O 67: Poster Session V: Ultrafast electron dynamics at surface and interfaces I

Time: Wednesday 10:30–12:30 Location: P

O 67.1 Wed 10:30 P

Improved projection-operator diabatization for electron transfer on periodic surfaces — •Simiam Ghan[1], Karsten Reuter[1,2], and Harald Oberhofer[1] — [1]Chair for Theoretical Chemistry, Technical University of Munich, Garching, Germany — [2]Fritz Haber Institute of the Max Planck Society, Berlin, Germany

We discuss the recently-proposed[1] projection-operator diabatization method POD2GS for calculating electronic coupling in donor-acceptor charge transfer systems. The new scheme offers accurate electronic couplings by constructing diabats which remain localized on their respective fragments, as demonstrated for the Hab11 benchmark suite with molecular dimers.

Here, we apply this improved scheme to explore electron transfer from photoexcited adsorbates to surfaces, a problem for which the original POD method has been widely used. Specifically, we report results for the case of monolayers of core-hole excited Argon on ferromagnetic substrates, where accurate spin-dependent electron transfer lifetimes have been measured experimentally. Aspects of periodic boundary conditions in the electron transfer model are discussed; in particular, we examine the validity of the Γ-point approximation which is commonly used with POD models for electron transfer on surfaces. [1] S. Ghan *et al.*, J. Chem. Theory Comput. **16**, 7431 (2020).

O 67.2 Wed 10:30 P

The ambivalent competition of Coulomb and van-der-Waals interactions in Xe-Cs$^+$ aggregates on Cu(111) surfaces — •John Thomas[1], Cord Bertram[1,2], Janos Daru[2], Ping Zhou[1], Dominik Marx[2], Karina Morgenstern[2], and Uwe Bovensiepen[1] — [1]Physik, Universität Duisburg-Essen — [2]Chemie, Ruhr-Universität Bochum

The properties of heterogeneous interfaces are important because of their fundamental and technological perspectives. We aim at understanding the contributions of the Coulomb and van-der-Waals interactions in Xe-Cs$^+$ aggregates on Cu(111). By combining time-resolved Two-Photon Photoelectron Spectroscopy (2PPE), Scanning Tunneling Microscopy (STM), and coupled cluster calculations, we investigate the microscopic structure and the ultrafast dynamics excited by photo-induced electron transfer. We observe by time-resolved 2PPE that adsorption of Xe results in a fivefold increase of the Cs 6s electron lifetime, an effect attributed to the repulsion of the Cs 6s wave function by the electron density of Xe. Furthermore, we observe by STM that the Cs$^+$...Cs$^+$ distance shrinks from 2-7 nm to 1-3 nm for the aggregates compared to bare Cs$^+$/Cu(111). The adsorption of Xe on Cs/Cu(111) results in a dual, i.e. attractive or repulsive, response of Xe depending on the positive or negative charge of the respective counterparticle, which emphasizes the dominant role of the Coulomb interaction between an alkali and a noble gas atom on the Cu(111).

This work was supported by the Cluster of Excellence RESOLV, funded by the Deutsche Forschungsgemeinschaft.

O 67.3 Wed 10:30 P

Ultrafast Dynamics of Hot Electrons and Holes by Femtosecond Photoelectron Spectroscopy in Au/Fe/MgO(001) — •Florian Kühne[1], Yasin Beyazit[1], Detlef Diesing[2], Ping Zhou[1], and Uwe Bovensiepen[1] — [1]University of Duisburg-Essen, Physics, Germany — [2]University of Duisburg-Essen, Chemistry

Optically excited electrons and holes are of particular interest in solid state physics, because they allow a microscopic understanding of interactions in non-equilibrium states. Here we aim at discerning electronic relaxation by local inelastic processes and non-local transport. To analyze the ultrafast dynamics of charge carriers in the vicinity of the Fermi energy E_F, femtosecond time-resolved linear photoelectron spectroscopy was applied and we report on results obtained by using 1.55 eV pump and 6 eV probe photons on Au/Fe/MgO(001), complementary to previous work in Beyazit et al., PRL **125**, 076803 (2020). In case of the back side pumping, hot electrons are excited in the Fe, are injected into Au and propagate to the surface, where they are probed by photoelectron emission spectroscopy. We observe a positive shift in the time delay of the transient intensity increasing with d_Au in comparison to the front pump data, which is attributed to transport effects in Au. The analyzed electron distribution in the vicinity of E_F indicates a symmetric excitation of electrons and holes. It can be described by a Fermi-Dirac distribution function. We estimate a maximum increase in the electron temperature by 50 K, which builds up within 100fs and then decays by energy transfer to phonons.

This work was funded by the DFG through the CRC 1242.

O 67.4 Wed 10:30 P

Ultrafast laser-induced electronic dynamics of perylene@MoSe$_2$ monolayer — •Matheus Jacobs[1], Jannis Krumland[1], and Caterina Cocchi[1,2] — [1]Institut für Physik und IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany — [2]Carl von Ossietzky Universität Oldenburg Institut für Physik, Oldenburg, Germany

Hybrid interfaces formed by atomically thin semiconductors, such as transition-metal dichalcogenides, and physisorbed organic molecules have received considerable attention in the last years due to their potential for opto-electronic applications. In particular, interfacial charge transfer in the earliest stage of the photoexcitation plays a crucial role in the electronic and optical response of these systems[1]. Therefore, it is of great relevance to gain insight into the dynamics of the involved processes. In the framework of real-time time-dependent density functional theory, we investigate the ultrafast electronic dynamics at the interfaced formed by perylene physisorbed on a MoSe$_2$ monolayer. We monitor the evolution of the electrons in k-space when the hybrid system is excited by a resonant time-dependent electric field. Our results provide a valuable starting point to explore further relevant effects, such as vibronic coupling.

