ADSORPTION OF AROMATIC MOLECULES ON THE PLATINUM (111) SURFACE

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ABSTRACT

Aromatic molecules are promising building blocks for active and carrier-injection layers in organic electronics. The interaction of the first adsorbed layer of such molecules with the substrate is fundamental in determining the growth of these layers. For this reason such adsorbed systems have to be carefully modelled, in particular including the van der Waals (vdW) interaction which plays a crucial role in determining the correct adsorption geometry and energy. Platinum can be used in devices as a high work function electrode and its high reactivity as a transition metal may lead to a covalent-like contribution to the adsorption interaction. Our study investigates two members of acene family, namely benzene (Bz, C_6H_6) and pentacene (Pc, $C_{22}H_{14}$), adsorbed on the (111) surface of platinum.

COMPUTATIONAL DETAILS

The ground state configuration for both molecules has been calculated by means of the **DFT** framework using the **GGA-PBE** exchange correlation functional including **vdW** corrections. The simulations have been carried out using the **Quantum ESPRESSO** suite (QE) and confirmed using VASP and FHI-AIMS.

Slabs were constructed with 3 and 6 layers. The first layer in the former and the topmost two layers in the latter were left free to relax, with a vacuum region above the surface, measuring 11 and 33 Å respectively. In both cases an electric dipole correction technique has been applied.

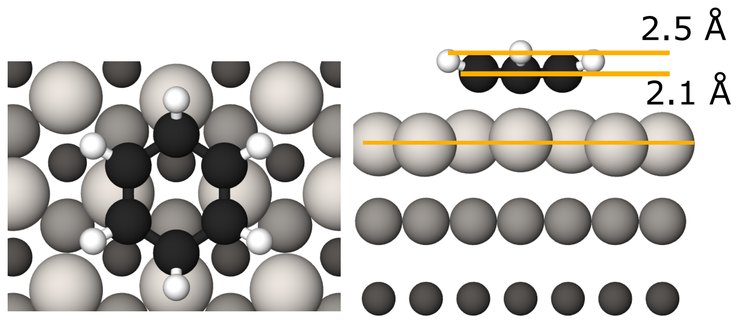
MODELLING VDW INTERACTION

In our simulations we included different corrections to account for the dispersion interaction. In particular we have chosen to apply the pairwise methods Grimme **D2** [1], **Tkatchenko-Scheffler** [2] (TS) and **vdW$_{surf}$** [3] or to add a non-local correction term of the family of vdW-DF1 [4] in the form of **optB88** [5] .
The TS self-consistent algorithm is not yet implemented in QE, hence we wrote a new routine from the D2-based one to accomodate the coefficients derived from TS, for C and H, and from vdW $_{surf}$ for Pt. We call this approach adapted TS (**aTS**). The geometries obtained with aTS have been verified with other softwares and vdW methods.

Bz/Pt(111): 3x3 supercell with 4x4x1 k-point grid mesh, 12x12x1 for DOS

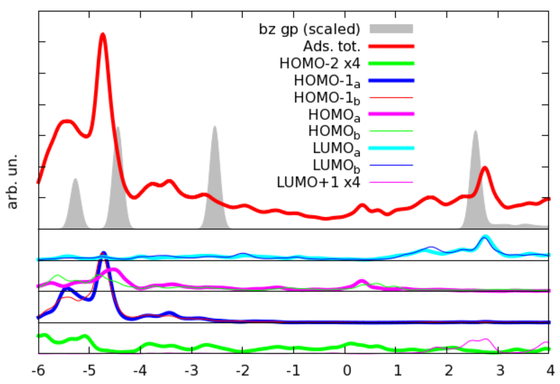
Adsorption geometry

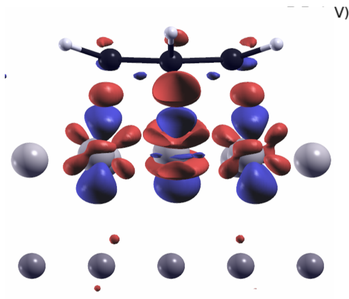
E_{bind} [eV]	
ads. site	aTS
top0	0.10
top30	0.36
bri0	0.96
bri30	**1.74**
fcc0	1.17
fcc30	0.77
hcp0	1.23
hcp30	0.87

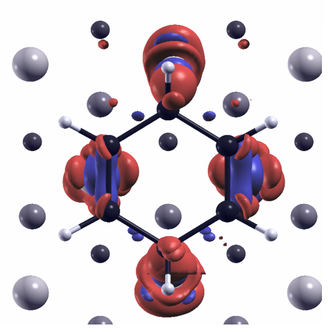


Very small differences in height with changing adsorption sites and vdW correction.

Electronic properties

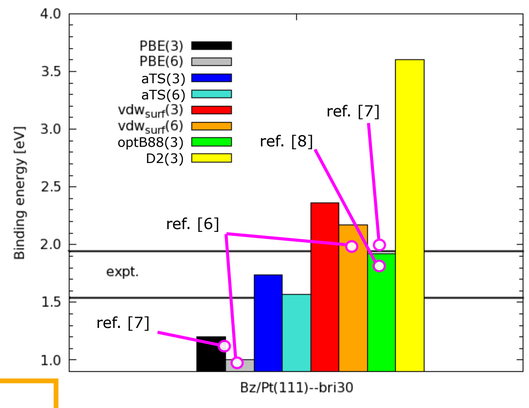






The DOS projected onto the molecular orbitals displays a strong hybridization of the molecule with the substrate.
This effect is also verified by the differences in charge densities for which a charge transfer of 0.3 *e* from the substrate to the molecule is obtained.

