Hybrid Molecular-Based Interfaces from first principles

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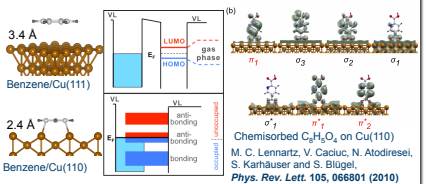
Introduction

The hybrid systems consisting of physisorbed or chemisorbed molecules on surfaces are a key component in the technologically emerging molecular electronics and molecular spintronics fields. From a theoretical point of view, a major challenge in the density functional theory (DFT) is to properly describe the non-local correlation effects responsible for the van der Waals (vdW) interactions that are crucial for bonding in the physisorbed molecular systems. Therefore, we explored how to mitigate this DFT limitation via a first-principles non-local correlation functional (vdW-DF) or a semi-empirical approach and applied them to investigate a prototypical non-aromatic molecule as cyclooctatetraene (C_8H_8) on several metal surfaces [1] and the clean and intercalated graphene on Ir(111) [2-4]. In particular, our *ab initio* vdW-DF calculations performed for naphthalene ($C_{10}H_8$) on graphene/Ir(111) demonstrated that the intercalated atomic layers with an electropositive or electronegative character can modulate the strength of the vdW interactions between a π-conjugated molecule and the *n*- or *p*-doped graphene on Ir(111) [4]. Furthermore, on this basis, we also investigated how the physisorbed and chemisorbed molecules can be used to tune the strength and spin texture of the Rashba spin-split surface states of the $BiAg_2$/Ag(111) surface alloy [5,6].

Molecule-surface interfaces

Physisorption vs chemisorption



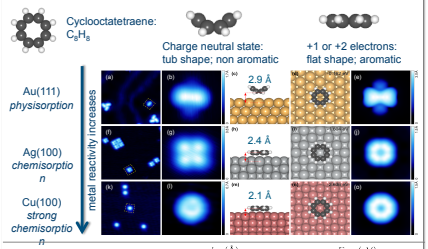
M. C. Lennartz, V. Caciuc, N. Atodiresei, S. Karhäuser and S. Blügel, ***Phys. Rev. Lett.* 105, 066801 (2010)**

Hybrid molecule-surface systems:

- physisorbed systems: sharp molecular electronic states
- chemisorbed systems: hybrid molecule-surface electronic states

Hybrid van der Waals systems

Organic molecules on metal surfaces [1]

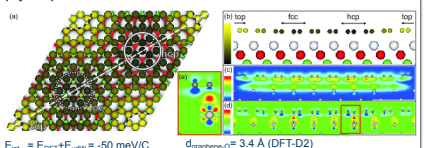


Surface	C – C (Å)	C = C (Å)	d_{eq} (Å) PBE	d_{eq} (Å) DFT-D3	d_{eq} (Å) vdW-DF2	E_{ads} (eV) PBE	E_{ads} (eV) DFT-D3	E_{ads} (eV) vdW-DF2
Au(111)	1.474	1.349	2.86	2.71	3.26	-0.162	-0.679	-1.040
Ag(100)	1.436	1.416	2.39	2.39	2.58	-1.604	-2.174	-1.714
Cu(100)	1.443	1.418	2.10	2.10	2.26	-2.636	-3.389	-2.628

Change of the molecular geometry due to strong hybridization!

Graphene on Ir(111) [2]

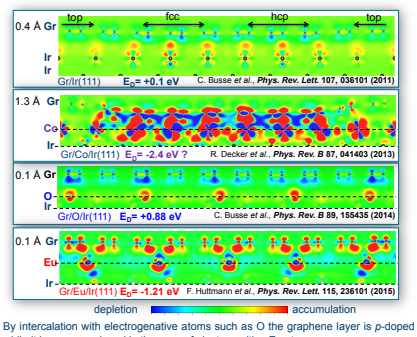
(10x10) graphene on (9x9) Ir(111): physisorption with chemical modulation



$E_{int} = E_{DFT}+E_{vdW}$ = -50 meV/C
E_{DFT} = +20.0 meV/C
E_{vdW} = -70.0 meV/C

On Ir(111), the DFT calculations including the vdW interactions revealed that at the top site graphene (Gr) is physisorbed. However, the analysis of the charge density difference clearly indicated that at the fcc and hcp sites a weak chemical bond is formed at the graphene-Ir(111) interface.

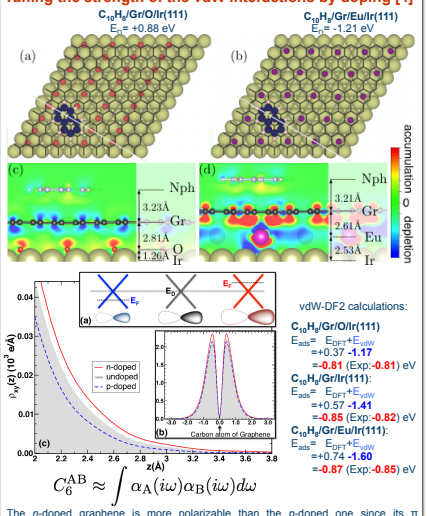
Doping graphene by intercalation [3,4]



By intercalation with electrogenative atoms such as O the graphene layer is *p*-doped while it becomes *n*-doped in the case of electropositive Eu atoms.

