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

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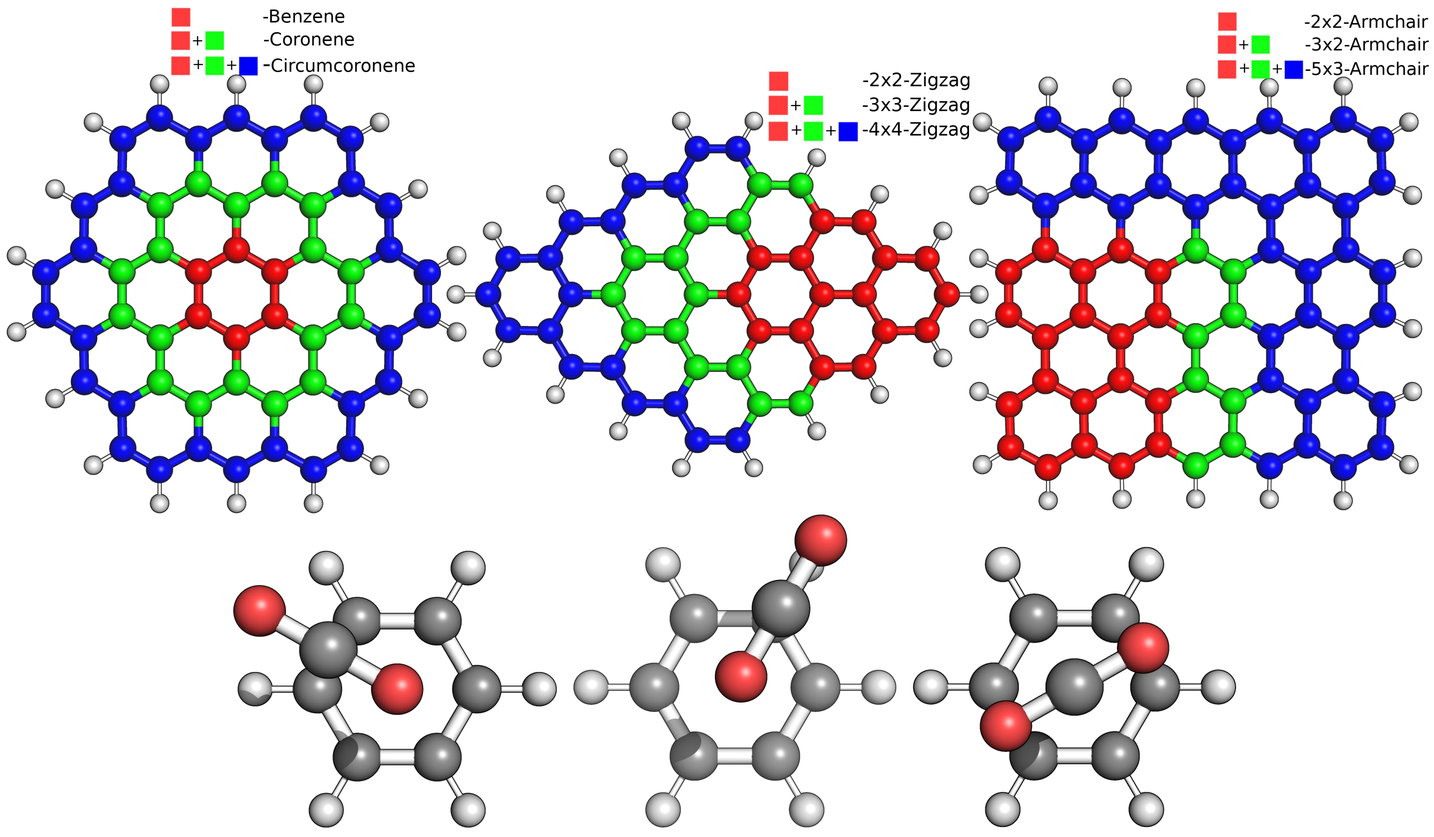
Introduction:

- Graphene based sensors are one example of novel nanodevices
- Understanding Sensor ⇔ adsorbent non-covalent interactions is the key to improve sensor performance
- CO_2 / Graphene is an excellent model system to study
- GOAL: Assess method/model combination obtain most accurate adsorption energies

