

O 120: Focus Session: Nonequilibrium Electron Transfer Across Interfaces in Real Time

(Photo)electrocatalytic devices, 2D material heterostructures and much interesting biophysics all require transferring electrons across interfaces between condensed phases. Despite this motivation, and much effort, gaining experimental insight into *how* electrons move across such interfaces has proven extremely challenging. Part of the challenge lies in the difficulty of experimentally characterising molecular level structure at such buried interfaces. More profoundly, however, even if an appropriate experimental approach is available, characterisation of an interfacial system held at a, nonequilibrium, steady-state is not generally useful in providing mechanistic insight into electron transfer (one cannot distinguish the relationship of minority species). Overcoming this challenge requires perturbation/relaxation techniques: one creates a temporally short non-equilibrium condition in which electron transfer is initiated and characterises the interface as the system relaxes to steady-state conditions over timescales from femto to milliseconds. Within the last several years work along these lines has appeared in a variety of usually disconnected communities. This Focus Session aims to bring together electrochemists approaching electron transfer using all-electrical relaxation techniques, chemical physicists studying (photo)electrocatalysis by initiating electron transfer using femtosecond optical pulses and probing using photons or photoelectrons and solid state physicists conducting similar experiments investigating charge transfer in solid heterostructures.

Organizers: Andrea Eschenlohr, R. Kramer Campen, Uwe Bovensiepen, U. Duisburg-Essen

Time: Friday 10:30–13:00

Location: TRE Ma

Invited Talk

O 120.1 Fri 10:30 TRE Ma

Ultrafast charge transfer dynamics in 2D heterostructures — ●GIULIO CERULLO, STEFANO DAL CONTE, ZILONG WANG, and CHIARA TROVATELLO — Dipartimento di Fisica, Politecnico di Milano, 20133 Milano, Italy

In the last few years, the research on 2D materials has developed towards the engineering and realization of new heterostructures (HS) based on stacking two or more 2D crystals on top of each other. In such HSs, the electronic structure of the single layers is well retained because of the weak interlayer van der Waals coupling. Nevertheless, new physical properties and functionalities, depending on the type and the stacking sequence of layers, arise beyond their constituent blocks. These new HS have high potential in the field of flexible optoelectronics because they combine strong light matter interaction, high flexibility and high charge carrier mobility. The experimental study of the interlayer charge scattering process in such HS is of paramount importance for developing 2D HS-based optoelectronic devices. In this work we use optical pump-probe spectroscopy to study photoinduced charge transfer dynamics in two different 2D HS: a TMDs heterobilayer (WSe₂/MoSe₂) and a graphene/WS₂ HS. We resolve interlayer exciton formation (200-fs) and decay dynamics in WSe₂/MoSe₂. We also monitor photothermoionic charge transfer dynamics from graphene to WS₂ when pumped well below the semiconductor bandgap, due to hot carriers injection across the HS Schottky barrier.

O 120.2 Fri 11:00 TRE Ma

Ultrafast charge transfer and vibronic coupling in donor/acceptor interfaces — ●MATHEUS JACOBS, JANNIS KRUMLAND, ANA M. VALENCIA, and CATERINA COCCHI — Institut für Physik und IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Donor-acceptor (DA) interfaces are ubiquitous in materials for optoelectronic applications and strongly characterize their intrinsic properties. Interfacial charge transfer, in particular, plays a crucial role in the electronic structure and optical response of these systems. For this reason, it is essential to gain insight on the fundamental processes involved at the interface also beyond the static picture. In the framework of real-time time-dependent density-functional theory coupled to Ehrenfest molecular dynamics, we investigate the microscopic mechanisms driving ultrafast charge transfer at DA interfaces. Specifically, we address the role of vibronic coupling in systems perturbed by an external laser pulse. For this purpose, we consider prototypical inorganic/organic and all-organic interfaces formed by the acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F₄TCNQ) by doping a hydrogenated silicon cluster and an oligothiophene molecule. From the analysis of charge distribution across the interface, of the induced electron density, and of the bond length dynamics, we demonstrate that the nature and amount of charge transfer results from a complex interplay between coupled electronic and vibrational degrees of freedom, which is crucially dependent on the material composition.

Invited Talk

O 120.3 Fri 11:15 TRE Ma

Dynamic non-linear multi-frequency analysis: investigating the electron-transfer theory — ●FABIO LA MANTIA — Universität Bremen, Energiespeicher- und Energiewandlersysteme, Bibliothekstr. 1, 28359 Bremen, Germany

The possibility to study and analyze the frequency response of electrochemical systems in dynamic conditions has shown the powerful advantage over classic electrochemical impedance spectroscopy (EIS) to be not limited only to stable systems. This is achieved by superimposing to a slow changing perturbation (dc) a broadband multi-sine perturbation (ac), which can cover several decades of frequency. However, typically the design of the multi-sine allows recovering and collecting only the first order frequency responses, typically named dynamic impedance spectra, for example through fast Fourier-transform EIS (FFT-EIS) or dynamic multi-frequency analysis (DMFA). In doing so, the information on the temporal asymmetry of the electrochemical reaction, carried by the intermodulation between any two frequencies of the multi-sine, is lost and cannot be recovered. In this work, after defining the concept of dynamic intermodulation, the multi-sine perturbation signal is redesigned in order to allow recovering and analyzing it. Non-linear dynamic multi-frequency analysis (NL-DMFA) will be used for investigating the electron transfer reaction to a redox couple in solution. The dynamic impedance and intermodulation spectra will be used in order to extract information on the dependence of the symmetry coefficient on the electrode's potential and its correlation to the Marcus theory of electron transfer.

