

O 7 Surface reactions I

Time: Monday 11:15–13:00

Room: WIL C207

O 7.1 Mon 11:15 WIL C207

Comparison of chemically and photo induced electronic excitations on gold surfaces — ●BEATE MILDNER, PETER THISSEN, ECKART HASSELBRINK, and DETLEF DIESING — Institut für Physikalische Chemie, Universität Duisburg Essen

Within an adiabatic picture exothermic surface reactions dissipate their excess energy into adsorbate and substrate vibrations. Deviations from this behavior are manifested in internal electronic excitation of the reaction products or in electronic excitations of the metal. The latter ones can be detected by the emission of electrons from the surface. However, this is only possible, when the energy of the electrons is larger than the work function of the metal. Electronic excitations with smaller energies can be detected as internal currents in tunnel or Schottky devices, whose barriers are smaller than the metals work function. We use Ta-TaOx-Au tunnel junctions as detectors for electronic excitations. In the course of the recombination reaction of atomic hydrogen on the gold surface chemically induced tunnel currents are observed. The band structure of the tunnel devices can be modified by the application of a bias voltage between the Ta and Au layers allowing an energy selective detection of the chemically excited charge carriers. This experiment is compared with the energy selective detection of photo induced tunnel currents. We used laser diodes with $h\nu = 1.95, 1.53, 1.37, 1.27$ eV. The spectrum of the chemically induced excitations agrees best with that observed for a photo excitation with $h\nu = 1.27$ eV, a value which is close to the exothermicity of the Langmuir-Hinshelwood reaction between two adsorbed hydrogen atoms of approx. 1.4 eV.

O 7.2 Mon 11:30 WIL C207

Description and analysis of non-adiabatic effects in surface processes using a mixed quantum-classical framework. — ●CHRISTIAN CARBOGNO and AXEL GROSS — Abteilung Theoretische Chemie, Universität Ulm, Albert-Einstein-Allee 11, 89069 Ulm

Impressive improvements in treating excited states have been achieved during the last decade and now allow a numerical calculation of *ab initio* potential energy surfaces for many systems. Nevertheless, to perform dynamical simulations on these surfaces still represents a considerable challenge: A full quantum treatment of both electrons and nuclei is computationally not feasible at the moment for complex, realistic systems. We have used a mixed quantum-classical approach [1] in order to describe the dynamics of electronically non-adiabatic processes at surfaces [2]. The computational efficiency of this method allows a high-dimensional treatment of these processes by including many nuclear degrees of freedom and/or electronic states. We have studied the influence of several physical and numerical parameters (e.g. number of electronic states) on the non-adiabatic reaction dynamics and compared the results with the experiment and full quantum simulations, in particular for charge-transfer processes in molecule-surface scattering and for laser-induced desorption from surfaces [2].

[1] J. C. Tully, *J. Chem. Phys.* **93**, 1061 (1990)[2] C. Bach *et al.*, *Israel J. Chem.* **45**, 45 (2005)

O 7.3 Mon 11:45 WIL C207

Non-adiabatic spin-transfer and electronic friction during chemisorption simulated with TDDFT — ●ECKHARD PEHLKE and MICHAEL LINDENBLATT — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität Kiel, 24098 Kiel

When atoms interact with a surface, part of their chemisorption energy is transferred into electron-hole pair excitations. This can result in the emission of exoelectrons, or chemicurrents over Schottky barriers as observed by Nienhaus *et al.* [1]. We simulate such non-adiabatic processes using time-dependent spin-density functional theory together with Ehrenfest dynamics for the motion of the nuclei. Results for the chemisorption of H-atoms on the Al(111) surface will be presented. Upon approach of the surface, the local spin polarization of the hydrogen atom is transferred to the substrate electrons. For an incoming H-atom with thermal energies, the energy dissipated into electron-hole pairs amounts to order of 0.1 eV for the initial part of the trajectory up to the first reflection of the H atom at the surface potential. The variation of the local spin polarization at the H-atom is compared to the Newns-Anderson model by Mizieliński *et al.* [2].

[1] H. Nienhaus, *Surf. Sci. Rep.* **45**, 1 (2002).[2] M.S. Mizieliński, D.M. Bird, M. Persson, S. Holloway, *J. Chem. Phys.* **122**, 084710 (2005).