Methods:

- 9 cluster models / 3 adsorption sites / 2 orientations
- Coupled-Cluster (CCSD(T)) and experimental data is used as reference



For **accurate interaction energies**, combine **density functional theory** with **symmetry adapted perturbation theory** and **extrapolate the surface size to infinity**

Results 1: Method Assessment for Benzene Against CCSD(T)

- All functionals predict the same relative complex stabilities
- Parallel are more stable than orthonormal orientations
- DSD-BLYP-D3 provides best energies & geometries compared to CCSD(T)
- All interaction energies are too small compared too experiment → larger models are necessary

Table 1: Interaction energies (given in kJ/mol) for CO_2 on benzene, at different adsorption sites and orientations, calculated with several electronics structure methods.

	Glob. min.	bridge par.	top par.	hollow par.	bridge orth.	top orth.	hollow orth.
CCSD(T)	-7.6	-7.2	-6.9	-7.1	-0.4	-0.4	-0.5
PBE-D3//SAPT0	-11.9	-11.4	-10.9	-10.7	-1.0	-1.1	-1.4
PBE-D3	-10.2	-9.9	-9.6	-9.5	-2.1	-1.7	-1.7
B3LYP-D3	-10.9	-10.5	-10.2	-10.0	-0.9	-0.9	-1.3
ωB97X-D3	-11.3	-10.9	-10.5	-10.3	-1.5	-1.0	-1.0
ωB97X-V	-10.6	-10.2	-9.8	-9.8	-1.8	-1.2	-1.2
DSD-BLYP-D3	-9.2	-8.8	-8.4	-8.4	-1.1	-0.8	-0.8

Results 2: Size-dependency

- Relative stabilities are size-independent
- The larger the surface model, the stronger the adsorption
- Extrapolate the surface size:

$$\lim_{x \to 0} \left(\frac{m}{x} + n \right),$$

with x-number of carbon atoms

- Interpolation with DSD-BLYP-D3/SAPT yield excellent agreement with experiment

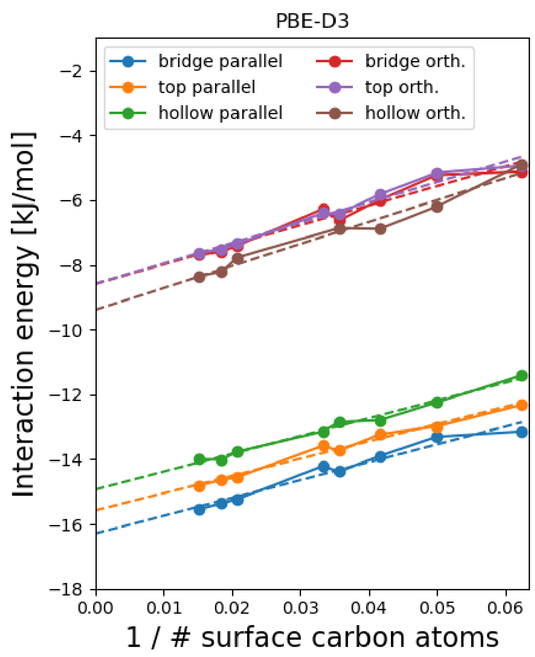


Table 2: Extrapolated interaction energies (in kJ/mol) of CO2 adsorbed on an artificial infinite graphene model calculated with several density functionals and SAPT0.

	Global Min	bridge par.	top par.	hollow par.	bridge orth.	top orth.	hollow orth.
PBE-D3	-16.3	-16.3	-15.6	-14.9	-8.6	-8.6	-9.4
ωB97X-V	-18.6	-18.5	-17.4	-16.7	-9.7	-9.7	-10.4
DSD-BLYP-D3		-18.9	-18.0	-17.3	-10.8	-10.3	-11.6
PBE-D3//SAPT0	-24.8	-24.8	-23.2	-22.0	-14.2	-14.1	-15.9
DSD-BLYP-D3//SAPT0		-26.8	-25.1	-23.8	-16.2	-15.2	-18.2
PBE-D3 (periodic)		-15.6	-15.2	-14.4	-8.5	-8.5	-9.0
Experiment [2]	30.1 ± 1.5						
Experiment [3]	26.1 ± 2						

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