■ Host–Guest Systems

A Systematic Protocol for Benchmarking Guest–Host Interactions by First-Principles Computations: Capturing CO₂ in Clathrate Hydrates

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Abstract: Clathrate hydrates of CO₂ have been proposed as potential molecular materials in tackling important environmental problems related to greenhouse gases capture and storage. Despite the increasing interest in such hydrates and their technological applications, a molecular-level understanding of their formation and properties is still far from complete. Modeling interactions is a challenging and computationally demanding task, essential to reliably determine molecular properties. First-principles calculations for the CO₂ guest in all sI, sII, and sH clathrate cages were performed, and the nature of the guest–host interactions, dominated by both hydrogen-bond and van der Waals forces, was systematically investigated. Different families of density functionals, as well as pairwise CO₂@H₂O model potentials versus wavefunction-based quantum approaches were studied for CO₂ clathrate-like systems. Benchmark energies for new distance-

dependent datasets, consisting of potential energy curves sampling representative configurations of the systems at the repulsive, near-equilibrium, and asymptotic/long-range regions of the full-dimensional surface, were generated, and a general protocol was proposed to assess the accuracy of such conventional and modern approaches at minimum and non-minimum orientations. Our results show that dispersion interactions are important in the guest–host stabilization energies of such clathrate cages, and the encapsulation of the CO₂ into guest-free clathrate cages is always energetically favorable. In addition, the orientation of CO₂ inside each cage was explored, and the ability of current promising approaches to accurately describe non-covalent CO₂@H₂O guest–host interactions in sI, sII, and sH clathrates was discussed, providing information for their applicability to future multiscale computer simulations.

Introduction

Significant developments in electronic structure methods and rapid advances in computer science have enabled exciting progress in computer modeling of molecular systems and processes, providing reliable predictions for a variety of properties, which sometimes may rival experimental accuracy.^[1–3] There is a number of computational approaches available for describing molecular interactions, ranging from the most accurate wavefunction (WF)-based methods to the computationally viable density-functional theory (DFT) ones.^[4] Highly accurate WF approaches suffer from scaling of the computational cost with the system size, and thus are limited to systems of only a few atoms, whereas DFT methods could be applied to numerous molecular and condensed phase systems. In recent years, a tremendous amount of effort has been dedicated to the de-

velopment of new functional approximations and assessing their performance and accuracy.^[5,6] Although there is a hierarchy within the DFT formalism (Jacob's ladder),^[7] the conventional density functionals are incapable of describing correctly dispersion effects. Thus, recently, additional dispersion-corrected density functional approaches have been developed, which in general, substantially improve the description of non-covalent interactions.^[8–10] Systematic benchmark calculations have assessed the performance of such functionals on specific databases, and in this regard for a given type of non-covalent systems, the developed functional may perform differently, without there being a suitable choice.^[11–15]

Here, we focus on the accurate description of non-covalent interactions in guest–host systems, such as clathrate hydrates. Clathrates are cage-like structures, which can physically trap small molecules, such as CH₄, CO₂, H₂, etc., and thus, can be great potential materials for gas storage.^[16–18] Water-based clathrates are interesting as they have been proposed as environmentally friendly substances; indeed, methane clathrates occur in the natural environment in very large quantities, and together with the hydrogen clathrates are considered as potential energy sources,^[19,20] whereas carbon dioxide clathrates have been proposed as a method to capture and store this greenhouse gas from the atmosphere and control climate change.^[21–25] As a result, they have received considerable attention from both the scientific and industrial communities. The

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stability of the clathrates depends on the collective guest–host interactions, hydrogen-bonding, and other, mainly van der Waals (vdW), interactions can also be present, modifying the structural and dynamic properties.^[26] Known common structures include clathrate structure I (sI), II (sII), and H (sH), although types sI and sII are those mostly found in nature (especially sI), sH and others (C_0 , C_1 , etc) occur typically in high-pressure environments.^[27] In the sI hydrate, the unit cell is formed from two small 5^{12} pentagonal dodecahedral cavities and six slightly larger tetrakaidecahedral $5^{12}6^2$ cages, with 46 water molecules. The sII hydrogen clathrate contains sixteen 5^{12} and eight $5^{12}6^4$ cavities, with 136 water molecules in the unit shell, whereas in the sH hydrate unit shell there are three 5^{12} , two $4^35^66^3$, and one $5^{12}6^8$, with 34 water molecules per unit shell (see Figure 1).

Although several *ab initio* studies have addressed the intermolecular interactions of H_2O - H_2O , CO_2 - H_2O , and CO_2 - CO_2 complexes,^[28–34] there is little *ab initio* data on the CO_2 encapsulated in water cages.^[35–38] The lack of *ab initio* reference computations motivates us to carry out such high quality benchmark data for $CO_2@H_2O$ from first-principles approaches in sI, sII, and sH type cavities. Computer simulations are a key challenge for molecular-level understanding of clathrate behavior, especially in terms of interpreting the underlying mechanisms of various physicochemical processes (see Ref. [39] and references therein). Nowadays, most of the molecular dynamics (MD) simulations still rely on empirical or semiempirical force fields as an important tool for investigating processes, such as the nucleation, growth, structural organization, and cage occupancy of

clathrate hydrates, as well as the dissolution of the guest gas in water,^[40–50] whereas for *ab initio* simulations, issues such as computational efficiency, system-size scaling, and accurate electronic structure treatments are of importance, with density functional theory (DFT) approaches^[36,38,51–55] being, more recently, also valuable in studying such inclusion compounds. In this vein, energy benchmarks from accurate quantum-mechanical calculations are essential for testing both force fields and DFT methods. Therefore, clathrate hydrates offer the opportunity to validate the ability or inability of current DFT methods to simultaneously describe both the hydrogen bonding within the water network and the predominantly dispersion bound gas–water interactions. Within this study, we focus on a rigorous description of the structures and bonding of $CO_2@H_2O$ in sI, sII, and sH cages by reference WF-based methods, and the most computationally inexpensive brand of dispersion corrections, the DFT-D3 approach^[56] and its variants regarding the damping functions available in the literature D3(0),^[56] D3(BJ),^[57] D3M(BJ),^[13] and D3(OP).^[14]

