O 91: Scanning Probe Microscopy: Light Matter Interaction at Atomic Scales III

Time: Thursday 15:00–17:45 Location: MA 041

Topical Talk O 91.1 Thu 15:00 MA 041

SPM on the path to direct nano-optical measurements — •Martin Svec — Institute of Physics, CAS, CZ — Institute of Organic Chemistry and Biochemistry, CAS, CZ

Exploration of essential photophysics at the level of individual molecules and atoms requires highly specialized optical spectroscopies that work at the very limit of instrument sensitivity or have to use plasmonic nanostructures - in order to overcome the fundamental resolution limits achievable with visible and infrared light. Recent developments emerging in the field of Scanning Probe Microscopy (SPM) bring the unique opportunity to pursue intriguing, often hard-to-access interactions between light and matter with plasmonic tips at submolecular scale. The modes of operation can be switched between the electroluminescence, photoluminescence and tip-enhanced Raman spectroscopies, and applied to probe the eigenmodes, charges, vibronics and temporal evolution of the transient states (TCSPC) in molecular emitters at nanoscopic scales.

References

[1] ACS Nano 16, 1082 (2022)

[2] Nature Comm. 13, 6008 (2022)

[3] arXiv:2310.12546 (2023)

[4] arXiv:2309.04416 (2023)

O 91.2 Thu 15:30 MA 041

Triplet emitter electroluminescence from Pd-octaethylporphyrin (PdOEP) in a scanning tunneling microscope (STM) — Li-Qing Zheng[1], Fábio Costa[1,2], Abhishek Grewal[1], Anna Rosławska[1], •Klaus Kuhnke[1], and Klaus Kern[1,3] — [1]Max-Planck Institut für Festkörperforschung, 70569 Stuttgart, Germany — [2]Gleb Wataghin Institute of Physics, UNICAMP, Campinas 13083-859, Brazil — [3]Institut de Physique, École Polytechnique Fédéral de Lausanne, 1015 Lausanne, Switzerland

Triplet emitters produce significant emission (phosphorescence) even below their lowest singlet transition (fluorescence) due to spin-orbit coupling by a heavy metal center. While this property makes them interesting for OLEDs, the study of their luminescence at the single molecule level in high resolution STM is challenging.

We investigate isolated PdOEP molecules decoupled from Ag(100) and Ag(111) by an ultrathin NaCl layer. Singlet and triplet emission lines are observed in the STM at visible wavelengths, only about $100nm$ apart from each other. The singlet S_1 state of PdOEP emits photons even when the energy of one tunneling electron is lower than the emitted S_1 photon energy. The mechanism requires a relay (or shelving) state in which energy is stored in the molecule for the interval between two tunneling electrons. Emission is then expected to follow a quadratic current dependence. The S_1 emission, in contrast, exhibits a linear dependence, suggesting a relay state with nanoseconds life time. We discuss possible scenarios for the S_1 overbias emission.

O 91.3 Thu 15:45 MA 041

Tip-enhanced Raman spectroscopy of physisorbed molecular hydrogen — Akitoshi Shiotari[1], Shuyi Liu[2], Heiko Appel[3], Adnan Hammud[1], Toshiki Sugimoto[4], •Jun Yoshinobu[5], Martin Wolf[1], Mariana Rossi[3], and Takashi Kumagai[4] — [1]Fritz-Haber Institute of the Max-Planck Society, Berlin, Germany — [2]Huazhong University of Science and Technology, Wuhan, Republic of China — [3]Max-Planck-Institute for Structure and Dynamics of Matter, Hamburg, Germany — [4]Institute for Molecular Science, Okazaki, Japan — [5]Institute for Solid State Physics, University of Tokyo, Kashiwa, Japan

Hydrogen molecules on metals is an important model system for understanding physisorption. However, characterizing such weakly adsorbed molecules has been technically challenging. We demonstrate that tip-enhanced Raman spectroscopy (TERS), when combined with scanning tunneling microscopy (STM) at cryogenic temperatures, is capable of detecting physisorbed adsorbates. The rotational and vibrational modes of hydrogen molecules on a Ag(111) surface are characterized using TERS, revealing the nature of the nearly-free rotor. Additionally, we find that the electromagnetic mechanism predominantly contributes to the enhancement of Raman scattering, thus enabling sensitive detection and providing local information on the physisorption system.

