O 72: Poster: Scanning Probe Microscopy: Light Matter Interaction at Atomic Scales

Time: Wednesday 18:00–20:00 Location: Poster D

O 72.1 Wed 18:00 Poster D

Luminescence of molecules with STM – from electron to photon excitations — Benjamin Doppagne[1], Shuiyan Cao[1], Song Jiang[1], Katharina Kaiser[1], Luis Parra Lopez[1], Anna Rosławska[1], Kirill Vasilev[1], Tomas Neuman[1], Andrei G. Borisov[2], Javier Aizpurua[3], Michelangelo Roméo[1], Alex Boeglin[1], Frederic Cherioux[4], Eric Le Moal[2], Hervé Bulou[1], Fabrice Scheurer[1], and •Guillaume Schull[1] — [1]Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France. — [2]Institut des Sciences Moléculaires d'Orsay (ISMO), UMR 8214, CNRS, Université Paris-Saclay, 91405 Orsay Cedex, France. — [3]Center for Materials Physics (CSIC-UPV/EHU) and DIPC, Donostia-San Sebastián, Spain — [4]Université Bourgogne Franche-Comté, FEMTO-ST, UFC, CNRS, Besançon, France

STM-induced luminescence (STML) and tip-enhanced photoluminescence (TEPL) enable fluorescence imaging of molecules with sub-nanometer spatial resolution. While the former approach relies on tunneling electrons as an excitation source, the latter involves exciting the molecule with light. In this summary, I will highlight recent results from our team and compare the respective benefits of each method.

O 72.2 Wed 18:00 Poster D

Interactions between plasmons and excitons in single molecules — •Miguel Varea[1,2], David Mateos[1,2], Óscar Jover[1,2], Koen Lauwaet[1], Alberto Martín-Jimenez[1], and Roberto Otero[1,2] — [1]IMDEA Nanoscience, Madrid, Spain — [2]Dep. de Física de la Materia Condensada and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid

The interaction of localized plasmons and excitons in quantum emitters results in plexcitons, hybrid light-matter states, offering unique prospects for controlling single photon states. Scanning Tunneling Luminescence (STM-L) proves crucial in characterizing exciton-plasmon interactions, providing control over cavity dimensions and knowledge of molecular geometry. However, the incomplete comprehension of electron-tunneling luminescence processes hinders its full exploitation. Specifically, the optical behavior of metal-interfacing molecules lacks explanation when no insulation separates the molecule from the substrate. This study addresses this gap by studying changes in plasmonic modes within the cavity induced by organic molecules adsorbed on the metal surface. Despite a substantial drop in luminescence intensity due to the molecules, our analysis primarily links this decline to differences in the electronic structures of the molecules and the metal surface. By isolating the strictly optical effects of molecule presence, luminescence spectra become comparable, though not entirely identical. This contribution underscores the molecule-specific and aggregation-dependent nature of these modifications, paving the way for using STM-L to explore plasmon-exciton coupling at the nanoscale.

O 72.3 Wed 18:00 Poster D

Luminescence on the atomic scale in a Terahertz Scanning Tunneling Microscope — •Johannes Schust, Kurt Lichtenberg, Felix Huber, Susanne Baumann, and Sebastian Loth — Institute for Functional Matter and Quantum Technologies, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany

The interplay between light and matter has a key role in solid-state research, and it constitutes a fundamental element of numerous contemporary technologies. Therefore, exploring the photonic properties of novel quantum systems is of high significance, while pushing the frontiers of both temporal and spatial resolution remains a persistent challenge. Here, we implement electroluminescence sensing into an ultra-fast Terahertz scanning tunneling microscope (STM), i.e. extend the system's capability to couple light directly out of the junction. Our exceptional vacuum chamber design features a thin slot that hosts the whole measuring unit in a flow-cryostat, while quartz windows on both sides give optical access and allow for the strait-forward adjustment of all further components at ambient conditions, precluding any complicated in-vacuum optical adjustments. Versatile optical concepts can be easily implemented and modified to the experimental needs in that way. With our unique setup, we harness the remarkable time resolution obtained by single Terahertz voltage pulses for time-resolved electroluminescence experiments. In particular, we will unravel field-induced electroluminescence with femtosecond time resolution, while simultaneously addressing samples with the atomic resolution provided by scanning probe microscopy.

