Physisorption of three amine terminated molecules (TMBDA, BDA, TFBDA) on the Au(111) Surface: The Role of van der Waals Interactions

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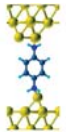
Abstract

Recently, the electronic properties and alignment of **tetramethyl-1,4-benzenediamine (TMBDA), 1,4-benzenediamine (BDA) and tetrafluro-1,4-benzenediamine (TFBDA) molecules** were studied experimentally. Discrepancies were found for both the binding energy and the molecule tilt angle with respect to the surface, when results were compared with density functional theory calculations [1].

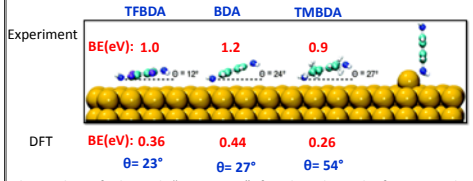
We have included the **effect of vdW interactions** both between the molecules and that of the molecule with the Au(111) surface and find binding energies which are in very good agreement with experiments. We also find that at **low coverages** each of these molecules would adsorb **almost parallel** to the surface. N-Au bond lengths and charge redistribution on adsorption of the molecules are also analyzed. Our calculations are based on DFT using vdW-DF exchange correlation functionals. For BDA (since we are aware of experimental data), we show that for **higher coverage**, inclusion of intermolecular van der Waals interactions leads to tilting of the molecules with respect to the surface and **formation of line structures**. Our results demonstrate the central role played by intermolecular interaction in pattern formation on this surface.

Introduction

1. Amine-terminated molecules are applied as single molecule electrical junctions. In particular 1,4-diaminobenzene (BDA) seems to be particularly useful as it provides less variation and hence better control in conductance than that observed for other linkers [2].



2. Experiment and DFT calculations [1]:



The authors find good "agreement" for the tilt angle for BDA. The disagreement for the others was ascribed to the lack of vdW interactions in the DFT calculations.

➢**Why would a symmetric molecule with a benzene ring adsorbs on Au(111) with a large tilt angle, while benzene itself prefers to align parallel to the metal surface?**

➢**Can PBE functional predict quantitatively reliable results for systems in which vdW interactions are expected to play a role?**

Computational details

➢Simulations are carried out using Density Functional Theory

➢Code: QUANTUM ESPRESSO

➢Ultrasoft Pseudopotential

➢Exchange-Correlation: GGA-revPBE [3] and vdW-DF[4]

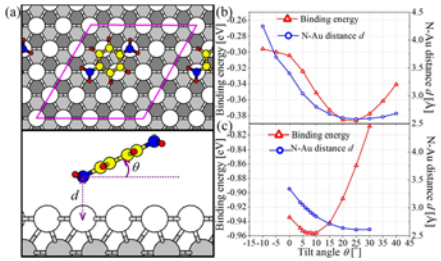
➢The Roman-Perez and Soler algorithm [5] is used to speed up the calculation.

➢Simulation model:

- Au(111) slab: 5 atomic layers of (4x4) and $\begin{pmatrix} 3 & 1 \\ 0 & 4 \end{pmatrix}$ surface unitcells parallel to surface.
- 17Å of vacuum

➢ Brillouin Zone: (3x3x1) uniform mesh of K-points for (4x4) substrate and (5x3x1) mesh for $\begin{pmatrix} 3 & 1 \\ 0 & 4 \end{pmatrix}$ substrate.

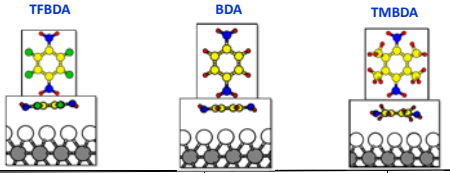
Isolated BDA/Au(111): Suggested adsorption site



➢(a) Top and side view of the BDA molecule–surface configuration. BDA adsorbs with a N atom on top of a surface Au atom.

➢The dependence of the binding energy and the molecule–surface separation d on the molecule tilt angle calculated within (b) GGA-PBE and (c) nonlocal vdW-DF methods.

Isolated TFBDA, BDA and TMBDA Molecules on Au(111)

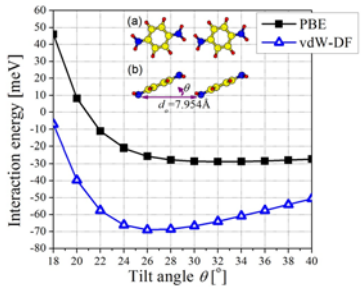


Molecule	Tilt Angle [°]				Binding Energy [eV]			N- Au distance [Å]	
	Exp [1]	Exp [6]	PBE [1]	vdW-DF	Exp [1]	PBE [1]	vdW-DF	PBE[1]	vdW-DF
TFBDA	12	---	23	-5	0.9	0.26	0.92	2.8	3.29
BDA	24	---	27	9	1.0	0.36	1.00	2.6	2.73
TMBDA	27	0	54	0	1.2	0.44	1.41	3.1	3.6

➢ The results for the binding energy, binding distance, and tilt angle for the three molecules are summarized in the table above together with previous GGA-PBE results and experimental data.

➢ As expected, inclusion of vdW interactions between the molecule and the metal surface leads to very good agreement with the experimental values for the binding energy for each molecule.

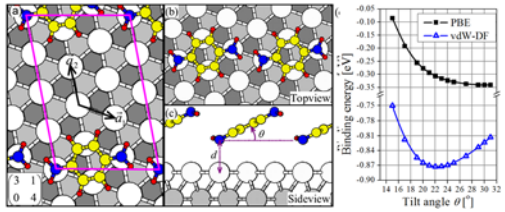
BDA Case: Interaction Energy Between Molecules



➢The PBE functional does not lead to a noticeable attractive interaction energy between the molecules, while vdW-DF show the formation of such an interaction with an energy of 70 meV .

➢Very interestingly, the interaction energy of two interacting BDA molecules separated by d_0 is found to be maximum at θ= 26° (vdW-DF). The difference in the interaction energy between 0° and 26° is as high as 620 meV (- 70 versus + 550 meV with vdW-DF).

High coverage: BDA line structure on Au(111)

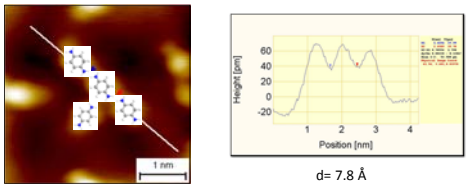


➢The results show that the PBE functional does not display any minimum of binding energy vs. tilt angle θ in the range 15° to 31°.

➢On the other hand, the vdW-DF functional finds a minimum at θ=22° which is also in good agreement with experimental data.

Experiment: BDA line structure on Au(111)

STM image of BDA molecules on Au(111) surface 0.1V, 2%, 5pA, 1ms



d= 7.8 Å

➢The presence of BDA line structure is confirmed in preliminary STM data[7].

➢The distance between neighboring molecules in STM measurements is found to be approximately the same as that in our model molecular line structures.

Conclusions

➢ For low coverages, amine terminated molecules align almost parallel to the gold surface.

➢ At higher coverages, we predict a line structure of BDA molecule on Au(111) surface.

➢ *Intermolecular* interactions plays an important role in raising the tilt angle.

➢ Inclusion of vdW interactions into DFT simulations is necessary to obtain the full picture of adsorption of these amine molecule on Au(111).

References

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For detailed information:
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