The article is organized as follows: in Computational Details, we present the electronic structure calculations used for the study, as well as some of the analytical pairwise potentials reported so far for the CO_2 - H_2O system; in the Results and Discussion section, we analyze the performance of the many-body $CO_2@H_2O$ interactions within specific cavities of clathrate hydrates with a particular emphasis on the dispersion effects for such guest–host systems; and finally, we summarize our findings and list some concluding remarks.

Computational Details

CO_2 is known to form sI clathrate hydrates at low pressures,^[58] whereas the formation of sII and sH hydrates seems to require, so far, the presence of additional co-guest molecules, thus, up to now only binary clathrate hydrates of such types have been synthesized.^[59–61] As sII and sH clathrate hydrates have been synthesized at high pressures for other guest gases (for example, methane), and given the possible high storage capacity of their cages, apart from sI cages (with $N=20$ and 24 water molecules), we also consider here the sII and sH cavities, formed by $N=20$, 28, and 36 water molecules, for evaluating the $CO_2@H_2O$ interactions (see Figure 1). Such specific size water systems are the building blocks of fairly rigid 3D hydrate lattices, and thus can be used as theoretically tractable models to probe the relevant guest–host interactions for deriving intermolecular potentials to be used under different thermodynamic conditions.

Geometries for different size clathrate cages of the sI, sII, and sH types (small 5^{12} , medium $4^35^66^3$, and large $5^{12}6^2$, $5^{12}6^4$, $5^{12}6^8$) were extracted^[54] from the 3D crystalline framework as it is given in Ref. [62]. For all water molecules in each sI, sII, and sH unit shell, the positions of the oxygen atoms were obtained from the X-ray diffraction experiments, whereas the hydrogen atom configurations have been calculated from optimizations by using the TIP4P water model,^[62] for zero dipole moment unit shell configurations that simultaneously satisfy the ice rules.^[63]

The coordinate system in the cages is aligned as shown in Figure 1. The origin is at the center of mass of the cage, with the X,Y axes lying in the equatorial plane, whereas the Z axis is perpendicular to the parallel tetragon/pentagon and/or hexagon faces;

Figure 1. Relative orientation of the CO_2 in the small, medium, and large cages of the sI, sII, and sH clathrate hydrate.

the center of mass of the CO₂ is placed in the origin of the coordinate system with θ and ϕ being the polar and azimuthal angles, indicating the orientation of the linear CO₂ molecule with respect to the body-fixed coordinate system, keeping fixed the CO₂ bond lengths at their equilibrium values ($r_1 = r_2 = 2.192$ bohr).

Interaction model potentials

As we mentioned above, several interaction model potentials, both semiempirical and ab initio, have been reported in the literature for describing the CO₂-H₂O potential energy surface (PES).^[29,30,33,34,44,49] Thus, the potential form for the encapsulated CO₂ molecules is expressed as a sum of such pairwise interactions between the CO₂ molecule and the number, N_w , of H₂O molecules forming each cage [Eq. (1)]:

$$V_{\text{CO}_2-\text{cage}} = \sum_{N_w=1}^{20/36} V_{\text{CO}_2-\text{H}_2\text{O}}(x, y, z, \theta, \phi) \quad (1)$$

On the one hand, semiempirical models have been adjusted to describe properties of the system at specific thermodynamic conditions. The most popular models for the CO₂ are the MSM, EPM2, TraPPE, and ZD,^[64–67] whereas for the H₂O, we used the SPC/E, TIP4P, TIP4P/ice, and TIP4P/2005 models.^[68–71] By employing the standard Lorentz–Berthelot combination rules, we obtained the corresponding parameters (see Table S1 in the Supporting Information) of all semiempirical models considered in this work. Here, we should also mention the VAS model by Anderson and co-workers,^[33] a site–site ab initio-based CO₂-H₂O intermolecular potential fitted to MP2 data and combined with the TIP4P/ice water model. On the other hand, ab initio potentials are usually designed to account for complex short-range interactions and subtle weak (long-range) interactions by fits to huge datasets of electronic structure calculations of the system including many-body contributions for the CO₂-H₂O complex. Here, we used two recent, high-level PESs reported in the literature for the CO₂-H₂O from Refs. [29,34]. The most recent rigid-monomer PES by Makarewicz,^[29] called hereafter PES^(a), has employed a complex analytical expression of Morse type terms including damped long-range electrostatic and dispersion contributions to represent the five-dimensional CO₂-H₂O intermolecular PES fitted to approximately 23 000 MP2/aug-cc-pVTZ energies. The other CO₂-H₂O PES used here (called PES^(b)), was reported by Bowman and co-workers,^[34] and is a fully flexible-monomer permutational invariant PES fitted to roughly 540 000 CCSD(T)-F12b/aug-cc-pVTZ electronic energies.

