

O 76: Plasmonics and Nanooptics III: Light-Matter Interaction and Spectroscopy II

Time: Thursday 10:30–12:45

Location: WIL A317

O 76.1 Thu 10:30 WIL A317

Continuous-wave multiphoton-induced electron transfer in a biased tunnel junction driven by intense plasmonic fields —CHENFANG LIN¹, ●MELANIE MÜLLER^{1,2}, FARUK KRECINIC¹, HIROKO YOSHINO¹, ADNAN HAMMUD¹, ANLIAN PAN², MARTIN WOLF¹, and TAKASHI KUMAGAI³ — ¹Fritz Haber Institute, Faradayweg 4-6, Berlin — ²Hunan University, Hunan 410082, China — ³Institute for Molecular Science, Okazaki 444-8585, Japan

Understanding photoinduced tunneling processes in the presence of intense plasmonic fields is of crucial importance for the design of plasmon-induced hot carrier technology and optical rectennas. However, in contrast to femtosecond laser excitation, the observation of multiphoton-induced electron transfer and the understanding of the role of hot carriers under intense continuous-wave (cw) illumination remains scarce. Here we exploit the strong spatial confinement of light inside the plasmonic gap of a scanning tunneling microscope (STM) to drive photocurrents with cw optical fields at local peak intensities up to 10^9 W/cm² at low incident power. We find that the photoinduced tunneling current scales nonlinear (linear) with laser intensity at low (high) STM bias. To yield insight into the photoinduced tunneling process we analyze the photocurrent-voltage dependence for different laser wavelength and powers. We discuss two possible origins of the multiphoton-induced electron transfer, namely transport of photoexcited hot electrons and photon-assisted quantum tunneling into light-dressed states.

O 76.2 Thu 10:45 WIL A317

Atomically resolved optical spectroscopy and microscopy in a scanning-tunneling microscope: Theory and experiment —●TOMAS NEUMAN^{1,2}, ANNA ROSLAWSKA¹, BENJAMIN DOPPAGNE¹, ANDREI G. BORISSOV², MICHELANGELO ROMEO¹, FABRICE SCHEURER¹, JAVIER AIZPURUA³, and GUILLAUME SCHULL¹ — ¹Universite de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000, Strasbourg, France — ²Institut des sciences Moleculaires d'Orsay (ISMO), UMR 8214, CNRS, Universite Paris-Saclay, 91405 Orsay Cedex, France — ³Center for Materials Physics and DIPIC, Paseo Manuel de Lardizabal 5, Donostia-San Sebastian 20018, Spain

We present a joint theoretical and experimental study of the optical properties of individual small organic molecules excited electrically by the plasmonic tip of a STM. We investigate how these properties vary as a function of the tip position with atomic-scale resolution. We show that the variation of the spectral position and width of the electroluminescence emission line of the molecular exciton can be linked with the DC Stark effect (induced by the static voltage across the tip-substrate gap) and the plasmonic Purcell effect due to the plasmonic response of the tip, respectively. We interpret the spectral line shift map as an image of the difference between the excited- and ground-state electron densities of the molecule, and the tip-position-dependent map of the excitonic line-width variation as an image of the transition electron density. In contrast, the map of light intensity emitted by the molecule reveals the information about the electronic mechanism leading to the tip-mediated generation of the exciton.

O 76.3 Thu 11:00 WIL A317

Modeling of molecular systems probed by near-field spectroscopy — ●SOFIA CANOLA, JIŘÍ DOLEŽAL, RODRIGO FERREIRA, and MARTIN ŠVEC — Institute of Physics, Czech Academy of Sciences, Praha, Czech Republic

Spectroscopy coupled to scanning-probe microscopy is a powerful tool to analyze molecular properties at a single molecule level with sub-molecular resolution. In this technique, some intrinsic limitations and selection rules of conventional spectroscopy are overcome. This aspect, together with the high resolution of the signal and the precise control over the sample, allow to obtain information otherwise not accessible, such as for example the structural arrangement of the molecule, the electronic structure of its ground or excited molecular electronic state, its charging state or its response to stimuli. To fully unpack and rationalize the information, a theoretical interpretative framework must accompany the experimental findings. A crucial aspect is the ability to describe the molecular spectroscopic response in the near-field while including all the relevant aspects of the setup. High-level quantum-chemical calculations are needed, capable of reliably model-

ing the molecular system in its complexity and providing the appropriate response function. In this contribution, we present the results from the application of this technique to small conjugated molecules, with particular focus on the modeling aspects and the interesting molecular properties that become accessible when experiments and theory complement.