O 72.4 Wed 18:00 Poster D

Time-Resolved Measurements with THz-STM on Semiconducting MoTe$_2$ — •Vibhuti Rai, Junyoung Sim, Carlos Williams, Sergey Trishin, Nils Bogdanoff, Tom Seifert, Tobias Kampfrath, Christian Lotze, and Katharina J. Franke — Freie Universität Berlin, Department of Physics, Arnimallee 14, 14195 Berlin, Germany

To access time scales of elementary excitations, pump-probe schemes using ultrashort laser pulses are the method of choice. Combining these with scanning tunnelling microscopy (STM) would not only give the required time resolution but also provide spatial resolution on the sub nanometer scale [1]. In this work, we use a home-built THz setup combined with an STM working at 5K in ultra-high vacuum. We study the charge carrier dynamics of the semiconducting MoTe$_2$ bulk sample [2]. An infrared pump pulse is used to excite the sample across its direct band gap of 1eV. To probe the dynamics, we use the THz field as a transient bias that modulates the tunnelling junction. By delaying the IR pulse with respect to the THz pulse, we explore the dynamics of the excited states and also use them further to spatially resolve and study surface defects.

O 72.5 Wed 18:00 Poster D

Coupling Single-Cycle Terahertz Fields into a STM: Characterization and Time-Resolved Measurements — •Junyoung Sim, Vibhuti Rai, Carlos Williams, Sergey Trishin, Nils Bogdanoff, Tom Seifert, Tobias Kampfrath, Christian Lotze, and Katharina Franke — Freie Universtiät Berlin, Department of Physics, Arnimallee 14, 14195 Berlin, Germany

Scanning tunneling microscopy (STM) is an ideal tool to study the structure and electronic properties of atomic-scale nanostructures on surfaces. Excitation-relaxation dynamics in these systems occur typically on timescales of picoseconds or even faster, which is beyond the electronic bandwidth of STM. To explore this ultrafast regime, Cocker et al. coupled ultrashort terahertz (THz) pulses into a STM junction and implemented a pump-probe detection scheme [1].

In this work, we follow a similar approach by setting up a THz source and coupling it to a 5K- STM. Here, we provide a preliminary characterization of our set up with a few benchmarking experiments. We measure the near-field THz pulse that modulates the photocurrent excited by a preceding optical pulse between STM tip and Ag(111) surface. We also probe field emission resonance by the transient voltage from the THz pulse. We then perform infrared-pump THz-probe measurement to investigate the dynamics of excitation processes across the bandgap on the semiconducting transition metal dichalcogenide MoTe2 [2].

[1] Cocker et al. Nature Photonics 15, 558-569 (2021)

[2] Sankar et al. Chem. Mater., 29, 2, 699-707 (2017)

O 72.6 Wed 18:00 Poster D

Azobenzene derivatives in the vicinity of Cobalt islands on a gold surface — •Bensu Günay, Christophe Nacci, and Leonhard Grill — Chemistry department, University of Graz, Graz, Austria

The purpose of this study is to investigate whether plasmonic effects can affect the isomerization behavior of molecular switches in the vicinity of cobalt islands on a metallic surface. We have chosen azobenzene derivatives, a prototypical molecular switch, as functional units and an Au(111) surface as substrate, which was studied by low-temperature scanning tunneling microscopy. The combination of these molecules with the gold surface is well known [1] and therefore represents a suitable model system. While in previous studies, switching of the molecules was typically induced by voltage pulses [1], we have induced isomerization here by light. Importantly, Cobalt islands were grown on the surface with the purpose of localized plasmonic effects around these islands. The surface, which was illuminated for different durations at various wavelengths, was then studied in view of different switching rates in the vicinity of the Cobalt islands as compared to remote locations.

[1] M. Alemani et al., JACS 128, 14446 (2006)

O 72.7 Wed 18:00 Poster D

Characterization of C_{60} derivatives by Atomic Force Microscopy — •Paul Mosser[1], Antoine Hinaut[1], Thilo Glatzel[1], Shi-xia Liu[2], Silvio Decurtins[2], and Ernst Meyer[1] — [1]Department of Physics, University of Basel, Klingelbergstrasse 82, CH 4056 Basel, Switzerland — [2]Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH 3012 Bern, Switzerland

Pristine C_{60} as a rigid spherical molecule is a 3D strong electron acceptor. The absorption spectrum of fullerene changes greatly as it approaches a metal surface, and a significant dependence on the distance between the molecule and the substrate is expected. For this purpose, functional groups with the binding affinity of Au substrates can be covalently attached to the fullerene core with any regioisomeric pattern and used to tune the coupling of the compounds with the local plasmons. In this work, N-pyridyl-3,4-fulleropyrrolidine (C_{60}-Py) is studied as it is supposed to form Au-N bonds on a gold surface. C_{60}-Py were evaporated on an Au(111) surface and characterized using nc-AFM and KPFM at room temperature and under UHV conditions. The high-resolution AFM images of C_{60}-Py islands show a periodicity difference compared to pristine C_{60} islands showing that the pyridyl-pyrrolidine group has an influence on the self assembly on Au(111). KPFM measurements show a contrast in CPD between Au, the pristine C_{60} islands and the C_{60}-Py islands of 200mV.

