Computational study of the interplay between intermolecular interactions and CO_2 orientations in type I hydrates

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Hydrates are non-stoichiometric inclusion solids where water molecules form a crystalline regular network through hydrogen bonding, leaving cage structures that may enclathrate small guest molecules, such as carbon dioxide (CO_2). Numerous research efforts from different scientific and technological communities have been devoted to study CO_2 gas hydrates, due to the applications and industrial processes where they are involved, as for instance their potential to capture and store greenhouse effect gases, especially CO_2 sequestration. One very attractive idea, although not yet accessible in practice, is the exchange of CO_2 for the CH_4 trapped inside naturally occurring hydrates in the ocean seabed and permafrost soils. This process would connect the potential future exploitation of hydrates as a methane source with the long term storage of this greenhouse gas, meaning a high added- value environmental side effect. The feasibility of this application depends to a great extent on the detailed knowledge of the structural properties and dynamics of CO_2 molecules inside the hydrate, a key to guess the optimal replacement process.

Orientation molecules within the hydrate cavities is the key to understand these processes. Carbon dioxide (CO_2) molecules show a rich orientation landscape when they are enclathrated in type I hydrates. Previous studies have described experimentally their preferential orientations, and some theoretical works have explained, but only partially, these experimental results. In the present work [1], we use classical molecular dynamics and electronic density functional theory to advance in the theoretical description of CO_2 orientations within type I hydrates. Our results are fully compatible with those previously reported, both theoretical and experimental, the geometric shape of the cavities in hydrate being, and therefore, the steric constraints, responsible for some (but not all) preferential angles. In addition, our calculations also show that guest-guest interactions in neighbouring cages are a key factor to explain the remaining experimental angles. Besides the implication concerning equation of state hydrate modeling approximations, the conclusion is that these guest-guest interactions should not be neglected, contrary to the usual practice.
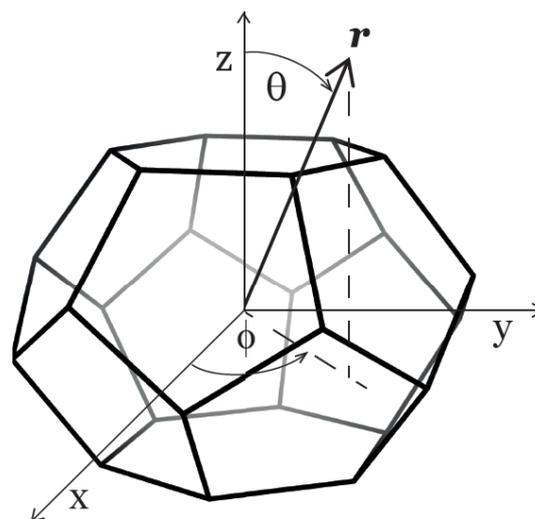
[1] M. Pérez-Rodríguez, A. Vidal-Vidal, J. M. Míguez, F. J. Blas, J.-P. Torré, and M. M. Piñeiro, Phys. Chem. Chem. Phys. **19**, 3384 (2017).

Figure 1: T cell showing the reference Cartesian axes (x, y, z), and related orientation angles (θ, ϕ) of vector **r**. θ is the angle with respect to positive z, and ϕ is the angle with respect to the positive x in the (x, y) plane.
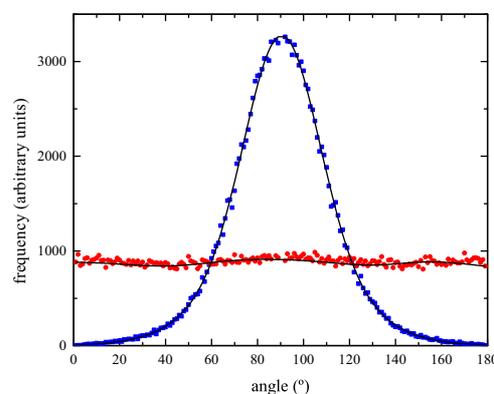

Figure 2: Frequency plot of θ (blue squares) and ϕ (red circles) orientation angles of a CO_2 molecule inside a T cage, calculated from MD simulations.