on semiempirical

force fields, while comparatively fewer studies have considered adequate first-principles interaction energy calculations. Such considerations have been highlighted in several investigations revealing the importance of preferential orientation of the guest-host, and guest-guest effects in the $\text{CO}_2@\text{sI}$ case. [46, 51, 58, 59, 60, 54] It is important, therefore, to explore the nature of the molecular interactions present in condensed phase CO_2 gas hydrates, as well as the performance of modern first-principles computational approaches, that could be employed to describe them. Evaluating the performance of electronic structure methodologies [61], such as the density functional theory (DFT), requires comparison with reference data from high level *ab initio* calculations, that is, in general, lacking for condensed phase hydrates. Also, we should highlight that in describing the hydrogen-bond water lattice plus the dispersion gas-water forces, present in gas clathrate hydrates, one should incorporate an accurate description of the van der Waals (vdW) interactions in such technologies. [62, 63, 64, 65, 66] However, valuable information has been gained from comparisons to isolated clathrate-like cluster models (like the building block cages of the clathrate hydrates, see Refs. [67, 60, 68, 54] and references therein), where highly accurate quantum chemistry methods are nowadays limited to, [23, 69] leading to significant improvements in the performance of dispersion-corrected DFT-D approximations. [62, 63, 64, 65, 66] In particular, the semiempirical D2, D3 and D4 dispersion schemes and their variants [70, 71, 72, 73, 74], as well as the exchange-hole dipole-moment (XDM) model [75, 76, 77, 78], and the nonlocal vdW-DF family of functionals [79, 80] have been extensively used for an accurate description of the vdW interactions in both gas and condensed phase molecular systems.

Thus, the objective of this study is to discuss energetic aspects relative to the structural stability and progressive occupation of the $\text{CO}_2@\text{sI}$, using current state-of-the-art computational tools, in order to improve our understanding of their complex behavior from clathrate-like clusters to periodic molecular crystals. The open questions, such as why CO_2 forms sI clathrate or which is the mechanism of hydrate formation, its storage capacity, and its phase transitions, is it possible to exchange CO_2 for CH_4 in hydrates, *etc*, could be addressed by proper modeling of the many-body cooperative effects in such non-covalent guest-host interactions. Following current challenges for investigating condensed phase systems within DFT [80, 81] approaches and recent efforts on machine-learned DFT functionals development [82], comparisons will be presented for a variety of functionals and corresponding dispersion corrections for evaluating guest-host(lattice) effects. Importantly, such systematic and detailed comparisons on DFT-D methods performance could reveal trends in the interactions from clathrate-like nanoscale clusters to the entire periodic crystalline frameworks, [83] drawing connections between finite-size and condensed-matter systems, and exploring the factors playing a stabilizing role of direct relevance in CO_2 storage applications. This information is also essential in building up improved data-driven (bottom-up/top-down) potential/force-field models, with profound implications and direct benefits to data science research [84]. Currently, emerging approaches offer promising alternatives of such models based

on large and high-quality reference datasets [85] and trained via active learning algorithms [86].

3 Computational setup

Figure 1: (Left panel) The CO₂@5¹² and CO₂@5¹²6² sI building blocks clathrate-like cages. (Right panel) CO₂@sI clathrate hydrate crystal structure. The red color corresponds to the oxygen atoms, the white to hydrogens, and the gray to carbons. The black box shows the unit cell, with α being its lattice constant.

The CO₂@sI clathrate hydrate crystal structure is shown in Fig. 1 (see the right panel), together with its cubic ($Pm\bar{3}n$) unit cell (see inset plot in right panel). In the CO₂@sI hydrate, as it is shown in Fig. 1, the water hydrogen bonded network forms two types of cavities (see left panel): a 12-sided pentagonal dodecahedron (called 5¹² or small or D cage in the literature), and a 14-sided tetrakaidecahedron (called 5¹²6² or large or T cage).

The cubic unit cell contains 46 water molecules forming a total of 8 cavities: two 5^{12} cages with 20 water molecules each, and six $5^{12}6^2$ cages, with 24 water molecules each, in total 54 molecules (162 atoms) in the fully occupied $\text{CO}_2@\text{sI}$ unit cell. The empty sI clathrate crystal structure is taken from the 3D crystalline framework given in Ref. [20]. The oxygen atoms positions have been extracted from the X-ray diffraction experiments, and hydrogen atoms orientations have been optimized using the TIP4P model for satisfying both zero dipole moment and ice rules for the unit cell configuration. [20] The DENEb software package [87] was used to construct building block cages, as well as partial and fully occupied $\text{CO}_2@\text{sI}$ crystal unit cells.