O 91.4 Thu 16:00 MA 041

Tip-enhanced Raman spectroscopy in plasmonic nanocavities: enhancement factors and applications — •Borja Cirera[1], Martin Wolf[2], and Takashi Kumagai[3] — [1]Material Science Institute of Madrid, Madrid, Spain — [2]Fritz Haber Insitute, Berlin, Germany — [3]Institute for Molecular Science, Okazaki, Japan

Tip Enhanced Raman Spectroscopy (TERS) in plasmonic nanocavities has reached subnanometer resolution, visualizing chemical heterogeneities and vibrations of adsorbates in the real space. The capabilities of TERS at the atomic scale are a great complement to the existing scanning probe microscopy (SPM) techniques to properly investigate the local physico-chemical properties of the adsorbates. The required Raman sensitivity generally relies on atomically-confined electromagnetic fields in (sub-)nanoscale gaps. Here, the latest results of a single C60 between a silver tip and various metallic and semiconductor substrates are presented. These model systems allow us to discuss the diverse factors contributing to the observed intensity in single molecule junctions, finding a drastic increase in the signal upon molecular point contact (MPC) formation. The resulting exceptionally chemical sensitivity is operative even for weak and non-plasmonic substrates such as Pt(111) and Si(111). These results open the possibility to probe adsorbates on catalytically relevant substrates and a wide range semiconductors, increasing the versatility of TERS beyond coinage metals. The simultaneous access to Stokes and anti-Stokes bands can also be used to investigate heating-cooling processes in non-equilibrium quantum transport systems, of great relevance in molecular electronics.

O 91.5 Thu 16:15 MA 041

Activating the fluorescence of a Ni(II) complex by energy transfer — Tzu-Chao Hung[1,2], Yokari Godinez-Loyola[3], Manuel Steinbrecher[1], Brian Kiraly[1], Alexander A. Khajetoorians[1], Nikos L. Doltsinis[3], Cristian A. Strassert[3], and •Daniel Wegner[1] — [1]Radboud University, Nijmegen, The Netherlands — [2]University of Regensburg — [3]University of Münster

Luminescence of open-shell 3d metal complexes is often quenched due to ultrafast intersystem crossing (ISC) and cooling into a dark metal-centered excited state. We demonstrate successful activation of fluorescence from individual nickel phthalocyanine (NiPc) molecules in the junction of a scanning tunneling microscope (STM) by resonant energy transfer from other metal phthalocyanines at low temperature. By combining STM, STS, STM-induced luminescence and time-dependent density functional theory, we provide evidence that there is an activation barrier for the ISC, which in most experimental conditions is overcome. We demonstrate that, when placing a donor MPc (M = Zn, Pd, Pt) molecule close to NiPc by means of STM atomic manipulation, resonant energy transfer can excite the acceptor NiPc without overcoming the ISC activation barrier, leading to Q-band fluorescence. This work demonstrates that the thermally activated population of dark metal-centered states can be avoided by a designed local environment at low temperatures paired with a directed molecular excitation into vibrationally cold electronic states.

O 91.6 Thu 16:30 MA 041

Gating single-molecule photoluminescence with electrons — •Anna Rosławska[1,2], Katharina Kaiser[1,3], Michelangelo Romeo[1], Fabrice Scheurer[1], and Guillaume Schull[1] — [1]Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France — [2]Max-Planck-Institut für Festkörperforschung, D-70569, Stuttgart, Germany — [3]IV. Physikalisches Institut, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen

The ability to switch an optically-active molecule from a bright to a dark state by modifying its redox state is one of the most striking modifications of optical properties of a chromophore. Here, we show that this mechanism can be applied to a single molecule located in the double barrier tunneling junction of a scanning tunneling microscope (STM). We achieve nearly full tip-enhanced photoluminescence (TEPL) quenching by controlling the population of a transiently charged state by adjusting the tip-molecule distance, the applied bias voltage, and the in-plane position of the tip with respect to the molecule. This versatile gating of the fluorescence yield of a single molecule with sub-nm precision is explained using a straightforward many-body description of our system.

O 91.7 Thu 16:45 MA 041

Electrically driven cascaded photon-emission in a single molecule — •Katharina Kaiser[1,2], Anna Rosławska[1,3], Michelangelo Romeo[1], Fabrice Scheurer[1], Tomáš Neuman[4], and Guillaume Schull[1] — [1]CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, France — [2]IV. Physikalisches Institut, Georg-August-Universität Göttingen, Germany — [3]MPI für Festkörperforschung, Stuttgart, Germany — [4]Institute of Physics of the Czech Academy of Sciences, Prague, Czechia

In STM-induced luminescence (STML) of single molecules, the intricate interplay between charging dynamics and excited state formation and decay can be accessed by studying correlations between consecutively emitted photons. This not only provides access to the time constants of the processes involved, but also sheds light on the quantum mechanical nature of a single molecule emitter. Until now, such studies were mainly focused on one transition only. For molecules adsorbed on thin insulating films, however, there are many accessible states, depending on the STM setpoint. Taking advantage of this, we investigate the interplay between the exciton and trion formation and decay in individual ZnPc molecules. We show that, upon trion formation, we can drive the correlated emission of photons from two different excited states within one molecule. In addition, by tuning the rate at which the molecule is charged we can control the population dynamics of the states involved. This allows us to disentangle which states play a role in the formation of excited states in a molecule in STML, and provides a direct means to manipulate excited state dynamics.

