

O 5 Zeitaufgelöste Spektroskopie I

Zeit: Freitag 10:45–13:00

Raum: TU EB107

O 5.1 Fr 10:45 TU EB107

Ultrafast adaptive nano-photonics — ●WALTER PFEIFFER¹, TOBIAS BRIKNER¹, JOHANNES SCHNEIDER¹, and F.J. GARCÍA DE ABAJO² — ¹Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Centro Mixto CSIC-UPV/EHU, Apartado 1072, 20080 San Sebastián, Spain

The time-resolved investigation of nanoscale transport phenomena requires localizing pump and probe excitation both for different times and at different locations. This requires a method for controlling independently the electric field evolution at closely neighboring locations. Here we present a rather general scheme that allows us to achieve this control over the spatial and temporal field distribution below the diffraction limit in the optical near field of a metal nanostructure. The scheme is based on interferences of optical near-field modes that are controlled by the excitation with polarization-shaped laser pulses. It is demonstrated that the interaction of optimally polarization-shaped femtosecond laser pulses with metal nanostructures allows controlling the spatial and temporal evolution of the electromagnetic near field. This control with simultaneous but independent nanometer length and femtosecond time resolution opens a new realm for ultrafast spectroscopy on the nanoscale and will allow novel quantum control schemes.

O 5.2 Fr 11:00 TU EB107

Ultrafast Photoemission Microscopy — ●FRANK-J. MEYER ZU HERINGDORF, DAGMAR THIEN, LIVIU I. CHELARU, OLIVER HEINZ, PING ZHUO, DIETRICH VON DER LINDE, and MICHAEL HORN-VON HOEGEN — Institut für Experimentelle Physik, Universität Duisburg-Essen (Campus Essen), 45117 Essen, Germany

The combination of ultrafast spectroscopy with photoemission microscopy is a rather challenging venture, that has so far only been attempted at few places around the world. Here we describe a novel experimental setup at the University of Duisburg-Essen that combines photoemission electron microscopy (PEEM) with pulsed fs-laser sources to study the energy dissipation of excited electrons in self organized nanostructures. The presentation describes the recent status of the setup and first experimental results of self-organized Ag nanostructures on Si(001).

O 5.3 Fr 11:15 TU EB107

Second-harmonic generation from nanoscopic metal tips: Generalized symmetry selection rules for single nanostructures — ●CATALIN C. NEACSU¹, GEORG A. REIDER², and MARKUS B. RASCHKE¹ — ¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, D-12489 Berlin — ²Institut für Photonik, Technische Universität Wien, A-1040 Wien

Second-harmonic generation from individual nanoscopic metal tips has been investigated. As a partially asymmetric (*comm*) nanostructure with the mirror symmetry broken in the axial direction the tip geometry allows for the first time to directly distinguish otherwise inseparable local surface and nonlocal bulk second-harmonic polarizations. Distinct second-harmonic-emission directions and polarization selection rules are observed that are different compared not only to linear light scattering but also compared to SHG from both, planar interfaces as well as spherical or ellipsoidal nanoparticles. In addition, the local field enhancement at the tip apex has been quantified ranging from 8 to 25 for Au tips with radii of 50 nm down to 10 nm and drops significantly for W or PtIr as tip material. The large sensitivity of SHG with respect to this local field enhancement together with the new selection rules being generally applicable to partially asymmetric nanoscopic systems provide new degrees of freedom for surface-specific second-harmonic investigations of nanostructures and the optical coupling in scattering-type near-field microscopy.

