## O 106: Scanning Probe Microscopy: Light Matter Interaction at Atomic Scales IV

Time: Friday 10:30–12:45 Location: MA 041

O 106.1 Fri 10:30 MA 041

**Probing Local Structural and Chemical Properties of Borophene via Tip-Enhanced Raman Spectroscopy** — Linfei Li and •Nan Jiang — University of Illinois Chicago, Chicago, IL, 60607

Two-dimensional boron (i.e., borophene) has recently been synthesized and computationally predicted to have promising physical properties for a variety of electronic and energy technologies. However, the fundamental chemical properties of borophene that form the foundation of practical applications remain unexplored. Here, we present atomic-level chemical characterization of borophene materials using ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS). Atomic-level chemical characterization of SL and BL borophene was achieved by TERS with an angstrom-scale vibrational fingerprint observation. Following that, we measure the interfacial interactions of a vertical Van der Waals heterostructure of borophene with tetraphenyldibenzoperiflanthene (DBP) molecules. TERS reveals subtle ripples and compressive strains of the borophene lattice underneath the molecular layer. The induced interfacial strain is demonstrated to extend in borophene by ~1 nm beyond the molecular region. Furthermore, we use our method to probe the local chemical properties of oxidized borophene. The results show that single oxygen adatoms on borophene can be identified and mapped with ~4.8 Å spatial resolution and single bond (B-O) sensitivity.

O 106.2 Fri 10:45 MA 041

**Tip-enhanced Raman spectroscopy study on anatase TiO$_2$ surfaces** — •Kyungmin Kim[1,2], Daiki Katsube[3], Takashi Kumagai[4], Martin Wolf[2], Masayuki Abe[1], and Akitoshi Shiotari[2] — [1]Osaka University, Toyonaka, Japan — [2]Fritz Haber Institute, Berlin, Germany — [3]RIKEN, Wako, Japan — [4]Institute for Molecular Science, Okazaki, Japan

Anatase, a crystalline phase of titanium dioxide (TiO$_2$), is traditionally considered to exhibit higher catalytic activity compared to rutile. Within the various surface orientations of anatase, the (001) surface and its (1x4) reconstructed counterpart have been identified as particularly reactive. The characterization of adsorbates and defects on these surfaces is crucial for comprehending the catalytic properties of the anatase surface. However, achieving this has been technically challenging. In this study, a single-crystal anatase TiO$_2$ thin film was fabricated on a SrTiO$_3$(100) substrate using the pulse laser deposition (PLD) technique. Following deposition, reflection high-energy electron diffraction (RHEED) measurements were conducted to verify the (1x4) surface reconstruction. The Anatase TiO$_2$ film exhibited a thickness of approximately 100 nm. Furthermore, we showcase the utility of tip-enhanced Raman spectroscopy (TERS) in conjunction with scanning tunneling microscopy (STM) under cryogenic conditions for vibrational spectroscopy and nanoscale resolution imaging in characterizing adsorbates and defects on the anatase TiO$_2$ surface.

O 106.3 Fri 11:00 MA 041

**Atomic scale chemical contrast in a plasmon-driven reaction: An STM-TERS study on PTCDA families on Si(111)** — •Youngwook Park[1], Ikutaro Hamada[2], Adnan Hammud[1], Egbert Willem Meijer[3], Takashi Kumagai[4], Martin Wolf[1], and Akitoshi Shiotari[1] — [1]Fritz Haber Institute of the Max Planck Society, Berlin, Germany — [2]Osaka University, Suita, Japan — [3]Eindhoven University of Technology, Eindhoven, the Netherlands — [4]Institute for Molecular Science, Okazaki, Japan