O 72.8 Wed 18:00 Poster D

Understanding photocurrents in plasmonic tunnel junctions driven by continuous-wave optical fields — •Henrik Wiedenhaupt[1], Chenfang Lin[1,2], Adnan Hammud[1], Martin Wolf[1], Takashi Kumagai[1,3], and Melanie Müller[1] — [1]Fritz-Haber Institute of the Max-Planck Society, Berlin, Germany — [2]Hunan University, Changsha, China — [3]Institute for Molecular Science, Okazaki, Japan

Understanding the mechanism by which optical radiation is converted into direct electrical (DC) current through plasmonic nanogaps is important for the future design of optical rectennas. One question concerns the transition from quantum (photon-driven) to classical (field-driven) optical rectification in continuous-wave (cw) driven tunnel junctions. The transition from field- to photon-driven rectification can be characterized by (i) the relation of the tunneling time to the light period (adiabaticity criterion), and (ii) by the relation of the photon energy to the induced optical voltage (quantum detection criterion). The transition between these regimes depends on the size of the tunneling gap, its current-voltage nonlinearity, and the frequency and intensity of the light field. Here, we investigate photocurrents through a cw-driven plasmonic junction of a scanning tunneling microscope at optical frequencies. We aim to identify the transition from field- to photon-driven tunneling by studying the dependence of photocurrent-voltage curves on the STM gap size and the frequency and intensity of the driving cw-laser field.

O 72.9 Wed 18:00 Poster D

Excitation of single 4f metal-organic molecules with light — •Adrian Ebert[1], Lukas Gerhard[1], Lia Mayer[1], Shuran Liu[1], Marjan Krstic[2], Barbora Brachnakova[3], Senthil Kumar Kuppusamy[3], Julia Feye[4], Peter W. Roesky[4], and Wulf Wulfhekel[1] — [1]Institute for Quantum Materials and Technology, KIT — [2]Institute for Theoretical Solid State Physics, KIT — [3]Institute of Nanotechnology, KIT — [4]Institute for Organic Chemistry, KIT

We study light emitting 4f metal-organic complexes in a low temperature, ultra-high vacuum scanning tunneling microscope (STM). While the system has been successfully used to couple light out emitted from single molecules, it's also suitable to couple light in using the same optical path. The addition of a pulsed light source for coupling light into the STM junction will greatly extend the possibilities to study the exciton dynamics.

4f metal-organic complexes have an immense advantage in comparison to purely organic chromophores or chromophores based on d-electrons, because the 4f states are highly localized hampering non-radiative recombination leading to long lifetimes of the excited states. They combine the extremely sharp emission lines including spin-orbit coupling and hyperfine coupling with functionalization by the ligands to enhance the coupling to the photon field. In future opto-electronic quantum devices the complexes can act as single photon emitters and their up- and down-conversion can be used to couple photons of different wavelength.

O 72.10 Wed 18:00 Poster D

Plasmonic probe preparation for tip-enhanced Raman spectroscopy and photoluminescence on single molecules — •Petr Kahan, Amandeep Sagwal, Rodrigo Ferreira, and Martin Švec — Institute of Physics, Czech Academy of Sciences; Cukrovarnická 10/112, CZ16200 Praha 6, Czech Republic

Various approaches to preparation of plasmonic tips for tip-enhanced Raman scattering (TERS) and photoluminescence (PL) are known [1,2] and were applied to spectroscopy on single molecules. Such preparation procedures are rather complex and time-consuming, hence not adequate for routine applications where more tips need to be prepared and tested efficiently at low input costs. Here we explore a new methodology of the TERS/PL tips fabrication, based on etching [3] silver and gold wires, and subsequent ion sputtering [4], aiming to obtain high purity surface of the resulting tips, which is required for good plasmonic activity and avoiding any spurious Raman scattering from the tip contamination. We optimize the procedure based on screening of the tip quality using the scanning electron microscopy, being able to improve reproducibility and prospects of a successful application of such tips in demanding experiments measuring single-molecule luminescence and Raman spectroscopy with scanning probe techniques.