Electronic structure DFT calculations were performed for the periodic $\text{CO}_2@\text{sI}$ and empty sI unit cells, using the Quantum Espresso (QE) [88, 89] code. The plane-wave/pseudopotential approach within the projector-augmented-waves (PAW) method [90], as implemented in the QE code [88, 89] was employed. All reported results used the standard PAW pseudopotentials supplied within QE, with PBE-based pseudopotentials used for PBE, revPBE, PW86PBE, optB88, optB86b, and PW91 calculations, while BLYP-based pseudopotentials for the BLYP ones.

Once we checked the convergence, the energy cutoff for the plane-wave expansion of the wavefunctions was chosen at 60 Ry (816 eV) and charge density at 300 Ry (4081 eV). A Monkhorst-Pack $2 \times 2 \times 2$ k -point grid [91] in the reciprocal space was used per unit cell. The geometry optimizations were performed by relaxing all atomic positions with BFGS quasi-newton algorithm until components of all forces are smaller than 0.05 eV/Å. We used the standard implementation in the LIBXC library [92] for different exchange-correlation functionals available in QE package, such as the PBE, revPBE, PW86PBE, PW91, BLYP, optB88 and optB86b. Regarding the choice of these functionals in the present periodic calculations, we should note that is made on the basis of previous studies on similar gas hydrate systems [26, 48, 29], as well as available investigations on small-size clathrate-like cage systems, where current computational resources have allowed to examine the performance of functionals at higher rungs of the Jacob’s ladder, such as hybrid or range-separated ones [60, 54]. So, we further considered a variety of their dispersion-corrected analogs by means of various semi-classical and nonlocal density based corrections. In particular, the dispersion correction schemes employed are: the semiempirical D2 [93], the original zero-damping function D3(0) [94], the most popular Becke-Johnson damping function D3(BJ) [70], the D3M(0) [71] and the D3M(BJ) [71], using the DFTD3 program [95] implemented in the QE code [88, 89], and the DFTD4 program [96] for the most recent developed D4 [73, 74] model including many-body dispersion interactions beyond the pairwise terms. The XDM model, like the D3 scheme, contains three-body intermolecular dispersion contributions, was also considered here, using the POSTG code [97] with its damping function parameterized for different functionals [75]. Further, we present results from nonlocal density functionals, that include vdW interactions self-consistently in the density, such as the modified vdW-DF versions [62].

The cohesive energies per water molecule for the fully occupied $\text{CO}_2@\text{sI}$ and

the empty sI hydrates were computed as:

$$\Delta E_{coh}^{CO_2@sI}(\alpha) = \frac{E_{CO_2@sI}(\alpha) - 46E_{H_2O} - 8E_{CO_2}}{46}, \text{ and} \quad (1)$$

$$\Delta E_{coh}^{empty(sI)} = \frac{E_{empty(sI)}(\alpha_0) - 46E_{H_2O}}{46}, \quad (2)$$

where $E_{CO_2@sI}(\alpha)$ and E_{H_2O}/E_{CO_2} are the total energies of the fully occupied $CO_2@sI$ hydrate unit cell with a lattice constant α , and the isolated ground-state H_2O/CO_2 molecules, respectively, while $E_{empty(sI)}(\alpha_0)$ is the total energy of the empty sI hydrate unit cell at the equilibrium lattice constant α_0 . The binding energy per CO_2 molecule encaged in the empty sI is given by,

$$\Delta E^{CO_2@sI} = \frac{E_{CO_2@sI}(\alpha_0) - E_{empty(sI)}(\alpha_0) - 8E_{CO_2}}{8} \quad (3)$$

4 Results and Discussion

4.1 Benchmarking the density functional approaches: structural properties

In Fig. 2 we plot the cohesive energy of the $CO_2@sI$ (eq. 2) as a function of the lattice constant, α , by performing geometry optimizations of all atomic positions in the fully occupied sI unit cell (see right panel of Fig. 1) at the several α values, for each of the indicated DFT functionals. A total of 35 functionals was considered, such as PBE, BLYP, PW86PBE, revPBE, and PW91, and their respective dispersion corrections such as D2, D3(0), D3(BJ), D3M(0), D3M(BJ), D4 and XDM, as well as the optB88, optB86b and the non-local dispersion-corrected optB88-vdW and optB86v-vdW functionals. For each of these DFT/DFT-D functionals the equilibrium lattice constant, α_0 , and the $\Delta E_{coh}^{CO_2@sI}(\alpha_0)$ energy were determined by fitting the corresponding values of the total $E_{CO_2@sI}(\alpha)$ energy to Murnaghan's equation of state (MEOS) [98] (see Table S1 in supplementary material).