Electronic structure calculations

All wavefunction-based calculations were carried out by using MOLPRO 2012,^[72] whereas the DFT calculations were performed by using Gaussian 09^[73] and a modified version of Gaussian 03^[74] package of codes, with the additional dispersion corrections computed by using the DFTD3 program.^[75]

In such large systems (like the building blocks of the CO₂@sl/sll/sH clathrates) coupled-cluster calculations are usually not affordable, so we obtained our reference energies from density fitting DF-MP2 computations^[72] with a careful analysis against basis set superposition error (BSSE) and basis set incompleteness error (BSIE) for different basis sets, such as aug-cc-pVXZ (namely AVXZ),^[76] with $X = \text{D, T, and Q}$. Counterpoise (CP) corrections,^[77] E_{CP} are included to mitigate the BSSE effects in the interaction energies, ΔE [Eq. (2)]:

$$\Delta E = E_{\text{CO}_2-\text{cage}} - E_{\text{CO}_2} - E_{\text{cage}}, \quad \Delta E(\text{BSSE}) = \Delta E + E_{\text{CP}} \quad (2)$$

where $E_{\text{CO}_2-\text{cage}}$, E_{CO_2} , and E_{cage} are the total energies of the whole CO₂@(H₂O) _{$N_w=20,24,28,36$} , CO₂, and specific water sl, sll, or sH cage systems, respectively.

In all cases, reference energies were obtained from DF-MP2 calculations by using basis set extrapolation schemes to reach complete basis set (CBS) limit. We employed the two- and three-step conventional formulas proposed by Schwartz,^[78] $E_X = E_{\text{CBS}} + \frac{A}{X^2}$ (for the correlation energies, and called hereafter CBS^(a)), and Peterson et al.,^[79] $E_X = E_{\text{CBS}} + Ae^{-(X-1)} + Be^{-(X-1)^2}$ (for the total energies, and called CBS^(b)), respectively; as well as, the two step weighted average scheme of Lee et al.^[80] $E_{\text{CBS}} = \frac{1}{2} \frac{(\delta_X E_{X+1} - \delta_{X+1} E_X)}{(\delta_X - \delta_{X+1})}$ (namely CBS^(c)), with $\delta_X = E_X^{\text{CP}} - E_X$, $\epsilon_X = E_X^{\text{CP}} + E_X$, and E^{CP} is the interaction energy corrected for BSSE, E represents the uncorrected one. We also considered the simple arithmetic average, called half-counterpoise scheme (see Refs. [81,82]), $\Delta E_{\text{half}} = \frac{1}{2} (\Delta E + \Delta E(\text{BSSE}))$.

As a special case, owing to the computational demands of the larger $N_w = 20, 24, 28$, and 36 systems and to check the DF-MP2 level of theory, we also performed DF-MP2 and CCSD(T) calculations for the CO₂-H₂O dimer. As in previous studies,^[29,34] we selected a few representative configurations of the dimer for comparing the DF-MP2 binding and interaction energies against highly accurate data from CCSD(T) computations. The calculated energies using different correlation-consistent basis sets, including BSSE corrections and at their CBS limits are listed in Table S2 (see the Supporting Information). One should note that convergence with respect to the basis sets is very important, as even for the large AV5Z basis sets, the BBSE error counts around 20 cm^{−1} for both DF-MP2 and CCSD(T) methods for the CO₂-H₂O dimer. Also, as expected, DF-MP2 underestimates the binding of the CO₂-H₂O, with DF-MP2/CBS energies being by around 60 cm^{−1} lower than those obtained from the present CCSD(T)/CBS calculations, as well as from previous CCSD(T) and CCSD(T)-F12 studies.^[29,34] Thus, the DF-MP2 energies should be considered as an underestimate for the CO₂-H₂O binding energies, whereas for larger CO₂@H₂O systems, as there is no data available, it is hard to attempt a quantitative estimate. However, recent studies on similar guest-free clathrate-like cages have shown that DF-MP2/CBS energies are within less than 0.5 kcal mol^{−1} (≈ 170 cm^{−1}) for the best values available (see ref. [54] and references therein).

In the DFT calculations, we chose in total 15 DFT functionals (with (namely DFT-D) and without dispersion corrections) from four categories within the DFT Jacob's ladder: GGA functionals (BLYP, PBE, B97),^[73] meta-GGA functionals (M06L, M11L, TPSS, SCAN),^[73,83] hybrid-GGA/metaGGA functionals (B3LYP, PBE0, TPSSH, M062X),^[73] and hybrid range-separated GGA and metaGGA functionals (LC- ω PBE, CAMB3LYP, ω B97X, M11).^[73] The D3 dispersion correction was used throughout the study with the original zero-damping function D3(0),^[56] as well as the most popular Becke–Johnson damping function D3(BJ).^[57] In addition to the above standard dispersion corrections, we also considered the recent D3M(BJ)^[13] and D3(OP)^[14] versions. The former is a modified version of D3(BJ) with an emphasis on non-equilibrium particularly compressed geometries, whereas the later is a generalization of the D3(BJ) with a more balanced tail correction.

Validation protocol

Most benchmark studies are usually focused on databases including only near-minimum geometries. However, it was found that good performance at the minimum, does not necessarily imply the same behavior for other intermolecular configurations.^[11] Thus, non-minimum geometries should be selected, sampling the full potential energy surface, in order to assess the accuracy of differ-

ent DFT or model potential approaches. Semilocal functionals cannot reproduce correctly long-range behavior, whereas functionals including nonlocal dispersion perform, in general, quite well at long distances, however, their accuracy drops at short distances owing to the overestimation of exchange and the inadequacy of damping functions used in the atom-pairwise dispersion expressions.

Therefore, an analysis at multiple orientations of a molecular system could provide information that could serve to evaluate, and then to improve, DFT approaches or semiempirical models by screening those unphysical interactions as follows:

- 1) Configurations near the center of the cage should correspond to bound energies;
- 2) Around the minimum: correct orientational anisotropy behavior against reference data;
- 3) Interaction energies should converge from above to the reference values;
- 4) Around the edges of the cage: correct orientation behavior against reference data;
- 5) If more than two functionals/models fulfil the above criteria, then the one with the lowest mean absolute error and less computational cost should be chosen.