[1] Li, M. et al. Journal of Raman Spectroscopy 47, 808-812 (2016). [2] Yang, B. et al. JPCC 122, 16950-16955 (2018). [3] Walker, P. & Tarn, W. H. CRC handbook of metal etchants. (CRC press, 1990). [4] Hoffrogge, P., Kopf, H. & Reichelt, R. J Appl Phys 90, 5322-5327 (2001).

O 72.11 Wed 18:00 Poster D

Theory of photo and electroluminescence in a scanning tunneling microscope — •Tomáš Neuman[1], Sofia Canola[1], Anna Roslawska[2], Katharina Kaiser[3], Alex Boeglin[3], and Guillaume Schull[3] — [1]Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, 16200 Prague, Czech Republic — [2]Max-Planck Institute for Solid-State Research, DE-70569 Stuttgart, Germany. — [3]Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France

I will present a theoretical perspective on a microscopy technique that combines the atomic-scale resolution of a scanning-tunneling microscope (STM) with optics. I will explain how this method, taking advantage of phenomena such as the optical Stark shift or plasmonic Purcell effect, can reveal excited-state properties of nanoscale samples with unprecedented spatial resolution. Besides introducing the method and the mechanism of STM-induced luminescence (STML) applied to dye molecules, I will show theoretical considerations concerning some of its applications and extensions including the study of vibronic features in the STML spectra and imaging, phototautomerization of a single molecule, and a theoretical view on correlated photon emission from electrically driven organic molecules in an STM.

O 72.12 Wed 18:00 Poster D

Theoretical Study of Electronic and Optical Properties in Modified Graphene Nanoribbons — •Jian Cheng Wong[1], Jiang Song[2], Sofia Canola[1], Alex Boeglin[2], Guillaume Schull[2], and Tomáš Neuman[1] — [1]Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, 16200 Prague, Czech Republic — [2]Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France

The electronic and optical properties of graphene nanoribbons (GNRs) depend on geometric configurations such as width and edge structure. The spin properties of these GNRs have been widely studied both theoretically and by scanning tunneling microscopy experiments. However, studies exploring their optical properties remain scarce. Scanning tunneling microscopy-induced luminescence (STML) provides sub-nanometer-scale spatial resolution to study these properties using light emitted from the sample. Pioneering STML studies [1] on modified GNRs unravel localized excitations that exhibit interesting optical properties. Despite this recent experimental progress, comprehensive theoretical description of these optical excitations in structures of varying size and geometry remains to be theoretically explored. Using first-principles electronic structure methods, we elucidate the electronic and optical properties of these localized excitations.

[1] Song et al., Science, 379(6636), 1049-1054 (2023).

O 72.13 Wed 18:00 Poster D

Probing Deformations of Heptahelicene Molecules via

TERS — •Amandeep Sagwal[1,2], Rodrigo Cezar De Campos Ferreira[1], Jiří Doležal[1,3], and Martin Švec[1,4] — [1]Institute of Physics, Czech Academy of Sciences; Czech Republic — [2]Faculty of Mathematics and Physics, Charles University; Czech Republic — [3]Institute of Physics, École Polytechnique Fédérale de Lausanne; Switzerland — [4]Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences; Czech Republic

The Raman scattering from single molecules can be substantially enhanced by placing them within the nanocavity between a sharp plasmonic tip and sample using the Tip-Enhanced Raman Spectroscopy (TERS) technique [1][2]. TERS in ultrahigh vacuum and cryogenic conditions can also reveal the relations between adsorption geometry, electronic states, and vibrational modes of single molecules [3]. Here we study the behaviour of heptahelicene (BA7H) molecules on Ag (111) showing two different conformers i.e. so-called bright and dark [4]. TERS measurements are conducted using a laser with wavelength 633 nm, along with the lifting of molecules from the substrate. We observe significant energy shifts in the Raman peaks corresponding to the geometrical changes of the molecules and attempt to assign them to the normal vibrational modes of the molecules calculated by TD-DFT. [1] Lee, J., Crampton, K.T., Tallarida, N. et al. Nature 568, 7882 (2019). [2] Jaculbia, R. B. et al. Nat. Nanotechnol. 15, 105110 (2020). [3] R. C. de Campos Ferreira, et al. arXiv:2310.12546, (2023) [4] O. Stetsovych, J. Am. Chem. Soc., 140, 3, 940946 (2018)