O 5.4 Fr 11:30 TU EB107

Photoemission from surface states using higher harmonic radiation — ●ANDREA MELZER¹, JINXIONG WANG¹, ALVARO WULFF¹, MARTIN WEINELT², and THOMAS FAUSTER¹ — ¹Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7, D-91058 Erlangen — ²Max-Born-Institut, Max-Born-Str. 2A, D-12489 Berlin

Photon energies up to 45 eV are generated by focussing pulses from

a multipass amplifier into argon. The laser provides pulses with 1.4 mJ energy at 770 nm wavelength at a repetition rate of 1 kHz. The pulse length is 30 fs leading to an intensity of $\sim 5 \times 10^{14}$ W/cm² at the focus. A grating monochromator with two interchangeable toroidal gratings (250 and 950 lines/mm) is used to select the individual harmonics. Photoelectron spectra from surface states on fcc(111) surfaces are measured to characterize the photon energy, linewidth, polarization, intensity, and pulse length of the higher harmonic photon source. One-photon photoemission spectra can be recorded at gas pressures below 10 mbar with no detectable pressure increase in the ultrahigh vacuum chamber of the electron spectrometer.

O 5.5 Fr 11:45 TU EB107

Two-Photon Photoemission Spectroscopy of Thiophenol Self-Assembled Monolayers on Gold(111) — ●S. DANTSCHER, T. SCHUTZMEIER, C. KENNERKNECHT, and W. PFEIFFER — Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg

The aromatic molecule thiophenol forms ordered self assembled monolayers (SAM) on gold surfaces. Using two-photon photoemission spectroscopy we investigate the influence of this surface modification on the occupied and unoccupied electronic structure of both the substrate and the adsorbate.

The samples consist of 600 Å thick gold(111) films on mica that have been evaporated in UHV. The preparation of the SAMs from an ethanolic solution takes place in an inert nitrogen atmosphere. Femtosecond laser pulses with wavelengths of 400 nm and 266 nm are used for the photoemission measurements.

The adsorption of thiophenol results in a decrease of the work function of the sample from 4.8 eV to 3.7 eV. The photoemission spectra exhibit peaks related to the SAM formation that shift with applied laser intensity. These peaks are attributed to electronic states in a physisorbed molecular overlayer on the chemisorbed monolayer. This overlayer can easily be charged by injection of excited electrons.

Accompanying these experiments, density functional theory calculations of free and adsorbed thiophenol molecules were performed. The calculated static dipole moment of thiophenol on a small gold cluster is in agreement with the observed work function change.

O 5.6 Fr 12:00 TU EB107

Ultrafast electron dynamics in C₆F₆/Cu(111) analyzed with time-resolved photoelectron and resonant Auger-Raman spectroscopy — ●P. KIRCHMANN¹, P. LOUKAKOS¹, U. BOVENSIEPEN¹, M. WOLF¹, V. SETHURAMAN², A. PIETSCH², F. HENNIES², M. NAGASONO², A. FÖHLISCH² and W. WURTH² — ¹Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin — ²Universität Hamburg, Institut für Experimentalphysik, Luruper Chaussee 149, 22761 Hamburg

Ultrafast charge transfer processes in molecules adsorbed on a metal surface can be investigated by resonant Auger-Raman spectroscopy [1] and femtosecond time-resolved two-photon-photoemission (2PPE) [2]. To systematically compare both techniques we investigated the system C₆F₆/Cu(111). This study reveals a qualitatively different coverage dependence of the decay rate of the lowest unoccupied molecular resonance. In addition the decay rate for monolayer coverages measured by the two methods is different by a factor of five. This is attributed to the fact that Auger-Raman spectroscopy detects intra-molecular charge delocalization as well as the delocalization between the molecule and its environment. In contrast, 2PPE probes the intraband scattering within delocalized states of the molecular adlayer as well as the population decay by interband scattering to the substrate. Thus different relaxation channels are measured with the two approaches. The project was funded by the DFG through SPP 1093.