O 91.8 Thu 17:00 MA 041

Statistical properties of light emission in current-driven single-molecule STM-junctions — •Andrés Bejarano[1,2], Rémi Avriller[2], Thomas Frederiksen[1,3], and Fabio Pistolesi[2] — [1]Donostia International Physics Center (DIPC), E-20018 Donostia-San sebastián, Spain — [2]Univ. Bordeaux, CNRS, LOMA, F-33405 Talence, France — [3]Ikerbasque, Basque Foundation for Science, E-48013 Bilbao, Spain

The atomic resolution of the scanning tunneling microscope (STM) enables fluorescence on the scale of single molecules. Recent experiments demonstrate the change from a broad plasmonic resonance to a sharp peak in the photon emission spectrum, by moving the tip laterally from the bare substrate towards the molecule [1]. These systems are of particular interest to the quantum cryptography community because they have been reported to emit non-classical light (antibunching) [2, 3]. We propose a microscopic model based on quantum master equation approach for the reduced density matrix of the central system. In particular, we focus on the description of the emission spectrum, conductivity and photon coherence. Additionally, by using full counting statistics, we calculate the Fano factor and correlations between emission and currents. The model provides a simple framework to explain the features observed experimentally in the photon spectrum and the electronic conductance. [1] B. Doppagne et al., Science 361, 251 (2018) [2] P. Merino et al., Nat. Commun. 6, 8461 (2015) [3] L. Zhang et al., Nat. Commun. 8, 580 (2017)

O 91.9 Thu 17:15 MA 041

Vibronically coupled excited states of asymmetric phthalocyanines from STM luminescence spectroscopy — •Sofia Canola[1], Kirill Vasilev[2], Fabrice Scheurer[2], Alex Boeglin[2], Fanny Lotthammer[3], Frederic Cherioux[3], Tomas Neuman[1], and Guillaume Schull[2] — [1]Institute of Physics of the Czech Academy of Sciences, Cukrovarnicka 10, 16200 Praha, Czech Republic. — [2]Universite de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France. — [3]Universite de Franche-Comte, CNRS, FEMTO-ST, F-25000 Besancon, France.

Interactions between molecular excited states, mediated by vibrations, rule the internal dynamic of the molecular electronic structure following excitation. Information on these interactions can be accessed via the vibronic features of the spectra that arise from different mechanisms of coupling between the electronic excitation and molecular vibrations (e.g. Franck-Condon or Herzberg-Teller). In this presentation, I will discuss a systematic experimental and computational study of the vibronic properties for a series of related zinc (II) phthalocyanine derivatives employing electroluminescence in a scanning tunneling microscope (STML). The optical properties of phthalocyanines have been widely studied due their biological and technological relevance, but many fundamental aspects are still to be clarified. From high-resolution vibronic spectra and the associated spatially resolved light emission maps, we can selectively probe different mechanisms of vibronic coupling and access novel microscopic details otherwise not accessible to conventional spectroscopy.

O 91.10 Thu 17:30 MA 041

Resonant TERS of a Single-Molecule Kondo System — •Rodrigo Cezar de Campos Ferreira[1], Amandeep Sagwal[1,2], Jiří Doležal[1,3], Sofia Sofia[1], Pablo Merino[4], Tomáš Neuman[1], and Martin Švec[1,5] — [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]Instituto de Ciencia de Materiales de Madrid; Spain — [5]Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences; Czech Republic

Single-molecule TERS under UHV and cryogenic conditions enables exploration of the relations between the adsorption geometry, electronic state, and vibrational fingerprints[1,2]. Here we precisely lift a PTCDA molecule from a metal surface to bring it into an open-shell spin one-half anionic state. We reveal a correlation between the Kondo resonance in the differential conductance spectroscopy and concurrent characteristic changes captured by the TERS measurements. Through the investigation of various adsorbed and tip-contacted PTCDA scenarios, we infer that the Raman scattering on the suspended PTCDA is resonant with a higher excited state. Theoretical simulation of the vibrational spectra enables a precise assignment of the individual TERS peaks to high-symmetry Ag modes, including the fingerprints of the observed spin state[3]. [1] Y. Zhang et. al. National Science Review, 6, 1169-1175 (2019).[2] R. Jaculbia et. al. Nat. Nanotechnol. 15, 105-110 (2020).[3] R.C.C. Ferreira et. al. arXiv:2310.12546 (2023).