Ultrafast electron transfer across polar molecule-metal interfaces: strong coupling vs. molecular screening

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Heterogeneous charge transfer plays a crucial role for the development of molecular electronics such as, for example, OLEDs. Depending on the side conditions, the respective charge transfer dynamics vary significantly. In particular, in the presence of (polar) molecules, the electron transfer (ET) reaction may be strongly influenced by the screening properties of the involved molecules, as they determine the timescales on which electron transfer occurs.

We adsorb D_2O and NH_3 on Cu(111) and Ru(001) surfaces as model systems for systematic investigation of the ultrafast ET dynamics at polar molecule-metal interfaces by means of time-resolved two-photon photoelectron (2PPE) spectroscopy. With a first laser pulse, electrons are excited in the metal and injected into the adsorbate layer (solvent) where they localize at favorable sites. The subsequent electron (back) transfer to the substrate is monitored with a second, time-delayed laser pulse. Our study unveils that, in the case of amorphous adsorbate structures, (i) molecular screening is observed for $\tau > 200$ fs after electron injection, (ii) before, ET is dominated by the strong coupling to the substrate states. Moreover, we vary the coupling strength of the excess electrons to the respective substrate by variation of the structure, morphology, and layer thickness of the adsorbate. In particular the structural and morphological transition from amorphous layers to 3D crystallites results in a considerable increase of excess electron residence times from ultrafast timescales up to several minutes.