Adsorption energy and vdW corrections



PBE underestimates the binding energy compared to experimental results; D2 overestimates the Pt vdW coefficient.

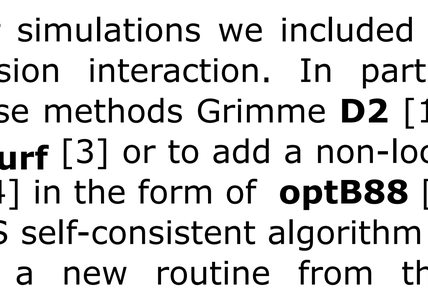
The calculated results are in agreement with the theoretical ones available in literature.

Using a thicker slab the induced energy change is not negligible.

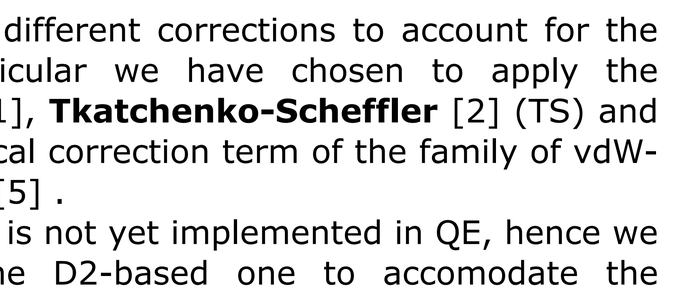
Pc/Pt(111): 7x4 supercell with 2x3x1 k-point grid mesh, 6x9x1 for DOS

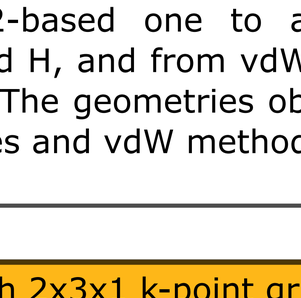
Adsorption geometry & STM spectra

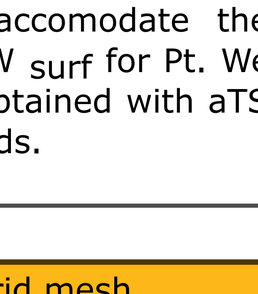
Most stable configuration: bri30



$d_{C\text{-}Pt}$ 1.95 Å $\Delta d_{C\text{-}C}$ 0.11 Å

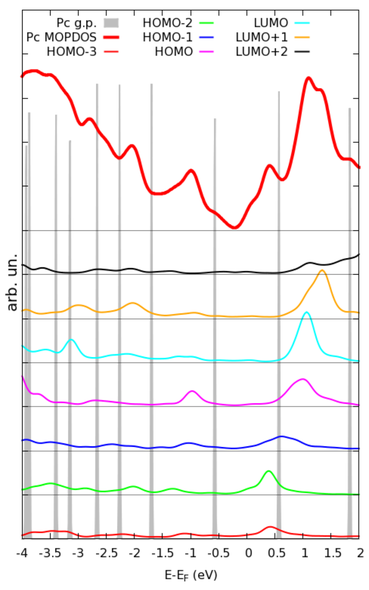


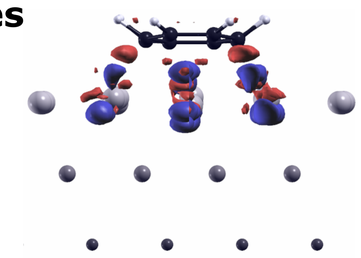


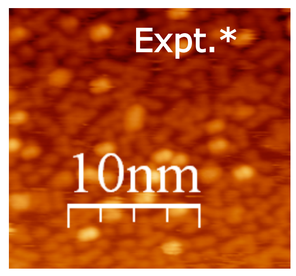


* experiments done by M. Gago at CSIC, Madrid

Electronic properties



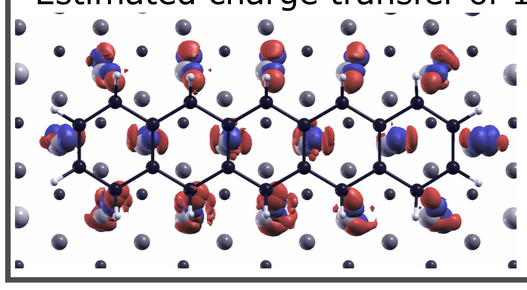




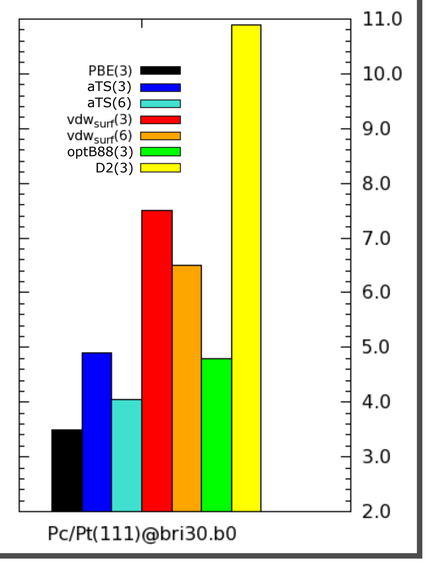
No ordered structures at high coverage

Strong molecule-metal hybridization

Estimated charge transfer of 1.5 *e*



Adsorption energy and vdW corrections



CONCLUSIONS

Our results for Bz/Pt(111) verify experimental and theoretical results available in literature.

In the calculated most stable configuration Pc adsorbs on Pt(111) in a gently bent configuration; the orientation of the molecule agrees with STM experimental results.

In both cases a strong molecule-substrate interaction is observed, due to the reactivity of platinum.

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