# Adsorption and nucleation of PTCDA molecules on a nanostructured KBr (001) surface

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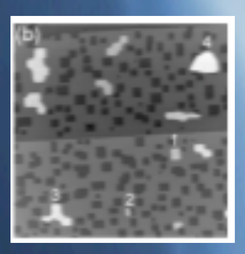
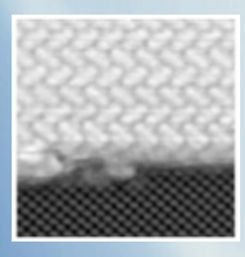
## Introduction

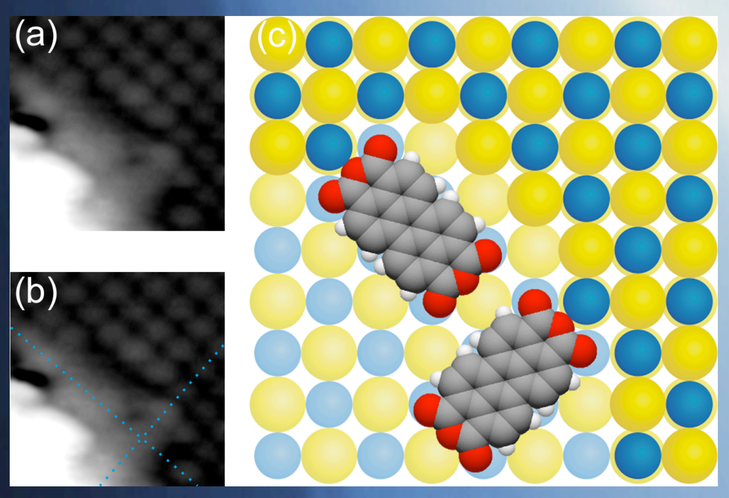
High-resolution SPM studies of organic molecules on insulating surfaces remain a crucial area in the development of practical molecular electronics. A great deal of focus has been placed on developing methods for **controlling the growth of organic layers** on the surface, particularly via **surface templating**. On insulating surfaces, irradiation is a powerful tool to engineer the surface and the treatment has been well characterized for alkali halides. In this work, we use **irradiation** to pattern the **KBr** (001) surface with regular pits, and then directly deposit 3,4,9,10-perylene-tetracarboxylic-dianhydride (**PTCDA**) molecules. NC-AFM measurements show that the majority of the resulting PTCDA islands conform to the rectangular shapes and nanometer-scale dimensions of the pits [1, 2].




• Deposited PTCDA totally (1) and partially (2) fills pits, as well as forming coalesced islands (3) and very large islands (4).

• High resolution images show the characteristic herring-bone structure of the molecules and atomic resolution on the KBr lattice.

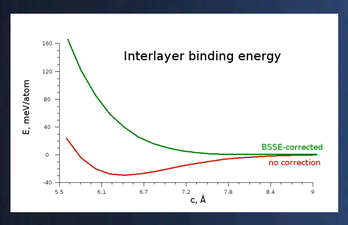



• High-resolution images also show a well-defined relationship between the molecules and the KBr lattice at kink sites.

## Methods

• *ab initio* calculations – SIESTA. All atoms apart from lowest layer of surface fully relaxed.

• Calculations include van der Waals interactions as implemented in the vdW-DF functional [3,4].



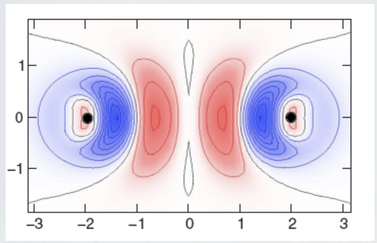

• Barriers calculated via drag method.

• Full BSSE corrections essential.

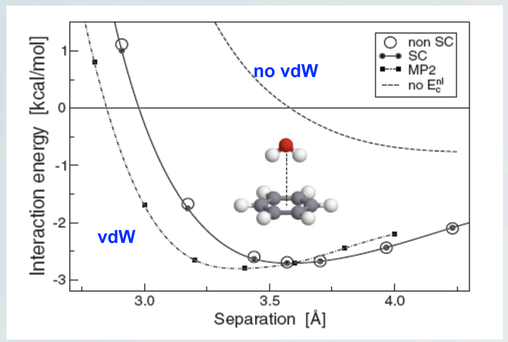
## vdW-DF

•As a **local method**, DFT completely neglects van der Waals interactions.

• This means it gets bonding in many important classes of material wrong.




Induced charge density in Ar dimer after introduction of vdW-DF.

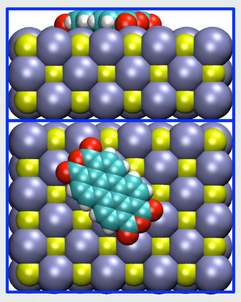



Comparison of binding energy of water on benzene with and without van der Waals.

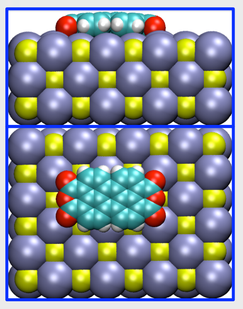
• Dynamic polarizability approximated in plasmon-pole model – can be included at the **self-consistent level** in calculations, as for any other functional.

• For the PTCDA on KBr system, the van der Waals contribution to the adsorption energy ranges from 0.4 to 1.5 eV, and from **58 – 98 % of the total adsorption energy**.