Structural properties of the periodic sI unit cell have been considered as a starting point in the evaluation of the chosen DFT functionals within such top-down approaches. The experimental lattice parameter values available in the literature from neutron and X-ray powder diffraction studies [37, 35, 38] were considered here as the reference data to compare with the equilibrium lattice parameters predicted by each of the DFT approaches. Such experimental values have been also reported under different temperature and pressure conditions for the $CO_2@sI$ hydrate. For example values such as $\alpha=11.8194 \text{ \AA}$ at $T=14 \text{ K}$ [99], $11.893 \text{ \AA}$ at $T=173 \text{ K}$ [35], $11.879 \text{ \AA}$ at 163 K [38] and $11.8194 \text{ \AA}$ at $T=7 \text{ K}$ [37] have been measured, with sample's pressures of 1.3 MPa and 1–6 MPa, reported in the X-ray and neutron diffraction experiments, respectively. The α_0 values were obtained from the present DFT calculations through potential energy optimizations for the fully occupied $CO_2@sI$ crystal cell, so one should compare them with experimental values at zero pressure and temperature.

Figure 2: Cohesive energies of the fully occupied $\text{CO}_2@\text{sI}$ clathrate hydrate as a function of the lattice constant α . Symbols indicate the computed values from the DFT/DFT-D periodic calculations using the QE code, while solid lines display their corresponding MEOS fits. Vertical dashed line corresponds to the experimental $\alpha_0=11.8194 \text{ \AA}$ value at the lowest temperature of 7 K [37], and its extrapolation to $T=0 \text{ K}$ [35].

Therefore, we employed the thermal expansion of $\text{CO}_2@\text{sI}$ hydrate given by analytical polynomial functions fitted to the available experimental data [37, 35, 100], that estimate a value [35] of $11.81945 \text{ \AA}$ at $T=0 \text{ K}$ (see Fig. 2). Regarding the increase of pressure, the composition of the samples will tend to 100% filling

of the cages, with the lattice parameter responding in an unknown yet way to increase cage occupancy and compression of the lattice under pressure [101, 102]. Such pressure effects will be discussed later on in the present study.

Figure 3: Relative error (%) of the equilibrium lattice constant α_0 of the unit cell obtained from the indicated DFT/DFT-D calculations compared to experimental value of 11.819 Å at T=0 K for the CO₂@sI clathrate hydrate system (see text). Vertical dashed black lines correspond to error values of 1 % with (+) and (-) signs indicating the overestimated and underestimated values, respectively (see Table S1 in supplementary material).

In this vein, we have examined the performance of the all DFT functionals presented in Fig. 2, by analyzing their errors in comparison to the low temperature experimental equilibrium lattice constant $\alpha_0 = 11.819$ Å. In Fig. 3 we display such errors (%), while in Table S1 (see supplementary material) we list them together with the corresponding calculated α_0 value for each DFT approach. According to these results, the pure revPBE, BLYP and PW86PBE functionals significantly overestimate the α_0 of the CO₂@sI crystal by 4.9, 3.2 and 1.5%, respectively, while by including dispersion corrections these errors are getting smaller down to 0.2% for the revPBE-D3(0), revPBE-D3(BJ), PW86PBE-XDM, PW86PBE-D3(BJ), PW86PBE-D4 and BLYP-D4. In contrary, PBE and PW91 functionals yield reasonable values within 0.2% to the experimental one, that are getting worse (around 2%) when dispersion schemes are applied. Also the optB88 and optB88-vdW estimated almost the same α_0 , that is too short by 1.9%, as well as the optB86b and optB86b-vdW with errors of 3.3 and 2.2%, respectively. By including dispersion corrections all DFT-D functionals yield shorter α_0 values compared to those of the pure DFT ones.

Figure 4: Cohesive energies of the empty sI clathrate hydrate as a function of the lattice constant α . Symbols indicate the computed values from the DFT/DFT-D periodic calculations using the QE code, while solid lines display their corresponding MEOS fits. The DMC cohesive energy of the empty sI hydrate unit cell from ref. [26] at the experimental $\alpha = 11.77$ Å value is also shown (see cross symbol).