O 76.4 Thu 11:15 WIL A317

Plasmon-Induced Molecular Switching of PTCDA on Si(111) Studied by STM-TERS —●YOUNGWOOK PARK¹, ADNAN HAMMUD¹, MARTIN WOLF¹, TAKASHI KUMAGAI², and AKITOSHI SHIOTARI¹ — ¹Fritz Haber Institute of the Max Planck Society, Berlin, Germany — ²Institute for Molecular Science, Okazaki, Japan

We studied a unique plasmon-induced molecular motion of perylene-tetracarboxylic dianhydride (PTCDA) single molecules on the Si(111)-7x7 surface by means of the atomic point contact (APC) tip-enhanced Raman spectroscopy (TERS) with a low temperature scanning tunneling microscope (STM) under an ultrahigh vacuum condition. In our APC-TERS scheme, a silver tip approaches close to the surface until the tip makes an atomic point contact with its counterpart. It was reported by our previous study that at the point contact with Si(111) the TERS signal was significantly enhanced. The PTCDA on the Si(111), fixed on the surface by four oxygen-silicon bonds, showed a distinctive APC-TERS pattern where the Raman intensity was dramatically enhanced at a certain gap distance during the tip approach, and then was attenuated at shorter tip-molecule distances. At the TERS "sweet spot", the STM current rapidly switched between two states, implying a fluctuating motion of PTCDA molecule between the tip and the surface. On the contrary to PTCDA, perylene-tetracarboxylic diimide (PTCDI) did not show such TERS "sweet spot" nor STM current switching. We believe this unique system could provide a better understanding on the plasmon-molecule interaction, as well as their implication on the enhancement mechanism in TERS.

O 76.5 Thu 11:30 WIL A317

Photoluminescence mapping of an anionic molecule —

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Only recently, the photoluminescence (PL) of a single molecule has been attained [1,2] with sub-nm resolution in a scanning tunneling microscope (STM). However, only a fluorescent peak from a neutral phthalocyanine has been observed. The observation of fluorescence from a charged molecule is still elusive, likely due to the plasmon-mediated excitation mechanism which is fundamentally different from the electroluminescence (EL) process where a charged exciton can be created via electron/hole tunneling into dication/dianion [3,4].

Here, we present STM-PL maps of PTCDA anion adsorbed on 3ML/NaCl. The anionic charge state of the adsorbed molecule [5] enables its direct excitation by a laser-induced gap plasmon. We show STM-PL photon maps of an individual molecule and small molecular clusters qualitatively comparable to STM-EL maps [5], but independent of the tunneling current. This brings a major advantage over electroluminescence as the current is a scaling factor in the photon map intensity and its elimination [5-7] creates unwanted artefacts.

[1] B. Yang et al. Nat. Photonics 14, 693 (2020). [2] H. Imada et al. Science 373, 95 (2021). [3] K. Kaiser et al. arXiv:2211.01051 (2022). [4] B. Doppagne et al. Science 361, 251 (2018). [5] J. Doležal et al. ACS Nano 16, 1082 (2022). [6] B. Doppagne et al. PRL 118, 127401 (2017). [7] Y. Zhang et al. Nature 531, 623 (2016).

O 76.6 Thu 11:45 WIL A317

A Setup for Fluorescence-Detected Two-Dimensional Electronic Spectroscopy of Single Molecules —

●SANCHAYEETA JANA, SIMON DURST, LUCAS LUDWIG, and MARKUS LIPPITZ — Chair for Experimental Physics III, University of Bayreuth, Bayreuth, Germany

Fluorescence-Detected Two-Dimensional Electronic Spectroscopy is a recent ultrafast technique that yields information about the coupling between the states of a system. At the same time, fluorescence-detected single molecule spectroscopy is a well-established technique since more than 30 years. By combining these two techniques one

should be able to measure 2d spectra of single molecules to get new insight in molecular dynamics on ultrashort time scales.

Here we present our work towards this goal. We use four phase-modulated ultrafast pulses to excite the molecule with the help of a high NA objective. The fluorescence is registered by single-photon detectors and demodulated at several mixing frequencies to get the rephasing and non-rephasing signals. The novelty of our technique is that we can measure Fluorescence Correlation Spectroscopy (FCS) and Time-Correlated Single Photon Counting (TCSPC) simultaneously to monitor the number of molecules in our excitation focus and the fluorescence lifetime.