On the basis of such criteria, we propose a validation protocol that allows us to critically examine different functional approaches (or analytical model potentials available), and provide a global conclusion for their performance and accuracy in future computer simulations of CO₂ clathrate hydrates. Such validation protocol is based on energy error analysis not only at equilibrium configurations, but also along the scans of relevant orientations of the encapsulated CO₂ (see Figure 2).

Results and Discussion

Interaction energies: Analysis around the minima

In Figure 3, we plot 1D minimum energy profiles of the $V_{\text{CO}_2-\text{cage}}$ [see Eq. (1)] PESs with the CO₂ inside the 5¹², 4³5⁶6³, 5¹²6², 5¹²6⁴, and 5¹²6⁸ cages (see upper to lower panels, respectively), as a function of the distance R joining the center of masses of the cage and the CO₂ molecule, keeping fixed the orientation of the R vector with its polar angle $\theta_R = 45^\circ$ and the azimuthal angle $\phi_R = 60^\circ$. Along the R coordinate, we optimized the internal orientation angles θ and ϕ of the CO₂ with respect to the indicated cage by using the analytical semiempirical and ab initio-based potentials discussed above. For all cages, one can see clear differences between the pairwise semiempirical and ab initio interactions. In the small 5¹² and medium 4³5⁶6³ cages, both ab initio potentials show deeper wells with respect to the semiempirical ones, with a difference of around 1500 cm⁻¹. In the large 5¹²6² cage, the difference is around 1000 cm⁻¹ for the ab initio PES^(b) by Bowman and co-workers,^[34] whereas the well-depth of the PES^(a) by Makarewicz^[29] is just slightly more deep than the TIP4Pice/ZD model. For the 5¹²6⁴ and 5¹²6⁸ cages, both PES^(a) and PES^(b) show double-minima topology with similar equilibrium geometries,

Figure 2. Proposed criteria for the validation protocol.

although with different well-depths, with these of PES^(a) being closer to the semiempirical values than those of PES^(b).

The semiempirical PESs are combinations of different CO₂ and H₂O potentials, and one can clearly see trends in their behavior. As it can be appreciated, the strength of the interaction is dictated by the water–water model with the following trend: TIP4P/ice > TIP4P/2005 > TIP4P > SPC/E for the small cages; whereas in the large cages the same trend is also found, although the curves for SPCE and TIP4P seem to be overlapped. This can be attributed to the parameterization of each model to different thermodynamical conditions. Regarding the position of the minima, in the small cages, all the potentials predict the same position at the center of the cage ($R = 0$ Å), whereas in the large 5¹²6² one, the position of the minima is shifted, and for the ab initio PESs is located at -0.38 Å (a shift of 0.18 Å with respect to the semiempirical potentials). For the 5¹²6⁴ and 5¹²6⁸ cages, the minima are located at R distances shifted by 4.5 – 5.2 Å and around 7 Å, respectively. As the size of the cavity should influence the interaction (allowing almost free rotations of the CO₂), one would expect that the well-depths should differ between small and large cages. We should also point out here that ab initio curves show higher anharmonicity compared with the semiempirical ones, and this could also affect their stability when zero-point energy effects are included.

In Figure 3, we also show the reference values for the interaction energies obtained from converged DF-MP2 calculations at the center of each cage, $R = 0$ Å. Performing such computations is in fact a challenging task, as the large basis sets needed to reach the CBS limit are unaffordable, huge BSSE errors are present, and thus a very careful examination is required for extracting unbiased conclusions. So, in Table 1, we present the convergence of the DF-MP2 calculations for different correlation-consistent basis sets with and without CP corrections, as well as the results of the half-counterpoise and the two- and three-step CBS extrapolation schemes for all above-mentioned clathrate cages. As expected, both uncorrected and corrected interaction energies converged from below and above to their CBS limits, respectively. Similarly, as has been found in previous studies,^[13,81,84] the arithmetic average (half) between the uncorrected and the CP-corrected energy value converges faster to the CBS limit. However, as we can see, a

Figure 3. Potential energy profiles, $V_{\text{CO}_2\text{-cage}}$ [Eq. (1)], as a function of the distance $R = \sqrt{x^2 + y^2 + z^2}$ between the center of masses of the CO_2 and the 5^{12} , $4^3 5^6 3$, $5^{12} 6^2$, $5^{12} 6^4$, and $5^{12} 6^8$ cages, with $\phi_R = 60^\circ$ and $\theta_R = 45^\circ$.

large BSSE error still contaminates even the AVQZ(-half) energy values, so we choose to employ for the reference energies the CBS values from the CBS^(c)(TQ) extrapolation scheme.^[80]

By comparing now in Figure 3 the DF-MP2/CBS^(c) data at $R = 0 \text{ \AA}$ with the analytical pairwise potential value, one can see that for the small 5^{12} and $4^3 5^6 3$ cages, none of the (semiempirical or ab initio) representations are close to the reference values of -2150.75 cm^{-1} and -2629.23 cm^{-1} , respectively. For the remaining (large) cages, the semiempirical TIP4Pice/ZD model, and the PES^(a) potential in the case of the $5^{12} 6^2$ cage, provide estimates near to the reference DF-MP2/CBS^(c) energy values of -2371.36 cm^{-1} , whereas for the $5^{12} 6^2$, $5^{12} 6^4$ and $5^{12} 6^8$ cages, TIP4P2005/ZD predicts values close to the DF-MP2/CBS^(c) ones of -1752.83 and -1218.36 cm^{-1} , respectively.