Thus, as a first step, we choose only those functionals that their lattice constants differing by less than 1% from the experimental value, and thus, on the basis of the description of the structural properties of the CO₂@sI the PBE, revPBE-D3(0), revPBE-D3(BJ), PW86PBE-XDM, PW86PBE-D3(BJ), PW86PBE-D4, BLYP-D2, BLYP-D4 and PW91 functionals should be considered hereafter (see Fig. 3) in the present study. We should note that among the selected DFT/DFT-D functionals with relative errors less than 1% only the PBE and PW91 failed to account for the entire vdW interactions, while the revPBE, PW86PBE and BLYP functionals, in this case, improve their performance by including dispersion corrections through D2, D3, D4 or XDM approaches.

In the same manner, we further checked the performance of the selected DFT/DFT-D functionals for the empty sI unit cell. In Fig. 4 we display the calculated cohesive energy as a function of the lattice constant α for such functionals, and compare it with a recent value from diffusion Monte Carlo (DMC) calculation [26] at the experimental lattice constant $\alpha=11.77$ Å [103]. One can see that cohesive energies obtained from the BLYP-D4, revPBE-D3(0) and revPBE-D3(BJ) calculations are the closest to the reported DMC value of -13.606 kcal/mol, while the remaining ones predict an overbinding of the sI water framework. Also the corresponding equilibrium α_0 values are estimated by fits to MEOS at 11.800 Å for most functionals, except for the PBE and PW91 ones that predict a shorter value of 11.601 Å (see Table S2 in supplementary material). These zero-pressure lattice constant α_0 values for the empty sI cell are very similar to those obtained for the fully occupied CO₂@sI crystal, indicating the rigidity of the whole water framework arrangement above the encapsulation of single CO₂ molecules in each of the cages.

Computational simulations consist valuable tools to recreate conditions, thus we also examined the effect of pressure on the structure of the filled CO₂@sI and empty sI unit cells. Fig. 5 displays the pressure as a function of lattice constant α for the indicated DFT/DFT-D functionals, as calculated from the total energy vs volume computed points through the MEOS fits. In the inset plots the normalized pressure-volume diagrams up to 1 GPa are shown, where one can see that by increasing pressure both unit cells for the empty and filled clathrates are more compressible, although no significant reductions are expected for the α_0 values under moderate pressure values of few MPa, reported in the experiment [37, 99, 35]. The bulk moduli (bulk modulus, B_0 , and bulk modulus pressure derivative, B'_0 , at zero pressure) are also estimated from the fittings to the MEOS equation, for both CO₂@sI clathrate and empty sI hydrate from the DFT/DFT-D calculations. We should mention that MEOS equation assumes linear dependence of the bulk modulus with pressure, $B=B_0+B'_0 \times P$, with B'_0 to be constant, and thus is valid for low compressions with $0 < P < B_0/2$. Using an initial guess of $B'_0=4$, values of $B_0=9.95/10.82$ GPa and $B'_0=5.42/5.70$ are obtained in the revPBE-D3/D3(BJ) calculations, while using the PW86PBE functional with XDM/D3(BJ)/D4 dispersion yield larger bulk modulus values of 13.64/13.51/12.53 GPa and B'_0 of 6.03/5.68/5.48 for the bulk CO₂@sI clathrate. Similar results are obtained in the case of the empty sI hydrate, with the corresponding values being $B_0=9.62/10.27$ GPa and $B'_0=5.25/5.63$ from the revPBE-

D3/D3(BJ) calculations, and 12.31/12.70/12.13 and 5.55/5.55/5.92 from the PW86PBE/XDM/D3(BJ)/D4 ones.

Figure 5: Pressure effects on the lattice constant α of the $\text{CO}_2@\text{sI}$ clathrate (left panel), and the empty sI hydrate (right panel). In the inset plots the corresponding normalized pressure-volume diagrams are shown for values up to 1 GPa. Symbols correspond to the computed values from the indicated DFT/DFT-D periodic calculations using the QE code, while solid lines display their corresponding MEOS fits (see text).

