

Electron Dynamics in Self-Assembled Monolayers of Azobenzene-Functionalized Alkanethiols on Gold

Charge and energy transfer processes at organic-metal interfaces are of key relevance in molecular electronics and functionalization of surfaces with molecular switches. Therefore the electronic structure and femtosecond electron dynamics of self-assembled monolayers (SAMs) of azobenzene-functionalized alkanethiols on gold have been investigated with time-resolved two-photon photoemission spectroscopy (2PPE).

Two excited electronic states at 2.4 and 3.6 eV above the Fermi level are attributed to unoccupied states in the chromophores, which are populated via charge transfer from the metal substrate. Their lifetimes are in the order of 100 fs for an alkyl chain length of 3 CH₂ units. The same timescale has been deduced from resonant core-level spectroscopy for the charge transfer across such an alkyl chain from excited molecular states ~1 eV above the Fermi energy.

In the densely packed monolayer of the azobenzene derivative, photoisomerization is strongly suppressed due to interaction among the azobenzene moieties. Mixing the azobenzene derivative with an alkanethiol allows to introduce free space into the SAM and thereby to control the chromophore interactions. Accordingly the optical properties and the switching ability can be tuned.

Primary authors: WEINELT, Martin (Freie Universitaet Berlin); Mr MOLDT, Thomas (FU Berlin)

Co-author: Dr GAHL, Cornelius (Fachbereich Physik, FU Berlin)

Presenter: Dr GAHL, Cornelius (Fachbereich Physik, FU Berlin)

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