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Adsorption study of terephthalic and benzoic acids on HOPG with Metastable Induced Electron Spectroscopy

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Motivation

The adsorption behavior of benzoic acids on conducting interfaces like HOPG is of high interest for the understanding of the building mechanism of 2D and 3D frameworks on surfaces. Thus, the knowledge about the molecular orientation and the molecule-substrate interaction is of great importance. Here we present our results on the adsorption of 4-substituted benzoic acids (R = hydroxy-, methoxy-, propoxy- , pentyloxy- and decyloxy-chains) and terephthalic acid (TPA) on HOPG [1]. The molecular films were studied with Metastable Induced Electron Spectroscopy (MIES) and Ultraviolet Photoelectron Spectroscopy (UPS(HeI)). For the TPA monolayer we find hints for a more planar orientation of the molecules. The benzoic acid molecules show a similar adsorption behavior on HOPG. For the 4-(decyloxy) benzoic acid we assume a possible reorientation of the alkyl chains after the first monolayer.

Experimental

UPS: He I (21.2 eV)

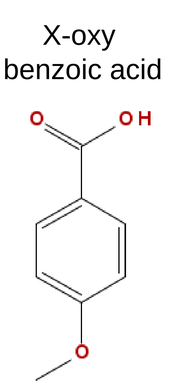
MIES: He* 2^3S_1 (19.8 eV)

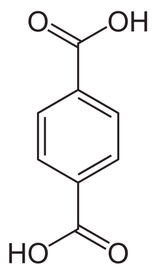
UHV systems with base pressure < 2.0×10^{-10} Torr

Substrate: **H**igly **O**riented **P**yrolytic **G**raphite (**HOPG**)

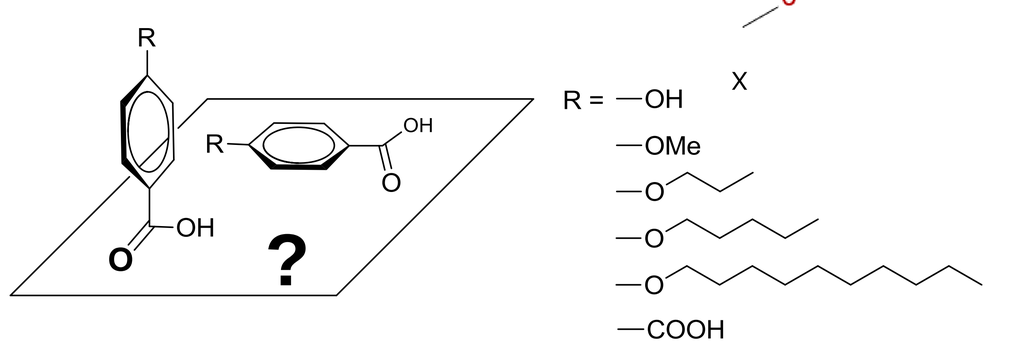
The sample surfaces were prepared by vapour deposition of the ultrapure benzoic acid on an HOPG substrate.