Overall the bulk moduli for the $\text{CO}_2@\text{sI}$ and sI hydrates follow the same behavior using revPBE-D3/D3(BJ) or PW86PBE/XDM/D3(BJ)/D4 functionals, with B_0 values being slightly larger for the $\text{CO}_2@\text{sI}$ than the sI, and thus the empty sI hydrate is found to be more compressible than the fully filled $\text{CO}_2@\text{sI}$ clathrate. These values are consistent with the rate the relative volume (V/V_0) decreases as pressure increases, as shown in the inset plots of Fig. 5 for bulk $\text{CO}_2@\text{sI}$ and sI hydrates. Also, the present B_0 and B'_0 values are close to those reported previously for the bulk CO_2 sI hydrate from theoretical studies from using various EOS fittings [48, 51]. In particular, values of $B_0=10.4$ GPa and $B'_0=6.27$ have been estimated from the revPBE calculations by MEOS fittings [48], and a value of $\alpha_0=11.90$ Å, while values of $B_0=15.42$ GPa and $B'_0=5.59$ for $\alpha_0=11.642$ Å have been reported from previously PW86PBE DFT-XDM ones [51]. One can see that the effect of including dispersion interactions is reflected in reduction of the lattice parameter α_0 , and thus enhance of bulk modulus.

4.2 Analyzing the $\text{CO}_2@\text{sI}$ stability: Binding and cohesive energies

In turn, for a better analysis of the performance of the DFT functionals, and further understanding on the description of the underlying interactions we con-

tinue by calculating the cohesive $\Delta E_{coh}^{CO_2@sI}(\alpha_0)$ and $\Delta E_{coh}^{empty(sI)}$ energies of the $CO_2@sI$ and empty sI hydrates (see Eq. 2), respectively, as well as the binding $\Delta E^{CO_2@sI}$ energies of the CO_2 to the sI hydrate (see Eq. 3). Such energies obtained for all examined DFT functionals are displayed in Figs. 2, 4 and 6, and listed in Table S1 (see supplementary material).

In Fig. 2 and Table S1 one can see a considerable variety among the DFT results. By examining the variation of the $\Delta E_{coh}^{CO_2@sI}(\alpha_0)$ and $\Delta E_{coh}^{empty(sI)}$ cohesive energies per water molecule for the full occupied $CO_2@sI$ and empty sI unit cells, respectively, we should notice that revPBE and PW91-D2 values are the higher (-18.417 and -17.207 kcal/mol/ H_2O) and lower (-9.855 and -6.142 kcal/mol/ H_2O) estimates, respectively, for both full and empty sI crystals, while among the functionals yielding the best estimates (within 0.2%) of the lattice constant from the experimental value, energies between [-14.270, -17.034]/[-13.456, -15.691] kcal/mol/ H_2O were obtained for the full/empty sI hydrates, respectively. We found that the inclusion of vdW interactions through any dispersion DFT-D scheme contributes in the stability of both $CO_2@sI$ and sI hydrates for all examined functionals. Although, the pure PBE and PW91 functionals were provided better estimates for α_0 than their DFT-D analogs, we found that they underestimate the cohesive energies due to the lack of the dispersion corrections.

Next in Fig. 6 we examined the binding energies, $\Delta E^{CO_2@sI}$, of the CO_2 to the sI hydrate (see Eq. 3), together with the formation energy of empty sI hydrate for all DFT/DFT-D functionals considered in this study. As we can see most of the DFT-D functionals yield close values for $\Delta E^{CO_2@sI}$ and $\Delta E_{coh}^{empty(sI)}(\alpha_0)$ energies, few of them (BLYP-D4 and optB88) predict that there is no binding between CO_2 and sI hydrate framework, while the revPBE significantly overestimates such binding, as well as revPBE-XDM, optB86b-vdW and optB88-vdW functionals. For the formation energy of the sI hydrate, most of the functionals yield similar values and trends, even when dispersion corrections are included, with the exception of the revPBE and its dispersion-corrected versions, as well as the optB88 and optB88-vdW, that predict lower values than all the others.

Given the lack of reference data for the $CO_2@sI$ hydrates and considering the nature of non-covalent interactions present in such clathrate hydrate systems, we decide to check average energy values for assessing the performance of the DFT approaches. Thus, taking into account that dispersion corrections should improve energies of the pure functionals, as well as the similar energy values obtained from all D2, D3, D4 and XDM schemes, we compute the average values in binding energy of the fully occupied $CO_2@sI$ clathrate and the formation energy of the empty sI hydrate of all examined functionals. Such averages count to -5.844 and -14.423 kcal/mol/molecule, respectively (see vertical solid (blue/red) lines in Fig. 6). Also we calculated average values for these energies by considering only the functionals that provide the best estimates of the experimental lattice constant, and values of 5.783 and -14.357 kcal/mol/molecule were obtained, while if you consider those yielding the closest binding energy values,

