# Computational quantum chemistry approaches in $CO_2$ clathrate-hydrates

*Adriana Cabrera-Ramirez*[1,2], *Daniel J. Arismendi-Arrieta*[3], *Álvaro Valdés*[4], *Rita Prosmiti*[1]

[1] Institute of Fundamental Physics (IFF-CSIC), Serrano 123, 28006 Madrid, Spain
[2] Doctoral Programme in Theoretical Chemistry and Computational Modelling, Doctoral School, Universidad Autónoma de Madrid, 28046, Madrid, Spain
[3] Department of Chemistry, Ångström Laboratory, Uppsala University, P.O. Box 538, 75121 Uppsala, Sweden
[4] Escuela de Física, Universidad Nacional de Colombia, Sede Medellín, A. A. 3840, Medellín, Colombia

adrianacabrera@iff.csic.es

Clathrate hydrates are crystalline compounds formed by guest molecules within a three-dimensional host lattice of water cages. These structures have been involved in current technological and industrial applications. Specifically, the $CO_2$ clathrate has been proposed as a potential molecular material in the fight against environmental problems related to greenhouse gases capture and storage.

The objective of this work is to understand of formation, energetics and structural stability of sI clathrate hydrates to describe the underlying processes at molecular level and determine the guest-host/host-host interactions dominated by hydrogen bonds and van der Waals forces. In particular, we consider two approaches: bottom-up and top-down. The first approach proposes to study the intermolecular interactions in finite-size systems of individual aperiodic cages, such as guest-free and guest-host $CO_2$ clathrates, and then extrapolate to their entire periodic unit cells. The second approach considers the unit cell that reproduces a periodic crystalline structure, and thus, guest-lattice effects are studied by a systematic evaluation of different density functionals. We consider functionals, including local and non-local dispersion corrections such as the exchange-hole dipole moment (XDM) and the semi-empirical model (DFT-D), as well as vdW-DF and vdW-DF2, respectively.

Our findings show that DFT-D approaches are able to describe properly the underlying interactions, once dispersion corrections are applied. Further, the results obtained allow to generate reference interaction energies from accurate quantum-mechanical calculations by testing different approaches on $CO_2$@sI systems. Such studies provide high-quality information with new insights that allow the construction of new reliable data-driven models and in turn have greater control of the properties of this promising material.

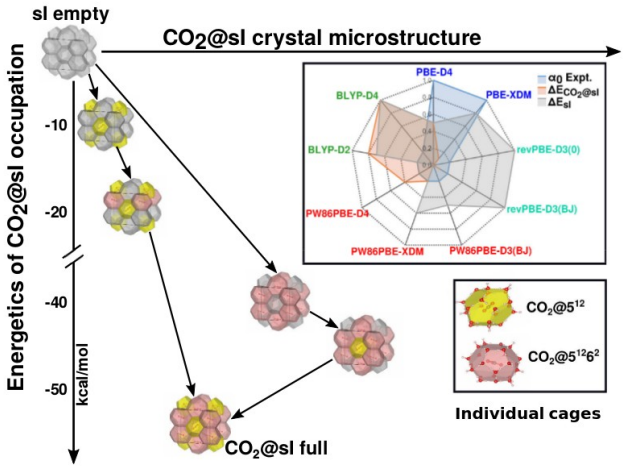


*Figure 1: DFT-derived energetics for the gradual storage of $CO_2$ molecules into sI crystal.*

**Index Terms:** clathrate-hydrate, density functional theory, carbon dioxide.

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