X-oxy benzoic acid

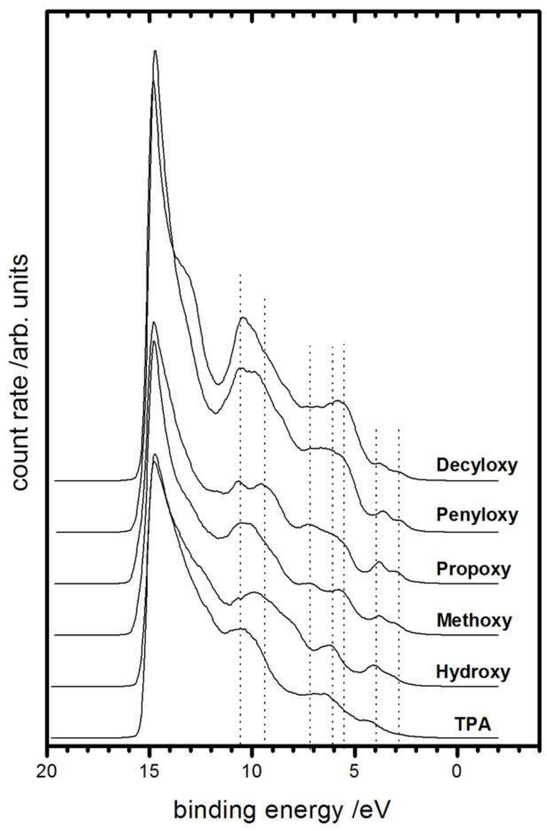


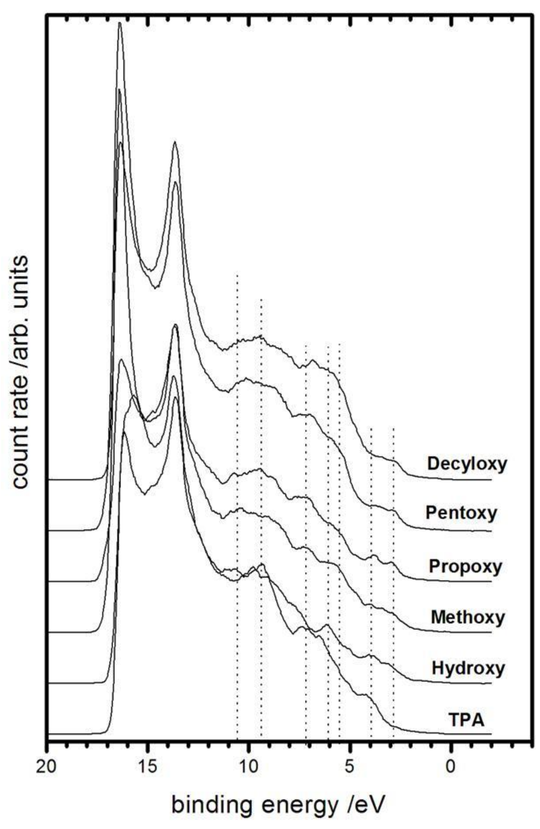


TPA



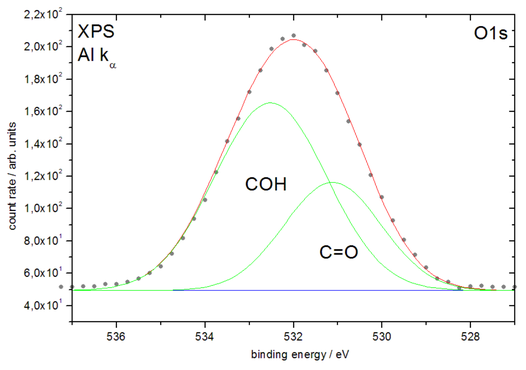
Electronic structure of benzoic acids on HOPG

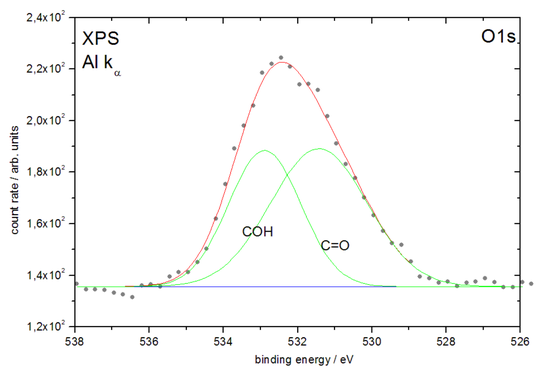




- Peaks between 3 eV and 5 eV show the characteristic splitting of the π-orbitals [1,2]
- In MIES peaks around 6.5 eV, 10 eV and 12 eV show the components from the COOH group
- For the 4-substituted benzoic acids changes in the electronic structure are clearly visible due to the attached functional groups; in MIES strong influence of the alkyl chains at around 5,5 eV and 11 eV [2,3]