Given the limitations of the current pairwise models to accurately describe such systems, it seems appropriate to explore alternatives for including cooperative many-body effects in the interactions of the CO_2 within clathrate hydrate cavities of sl, sII, and sH phases. In this sense, DFT approaches offer such an option, as they could balance computational cost and accuracy for a representation of such interactions from direct first-principles calculations.

Thus, as a first step, we carried out partial optimizations of the CO_2 orientation at the center of each cage, $R = 0 \text{ \AA}$, at the DF-MP2/AVTZ level of theory, with their binding energies obtained from CBS^(c)(TQ) calculations. We recorded the energies in a grid of (θ, ϕ) with θ ranging from 0 to 90° , in steps of 30° , and for ϕ from 0 to 360° , in steps of 45° .

In turn, we employed such configurations for carrying out DFT calculations with different functionals including dispersion corrections, and then we used these data for a qualitative and quantitative error analysis. On the one hand, for the qualitative error analysis, we employed the first and second criteria of the validation protocol introduced here (see Figure 2). In Figure 4, we show the results obtained from different DFT functionals, with and without dispersion corrections, as well as from the analytical pairwise model potentials for the two cages of the

Table 1. Convergence of the reference DF-MP2 calculations. Energies are in cm^{-1} .

System/	$\text{CO}_2@5^{12}$	$\text{CO}_2@4^3 5^6 3$	$\text{CO}_2@5^{12} 6^2$	$\text{CO}_2@5^{12} 6^4$	$\text{CO}_2@5^{12} 6^8$
Basis set			$\Delta E/\Delta E(\text{BSSE})$		
AVDZ	−4383.0/−1635.8	−4631.4/−2159.9	−4196.8/−2141.1	−3307.1/−1649.6	−2312.9/−1171.1
AVTZ	−3149.0/−1996.7	−3612.0/−2488.3	−3245.5/−2303.9	−2492.3/−1722.5	−1788.7/−1204.6
AVQZ	−2589.5/−2083.1	−3055.7/−2568.1	−2743.2/−2342.7	−2064.5/−1740.1	−1453.5/−1212.7
AVQZ(half)	−2336.3	−2811.9	−2542.9	−1902.3	−1333.1
CBS(TQ) ^(a)	−2147.2	−2627.9	−2388.7	−1753.2	−1219.1
CBS(DTQ) ^(b)	−2128.9	−2610.6	−2363.2	−1749.4	−1216.9
CBS(TQ) ^(c)	−2150.8	−2629.2	−2371.4	−1752.8	−1218.3

CO ₂ @5 ¹²						CO ₂ @5 ¹² 6 ²					
	BLYP ¹	D3(0) ²	D3(BJ)	D3M(BJ)	D3(OP) ²	BLYP ¹	D3(0) ³	D3(BJ) ⁴	D3M(BJ) ³	D3(OP) ³	
B97		D3(0) ¹	n/a	n/a	n/a	B97	D3(0)	n/a	n/a	n/a	
PBE ¹		D3(0)	D3(BJ)	D3M(BJ)	D3(OP)	PBE ¹	D3(0) ³	D3(BJ) ²	D3M(BJ) ³	D3(OP) ³	
M06L ³		D3(0) ³	n/a	n/a	n/a	M06L	D3(0)	n/a	n/a	n/a	
M11L		n/a	n/a	n/a	n/a	M11L ³	n/a	n/a	n/a	n/a	
TPSS ¹		D3(0) ²	D3(BJ) ¹	n/a	D3(OP) ¹	TPSS ¹	D3(0)	D3(BJ)	n/a	D3(OP) ³	
SCAN ¹		D3(0) ²	D3(BJ) ²	n/a	n/a	SCAN ¹	D3(0)	D3(BJ) ³	n/a	n/a	
B3LYP ¹		D3(0) ²	D3(BJ)	D3M(BJ)	D3(OP)	B3LYP ¹	D3(0)	D3(BJ) ²	D3M(BJ)	D3(OP)	
PBE0 ¹		D3(0)	D3(BJ)	D3M(BJ)	D3(OP)	PBE0 ¹	D3(0)	D3(BJ)	D3M(BJ)	D3(OP)	
M062X		D3(0)	n/a	n/a	n/a	M062X	D3(0)	n/a	n/a	n/a	
TPSSH ¹		D3(0)	D3(BJ) ¹	n/a	D3(OP)	TPSSH ¹	D3(0)	D3(BJ)	n/a	D3(OP)	
CAMB3LYP ¹		D3(0) ²	D3(BJ)	n/a	n/a	CAMB3LYP ¹	D3(0)	D3(BJ)	n/a	n/a	
LC-ωPBE ¹		D3(0) ²	D3(BJ)	D3M(BJ) ¹	n/a	LC-ωPBE ¹	D3(0)	D3(BJ)	D3M(BJ)	n/a	
ωB97X ¹		D2(0) ²	n/a	n/a	n/a	ωB97X	D3(0) ¹	n/a	n/a	n/a	
M11 ³		D3(0) ⁰	n/a	n/a	n/a	M11	n/a	n/a	n/a	n/a	
SPCE/	EMP ²	EPM2 ²	MSM ²	TraPPE ²	ZD ²	SPCE/	EMP ²	EPM2 ²	MSM ²	TraPPE ²	ZD ²
TIP4P/	EMP ²	EPM2 ²	MSM ²	TraPPE ²	ZD ²	TIP4P/	EMP ³	EPM2 ³	MSM ³	TraPPE ²	ZD ³
TIP4P2005/	EMP ²	EPM2 ²	MSM ²	TraPPE ²	ZD ²	TIP4P2005/	EMP ³	EPM2 ³	MSM ³	TraPPE ²	ZD ³
TIP4Pice/	EMP ²	EPM2 ²	MSM ²	TraPPE ²	ZD ²	TIP4Pice/	EMP ³	EPM2 ²	MSM ³	TraPPE ²	ZD ³
AB INITIO	PES ^{(a)3}	PES ^(b)				AB INITIO	PES ^{(a)3}	PES ^{(b)3}			

Figure 4. Qualitative screening of the indicated DFT functionals, with and without dispersion corrections and analytical potential models. Green indicates a successful fulfilling of all screening criteria, whereas red is used when any of the screening criteria is not fulfilled. In this case, 1 stands for when the criterion of bound configuration fails, 2 for the criterion of the minimum's orientation, and 3 for the criterion of the maximum's orientation.

