

O 61: Plasmonics and Nanooptics 2

Time: Thursday 10:30–12:45

Location: H2

Topical Talk

Single Molecule Nonlinearity in a Plasmonic Waveguide —
 ●MARKUS LIPPITZ — Experimental Physics III, University of Bayreuth

Plasmonic waveguides offer the unique possibility to confine light far below the diffraction limit. Past room temperature experiments focused on efficient generation of single waveguide plasmons by a quantum emitter. However, only the simultaneous interaction of the emitter with multiple plasmonic fields would lead to functionality in a plasmonic circuit. Here, we demonstrate the nonlinear optical interaction of a single molecule and propagating plasmons. An individual terylene diimide (TDI) molecule is placed in the nanogap between two single-crystalline silver nanowires. A visible wavelength pump pulse and a red-shifted depletion pulse travel along the waveguide, leading to stimulated emission depletion (STED) in the observed fluorescence. The efficiency increases by up to a factor of 50 compared to far-field excitation. Our study thus demonstrates remote nonlinear four-wave mixing at a single molecule with propagating plasmons. It paves the way toward functional quantum plasmonic circuits and improved nonlinear single-molecule spectroscopy.

O 61.2 Thu 11:00 H2

Excitation of coherent phonon modes in plasmonic gold nanoparticles —
 ●DOMINIK HÖING^{1,2}, ROBERT SALZWEDEL⁴, MALTE SELIG⁴, KARTIK AYYER^{2,3}, JOCHEN KÜPPER^{2,3}, ANDREAS KNORR⁴, and HOLGER LANGE^{1,2} — ¹Institute of Physical Chemistry, Universität Hamburg, Hamburg, Germany — ²The Hamburg Centre for Ultrafast Imaging, Hamburg, Germany — ³Center for Free-Electron Laser Science, Hamburg, Germany — ⁴Institut für Theoretische Physik, Technische Universität Berlin, Berlin, Germany

The plasmonic properties of gold nanoparticles (AuNP) have been widely studied, because of their exhibition of strong light-matter coupling and hot carrier generation. The carrier dynamics that follow the optical excitation are presently understood as a series of events with increasing time-scales. Among them, the excitation of coherent acoustic phonon modes, also called breathing modes, is thought to result from the ultrafast heating of the lattice due to electron-phonon coupling. However, previous experimental studies were insufficient in detecting the onset of the breathing oscillation. Here, we use a combination of transient absorption spectroscopy, time-resolved X-ray scattering and a model combining quantum coherent and hydrodynamic theory to develop a different picture: We show that the gradient in electron density induced by the optical excitation instantaneously couples to coherent phonons, resulting in an immediate onset of the breathing oscillation with the optical excitation. Thus, the processes involved in the plasmon decay are more intertwined as previously assumed.

O 61.3 Thu 11:15 H2

Probing a plasmon-polariton quantum wave packet —
 SEBASTIAN PRES¹, BERNHARD HUBER¹, DANIEL FERSCH¹, ENNO SCHATZ², DANIEL FRIEDRICH², VICTOR LISINETSKII¹, RUBEN POMPE³, ●MATTHIAS HENSEN¹, BERT HECHT², WALTER PFEIFFER³, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²NanoOptics & Biophotonics Group, Experimental Physics 5, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ³Fakultät für Physik, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld, Germany

Beyond the classical picture, plasmon-polariton modes are treated as quasi-particles in quantum physics and they are considered essential for the realization of future nanoscale quantum functionality. Implementing and demonstrating such functionality requires local access to the quasi-particle's quantum state to monitor its corresponding quantum wave-packet dynamics. Here, we report the local probing of such an eigenstate superposition, linked to a nanoslit resonator, using plasmon-polariton-assisted electron emission as signal in coherent two-dimensional nanoscopy¹. We observe a quantum coherence oscillating at the third harmonic of the plasmon-polariton frequency and identify it, using quantum dynamical simulations, to arise from the superposition of energetically non-adjacent plasmon-polariton occupation number states. The simulations also contain an improved model for plasmon-polariton-assisted electron emission processes.

[1] M. Aeschlimann et al., *Science* 333, 1723-1726 (2011)

O 61.4 Thu 11:30 H2

Modelling Plasmon-Exciton Interaction using a Coupled-Oscillator Approach —
 ●SIMON DURST, CHRISTOPH SCHNUPFHAGN, and MARKUS LIPPITZ — Experimental Physics III, University of Bayreuth

Coupling effects between plasmonic and excitonic systems have attracted increasing interest in the last decade. In particular, Surface Lattice Resonances, diffractive modes supported by periodic arrays of metallic nanoparticles, allow for long-range coherent energy transfer and have been shown to strongly couple to interspersed excitonic emitters. Here, we will present experimental results showing strong coupling between Surface Lattice Resonances and the excitonic mode of a J-aggregate dye. The angle-resolved extinction spectra of this coupled system are modelled using a coupled oscillator model, which describes observed effects, such as a loss of contrast of the upper polariton branch or an asymptotic behaviour of the lower polariton branch well.