Hybrid van der Waals systems

Tuning the strength of the vdW interactions by doping [4]



vdW-DF2 calculations:

$C_{10}H_8$/Gr/O/Ir(111)
E_{ads}= E_{DFT}+E_{vdW}
=+0.37 **-1.17**
=**-0.81** (Exp:**-0.81**) eV

$C_{10}H_8$/Gr/Ir(111):
E_{ads}= E_{DFT}+E_{vdW}
=+0.57 **-1.41**
=**-0.85** (Exp:**-0.82**) eV

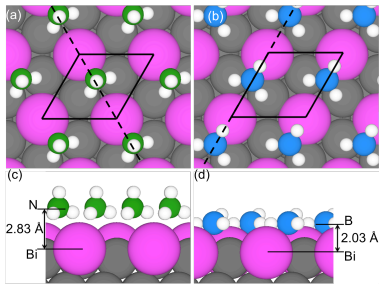
$C_{10}H_8$/Gr/Eu/Ir(111):
E_{ads}= E_{DFT}+E_{vdW}
=+0.74 **-1.60**
=**-0.87** (Exp:**-0.85**) eV

$$C_6^{AB} \approx \int \alpha_A(i\omega)\alpha_B(i\omega)d\omega$$

The *n*-doped graphene is more polarizable than the *p*-doped one since its π electronic states of the are more extended in space than in the later case. Overall, this feature leads to a different strength of the vdW interactions between the doped graphene layer and another π-system such as naphthalene ($C_{10}H_8$).

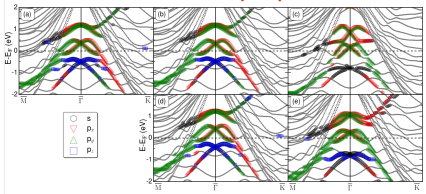
Tuning the spin-orbit coupling at hybrid interfaces

Inorganic molecules adsorbed on $BiAg_2$/Ag(111) [5]



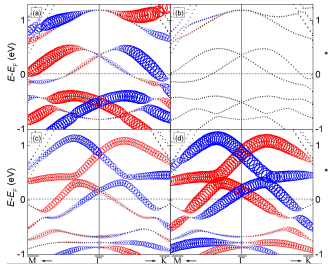
- on $BiAg_2$/Ag(111) ammonia (NH_3) is physisorbed while borane (BH_3) is weakly chemisorbed
- in the NH_3-$BiAg_2$/Ag(111) hybrid system the Bi atoms relax *outwards*
- in the BH_3-$BiAg_2$/Ag(111) hybrid system the Bi atoms relax *inwards*

Molecular-modulated Rashba spin-split surface states



On the $BiAg_2$/Ag(111) surface alloy the molecular adsorption gives rise to:
- (b) an increased magnitude of Rashba splitting of the occupied surface states for the NH_3-based hybrid system ($\lambda_{SO}^{NH_3 occ} = 0.10$ Å^{-1} vs $\lambda_{SO}^{Clean occ} = 0.09$ Å^{-1})
- (c) new Rashba spin-split unoccupied surface state for BH_3-$BiAg_2$/Ag(111)

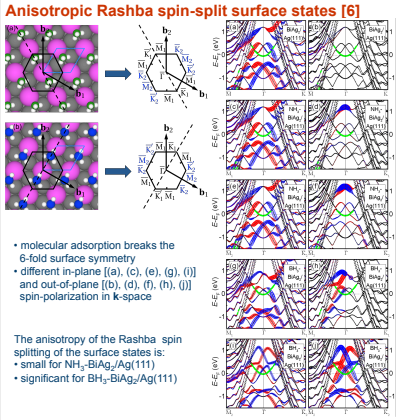
From in-plane to out-of-plane spin polarization of the surface states



- (a) in-plane and (b) out-of-plane spin polarization of clean surface
- (c) in-plane and (d) out-of-plane spin polarization of NH_3-surface hybrid system

Hybrid Rashba systems

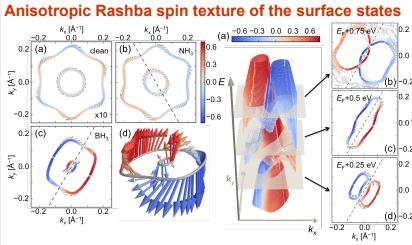
Anisotropic Rashba spin-split surface states [6]



- molecular adsorption breaks the 6-fold surface symmetry
- different in-plane [(a), (c), (e), (g), (i)] and out-of-plane [(b), (d), (f), (h), (j)] spin-polarization in **k**-space

The anisotropy of the Rashba spin splitting of the surface states is:
- small for NH_3-$BiAg_2$/Ag(111)
- significant for BH_3-$BiAg_2$/Ag(111)

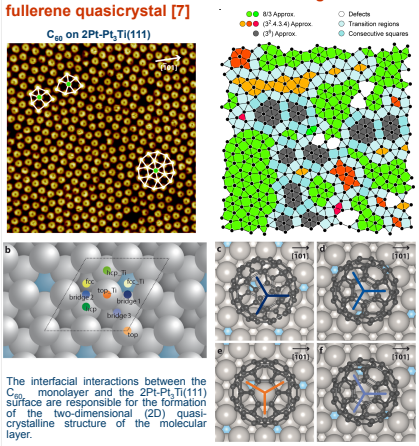
Anisotropic Rashba spin texture of the surface states



The reduction of the surface symmetry upon molecular adsorption results in:
- an energy-dependent anisotropy of the surface states in **k**-space
- a strong out-of-plane spin polarization for BH_3-$BiAg_2$/Ag(111)

Present and future investigations

Interface-driven formation of a 2D dodecagonal fullerene quasicrystal [7]



The interfacial interactions between the C_{60} monolayer and the 2Pt-Pt_2Ti(111) surface are responsible for the formation of the two-dimensional (2D) quasi-crystalline structure of the molecular layer.

Acknowledgments

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