Figure 6: Comparison of the binding energies of the fully occupied $\Delta E^{CO_2@sI}$ hydrate (blue color bars) and formation energies of the empty sI hydrate $\Delta E^{empty(sI)}$ (red color bars) obtained from the indicated DFT/DFT-D periodic calculations. Vertical solid lines correspond to the averaged values of the $\Delta E^{CO_2@sI}$ (blue color) and $\Delta E^{empty(sI)}$ (red color) over all or selected DFT-D binding and formation energies (see text). Black dashed lines correspond to binding energies reported previously in the DF-MP2/CBS calculations [60] for the individual T (long-dashed line) and D (dashed line) $CO_2@sI$ cages, while the red color dot-dashed line is the $\Delta E^{empty(sI)}$ energy from the DMC calculations [26].

then values of -6.600 and -14.799 kcal/mol/molecule were found. So, we choose to consider as reference values at this step this latter energies (see vertical solid color (blue/red) lines in Fig. 6). We should note that this later value is closer to the binding energies of -6.148 and -6.779 kcal/mol, that have been reported for the individual 5^{12} and $5^{12}6^2$ cages of the $\text{CO}_2@\text{sI}$ [60] from finite-size cluster wavefunction-based DF-MP2/CBS[TQ] (density-fitting second-order Møller-Plesset perturbation theory [104] at complete basis set limit) reference calculations (see vertical dashed black lines in Fig. 6). For the formation empty sI energies we consider as reference value the -13.606 kcal/mol/ H_2O at $\alpha_0=11.77$ Å reported previously from DMC calculations [26] for the sI hydrate.

For each set of functionals (see Fig. 6) the better agreement with the reference values for both binding and formation energies is obtained in the PBE-D3(0), revPBE-D3(0)/D3(BJ), PW86PBE-XDM/D3(0)/D3(BJ), BLYP-D3(0), PW91-XDM/D2 calculations. However, if one crosscheck (see Fig. 7) with the estimates of the lattice constant of the $\text{CO}_2@\text{sI}$ clathrate, then the revPBE-D3(0)/D3(BJ) and PW86PBE-D3(BJ)/D4/XDM seem to best-perform, with the PW86PBE-D4 underestimating the $\Delta E^{\text{CO}_2@\text{sI}}$ binding energy, while the PW86PBE-D3(BJ) and PW86PBE-XDM yield similar results, so we choose to consider the latter one further on in the present study.

Figure 7: Relative errors (in %) in the DFT computed lattice constant α_0 , and normalized errors (in %) in the binding, $\Delta E^{\text{CO}_2@\text{sI}}$, and formation, $\Delta E^{\text{empty}(\text{sI})}$, energies for the indicated functionals compared to available experimental or theoretical reference data (see text).

4.3 Evaluating the influence of gradual CO₂@sI cage occupation

The single occupancy of the CO₂@sI clathrate hydrate has been supported by previous studies [101, 46, 52], so we focused our study on such progressive occupancy of the crystal unit cell. We start from the empty sI unit cell, and in each step the system is optimized by including one more CO₂ molecule. In this way the binding energies with respect to the guest-free or partially filled system were calculated, and in Fig. 8 all such single filling processes are shown, starting from one up to eight guests. The present results of the energetics involving the occupation of the sI cages by CO₂ molecules are obtained from PW86PBE-XDM calculations. The numbers in each panel in Fig. 8 stand for the energy gained in the corresponding step with respect to the empty or partial occupied sI clathrate and the free CO₂ molecules.

Figure 8: Schematic representation of the gradual CO₂ occupation of the sI crystal. The highlighted red and yellow cavity indicates that a T or D cage is occupied, respectively.

The results of Fig. 8 show that binding is more favorable for the T cage, so the occupation is preferably in a large cage. It is found that there is a significant preference of CO₂ for occupying the T cage, in agreement with previous studies [46, 51, 59, 52, 60, 54] for both finite-size clathrate-like clusters and periodic calculations. We estimated an average energy of -6.740 and -4.835 kcal/mol for the CO₂ in the large and small sI clathrate cages, respectively. According to our computations the energy difference between the occupation of the small and large CO₂@sI cages is around 1.9 kcal/mol, with a total energy difference between the empty sI to full occupied CO₂@sI, with all eight cages filled, of -51.01 kcal/mol.

Such preference in the occupation of the T cages is related with the linear shape of the CO₂ guest, and its interactions with the surrounding host water lattice. The small sI cage has a smaller radius than the large cage, and thus shorter intermolecular CO₂-H₂O distances that probably affect the binding energy due to the repulsive energies that seek to stabilize the structure. The D cage is formed by twelve pentagons, while the T cage contains twelve pentagons and two hexagons with equatorial plane parallel to hexagonal faces, with the T cage radius being longer, and so CO₂ could easier move therein. Such conclusion has been evidenced in experiments at 173 K, where it has been found that the T cages were all filled, while the D ones were only partially [35].