CO₂@sl clathrate hydrate. We indicate in Figure 4 (see red and green colored boxes) when the functional or the analytical potential predicts a no-bound configuration, or an orientation of the CO₂ in the cage that does not agree with those from the reference DF-MP2 calculations. This serves to filter those DFT or analytical potentials to provide a global comparison. Thus, by checking through all possible choices, we found that apparently only five functionals fulfill the criteria of the proposed validation protocol. These functionals are: B3LYP with D3(BJ), D3M(BJ), and D3(OP), PBE0 with D3(0), D3(BJ), D3M(BJ), and D3(OP), TPSSH-D3(OP), CAMB3LYP-D3(BJ), and LC- ω PBE-D3(BJ). We should also note that none of the analytical pairwise models were able to fulfil the protocol's criteria.

On the other hand, for the quantitative validation, in Figure 5, we present the relative errors of all DFT functionals, with and without dispersion corrections, against the reference DF-MP2/CBS^(c) interaction energies at their equilibrium orientation. For the sake of completion, we also include results for both semiempirical and ab initio analytical interaction potentials. The corresponding DF-MP2/CBS^(c), DFT, and models data are given in Table S3 in the Supporting Information, together with complementary data for different geometries. For the 5¹² cage (see left panel), the interaction energy at the DF-MP2/CBS^(c) level, ΔE , is -2150.8 cm^{-1} ($-6.148 \text{ kcal mol}^{-1}$) for the CO₂ at $(R, \theta, \phi) = (0 \text{ \AA}, 60^\circ, 90^\circ)$, whereas for the large 5¹²6² cage (see right panel), ΔE is -2371.4 cm^{-1} ($-6.779 \text{ kcal mol}^{-1}$), with the CO₂ lying on the XY-plane with $(\theta, \phi) = (90^\circ, 45^\circ)$ and $R = 0 \text{ \AA}$. Positive relative error energy values correspond to estimates for underbound systems, whereas overbound ones correspond to negative error values. As a result of a more compact structure (repulsive interactions), one can see that larger errors are obtained for the small 5¹² cage compared with the errors for the large 5¹²6² one. As was expected, generally dispersion-corrected functionals have smaller errors than their non-corrected analogs. Also, as we climb up the Jacob's ladder, relative errors

tend to decrease, although with no clear trend. In most of the cases, pure functionals tend to predict underbound or almost underbound complexes, with an exception the M06L, M062X, M11L, and M11 functionals, which predict overbound complexes. The SCAN and ω B97X are the only functionals that predict bound energy values, with low relative errors.

By combining now both qualitative and quantitative error analysis results (see Figures 4 and 5), and considering that gold-standard CCSD(T) energies might introduce a correlation energy that should increase the DF-MP2/CBS^(c) reference energy values, we could then assign a flexible upper and lower limit of $\pm 0.5 \text{ kcal mol}^{-1}$ for the obtained relative errors for the DF-MP2/CBS^(c) energies. In this sense, the number of functionals fulfilling the validation protocol is now reduced to the B3LYP, including the D3(BJ), D3M(BJ), and D3(OP) dispersion corrections, with the lower relative errors including the dispersion corrections being: D3(BJ) > D3(OP) > D3M(BJ). Such results are consistent with the fact that more recent damping dispersion corrections include non-equilibrium geometries, as well as a more balanced parameterization that consistently improves upon their previous generations.

Regarding the analytical potentials, the semiempirical ones tend to have larger errors compared with the reference values than the DFT-D dispersion-corrected functionals, whereas for the ab initio potentials, relative errors are of comparable size to the DFT energies, although the most recent PES^{(b)[34]} predicts overbound energies for all CO₂@sl, CO₂@sII, and CO₂@sH cages.

Interaction energies: Analysis around the edges of the cavities

Following the proposed validation protocol, after examining the interaction around the minima of the PESs, we proceed with the analysis around the edges of the cavities. The repulsive part of the interaction plays an important role in the study

Figure 5. Relative errors for the indicated DFT functionals and analytical potential models at $R=0$ Å for the two CO_2 @sl cages. Full color and pattern bars correspond to DFT calculations without dispersion corrections (pure functionals), and with the indicated D3 corrections, respectively. Similar color patterns are also shown for the analytical PESs.

of different processes, such as phase transitions, diffusion, absorption, or release of CO_2 within the cavities.