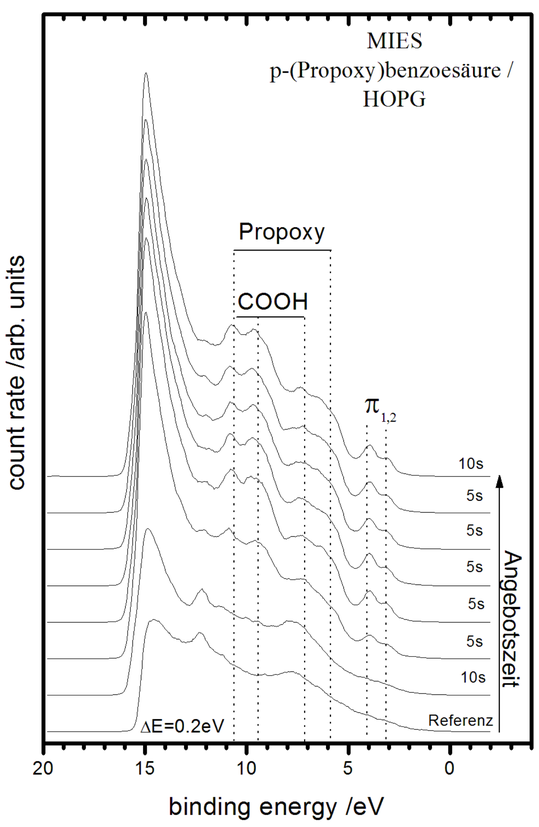
XPS results for p-(Hydroxy)benzoic acid

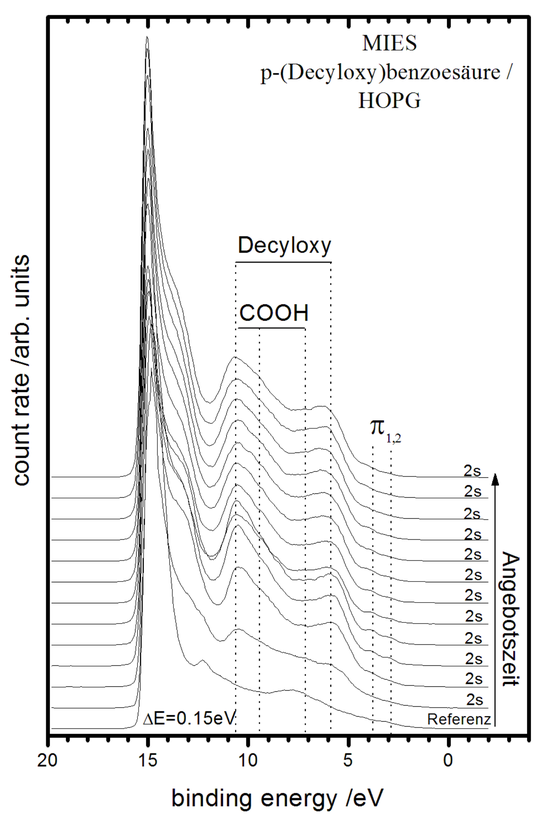




- The oxygen 1s detailspectrum shows a decrease of the C-OH group intensity during the X-Ray exposure
- We found a similar behaviour for p-(propoxy) benzoic acid
- Possible scission of the alkyl chain

Adsorption of benzoic acids on HOPG





- In MIES at the beginning of adsorption: the π-orbitals from both molecules are visible
- For p-(decyloxy) benzoic acid the π-orbitals show an intensity decrease during adsorption
- We assume a reorientation of the alkyl chains during the adsorption, which prevents the interaction of the metastable helium atoms with the π-orbitals

Summary

- All experiments indicate a flat lying orientation of the 4-substituted benzoic acid molecules on the HOPG surface for the first layer
- for longer alkyl chains a reorientation starts after completion of the first layer
- X-Ray induced damage resulting in a possible scission of the alkyl chain

References

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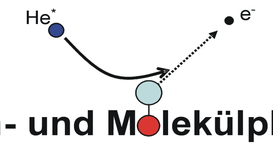

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