Moreover, recent experimental and theoretical investigations on the CO₂ orientation on the individual and two-adjacent cage systems the CO₂@sI clathrates have shown [35, 105, 38, 46, 52, 60, 54] that the orientational preference of the CO₂ in the sI cages permits it to rotate easily, and thus it may enhance the stability of these clathrate's cages. In Fig. 9 we present (see right-upper panel) a view along the x-axis of the fully occupied CO₂@sI crystal cell, obtained from all atomic positions relaxation calculations, together with the corresponding different views along the x and z -axis of the individual building block D and T sI cages (see left panels). One can see the orientation of the CO₂ molecules in the CO₂@sI unit cell, and in Table S3 (see supplementary material) we list the (r, θ, ϕ) coordinates of each CO₂ inside the T and D cages of the sI hydrate, where r is the distance between the carbon atom of the encapsulated CO₂ and the center of mass of the corresponding cage (see inset plots in Table S3), while θ and ϕ are the polar and azimuthal angles, respectively.

For each cage in the CO₂@sI crystal cell, we kept fixed the orientation of the (x, y, z) axes as shown in the right-upper panel of Fig. 9. We labeled as a, b, c, d, e, f, h and g the eight CO₂ positions in the CO₂@sI unit cell (see right-upper panel), while in the right-lower panel of the figure the connectivity of the first-neighbor cages in the CO₂@sI crystal is displayed. The positions a and b correspond to the small D cages, while the remaining six c-h to the large T sI cages. One can see in Table S3 that the θ/ϕ angles for the CO₂ in the a and b D cages are different with values around 50/80, and 70/70°, respectively, with the CO₂ located almost at the center of both cages in accord with previous experimental and theoretical results [35, 105, 38, 46, 51, 52, 60, 54]. By examining the CO₂ orientations trapped into the T cages of the crystal (see c-h positions in Fig. 9) we found that θ angle values are ranging between 75

to 100° that corresponds to deviations of 15° (anti-clockwise) to 10° (clockwise) of their equatorial planes parallel to hexagonal faces, as shown in left panel of Fig. 9. The ϕ angles are covering a wide value range, with the locations of the CO_2 inside the T-cages being shifted at r values between 0.1 and 0.2 Å, in close accord with the experimental data available [35, 38].

Figure 9: Top-side views of the orientation of the CO_2 molecules inside the building block sI cages (left panel), and fully CO_2 occupied sI unit cell (right-upper panel) from the periodic PW86PBE-XDM calculations. Connectivity first neighbor cages map in the $\text{CO}_2@\text{sI}$: solid, dashed and dotted lines for the DT, TT(5) and TT(6) cage arrangements.

For further comparisons, we also checked the relative orientation between two CO₂ molecules trapped in two neighbor cages, and the $(R, \theta_1, \theta_2, \phi_1)$ coordinates are given in Table S3, together with the connectivity between them (see right-lower panel of Fig. 9 and Fig. S1). Three different cage arrangements are present in the CO₂@sI crystal, such DT, TT(5) and TT(6) with the large T cages sharing a pentagonal and hexagonal face, respectively. The a-position CO₂ forms DT cage systems with all c–h T cages, while the b with those at f–h positions. In turn the c–d, e–f and g–h form TT(6) systems, while TT(5) are those from the c or d with e–h, as well as the e or f with the g–h cages (see Table S3 and Fig. S1 in supplementary material). By analyzing the relative orientations of all such arrangements, trends can be drawn on the effect of the guest-cages and first-neighbors on the interactions in the crystal cell.

One can see that the intermolecular distance R is the shorter between 5.77–6.14 Å in the TT(6) cage arrangement, while values of 6.39–6.82 and 6.95–7.44 Å are found in those of the DT and TT(5) cases, respectively, indicating the importance of the CO₂ interaction with the surrounding water molecules framework, while due to the larger separation of the trapped molecules the asymptotic long-range CO₂–CO₂ contributions [106] are mainly of dispersive nature. Further, recent DF-MP2/CBS reference calculations have been reported in both individual and two-adjacent sI cages [60, 54], that correspond, by taking into account the outer-hydrogen (proton) arrangements in all finite-size cluster cases, to the a and c cages of the CO₂@sI, as well as the a–c, c–d, and c–g two-cage systems in the present PW86PBE-XDM calculations. By examining the orientation of CO₂ in these CO₂@sI cages (see Table S3 in supplementary material) from the PW86PBE-XDM calculations, we show that they compare very well with those obtained from the previous reported clathrate-like calculations [60, 54]. Thus, the present results on the entire periodic CO₂@sI crystal confirm the rigidity of the clathrate framework and the contribution of the guest-cage and guest-lattice interactions on the structural stability of the CO₂@sI.

