Control of the deprotonation of Terephthalic Acid assemblies on Ag(111) studied by DFT calculations and low temperature scanning tunneling microscopy†

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1 Abstract

This paper deals with the investigations of Terephthalic Acid (TPA) molecules deposited on a low reactive Ag(111) surface and studied by scanning tunneling microscopy (STM) at low temperature and DFT calculations. These investigations show that two deprotonation states energetically equivalent can be produced at the single molecule level. On self assemblies, the mobility of H atoms at 77 K favours the motion of created defects in the layer. The STM observations and DFT calculations show that the most stable structures are obtained when only one hydrogen atom is removed from a O-H...O bond and when these deprotonated molecules are located in adjacent TPA rows.

2 DFT calculations on single TPA on Ag(111)

	TPA	TPA-1H	TPA-2H
E_{ads} (eV)	-1.43	-3.51	-5.51
E_{vdW} (eV)	-1.61	-1.68	-1.75
ΔE_F (eV)	+0.16	+0.10	+0.05
$\Delta\Phi$ (eV)	-0.07	+0.11	+0.26
$\Delta q_{Ag->Mol}$ (e)	+0.14	+0.75	+1.37

Table 1 : Results of the DFT calculations for a single TPA adsorbed on Ag(111). This substrate serves as a reference for all the calculated parameters (for Ag(111): E_F=-1.75 eV, Φ_{wf}=4.24 eV).

3 DFT calculations on a TPA monolayer on Ag(111)

	TPA	1TPA-1H (1 single defect)	1TPA-2H	2x(1TPA-1H) (2 single defects)	2TPA-2x1H (1 double defect)
E_{ads} (eV)	- 7.76	-9.94	-11.70	-11.95	-11.86
$E_{vdW(Mol-Mol)}$ (eV)	-1.98	-1.95	-1.88	-1.91	-1.92
$E_{vdW(Mol-Surf)}$ (eV)	-6.57	-6.58	-6.59	-6.57	-6.55
ΔE_F (eV)	+0.67	+0.61	+0.53	+0.51	+0.54
$\Delta\Phi$ (eV)	-0.24	-0.14	+0.06	-0.01	0
$\Delta q_{Ag->Mol}$ (e)	+0.98	+1.40	+1.85	+1.86	+1.88

Table 2 Results of the DFT calculations for a TPA monolayer (2x2 unit cell) adsorbed on Ag(111) ($\Delta\Phi$ is calculated with respect to the bare Ag(111) surface). Adsorption energy, van der Waals contributions and charge transfer Δq are given for the complete layer, i.e. for the four molecules of the unit cell.

The second column gives the results for the pristine (2x2) TPA unit cell. The third concerns this unit cell without an H atom (single defect). The fourth deals with the (2x2) layer containing a TPA without its 2 H atoms while the fifth presents the results for two single defects in the (2x2) layer. The last column corresponds to a (2x2) layer with a double defect.

4 Radial distribution function of defects in the TPA layer

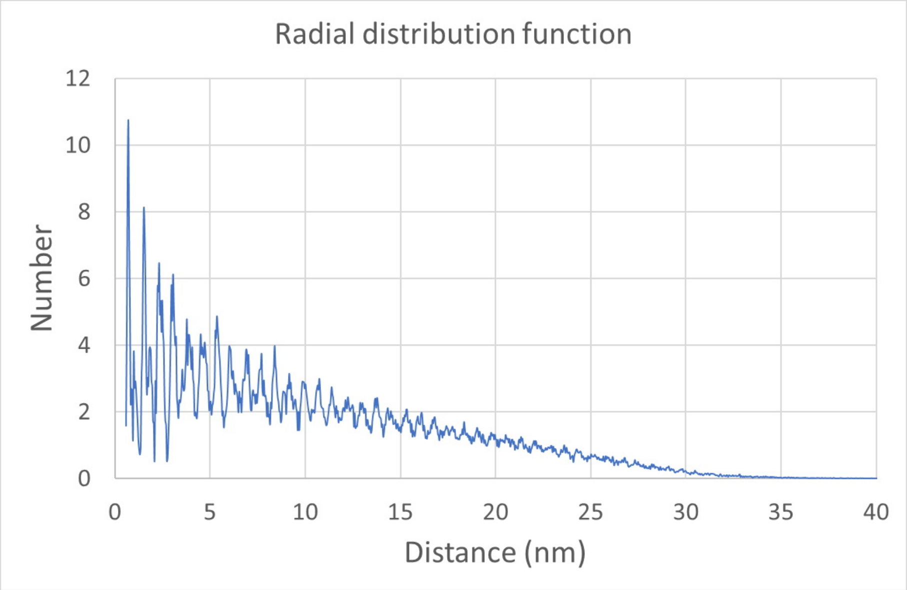

Figure 1 Radial distribution function calculated from Fig. 5c.