Thus, in Figure 6, we plot the interaction energies computed at the DF-MP2/CBS^(c) level of theory, and by the analytical pairwise potentials for a randomly chosen orientation of the CO_2 (for example, $\theta=61^\circ$ and $\phi=127^\circ$), as a function of R coordinate (lying along the Z axis) for the 5^{12} and 5^{126^2} cages of sl clathrate. For the small CO_2 @sl cage (see upper panel), the DF-MP2/CBS^(c) curve shows two symmetric energy barriers at around $360 \text{ kcal mol}^{-1}$, corresponding to the configurations of the CO_2 crossing to the center of a pentagonal face at the edges of the cage, whereas for the large CO_2 @sl cage (see lower panel), we can see two lower height asymmetric barriers of about 90 and $120 \text{ kcal mol}^{-1}$, as in this case CO_2 is facing hexagons (see Figure 1) with a different orientation of the hydrogen atoms at each of them. As mentioned previously, we only conducted calculations along the Z axis keeping fixed the CO_2 molecule in its linear configuration and choosing randomly its orientation following the proposed validation protocol. Given the size of the systems under study, full optimizations are too computationally expensive to be carried out, and beyond the scope of the present work. We should also note that the above reported barrier values will be clearly affected

Figure 6. Scan along the R coordinate/ Z axis (with $\phi_R=\theta_R=0^\circ$) showing the energetic barriers at the edges of the small and large CO_2 @sl cages. Solid-color/symbols lines correspond to semiempirical water/ CO_2 model potentials. Scaling factors should be used to recover the potential values for the indicated curves.

once minimum energy paths, as well as the presence of the 3D crystalline framework of hydrates, are taken into account.

Regarding the analytical models, they also present maxima at the edges of each cage with oscillatory behavior indicating the deficiencies in their parameterization at repulsive configurations and/or artifacts arising from the pairwise approach. As in the case of the well depths, the semiempirical water models also dictate the strength of the barriers' height in both cages. The fact that the barriers' height predicted by the semiempirical models is higher than the reference DF-MP2/CBS^(c) values is related to the properties they are built upon. Note that semiempirical potentials have been fitted to reproduce bulk macroscopic properties obtained from experimental data under given thermodynamical conditions. In addition, we also found that the apparently good predictions of the pairwise ab initio PES^{(b)[34]} for the CO₂@sl cages are just a fortuitous cancellation of errors, attributed to artifacts at short distances of the CO₂-H₂O potential, as well as its oscillatory behavior around the barrier in the small 5¹² cage.

Figure 7. Relative and % errors (δE and %δE) of the B3LYP-D3(BJ), B3LYP-D3M(BJ), and B3LYP-D3(OP) energies compared with the DF-MP2/CBS^(c) along the *R* coordinate/*Z* axis of the small and large CO₂@sl cages.

Given the good agreement found for the B3LYP-D3 functional with D3(BJ), D3M(BJ), and D3(OP) dispersion corrections, in Figure 7, we display the relative and percentage errors against the DF-MP2/CBS^(c) reference data along the *R* coordinate, lying in the *Z* axis direction, for both 5¹² and 5¹²6² clathrate cavities (see upper and lower panels). In both cases, the barriers' height predicted by the DFT functional is underestimated, with the small 5¹² cage showing higher relative errors than the large cage, owing to its more compact structure. The dispersion contribution is found to be very small, and in fact results in an overcorrection. By checking the relative errors for different configuration regions, such as near the edges (for *R* between 2–6 Å) and around the minima (for *R* around 1 Å), we obtained small values of average relative errors, indicating a very good agreement with respect to the reference data, and in case of the B3LYP-D3M(BJ) energies count approximately 6% and 4%, respectively.

Figure 8. Potential contour plots in the (φ, θ) plane for the small 5¹² (left panels) and large 5¹²6² (right panels) cages of the CO₂@sl clathrate in the (φ, θ) plane obtained from the indicated electronic structure calculations or analytical model potentials. Darker colors correspond to potential minima values, in kcal mol⁻¹.

Interaction energies: Orientational anisotropy

In Figure 8, we show potential contour plots in the (φ, θ) plane for the CO₂@sl clathrate to display angular anisotropy nearby the center, *R* = 0 Å, of the cages (see left and right panels for the small 5¹² and large 5¹²6² cages, respectively). Contour plots are depicted (from the upper to lower panels of the figure) for the reference DF-MP2/CBS^(c) energies, for the DFT energies using the B3LYP-D3M(BJ) functional, for the two analytical ab initio PES^(a), and PES^(b) potentials, and for two semiempirical models corresponding to the SPCE/EPM and TIP4Pice/ZD. Within the small CO₂@sl cage, the CO₂ is located at θ ≈ 60° and φ ≈ 90°, whereas in the large CO₂@sl cage, the CO₂ is able to

move almost freely around the equatorial plane of the cage and presents two degenerate minima at $\theta = 90^\circ$ and $\phi \approx 45$ or 225° (see also Figure 1). Such results are in very good agreement with respect to experimental single-crystal and powder X-ray diffraction as well as solid-state NMR studies,^[21,85,86] which measure the most frequently orientation of the CO₂ with respect to the equatorial plane of the sl cages.

Among all DFT/DFT-D calculations considered in the present study, we found that the B3LYP functional including the D3M(BJ) dispersion corrections shows the most quantitative agreement with respect to the angular anisotropy of the reference data for both CO₂@sl cages (see B3LYP-D3M(BJ) panels of Figure 8). The mean absolute error (MAE) for the whole range of ϕ and θ is 0.13 kcal mol⁻¹ in the small cage, and 0.14 kcal mol⁻¹ in the large one; with maximum absolute errors of 0.18 kcal mol⁻¹ in the small cage and 0.24 kcal mol⁻¹ in the large one.

In Figure 8, one can also see that the ab initio PES^(a) and PES^(b) pairwise potentials show a very good qualitative agreement with respect to the orientational anisotropy; however, it seems that many-body corrections should be included to achieve quantitative agreement. In turn, we found that semiempirical models are not able to globally represent, either qualitatively or quantitatively, the orientational anisotropy, especially for the CO₂ in the large 5¹²6² cage (see in the two lower panels of Figure 8 for SPCE/EPM and TIP4Pice/ZD models). Therefore, it should be carefully taken into account when rotational ability and orientational stability of such clathrate structures are of interest.

