

Computational insights on the FM-AFM experiments of the *p*-nitroaniline solid-liquid interface



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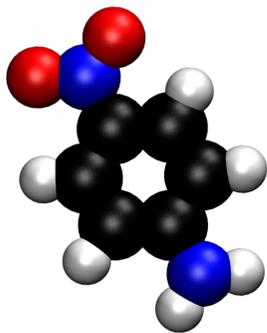
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Introduction

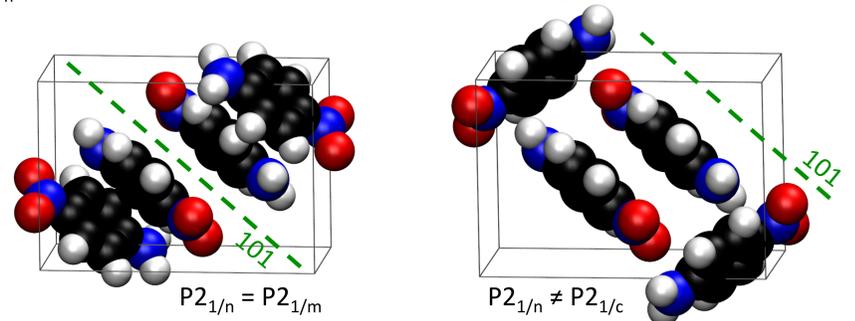
Solid-liquid interfaces play a fundamental role in many biomolecular and electrochemical applications at the nanoscale. Although spectroscopy and diffraction techniques can provide very accurate information about such interfaces, atomic force microscopy (AFM) has the advantage of probing the investigated system locally, thus allowing a deeper understanding of these type of interfaces.

Recently experiments on the *p*-nitroaniline (101) crystal surfaces in water have been performed in order to better understand the stability and the mechanisms of nucleation or dissolution at crystal surfaces [1]. *p*-Nitroaniline is an organic compound containing polar NH₂ and NO₂ groups at opposite ends of a benzene ring, and, although being a relative simple compound, it gives rise to enough complexity to serve as an excellent experimental case.



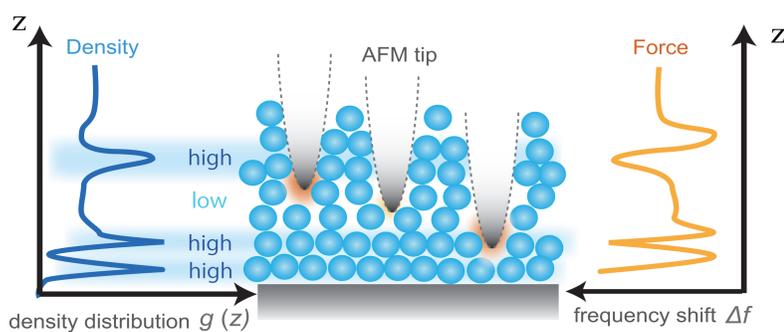
Computational model

Based on crystallographic data [3] two different *p*-nitroaniline crystals are constructed (because of ambiguity in interpreting the associated space group P2_{1/n}). This leads to two different (101) surfaces being exposed.



Both unit cell structures are iteratively relaxed in molecular dynamics (MD, using the CHARMM force field) and density functional theory (DFT) computations, while updating the charge distribution on the atoms each iteration. Bulk structures of both crystal configuration remain extremely stable in MD computations under ambient conditions, although the final unit cell of both structures is different (the size of the (101) surface remains constant).

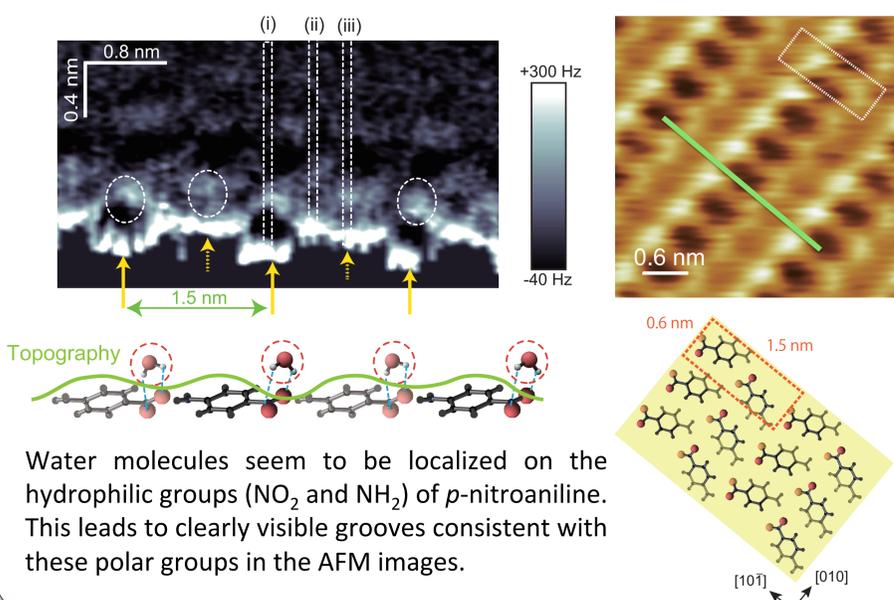
Solvation measurements with FM-AFM



The force can be measured very accurately as a function of the tip location. This obtained force distribution should relate to the local density distribution of the interfacial water [2].

Experimental results

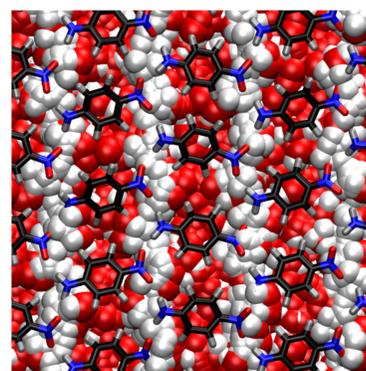
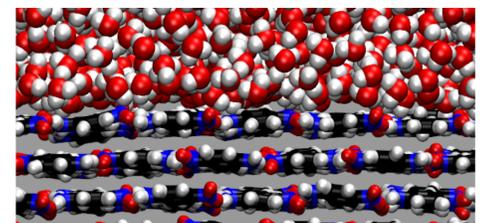
From the obtained topography images on terraces of the *p*-nitroaniline crystal, a repetitive unit can be identified (dotted lines in top right image), giving a bright and a less bright spot in each unit cell. In the cross sectional views (top left image) the nature of these bright and less bright spots are clearly seen. Major groves, like (i) are on top of the polar groups of the molecules forming a hydrogen bond network between them.



Water molecules seem to be localized on the hydrophilic groups (NO₂ and NH₂) of *p*-nitroaniline. This leads to clearly visible grooves consistent with these polar groups in the AFM images.

MD simulations of *p*-nitroaniline/water interface

Similar to our previous work in MD simulations of the calcite/water interface [4,5], we model a large exposed surface of the crystal together with sufficient bulk water, allowing the system to fully relax.



Preliminary results on the structuring of water at the *p*-nitroaniline surface (see figure to the left), show similar strong pairing of water molecules along the polar/hydrophilic grooves of the crystal. However, the water molecules are not extremely strongly bound to the crystal, as it is observed that a fair amount of diffusion of water molecules from the surface still takes place.

References

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