In this work we illustrate our experimental technique and discuss 2d spectra measured on a molecular sample at low concentration.

O 76.7 Thu 12:00 WIL A317

Luminescence from Cu₂O films and bulk crystals in the STM — ALEXANDER GLOYSTEIN, MINA SOLTANMOHAMMADI, and NIKLAS NILIUS — Carl von Ossietzky Universität, Institut für Physik, D-26111 Oldenburg, Germany

STM luminescence spectroscopy is employed to compare the optical response of bulk Cu₂O(111) and 1-10 nm thick Cu₂O/Au(111) films. Although both systems share similar structural and electronic properties and expose the same thermodynamically preferred ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction, their luminescence exhibits pronounced differences. The spectra of bulk Cu₂O are dominated by the recombination of free and defect-bound excitons, whereas a unique plasmonic response is detected for the oxide films. The latter arises from the electromagnetic coupling between STM tip and gold support, while the Cu₂O ad-layer exclusively controls the inelastic tunneling rates, i.e., the intensity, but not the spectral signature of the emission. Only upon tunneling into the Cu₂O band gap, a luminescence channel mediated by O vacancies is identified in the oxide film. The talk addresses the question why the unique exciton response of Cu₂O is covered by plasmon excitations even in films as thick as 10 nm.

O 76.8 Thu 12:15 WIL A317

Hot-carrier transfer across a nanoparticle-molecule junction: The importance of orbital hybridization and level alignment — JAKUB FOJT¹, TUOMAS ROSSI², MIKAEL KUISMA³, and PAUL ERHART¹ — ¹Department of Physics, Chalmers University of Technology, Gothenburg, Sweden — ²Department of Applied Physics, Aalto University, Aalto, Finland — ³Department of Physics, Technical University of Denmark, Kongens Lyngby, Denmark

While direct hot-carrier transfer can increase photocatalytic activity, it is difficult to discern experimentally and competes with several other mechanisms. To shed light on these aspects, here, we model from first-principles hot-carrier generation across the interface between plasmonic nanoparticles and a CO molecule. The hot-electron transfer probability depends nonmonotonically on the nanoparticle-molecule distance and can be effective at long distances, even before a strong chemical bond can form; hot-hole transfer on the other hand is limited to shorter distances. These observations can be explained by the energetic alignment between molecular and nanoparticle states as well as the excitation frequency. The hybridization of the molecular orbitals is the key predictor for hot-carrier transfer in these systems, emphasizing the necessity of ground state hybridization for accurate predictions. Finally, we show a nontrivial dependence of the hot-carrier distribution on the excitation energy, which could be exploited when optimizing photocatalytic systems.

O 76.9 Thu 12:30 WIL A317

Disentangling the Orientations of Spectrally Overlapping Transition Dipoles in Dense Dye Layers — CHRISTOPH SCHNUPFHAGN¹, THORSTEN SCHUMACHER¹, PAUL MARKUS², GEORG PAPASTAVROU², OLHA AFTENIEVA³, TOBIAS A. F. KÖNIG³, VOLODYMYR DUDKO⁴, MARIAN MATEJDES⁴, JOSEF BREU⁴, and MARKUS LIPPITZ¹ — ¹Experimental Physics III, University of Bayreuth — ²Physical Chemistry II, University of Bayreuth — ³Leibniz-Institut für Polymerforschung Dresden e.V. — ⁴Inorganic Chemistry I, University of Bayreuth

The transition dipole orientations of dye assemblies in heterostructures have a crucial impact on the efficiency of novel optoelectronic devices such as organic thin-film transistors and light-emitting diodes. These devices are frequently based on heterojunctions and tandem structures featuring multiple optical transitions. Precise knowledge of preferred orientations, spatial order, and spatial variations is highly relevant. We present a fast and universal large-area screening method to determine the transition dipole orientations in dye assemblies with diffraction-limited spatial resolution. Moreover, our hyperspectral imaging approach disentangles the orientations of different chromophores. As a demonstration, we apply our technique to dye monolayers with two optical transitions sandwiched between two ultrathin silicate nanosheets. A comprehensive model for dipole orientation distributions in monolayers reveals a long-range orientational order and a strong correlation between the two transitions.