

Graphene Interaction with Ni(111) Described by Modern Dispersive Forces

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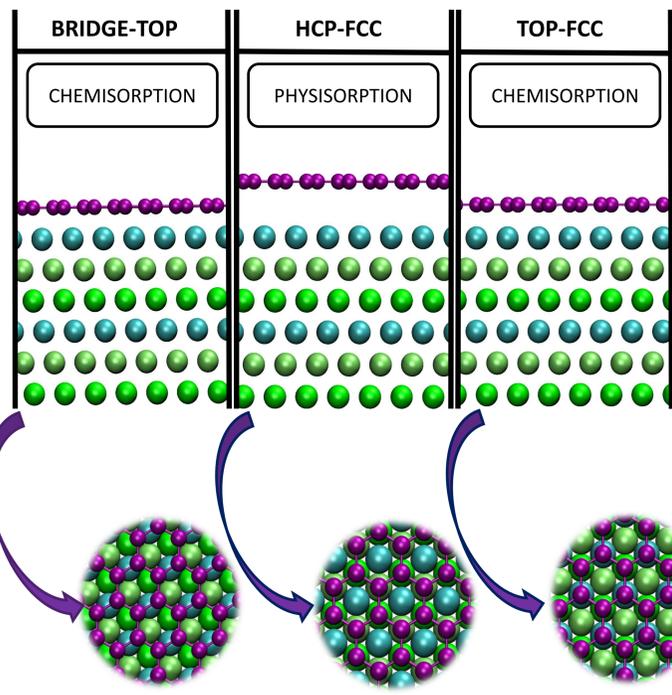
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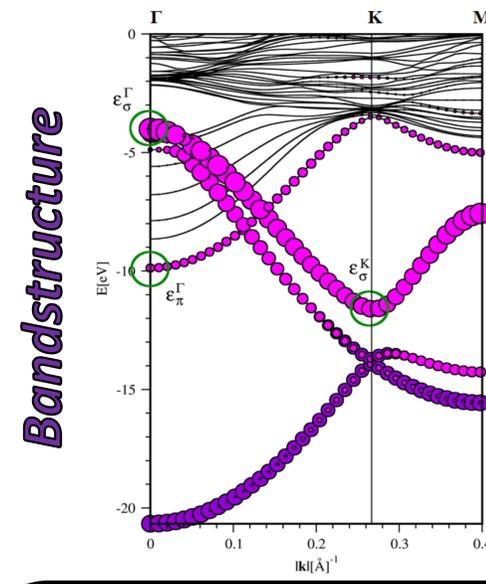
For the **synthesis** of high-quality and large-size patches of **graphene**^[1] by chemical vapor deposition, **Ni(111)** have quickly gained momentum against other metals since the lattice mismatch of graphene with respect to Ni(111) is propitiously small.² Here we present a **Density Functional Theory (DFT)** study on the suitability of **modern corrections** for the inclusion of **dispersion related terms (DFT-D)** performed by VASP in treating the interaction of graphene and metal surfaces, exemplified by the graphene/Ni(111) system with three different conformations.

INTRODUCTION



METHODS	BASIS	CORRECTIONS	
	DFT	DFT-D	
PBE	Grimmes	Tkatchenko-Schefflers	
	D2	TS	
	D3	TS-Self Consistent Screening	
	Becke-Jonson	TS-Many Body Dispersion	
	Andersson		

The performance of modern DFT-D corrections—Grimme D2³, D3⁴, BJ⁵ damping, and A⁶ corrections, as well as TS⁷, TS-SCS⁸, and TS-MBD⁹—applied in conjunction with PBE have been assessed relying on their description of the adsorption of graphene on Ni(111) featuring chemisorbed and physisorbed states. Two experimentally observed chemisorbed states, namely top-fcc and bridge-top, were examined, as well as an hypothetical physisorbed situation (hcp-fcc).