A localized surface plasmon is a promising tool to drive chemical reactions by enhancing light-molecule interactions. However, controlling reactions at an atomic level remains as a challenge. Here we demonstrate a sharp contrast in reactivity by minimal chemical modification of a single-molecule photoswitch. The switch comprises a plasmonic nanojunction of an Ag tip and a perylene-di-anhydride (PTCDA) molecule on a Si(111)-7x7 reconstructed surface. With a laser focused at the junction, the molecule toggles between the surface and the tip, accompanying bond breaking and forming of the molecule with the surface, as characterized by scanning tunneling microscopy (STM) and tip-enhanced Raman spectroscopy (TERS). Perylene-di-imide (PDI), an imide-analogue of PTCDA, remains silent on the surface, whereas a methyl substitution at the imide, Me2-PDI, recovers the reactivity. Such dramatic shift in reactivity is intriguing in that the modified part of the molecule (O, NH, and N-Me) even does not directly participate in the chemical bonds with the surface. The results suggest the possibility of a rigorous submolecular-level control of plasmon chemistry.

**Topical Talk** O 106.4 Fri 11:15 MA 041

**Characterization of just one atom using synchrotron x-rays** — •Volker Rose — Argonne National Laboratory, Lemont, IL, USA

The real-space observation of chemistry using scanning tunneling microscopy (STM) or synchrotron-based x-ray microscopy (XM) continues to have a tremendous impact on our understanding of nanoscale materials. However, although STM provides high spatial resolution, it lacks direct chemical contrast. On the other hand, XM can provide chemical sensitivity, but the spatial resolution is inferior. In order to overcome these limitations, we have developed a technique that combines the chemical contrast of synchrotron x-rays with the locality of STM.

In this presentation, we show that x-rays can be used to characterize the elemental and chemical state of just one atom [1]. Using a specialized tip as a detector, x-ray excited currents generated from an iron and a terbium atom coordinated to organic ligands are detected. The x-ray signal can be sensed only when the tip detector is located directly above the atom in extreme proximity, which confirms atomically localized detection in the tunnelling regime. Our work connects synchrotron x-rays with a quantum tunnelling process and opens a path to future x-ray experiments for the characterization of chemical properties of materials at the ultimate single atom limit.

This work was performed at the Advanced Photon Source and the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility under Contract No. DE-AC02-06CH11357. [1] Nature 618, 69-73 (2023).

O 106.5 Fri 11:45 MA 041

**Excited-state spectroscopy of individual molecules with atomic force microscopy** — •Lisanne Sellies, Jakob Eckrich, and Jascha Repp — University of Regensburg, Regensburg, Germany

The combination of scanning probe microscopy with an increasing number of spectroscopic techniques, such as Raman and luminescence, provides unprecedented microscopic understanding. Despite its very direct access to well-defined single-molecule model systems, the unambiguous assignment of observations to specific quantum transitions is not always straightforward [1,2], and typically only a small fraction of all transitions can be studied.

Here, we propose a novel type of single-molecule spectroscopy that enables access to many quantum transitions of different types, including radiative, non-radiative and charge-related transitions. The molecules of interest are deposited on thick insulating films, preventing tunneling of charges to and from the underlying support. By controlled charge exchange between the conductive tip of an atomic force microscope and the molecule, we bring a molecule into different electronic configurations. The detection proceeds via the force acting on the tip. Thereby, quantum transitions can be mapped out in energy, enabling access to the energies of the lower-lying electronic states of individual molecules, including out-of-equilibrium states. We demonstrate our technique by applying it on pentacene and PTCDA, shedding light on the recent STM luminescence experiments on PTCDA [1,2].

References: [1] K. Kimura et al., Nature 570, 210-213 (2019) [2] J. Dolezal et al., ACS Nano 16, 1082-1088 (2022)

O 106.6 Fri 12:00 MA 041

**Atomic-scale investigation of hot electron dynamics in a single molecule** — •Shaoxiang Sheng[1], Yang Luo[1], Alberto M. Jimenez[1], Andrea Schirato[2], Guiseppe Dalla Valle[2], Guilio Cerullo[2], Klaus Kern[1,3], and Manish Garg[1] — [1]Max Planck Institute for Solid State Research, Stuttgart, Germany — [2]Dipartimento di Fisica - Politecnico di Milano, Milan, Italy — [3]Institut de Physique, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

