

First-principles approaches on guest-free/guest-host interactions in clathrate hydrates.

A Cabrera-Ramírez¹, D J Arismendi-Arrieta², Á Valdés³, and R Prosimiti^{1*}

¹Institute of Fundamental Physics (IFF-CSIC), CSIC Serrano 123, 28006 Madrid, Spain, ²DIPC, Paseo Manuel de Lardizabal 4, 20018 Donostia-San Sebastián, Spain. ³Departamento de Física, Universidad Nacional de Colombia, Calle 26, Cra 39 E4004 Bogotá, Colombia.

Synopsis Modeling interactions is a challenging and computationally demanding task, essential to reliably determine molecular properties. Despite the increasing interest in clathrate hydrates and their technological applications, a molecular-level understanding of their formation and properties is still far from complete. In view of the complexity of the problem, our results highlight the importance of accurate and computational demanding approaches for building up predictive models for such inclusion compounds.

Recently, empty hydrate structures sI, sII, sH, and others have been proposed as low-density ice structures by both experimental observations and computer simulations, while CO₂ clathrates have been proposed as potential molecular materials in tackling important environmental problems related to greenhouse gases capture and storage [1]. Some of them have been synthesized in the laboratory, which motivates further investigations on the stability of such guest-free and guest-host clathrate structures. Thus, we focus our study on non-covalent interactions in such compounds, in order to validate the ability or inability of conventional and modern first-principles methods to simultaneously describe both the hydrogen bonding within the water network and the predominantly dispersion bound gas-water interactions.

Energy reference data from accurate high level quantum-mechanical calculations are essential for testing both force fields and DFT methods [2]. Therefore, we first propose a systematic protocol for benchmarking the intermolecular interactions in finite-size systems of individual aperiodic cages, such as those of guest-free and guest-host CO₂@sI, CO₂@sII, and CO₂@sH clathrates, and then for their entire periodic unit cells [3, 4] (see Fig. 1). We found that dispersion interactions are important in the stabilization energies of such clathrate cages, and the encapsulation of the CO₂ into guest-free clathrate cages is always energetically favorable. In addi-

tion, the orientation of CO₂ inside each cage was explored, and the ability of such current bottom-up and top-down promising approaches to accurately describe noncovalent CO₂@H₂O guest-host interactions in sI, sII, and sH clathrates will be discussed.

Finally, comparisons with semiempirical force fields (widely used in simulations) will be presented providing information for their applicability to future multiscale computer simulations.

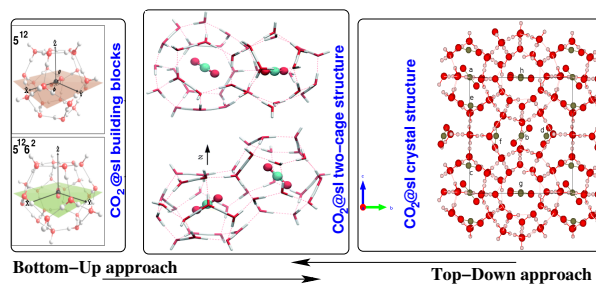


Figure 1. CO₂@sI: building blocks and crystal structures.

References

- [1] Falenty A *et al* 2014 *Nature Lett.* **516** 231; Matsui T *et al* 2017 *J. Chem. Phys.* **147** 091101; Koh C *et al* 2011 *Annu. Rev. Chem. Biomol. Eng.* **2** 237.
- [2] Valdés A *et al* 2015 *J. Phys. Chem. C* **119** 3945
- [3] Arismendi-Arrieta A *et al* 2018 *Chem. Eur. J.* **24** 9353; León-Merino I *et al* 2018 *J. Phys. Chem. A* **122** 1479
- [4] Cabrera-Ramírez A *et al* 2019 *J. Phys. Chem. C* submitted

*E-mail: rita@ff.csic.es