The radial distribution function of Fig. 5c is presented in Fig. 1. This curve gives the probability to find a defect in the neighborhood of another defect in terms of distance to this latter. For this calculation, a distance step of 42 pm has been used. The first and highest peak at about 0.73 nm corresponds to the nearest neighbor distance in the TPA self-assembly.

5 Dehydrogenation barriers to detach two H atoms from the same H-bonds "dimer" location in the (2x2) unit cell

For TPA molecules in a self-assembled monolayer (ML), a first hydrogen atom (encircled in Fig. 2, schema IS-ML) was detached. Similar to the case of single molecule, the detached H atom was adsorbed close to this newly created defect in order to allow a direct total energy comparison. The activation energy to detach this H atom was evaluated to be 0.91 eV, close to that on the single molecule (0.95 eV). As the detached H atom could diffuse easily away and desorbed as an H_2 molecule after recombination with another diffusing H atom, this singly dehydrogenated defect could be seen as a so-called "single defect" in an STM image.

To detach a second H atom, two situations have been considered. The first is to detach the H atom from the molecule involved in the H-bond "dimer" which has already lost one H atom (encircled in schema IntS-ML of Fig. 2) and create a "double defect". The activation barrier to overcome in this case is 1.33 eV (1.65 eV directly from the neutral TPA ML).

In the second case, the second H atom has been cleaved from a O...H-O bond located in the right column of the unit cell (encircled in schema IntS-ML of Fig. 3). The detached H atom was adsorbed close to this second "single defect" and to the previously detached H atom, in the free space between the two TPA columns. The activation energy necessary to be overcome here is higher than the first case (1.76 eV from the intermediate state or 2.08 eV from the neutral TPA ML, see the energy path on the bottom of Fig. 3).

These results show that at the annealing temperature of 370 K, the probability to detach one H atom is thus at least 500 000 times higher that the probability to detach two H atoms of the same TPA dimer. Thus, the most majority defects present in TPA MLs are "single defects". This conclusion is perfectly consistent with the scarcely observed "double defect" in STM images. As the reverse reaction (re-attachment of detached H atoms barrier) are respectively 1.09 eV and 0.59 eV, the most probably case should correspond to the desorption of H_2 molecules after recombination.

