Modelling non-covalent interactions of graphene and small gas molecules: An assessment of cluster models and methods

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Non-covalent interactions of gas phase molecules with graphene-based materials can be essential for modern nanosensors [1]. Quantum chemical methods, especially those based on density functional theory, are indispensable tools to model and predict non-covalent interactions. In this contribution, we present a benchmark study in which we assess methods and models for the CO_2 adsorption on graphene surfaces and compare the results with experiments [2,3]. The surfaces are represented by finite cluster models which vary in size and shape. The adsorption of CO_2 is modelled at three different sites for parallel and orthonormal orientations. For the smallest graphene surface model (benzene) we compare interaction energies and adsorption geometries to the golden standard of quantum chemistry, the CCSD(T) method, and to the experiment. Not surprisingly, we find that benzene is too small to reliably predict experimental values and we continue to examine the interaction energies with respect to the size of the graphene model. The results allow us to derive an extrapolation scheme with which values for an infinitely large graphene surface can be obtained. Those final results are in excellent agreement with the experiment. Finally, by means of symmetry adapted perturbation theory, we analyse the nature and size-dependency of the non-covalent interactions.

References

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Figures

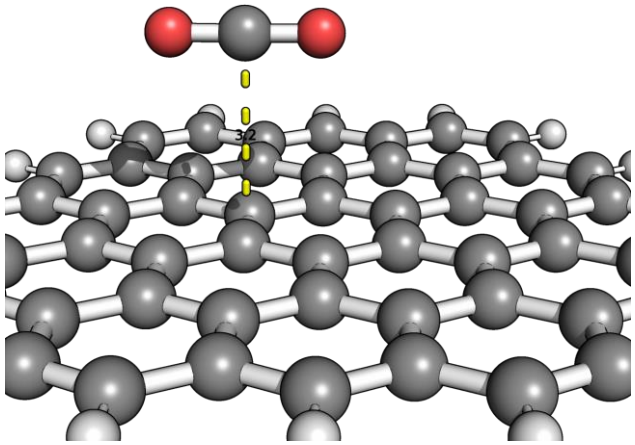

Figure 1: Example for the adsorption of CO_2 close to the bridge site of circumcoronene is shown. In addition, the yellow line indicates the distance between the surface and the centre of mass of CO_2.