[1] W. Wurth and D. Menzel, Chem. Phys. 251, 141 (2000)

[2] C. Gahl, K. Ishioka, Q. Zhong, A. Hotzel and M. Wolf, Faraday Discuss. 117, 191 (2000)

O 5.7 Fr 12:15 TU EB107

Vibrational dynamics of the C-O stretching mode of CO:Si(100) — ●KRISTIAN LASS, XU HAN, and ECKART HASSELBRINK — Fachbereich Chemie, Physikalische Chemie, Universität Duisburg-Essen, Standort Essen, Universitätsstr. 5, D-45141 Essen

Surface infrared-visible sum frequency generation (SFG) spectroscopy (using ps laser pulses) has been utilised to study the vibrational dynamics of the internal stretching mode of CO molecularly adsorbed on a Si(100) surface. The structure of the CO-adsorbed Si(100) surface is not known in detail; however, two slightly different adsorbed species have been suggested in the past. With our IR laser linewidth of 9 cm^{-1} , only one resonance was distinguishable, whose linewidth was significantly lower than our laser linewidth. Using a IR-pump-SFG-probe setup, the vibrational lifetime of the system could be determined to be about 2 ns. This value is unexpectedly short, in view of the fact that the vibrational excitation cannot couple to electron-hole pairs because of the large bandgap in Si. The lifetime appears to be independent of the carrier density of the Si crystal (within the accuracy of our experiment), as judged from the vibrational lifetime measured on crystals with different dopant densities.

O 5.8 Fr 12:30 TU EB107

Mechanism of femtosecond laser induced diffusion of oxygen on vicinal Pt(111) — ●K. STÉPÁN, J. GÜDDE, and U. HÖFER — Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps Universität Marburg, D-35032 Marburg

Laser-induced diffusion of atomic oxygen from step edges onto terraces of a vicinal Pt(111) surface has been studied by exploiting the sensitivity of optical second-harmonic generation (SHG) on surface symmetry. The excitation mechanism of the diffusion process has been investigated by measuring the diffusion rate as a function of fluence and delay between two femtosecond pump pulses. The strong nonlinear fluence dependence ($\propto F^{15}$) and a width of 1.5 ps in the two-pulse-correlation measurements show that the diffusion process can be understood within the same framework as the well studied phenomena of desorption induced by multiple electronic transitions (DIMET). For a quantitative modeling of the data we approximate the detailed coupling of adsorbate modes and excited substrate electrons with an electronic friction coefficient [1]. In contrast to the situation in most laser-induced desorption experiments, a friction coefficient that depends on the excitation density is required in to describe the whole data set. We interpret this dependence in terms of an indirect electronic excitation mechanism of the frustrated translation leading to diffusion. We suggest that the electronic excitation of the substrate couples primarily to the O-Pt stretch vibrations which then excite frustrated translations via an anharmonic coupling of modes.

[1] M. Brandbyge *et al.* Phys. Rev. B. **52**, 6042 (1995)

O 5.9 Fr 12:45 TU EB107

Dynamics of Electron Transfer, Trapping, and Solvation in $D_2O/Ru(001)$ — ●JULIA STÄHLER, UWE BOVENSIEPEN, CORNELIUS GAHL, and MARTIN WOLF — Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

The dynamics of excess electrons photo-injected into ultrathin ice layers on Ru(001) has been studied by femtosecond time-resolved two photon photoelectron (2PPE) spectroscopy. The electrons' residence time in the adlayer is limited due to the transfer matrix element between substrate and adsorbate. In amorphous ice layers, this leads to sub-ps-lifetimes of the solvated electrons. These are initially injected into the ice conduction band before they start to stabilize 2.9eV above the Fermi level [1]. In contrast, we observe excess electrons within crystalline $D_2O/Ru(001)$ that present lifetimes up to several minutes before they relax back to the metal. Variation of the UV excitation energy shows that these electrons are transferred to the delocalized image potential state within the ice layer before they localize more than 2eV above the Fermi level into preformed traps. During their extremely long lifetime an increase of binding energy is observed, which is attributed to a rearrangement of the polar environment. The notable temperature dependence of binding energy and photoelectron intensity will be discussed.

[1] U. Bovensiepen *et al.*, Isr. J. Chem. 45 (2005), in press