O 61.5 Thu 11:45 H2

Light emission from single self-decoupled molecules —
 ●VIBHUTI RAI¹, LUKAS GERHARD¹, GABRIEL DERENBACH¹, NICO BALZER², MICHAL VALÁŠEK², MARCEL MAYOR², and WULF WULFHEKEL¹ — ¹Institute for Quantum Materials and Technologies, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany — ²Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany

Realization of single molecules as electric light sources faces a dilemma: In order to emit light, they need to be decoupled from the metallic electrodes to prevent fluorescence quenching. To conduct, however, the molecular orbitals need to hybridize with the electrodes. This can be achieved by decoupling the molecular chromophore to a certain extent from the electrode via anchoring groups. In the past, such self-decoupled molecules often lacked reproducibility of the decoupling and energy of the emitted light. Here, we show reproducible and well defined electroluminescence of two different NDI chromophores linked to a gold substrate via a molecular tripod and via a vacuum barrier to the tip of a scanning tunnelling microscope [1]. The stability of the system allows to perform systematic experiments so far only possible for molecules decoupled via insulating layers.

[1] Edelmann, K. et al. *Rev. Sci. Instrum.* 89, 123107 (2018).

O 61.6 Thu 12:00 H2

Investigation of chemical interface damping on electrochemically functionalized flat gold and nanoporous gold surfaces —
 ●MAURICE PFEIFFER¹, XINYAN WU¹, ALEXANDER PETROV^{1,2}, and MANFRED EICH^{1,2} — ¹Institute of Optical and Electronic Materials, Hamburg University of Technology, Germany — ²Institute of Photoelectrochemistry, Helmholtz-Zentrum Hereon, Geesthacht, Germany

The chemical interface damping (CID) effect occurs at metal surfaces when applying surface modifications, such as oxidation. It results in an increase of the electron collision frequency of the metal, thus altering its optical properties. Previous research showed that this effect may also enhance the efficiency of photocatalytic water splitting by visible light [1]. We investigate the CID effect on flat gold as well as nanoporous gold samples with the latter having the advantage of a very high surface to volume ratio, making surface effects (like CID) more pronounced. Our experimental setup consists of a spectroscopic ellipsometer to investigate the optical properties. This device is equipped with an electrochemical cell in which we can reversibly oxidize the sample surface, allowing an in-situ study of the CID effect. Previous research investigated the CID effect on gold nanoparticles and observed an increase of the damping rate at the plasmon resonance [2]. Our results on flat gold reveal a similar increase of the damping, but additionally enable the investigation of broadband properties from which we expect further insights on the nature of the damping mechanism.

[1] Graf et al., *ACS Nano* 2021, 15, 2, 3188-3200 [2] Foerster et al., *Nano Lett.* 2020, 20, 5, 3338-3343

O 61.7 Thu 12:15 H2

Switching on the electroluminescence of single molecules adsorbed directly on a metal surface —
 VIBHUTI RAI¹, ●LUKAS

GERHARD¹, NICO BALZER², MICHAL VALÁŠEK², CHRISTOF HOLZER³, LIANG YANG², MARTIN WEGENER², CARSTEN ROCKSTUHL³, MARCEL MAYOR², and WULF WULFHEKEL¹ — ¹Institute for Quantum Materials and Technologies, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany — ²Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany — ³Institute of Theoretical Solid State Physics, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany

Exciting single molecules to emit light into the far-field requires them to be electronically decoupled from the contacting metallic leads. In the scanning tunnelling microscope (STM) geometry, typically this has been achieved by inserting insulating layers between the molecules and the metal substrate [1]. Here, we report our finding that it is possible to activate the electroluminescence (EL) of individual 2,6- core-substituted naphthalene diimide derivatives (Tpd-sNDI), adsorbed directly on a metal surface with the help of the STM tip. We observe that to emit light, both orbitals involved in the optical transition need to be electronically decoupled. The STM measurements were performed with a home-built, low temperature, ultra-high vacuum scanning tunnelling microscope (STM) with optical access [2].

[1] Zhang, Y. et al. Nature 531, 623 (2016).

[2] Edelmann, K. et al. Rev. Sci. Instrum. 89, 123107 (2018).

O 61.8 Thu 12:30 H2

First principles investigation of plasmonic hydrogen catalysis on metallic magnesium nanoparticles — OSCAR A. DOUGLAS-GALLARDO, CONNOR L. BOX, and REINHARD J. MAURER — University of Warwick, Coventry, United Kingdom

Plasmon-induced hot-carrier photochemistry is currently a promising avenue to achieve highly selective and efficient chemical transformation on plasmonic metal surfaces. A new class of materials made up of Earth-abundant-elements has gained increasing interest in the plasmonic area, as an alternative to the oft studied late transition metals (Au, Ag and Cu).

Here, we will present our results on the optical and electronic properties of metallic magnesium nanoparticles and their potential use as plasmonic hydrogen catalysts. We explore the optical and electronic properties with time-dependent density functional tight-binding (TD-DFTB) and molecular dynamics with electronic friction (MDEF) simulations. Our results show that Mg nanoclusters can produce highly energetic hot-electrons and they energetically align with electronic states of physisorbed molecular hydrogen, the occupation of which by these hot electrons can promote hydrogen dissociation. The reverse reaction, hydrogen evolution on metallic Mg, may also be promoted by hot electrons, but following a different mechanism.