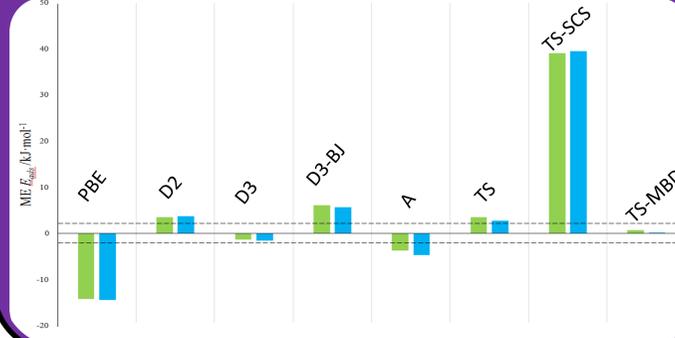
The energy levels ϵ of the graphene σ and π bands at Γ and K points have been compared to experimental Angle-Resolved Photoemission Electron Spectroscopy (ARPES). Bandstructure is well reproduced by any of the tested methods, so relative graphene band levels are determined by the adsorption distance. The well-known opening of the Dirac points caused by graphene/Ni(111) interactions is easily appreciable.

Obtained data are compared to accurate experimental values yielding a graphene-Ni(111) distance of 211±7 pm and adsorption energy values of 9.2±2.0 kJ·mol⁻¹ per C atom.

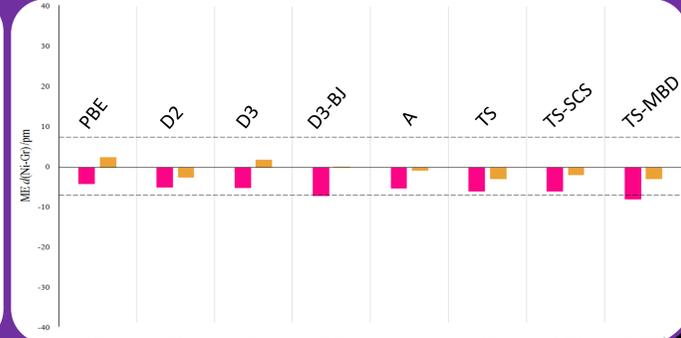
Tested Methodologies

All studied methods are well suited to describe the graphene-Ni(111) distance. However, only the fully *ab initio* TS-MBD and semi-empirical Grimme D3 corrections are able to well reproduce experimental E_{ads} values.

MEAN ERROR ABSORPTION ENERGIES

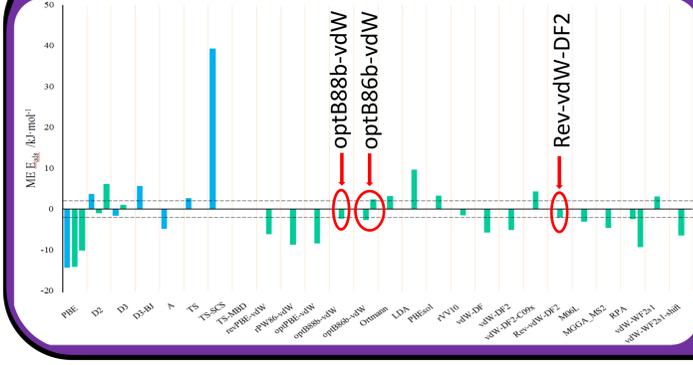


MEAN ERROR Gr-Ni DISTANCE

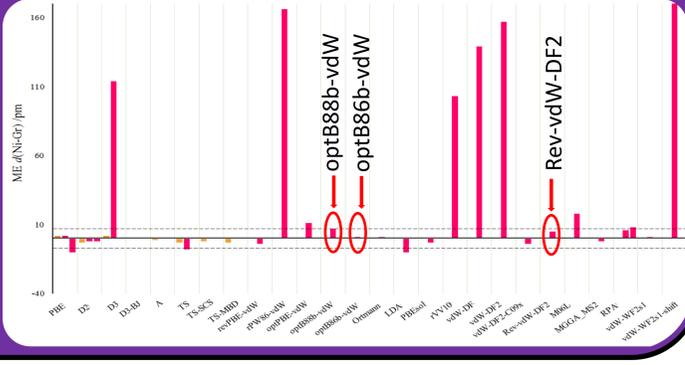


All Methods Compilation

MEAN ERROR ABSORPTION ENERGIES



MEAN ERROR Gr-Ni DISTANCE



Top-fcc conformation has been compared also with other functionals. As shown, some previous studied methods match experimental results, such the Rev-vdW-DF2 functional. Also the optB86b-vdW and optB88b-vdW functionals are fairly close.

CONCLUSIONS

Present results highlight how different approaches to introduce dispersion in DFT based methods may yield discrepant results, and so, one must take dispersion related interactions with great caution when studying systems of technologic interest. In this line, the present survey point D3 and TS-MBD as best suited for future accurate and affordable theoretical studies of nanotechnologic devices based on graphene-metal contacts.

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