

RIXS and ultra-fast molecule-surface charge transfer dynamics

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In devices such as dye-sensitised solar cells, the dynamics of charge transfer at the electron injection interface - from the molecule into the semiconductor substrate - play a key role and are typically very fast. The charge transfer dynamics of the molecule biisonicotinic acid adsorbed on a titanium dioxide surface was found to occur on the low femtosecond timescale - using a core-hole clock implementation of resonant photoemission (RPES) [1]. This process relies on the competing channels of core-hole decay and ultra-fast charge transfer to the surface. An electron emitted by a core-hole decay process in which the originally excited core-electron is a direct participant is easily distinguishable from the electronic debris by its kinetic energy and evinces electron localisation in the excited molecular orbital on the timescale of the core-hole lifetime. It has long been proposed that the photons emitted during radiative core-hole decay should be equally informative, allowing femto-second charge transfer to be probed in more realistic environments due to the large escape depth of the photons in what would be resonant inelastic x-ray scattering (RIXS) compared to the electrons of resonant photoemission (RPES). In the event that the originally excited core-electron is a direct participant in the decay process, radiative decay will give rise to what is essentially an elastically scattered soft x-ray photon, perhaps modified by any ultra-fast processes within the core-excited molecule. Our early RIXS core-hole clock results of biisonicotinic adsorbed on a rutile TiO₂ (110) surface were consistent with this simple idea that the abundance of elastically scattered photons would be diminished in the presence of the charge transfer out of specific molecular orbitals known to occur in this system on the order of a few femtoseconds [2]. Moreover, the other photons emitted in the experiment - the inelastic scattering - provide valuable insight character of the occupied molecular orbitals and their relationship to each other. This is most evident when the RIXS is mapped over all the highest occupied molecular orbitals as a function of core-excitation into all the lowest unoccupied molecular orbitals. Our recent experiments [3] performed at the SOLEIL synchrotron have focussed on obtaining two-dimensional RIXS maps of biisonicotinic acid monolayers and multilayers on the TiO₂ (110) surface and of the crystalline molecule. The high energy resolution reveals a complex vibrational structure around the LUMO resonances close to the elastic peak and how this is modified by coupling of the molecule to the oxide surface and the resulting ultra-fast charge transfer of electrons from those orbitals that overlap energetically with the conduction band edge.

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