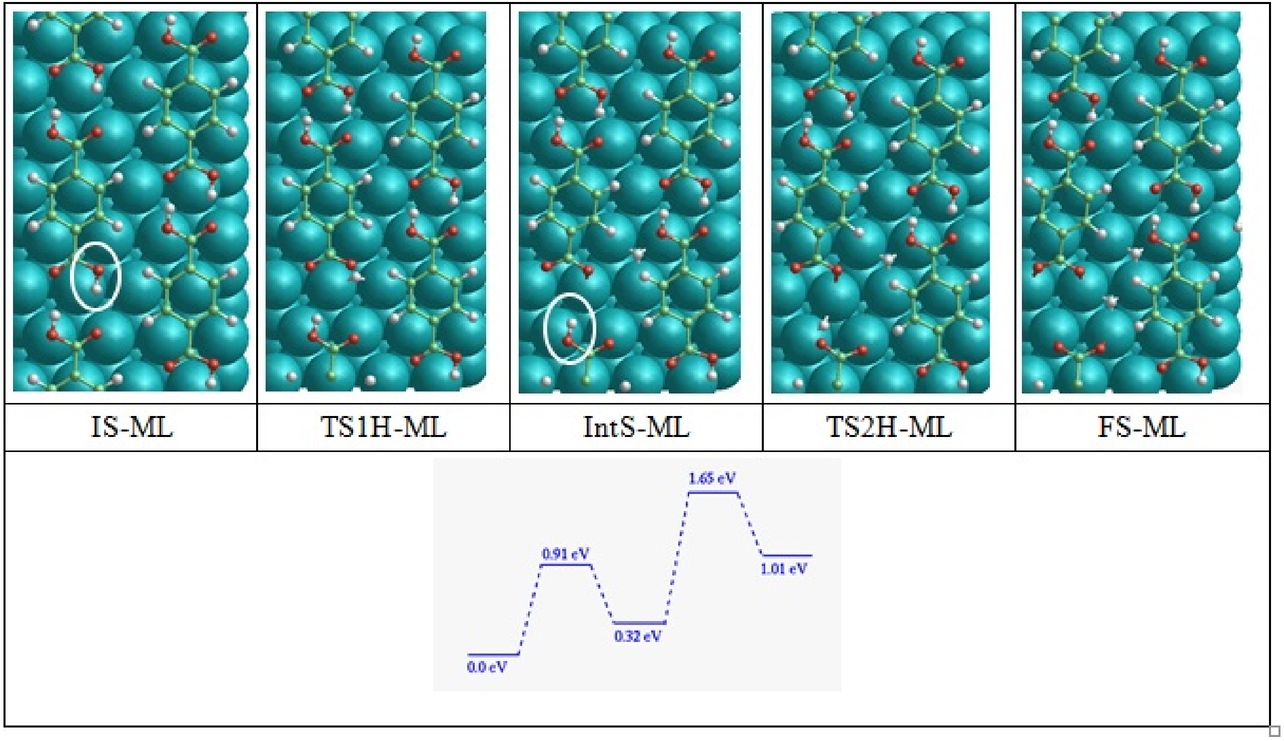

Figure 2 Calculated configurations for the creation of a double defect in a TPA row and associated energy paths.

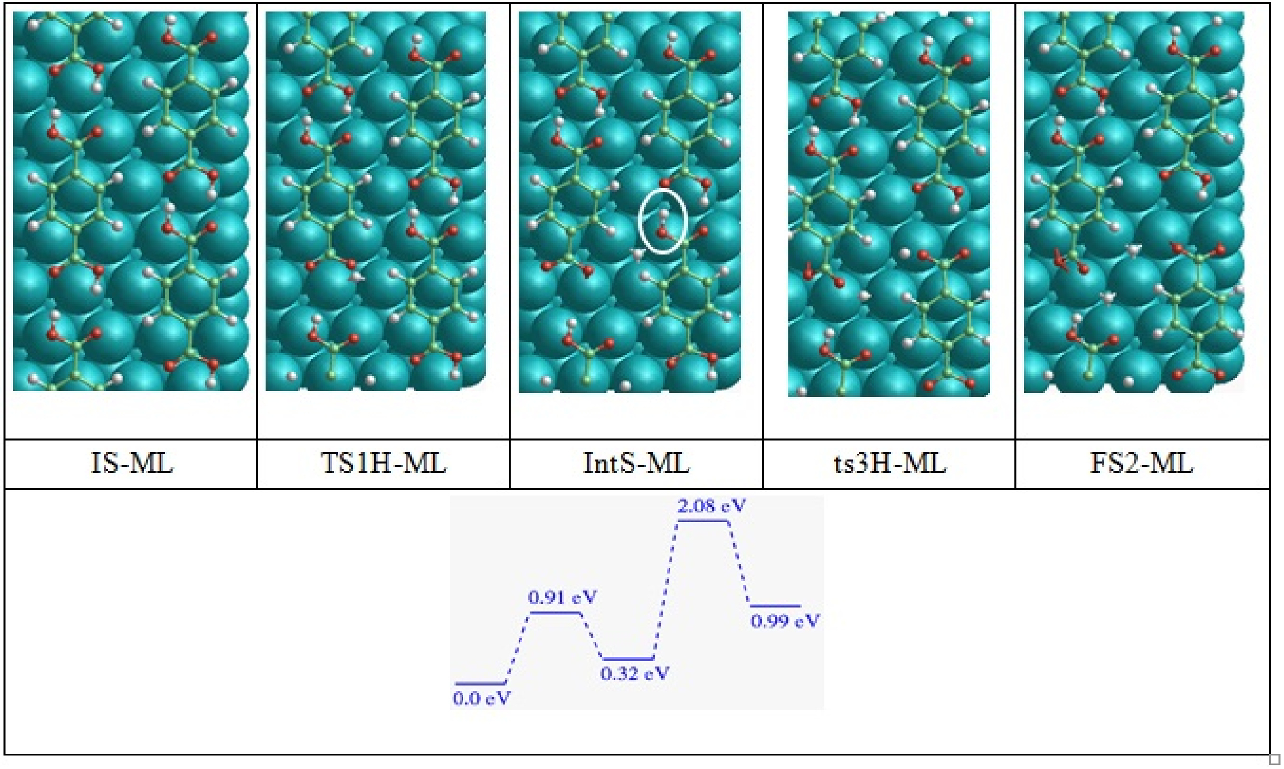

Figure 3 Calculated configurations for the creation of two single defects in a TPA monolayer and associated energy paths.