O 120.4 Fri 11:45 TRE Ma

New spectroscopical tools for single-molecule junctions — ●ALBERT ARAGONÈS¹, ISMAEL DÍEZ-PÉREZ², and KATRIN DOMKE¹ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²Department of Chemistry, Faculty of Natural & Mathematical Sciences, London, UK

Biological charge transport (CT) is the key step in many basic cellular processes such as respiration or photosynthesis and nature has developed highly specialized molecular building blocks to achieve it with unprecedented efficiency. Understanding the mechanisms behind biological CT is key to elucidate the changes in its regimes caused by specific structural variations of the associated molecular machinery. Such knowledge will ultimately lead us to tailor its electrical properties and exploit them as high performance bioelectronic devices with a wide variety of applications in organic electronics, sensing, biomanufacturing etc.

To investigate CT in single-molecule bioelectronic devices, we exploit Scanning Tunnelling Microscopy-based approaches in the break-junction mode (STM-BJ) under electrochemical control (EC-STM). It allows the trapping of individual molecules in a junction to characterize their main electrical signatures. This contribution will present novel light-induced tunneling transport studies carried out with Azurines molecules (blue copper proteins) under electrochemical

control. Evident effects over the electron transport mechanism have been demonstrated due employing laser illumination in resonance with the "Ligand-to-Metal Charge Transfer" transition of the Azurine.

O 120.5 Fri 12:00 TRE Ma

Charge transfer and the hydrogen evolution reaction on Pt: bridging timescales from femto- to milliseconds by ultrafast electrochemical and optical measurements — •GREGOR ZWASCHKA¹, YUJIN TONG^{1,2}, MARTIN WOLF¹, and KRAMER CAMPEN^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin — ²Universität Duisburg-Essen, Fakultät für Physik, Lotharstr. 1, 47057 Duisburg

Despite decades of study, the mechanism of the hydrogen evolution reaction (HER) on the best available catalyst, Pt, remains controversial. At least in part, understanding is complicated by the necessity to describe processes with timescales ranging from femtoseconds (interfacial charge transfer) to milliseconds (mass transport). We approach this problem by performing perturbation experiments with ultrashort laser pulses that drive the HER close to its reversible potential and induce charge transfer along the Pt-H bond in the underpotential deposition region. We disentangle the involved timescales by performing both i) time averaged electrochemical measurements under femtosecond laser irradiation and ii) time resolved sum frequency generation spectroscopy (SFG) of Pt-H after laser excitation. Ultrafast charge transfer is found to be a function of interfacial structure (electrode and electrolyte). Trends on single crystals and a microelectrode correlate with HER activity and allow insight into the reactions rate determining step. SFG provides information on Pt-H as a function of potential, electrolyte composition and temporal evolution during and after ultrafast charge transfer. Implications for the HER are discussed.

O 120.6 Fri 12:15 TRE Ma

Real-time first-principles simulations of excitation dynamics in organic systems — •JANNIS KRUMLAND¹, ANA M. VALENCIA¹, STEFANO PITTALIS², CARLO A. ROZZI², and CATERINA COCCHI¹ — ¹Humboldt-Universität zu Berlin, Germany — ²CNR-NANO Modena, Italy

Recently, the importance of vibronic coupling in the ultrafast dy-

namics following a photo-excitation in organic molecules has become more and more appreciated, e.g. in the context of charge transfer in photovoltaics. Gaining a deeper understanding of these processes is paramount to fully exploit their technological potential.

Towards a comprehensive description of the excitation dynamics in organic light-absorbing systems, we employ real-time time-dependent density functional theory, which provides a quantum-mechanical description of electron dynamics, coupled to the Ehrenfest scheme for classical molecular dynamics. The ultrafast pulse is explicitly included as a time-dependent external field, while solvents and substrates are modeled implicitly as polarizable continua. Considering ethylene, thiophene, and benzene molecules as building blocks of complex molecular systems, we demonstrate and rationalize the strong interplay between electronic excitations and coupled vibrational modes. The results obtained in such small compounds confirm the prominent role of vibronic coupling in the ultrafast dynamics of molecules.

Invited Talk

O 120.7 Fri 12:30 TRE Ma

Resolving Chemical Bond Dynamics at an Electrode Surface — •TANJA CUK — University of Colorado, Boulder, Boulder USA

Catalytic mechanisms at electrode surfaces guide the development of electrochemically-controlled energy storing reactions and chemical synthesis. The intermediate steps of these mechanisms are challenging to identify in real time, but are critical to understanding the speed, stability, and selectivity of product evolution. In my group, we employ photo-triggered vibrational and electronic spectroscopy to time-resolve the catalytic cycle at a surface, identifying meta-stable intermediates and critical transition states which connect one to another. The talk will focus on the highly selective water oxidation reaction at the semiconductor (SrTiO₃)-aqueous interface, triggered by an ultrafast light pulse in an electrochemical cell. Here, I will describe the dynamics from the birth of the initial intermediates that trap charge (Ti-O* and Ti-O*-Ti) through the next event, suggested to be the formation of the first O-O bond of O₂ evolution. The dynamics of charge screening at the interface, a hallmark of electrochemically controlled reactions, will be addressed in both aqueous and non-aqueous (battery) electrolytes. While many open questions remain, these experiments provide and benchmark the opportunity to quantify intermediates at an electrode surface and their associated dynamics.