The generation and detection of hot electrons have attracted broad attention due to their substantial potential for applications across a wide range of fields1. Extensive studies have been carried out to understand hot electron dynamics in various nanostructures2. Here, we investigate hot electron dynamics by utilizing pump-probe spectroscopy and measuring anti-Stokes emission in the tunnel junction of a scanning tunneling microscope. Our results reveal that the generation of hot electrons is highly localized and their decay in time is energy dependent. We also observe nonlinear four-wave mixing (FWM) signal when the pump and probe pulses overlap in time. Both the hot electron and FWM signals exhibit high sensitivity to the atomic-scale structures and show a large enhancement along the edges of a graphene nanoribbon owing to higher density of the electronic states. This study opens new perspectives in exploiting hot electron induced catalytic reactions in a single molecule and nonlinear optical response in materials at the atomic scales. References: 1. C. Clavero, Nat. Photonics, 8, 95-103 (2015). 2. A. Schirato, et al., Nanophotonics 12, 1-28 (2023).

O 106.7 Fri 12:15 MA 041

**Fluorescent single-molecule STM probe** — •Niklas Friedrich[1], Anna Roslawska[2], Xabier Arrieta[3], Michelangelo Romeo[2], Eric Le Moal[4], Fabrice Scheurer[2], Javier Aizpurua[3], Andrei G. Borisov[4], Tomas Neuman[4,5], and Guillaume Schull[2] — [1]CIC nanoGune BRTA, Donostia, Spain — [2]Université de Strasbourg, CNRS, IPCMS, Strasbourg, France — [3]Center for Materials Physics (CSIC-UPV/EHU), DIPC, Donostia, Spain — [4]Université Paris-Saclay, CNRS, Orsay, France — [5]Czech Academy of Sciences, Prague, Czech Republic

We present the functionalization of a plasmonic scanning probe tip with a single fluorescent molecule. The functionalization is performed by mechanically attaching an individual PTCDA molecule to the tip's apex atoms in an upright standing configuration. The electroluminescent character of the singly negatively charged PTCDA$^-$ is preserved, despite the molecule's direct contact with a metal electrode. We characterize the change in luminescence caused by different plasmonic tips, changing cavity geometries and varying bias voltage. Furthermore, we discuss theoretical considerations unraveling the photon emission mechanism.

The presented system showcases the possibility to use single molecules as nanoscale sensors able to retrieve optical properties of samples at the atomic scale.

http://arxiv.org/abs/2311.16805

O 106.8 Fri 12:30 MA 041

**Hot luminescence from single-molecule chromophores electrically and mechanically self-decoupled by tripodal scaffolds** — •Vibhuti Rai[1,2], Nico Balzer[3], Gabriel Derenbach[1], Christof Holzer[4], Marcel Mayor[3], Wulf Wulfhekel[1], Lukas Gerhard[1], and Michal Valášek[3] — [1]Institute for Quantum Materials and Technologies, Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany — [2]Freie Universität Berlin, Department of Physics, Arnimallee 14,14195 Berlin, Germany — [3]Institute of Nanotechnology, Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany — [4]Institute of Theoretical Solid State Physics, Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany

Control over the electrical contact to an individual molecule is one of the biggest challenges in molecular optoelectronics. Chemical route of anchoring individual chromophores via extended tripodal scaffolds is a promising approach for efficient electrical decoupling from metallic leads [1]. Here, we show that NDI chromophores coupled to a gold substrate via a tripodal scaffold and via a vacuum barrier to the tip of a scanning tunnelling microscope enable spectrally and spatially resolved electroluminescence. We show that specific vibrons of the chromophore which are mechanically decoupled from the substrate give rise to hot-luminescence (HL) bands. Vibrons which are coupled to the substrate do not show HL.

[1] Rai, V. et al. Phys. Rev. Lett. 130, 036201 (2023).