[1] M. Jacobs *et. al.*, Advances in Physics: X 5, 1749883(2020)

O 67.5 Wed 10:30 P

Pump-probe second harmonic spectroscopy of molecule/metal interfaces — Jinghao Chen, Ping Zhou, Uwe Bovensiepen, and •Andrea Eschenlohr — Faculty of Physics, University Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany

Achieving a microscopic understanding of charge transfer dynamics and the relaxation of optically excited electrons and holes at molecule/metal interfaces requires an interface-sensitive analysis on the respective femtosecond timescales. Second harmonic spectroscopy (SHS) [1] is such an interface-sensitive probe in centrosymmetric materials. We employ a non-collinear optical parametric amplifier in the visible wavelength range (1.9-2.5 eV) for pump-probe SHS with <20 fs pulse duration. A prototypical molecule/metal interface is prepared by adsorption of iron octaethylporphyrin (FeOEP) molecules on Cu(001) [2] and analyzed *in situ* in ultrahigh vacuum. We find a molecule-induced resonance at about 2.2 eV fundamental photon energy in the second harmonic spectrum of one monolayer of FeOEP/Cu(001). At this resonance, we observe a markedly slower relaxation time of the pump-induced changes in SHS compared to the bare Cu(001) surface, which indicates an increased lifetime of the electronic molecular state.

We thank H. Wende, J. Güdde and E. Riedle for valuable experimental advice, and the German Research Foundation for funding via SPP 1840 QUTIF and Sfb 1242.

[1] T. F. Heinz, C. K. Chen, D. Ricard, and Y. R. Shen, Phys. Rev. Lett. **48**, 478 (1982); U. Höfer, Appl. Phys. A **63**, 533 (1996).

[2] H. C. Herper et al., Phys. Rev. B **87**, 174424 (2013).

O 67.6 Wed 10:30 P

Energy transfer during resonant neutralization of hyperthermal protons at an aluminum surface studied with time-dependent density functional theory — •Lukas Deuchler and Eckhard Pehlke — Christian-Albrechts-Universität Kiel

Knowledge about the charge and energy transfer between an ion and a surface is crucial for the description of the plasma-surface interaction. In the present work, we report results from TDDFT based Ehrenfest molecular dynamics (MD) simulations for energy and charge transfer for a proton (H$^+$) with initial kinetic energy $2\,\mathrm{eV} - 50\,\mathrm{eV}$ incident normally on an Al(111) surface [1]. Simulations have been performed with the Octopus code [2]. The Al-surface is represented by an Al-cluster.

As pointed out by Winter [3], energy and angle shifts observed in the energy distribution of the scattered projectile should provide a means to experimentally estimate the neutralization distance. In this poster, we present the difference in initial kinetic energy between an H$^+$ and an H^0 projectile which is required to yield identical exit velocities of the H after neutralization. Notably, this difference changes sign within the studied range of kinetic energies.

[1] L. Deuchler and E. Pehlke, Phys Rev B **102**, 235421 (2020).
[2] X. Andrade et al., Phys. Chem. Chem. Phys. **17**, 31371 (2015).
[3] H. Winter, J. Phys.: Condens. Matter **8**, 10149 (1996).

O 67.7 Wed 10:30 P

Relaxation and Transport Processes of Hot Electrons in Au/Fe/MgO(001) — •Yasin Beyazit[1], Ping Zhou[1], Florian Kühne[1,2], Jan Philipp Meyburg[2], Detlef Diesing[2], and Uwe Bovensiepen[1] — [1]Faculty of Physics, University Duisburg-Essen — [2]Faculty of Chemistry, University Duisburg-Essen, Germany

This work presents an energy resolved analysis of relaxation and transport processes of excited electrons in the time domain. By employing femtosecond laser pulses with 2 eV pump energy and pulse width less than 35 fs we excite hot electrons in epitaxially grown Au/Fe/MgO(001). The photo-excited electrons exhibit local and non-local dynamics which lead to relaxation and transport processes of charge carriers. We perform time-resolved two photon photoelectron spectroscopy (tr-2PPE) with a particular excitation scheme; back side pumping and front side probing. The hot electrons are excited in the buried Fe layer 2 eV above the Fermi level E_F and experience subsequently spatiotemporal transport through the Fe-Au interface towards the Au surface and local inelastic relaxation. By analysis of the relaxation dynamics as a function of Au film thickness we determine the electron lifetimes of bulk Au and Fe and distinguish the relaxation in the heterostructures constituents. Furthermore, we show that the hot electrons propagate through the Au in a superdiffusive regime [1]. Additional measurements allow us to discuss contributions of secondary electrons. This study was funded by the DFG through SFB 1242. [1] Beyazit et al., PRL 125, 076803 (2020)