5 Summary and conclusions

We have performed first-principles computations for the entire periodic crystal of the CO₂@sI clathrate hydrate for evaluating guest–lattice effects and their influence on the crystal energetics. In particular, the outcome of the present top-down approach was combined with those from bottom-up protocols by benchmarking the performance of various density functionals. Different DFT/DFT-D functionals were considered, the best-performed were identified, and then employed to investigate the structural stability and energetics of single-CO₂ gradual occupation process of the sI crystal. The results obtained indicate that dispersion interactions are important in the stabilization of the CO₂@sI clathrate, as well as on the energetics of the empty sI hydrate crystal. Such quantification of the interaction, binding and cohesion energies provides information on the performance of the functionals through the establishment of a combined criterion adapted to the periodic system under study. The proposed

criterion considers the experimental values of the lattice parameter, taking into account thermal expansion and pressure compressibility effects, as well as the formation energies of CO₂@sI and sI hydrate crystals. The latter values are compared with previous reported estimates available from electronic structure DF-MP2 and DMC calculations, that served as lower energy limits. Among the DFT approaches studied, we found that the revPBE and PW86PBE functionals with D3, D3(BJ) and XDM dispersion corrections yield the best performance on the interaction between CO₂ guests and water sI lattice. They also predict the lattice parameter with an error less than 0.2%, with the PW86PBE-D3(BJ) or XDM estimates on binding CO₂@sI and cohesive energies in the empty sI unit cell within 1 kcal/mol to the reference data available.

The present computations reveal that the process of filling the CO₂@sI hydrate is energetically favorable with a total occupation energy of 51 kcal/mol. The preferences of CO₂ occupation in the sI crystal was investigated, and it was found that the T cages are preferred than the D ones. Also, adjacent T cages that share a pentagonal face are more preferential to be filled than those sharing an hexagonal face. Further, the enclathration of CO₂ in the sI structure is always favored either considering only the individual guest-cage interactions, either the complete guest-lattice unit cell, leading to the same conclusion on its orientation inside the small and large sI cages of the crystal.

Our results confirm that the preferential orientation of a single CO₂ in the large sI crystal cages has a major stabilizing effect on the hydrate, with the sI unit cell showing minor distortion upon the CO₂ capture. In this vein, previous studies in clathrate-like cage clusters have also shown a preferential orientation of the CO₂ in the large 5¹²6⁸ cage of the sH hydrate. Thus, interestingly together with the sI and sH clathrates, also the sII structure should also be evaluated to identify the underlying interaction effects influence the CO₂ storage in such systems from bottom-up/top-down approaches, and verify the outcome conclusions in the crystal environment. In turn, the impact of multiple cage occupancy on the stability of CO₂@sI/sII/sH clathrates is the next step to explore, and of high relevance in potential CO₂ storage material applications. Increasing the CO₂ content in different size/type of sI, sII and sH cages could provide valuable insights into the factors that lead to destabilization or not of such CO₂ clathrate hydrates.

In this context, a reliable description of the underlying potential interactions is presented here, however one should keep in mind that investigation on the thermodynamically stable structures of such CO₂ clathrate hydrates involves studies under different conditions of pressure and temperature. Thus, the stability of such multicomponent systems should be analyzed by considering not only the potential energy but also kinetic and thermodynamic terms, to explore the factors playing a stabilizing role. By using first-principles methodologies to characterize guest-host interactions and guest occupancy capacity within the hydrate cages can give insight understanding for application in the field of gas sequestration and storage. However, given the fact that up to date the majority of the research is still limited to laboratory experiments and theoretical simulations, further effort is needed to ascertain the capacity that can be vi-

able for CO₂ sequestration and storage in the form of hydrates. Therefore, we anticipate that the present new results will contribute in developing improved predictive (data-driven) models, and will enable further investigations to explore formation processes and phase transitions, identifying in this way the stability/metastability of such periodic crystalline networks.

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7 Keywords

CO₂ clathrate hydrates, electronic structure calculations, guest-host interactions, CO₂ storage

8 TOC

DFT-derived energetics for the gradual storage of CO₂ molecules into sl crystal unit cell.

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