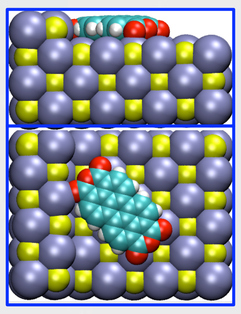
## Adsorption



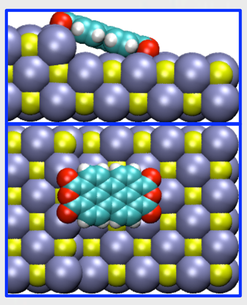
**Terrace 1.98 eV**



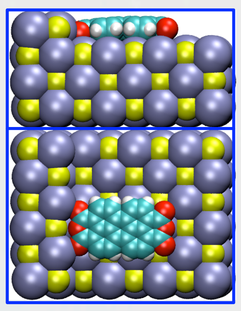
**Terrace 1.52 eV**



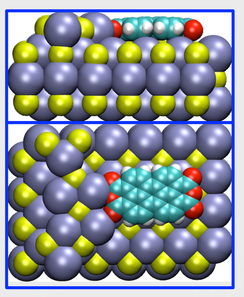
**Step 1.74 eV**



**Step 1.73 eV**

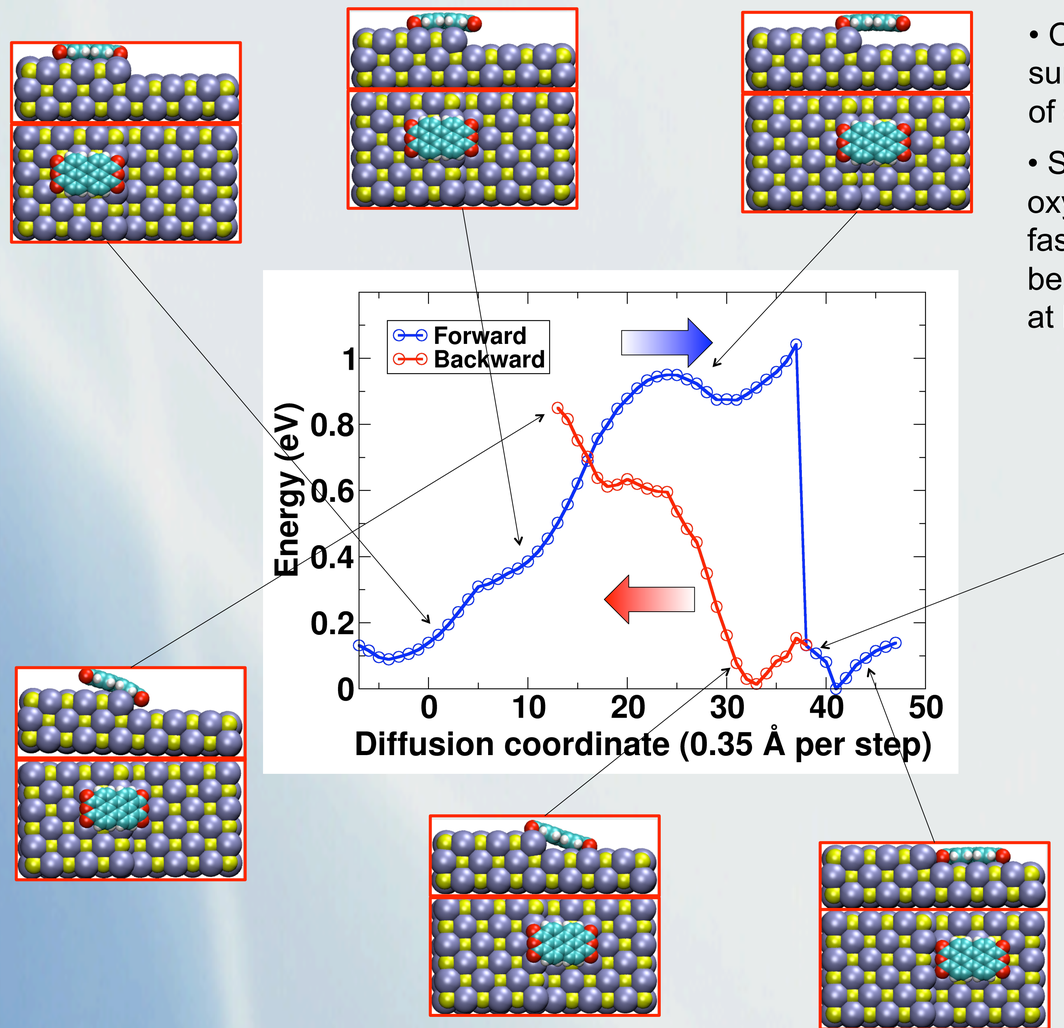


**Step 1.76 eV**



**Kink 2.30 eV**

## Diffusion




• Oxygens on molecule bond to K in the surface, while trying to minimize distortion of carbon *plane*.

• Step less favourable than terrace due to oxygen-bromine repulsion – combined with fast terrace diffusion (0.4 eV), molecules will be very **mobile** within pits. Pinned strongly at kink sites.

• Barrier to go from upper to lower terrace 0.60 eV and reverse is 0.76 eV. At room temperature, successful *crossings* are about **500 times more likely** from the upper terrace.

## Summary

• PTCDA molecules adsorb strongly at K kink sites, acting as markers for contrast interpretation and nucleation centres for film growth.

• The high mobility of molecules on the terrace explains why single molecules have only been seen at kink sites.

• Diffusion results explain the filling of pits on the surface observed in experiments.

[1] S. A Burke *et al.*, Phys. Rev. Lett. 100 (2008) 186104
[2] J. M. Mativetsky *et al.*, Nanotechnology 18 (2007) 105303
[3] M. Dion, et al., Phys. Rev. Lett. 92 (2004) 246401
[4] T. Thonhauser *et al.*, Phys. Rev. B 76 (2007) 125112