Concerning the remaining cages of the CO₂@sl and CO₂@sH clathrate hydrates, in Figure 9, we also present contour plots varying the orientation of the CO₂ molecule inside the 4³5¹²6³, 5¹²6⁴, and 5¹²6⁸ cages from the DF-MP2/CBS^(c) (see left panels) and B3LYP-D3M(BJ) (see right panels) calculations. Again, B3LYP-D3M(BJ) results are in good accord with the reference data for all cages studied. One can see that the potential minima are at around $\theta = 0^\circ$ and $\phi = 0$ or 360° for the CO₂@4³5¹²6³ and CO₂@5¹²6⁴ cases, whereas the CO₂ molecule prefers to be placed parallel to hexagons with $\theta = 90^\circ$ and $\phi = 90$ or 270° in the 5¹²6⁸ sH cage (see also Figure 1). This planar orientation of the CO₂ is also the most stable configuration in the 5¹²6² sl cage. As can be expected, the reorientation of the guest molecule depends on the cage size and their symmetry. So far the CO₂@sl structure has been observed, where the CO₂ is lying in the equatorial plane within the 5¹²6² cavity, caused by the spherical shape of the cage. The same occurs for the 5¹²6⁸ one of the CO₂@sH, whereas for all the other cavities of sl, slI, and sH there is no such orientational preference. In both the 5¹²6² and 5¹²6⁸ cages, the CO₂ can freely rotate in the equatorial plane, although as the size of the cage increases, the CO₂ lies further away from the center of the cage (see Figure 3). Such orientation permits the guest molecule to rotate easily, and may enhance the stability and rigidity of the CO₂ clathrates. As has been found,^[46] by including nuclear quantum effects for the CO₂@sl cages, the rotational ability of the CO₂ is hindered in the small sl cavity, whereas in the large 5¹²6² one, translational and rotational degrees of freedom are highly cou-

Figure 9. Potential contour plots in the (ϕ, θ) plane from DF-MP2/CBS^(c) (left panels) and B3LYP-D3M(BJ) (right panels) calculations, for the 4³5¹²6³ (upper panels), 5¹²6⁴ (middle panels), and 5¹²6⁸ (lower panels) cages of the CO₂@sl/sH clathrates. Darker colors correspond to potential minima values, in kcal mol⁻¹.

pled. However, in the latter study, the SCPE/EPM semiempirical potential was employed,^[46] which shows substantial differences with respect to the reference DF-MP2/CBS^(c) results (see Figure 8), so one should expect that anharmonicity could also be crucial to describe their stability, and thus should be explored taking into account realistic underlying interactions.

Summary and Conclusions

We have introduced a general protocol that can be used to examine globally the validity of any interaction against available reference data and gauge their performance for any guest–host system. Based on this scheme, by sampling representative minimum and non-minimum configurations on the potential surface of CO₂@sl/slI/sH cages, we have discussed, classified, and assessed the performance of a variety of promising DFT approaches, as well as various pairwise semiempirical and ab initio based models, with some of them emerged only recently.

Converged DF-MP2 reference data are reported on such systems for the first time, and were used to benchmark the performance of the two-body (semiempirical and ab initio models) and cooperative many-body approaches. We found that semiempirical interaction models underestimate the binding energies, whereas ab initio pairwise potentials tend to overestimate them. Among the DFT approaches studied, we found that the B3LYP with the D3(BJ), D3M(BJ), and D3(OP) dispersion corrections fulfils the proposed criteria and is able to describe the underlying interactions in all CO₂@sl/slI/sH cages.

Regarding the dispersion correction, we found that they are necessary to recover the bounded interaction within the cages, and thus contribute to the guest–host stability. Our results indicate that the D3M(BJ) scheme shows the best performance against the reference data compared with the different D3 damping schemes used in this study.

By analyzing the orientation of the CO₂ molecule inside the cages, we show that it depends on the size and symmetry of the cages. So far, CO₂@sl clathrates have been observed where the CO₂ lying within the 5¹²⁶2 cavity is on the equatorial plane owing to its spherical shape, as in case of the 5¹²⁶8 of the CO₂@sH cage, whereas for all other cages studied, no such orientational preference is found. This orientation implies rotational ability of the CO₂ in these cages and may play a decisive role in enhancing the stability of the crystalline framework.

The computational analysis is used to understand the nature of the bonding in these molecular materials and to interpret the guest positions in the hydrate cages obtained from experimental studies. Indeed, the present study is restricted to specific (relatively large) finite-size cages of the CO₂@sl/sll/sH systems. For an accurate description of the whole interaction in the CO₂ clathrate hydrates, one needs to include the corresponding 3D hydrate lattices; however, dealing with such finite-size/lattice effects requires even much larger molecular systems to be modeled under periodic boundary conditions. Although extrapolations from finite-size systems to bulk rely on assumptions, the output of systematic comparisons could reveal trends in the interactions, essential for a reliable description of extended systems. Further, the availability of accurate benchmark energies for large finite-size systems opens interesting possibilities of tracing out errors in DFT or potential model approaches as a function of system size, allowing us to draw connections between such errors in finite-size clusters and condensed-matter systems. Apart from cage/lattice effects, cage occupancy, as well as nuclear quantum effects and thermodynamic conditions are also expected to affect guest–host dynamics and the relative clathrate stability, thus should also be considered.

The open question of why CO₂ guests form a sl clathrate hydrate phase is still not addressed by the present calculations, but with a proper modeling of the CO₂@H₂O interactions in the clathrate hydrate cages, it is hoped that a step toward understanding the relationship between the local guest–host interactions and the choice of the clathrate hydrate phase structure will have been taken. Such findings allow us to improve our knowledge on many-body cooperative effects in non-covalent interactions for developing best potential models for reliable computer simulations.

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Conflict of interest

The authors declare no conflict of interest.

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