O 7.4 Mon 12:00 WIL C207

Influence of the isotope effect on chemicurrent detection — ●DAVID KRIX, RAMONA NÜNTHEL, and HERMANN NIENHAUS — Experimental Physics, University of Duisburg-Essen, 47048 Duisburg, Germany

Hot charge carriers created in the exothermic reaction of atomic hydrogen and atomic deuterium with silver have been detected with the use of thin film Ag/p-Si(111) Schottky diodes. In thin film diodes excited holes can penetrate the metal film. If the holes are sufficiently energetic they can surpass the Schottky barrier and can be detected as a so called chemicurrent. The intensity of the chemicurrent is influenced by the transport process in the device. An exponential attenuation depending on the film thickness is observed. The experimental data show an isotope effect in the absolute intensity and attenuation length for deuterium vs. hydrogen. Chemicurrents as much as three times larger have been observed while exposing the devices to hydrogen than is the case with deuterium. The attenuation length of hot holes is found to be larger for hydrogen than for the deuterium case. The results are in agreement with theoretical predictions of electronic excitations by chemical reactions within the electronic friction model.

O 7.5 Mon 12:15 WIL C207

Copper Dissolution Reaction (CDR) in the Presence of a Binary 2D-Compound: CuI on Cu(100) — ●MINH HAI NGUYEN THI, PETER BROEKMANN, and KLAUS WANDELT — Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, D-53115 Bonn

The anodic copper dissolution reaction (CDR), has been studied by means of Cyclic Voltammetry (CV) and in-situ scanning tunnelling microscopy (STM) at the electrochemical solid/liquid interface. Exposing the Cu(100) electrode surface to an acidic and iodide containing electrolyte (5 mM H₂SO₄, 1 mM KI) leads to the formation of an electro-compressible/decompressible c(p x 2)-I adsorbate layer at potentials close to the onset of the CDR. At these positive potentials mobile CuI species originating mainly from step-edges cause the local exceeding of the CuI solubility product, thereby giving rise to the nucleation and growth of a laterally well ordered 2D-CuI film. As this process occurs at potentials well below the potential regime of the 3D-CuI bulk formation we refer to it as under potential formation (UPF) of a binary compound. The formed 2D-CuI film exhibits symmetry properties and nearest neighbour distances that are similar to the (111) lattice of the crystalline bulk CuI phase (zinc blende type). Surprisingly, the 2D-CuI film on Cu(100) does not act as a passivation layer against the copper dissolution which proceeds via an inverse step flow mechanism.

O 7.6 Mon 12:30 WIL C207

Mass transport with pulses in an excitable surface reaction: Rh(110)/K/NO + H₂ — ●HONG LIU¹, LING ZHOU², SEBASTIAN GÜNTHER³, and RONALD IMBIHL¹ — ¹Institute for Physical Chemistry, Hannover University, Callinstr. 3-3a, D-30167 Hannover, Germany — ²Division of Engineering and Applied Sciences, Harvard University, Pierce Hall, 29 Oxford St., Cambridge, MA 02138, USA — ³LMU München, Department Chemie, Butenandstr.11 E, 81377 München, Germany

Pattern formation in the NO + H₂ reaction on a Rh(110) surface predoed with potassium has been studied with photoelectron emission microscopy (PEEM), low energy electron microscopy (LEEM), and with scanning photoelectron microscopy (SPEM) at ELETTRA. With the addition of potassium the NO + H₂ reaction retains its excitability, but one finds now that the pulses are transporting potassium. In areas where pulses collide, a strong enrichment of K takes place. Under certain conditions stationary patterns develop in which the K-enriched areas form a macroscopic network. Compared to the unpromoted system the direction of the traveling wave fragments has been rotated by 90°. A mathematical model is proposed which explains qualitatively the main observations.

O 7.7 Mon 12:45 WIL C207

Two-dimensional polymeric network formed via a surface reaction — ●CARSTEN BUSSE^{1,2}, SIGRID WEIGELT¹, KURT V. GOTHELF³, CHRISTIAN BOMBIS¹, THOMAS STRUNSKUS², CHRISTOF WÖLL², FLEMMING BESENBACHER¹, and TROLLE R. LINDEROTH¹ — ¹Department of Physics and Astronomy, and iNANO, University of Aarhus, DK-8000 Aarhus C, Denmark — ²Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, D-44780 Bochum, Germany — ³Department of Chemistry, and iNANO, University of Aarhus, DK-8000 Aarhus C, Denmark

Molecular assemblies on surfaces are often held together via weak forces (van-der-Waals interaction, hydrogen bonding). In order to form more stable, covalently bond structures, we explored chemical reactions between adsorbed molecules. A tri-aldehyde with a large, conjugated backbone was deposited under UHV-conditions in submonolayer coverage on Au(111). The resulting 2D-islands were exposed to a background pressure of a reactive di-amine. After annealing to 450 K, STM reveals the formation of a network structure that consists of large (molecular mass up to 6 kDA) polymer-like macromolecules. We were able to study the connectivity and the varying local binding patterns with sub-molecular resolution. The structure of the macromolecules leads to the conclusion that a chemical reaction between the aldehyde and the amine takes place. Increasing the initial tri-aldehyde coverage leads to a dense, monolayer-high polymer film covering the whole surface. Changing the structure of the educts leads to very similar reactions. We obtained additional information on this process by XPS and NEXAFS.