O 5: Scanning Probe Microscopy: Light-Matter Interactions at the Atomic Scale I

Time: Monday 10:30–13:00 Location: H6

O 5.1 Mon 10:30 H6

Simulated tip-enhanced Raman scattering fingerprints of doped triangulenes — •Orlando Silveira[1,2], Markus Junttila[1], Shawulienu Kezilebieke[2,3], and Adam Foster[1,4] — [1]Department of Applied Physics, Aalto University, Espoo, Finland — [2]Department of Physics, Nanoscience Center, University of Jyvaskyla, Jyvaskyla, Finland — [3]Department of Chemistry, University of Jyvaskyla, Jyvaskyla, Finland — [4]WPI Nano Life Science Institute (WPI-NanoLSI), Kanazawa University, Kakuma-machi, Kanazawa, Japan

Triangulenes are organic molecules promising for future applications in spintronics technologies, and fine tunning their electronic and magnetic properties will only extend the potential applications. A reliable possibility for such control is doping the triangulenes with different atoms such as nitrogen and boron. Usually, the reaction yield of triangulenes is quite small, and it is prohibitive to use techniques with high cross section such as Raman to chemically characterize the triangulenes. In the other hand, scanning probe microscopy (SPM) techniques have been successfully used for their structural characterization. In this work, we propose that the tip-enhanced Raman scattering (TERS) can be used for simultaneous chemical and structural characterization of the triangulenes. Our work offers a new perspective to study the triangulenes, as their vibrational properties have not yet been fully investigated, and the same simulation protocol used here can be applied to any other type of molecule.

O 5.2 Mon 10:45 H6

Plasmon-induced reaction in hydrogen-bonded molecular networks studied by laser-coupled STM — •Youngwook Park, Adnan Hammud, Martin Wolf, and Akitoshi Shiotari — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Hydrogen-bonded molecular networks are widely found in natural systems and play an important role in the development of functional molecular assemblies. Understanding chemical reactions within these networks requires molecular-level spatial resolution, which is challenging for photochemical studies. In this talk, we present a plasmon-induced reaction in 2D hydrogen-bonded assemblies, studied with a laser-coupled scanning tunneling microscope (STM). We investigated triphenylene-2,6,10-tricarboxylic acid forming a honeycomb network on Au(111) through hydrogen bonds. Our findings showed that photo-induced deformation of the network was localized to a few molecules beneath the Ag tip under visible laser illumination. In contrast, a PtIr tip, which lacks plasmonic activity in the visible range, failed to trigger the reaction. By varying the laser wavelength, we identified that non-thermal (hot) electrons generated by plasmons mediate the reaction. This was confirmed by initiating the reaction with non-thermal electrons from the STM tip without laser irradiation. Our results highlight the potential of plasmonic STM tips for precise control over molecular network structure and reactivity.

O 5.3 Mon 11:00 H6

Motion of molecular motors on ultra-thin NaCl islands on Cu(111) — •Monika Schied[1,2], Grant J. Simpson[1], Ken Kolar[1], Dongdong Liu[3], James M. Tour[3], and Leonhard Grill[1] — [1]University of Graz, Austria — [2]CNR-IOM, Italy — [3]Rice University, USA

Molecular motors are designed to overcome nature's random motion by converting external energy into controlled, uni-directional rotation. Studying them on a solid surface can be advantageous, as it offers confinement in two dimensions, making it easier to observe the directionality of their motion. In previous studies on metallic surfaces, indeed uni-directional rotation has been observed [1]. However, the activation of the motor functionality is likely suppressed due to the hybridisation of the molecular orbitals with the electron bath of the metal. In order to preserve the inherent electronic structure of the free molecule, we studied Feringa-type motors adsorbed on ultra-thin NaCl layers on Cu(111), which electronically decouples them from the metal substrate, while still permitting measurements with the low-temperature scanning tunnelling microscope (LT-STM). We excited the molecules with UV light, which – in contrast to voltage pulses – acts remotely without altering the local potential energy landscape with the STM tip. In this way, we could induce the motion of individual molecules.

[1] M. Schied et.al., ACS Nano 2023, 17, 4, 3958-3965

O 5.4 Mon 11:15 H6

Triggering chemical reactions in single molecules with ultrashort THz pulses — •Niklas Friedrich, Carmen Roelcke, Tzu-Chao Hung, Yaroslav Gerasimenko, Rupert Huber, and Jascha Repp — Institute of Experimental and Applied Physics, University of Regensburg, Regensburg, Germany

In lightwave-driven scanning tunnelling microscopy (LW-STM), the electric-field transient of ultrashort laser pulses focused into the junction of a tunnelling microscope acts as a bias-voltage transient and thereby controls tunnelling on ultrashort timescales. This allows unravelling the dynamics of quantum systems in pump-probe experiments with atomic spatial and femtosecond temporal resolution [1].

Here, we show that LW-STM can be used to trigger chemical reactions on ultrashort timescales. We study free-base naphthalocyanine molecules (H2Nc) on 2ML NaCl on Cu(111). In DC-biased experiments, this system switches between different tautomers upon injection of high-energy tunnelling electrons [2]. We find that the same reaction is facilitated by ultrashort voltage transients in LW-STM for transients far exceeding the voltage of the lowest unoccupied molecular orbital. Furthermore, even a stepwise deprotonation of the molecule is activated by the ultrashort laser pulses when increasing the voltage transient beyond a threshold value.

[1] Roelcke et al. Nat. Photon. 18, 595-602 (2024) [2] Liljeroth et al. Science 317, 1203-1206 (2007)

O 5.5 Mon 11:30 H6

Spatial coherent phonon spectroscopy on 2H-$MoTe_2$ using THz-STM — •Vibhuti Rai, Junyoung Sim, Florian Faaber, 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

Scanning tunneling microscopy (STM) offers subnanometer spatial resolution. However, it lacks the temporal resolution required to investigate the dynamics of various elementary excitations such as phonons. By integrating STM with a pump-probe scheme that utilizes two terahertz (THz) pulses acting as transient bias voltages, subpicosecond time resolution can be achieved [1,2]. Here, we demonstrate that our custom-built THz setup, combined with an STM operating at 5K in an ultra-high vacuum, can be used to excite and detect lattice vibrations on the surface of 2H-$MoTe_2$. The time-resolved spectrum shows a long-lasting oscillatory signal that is sensitive to surface defects [3,4]. Fourier analysis reveals the presence of two prominent excitation modes. We correlate the excited modes with coherent phonons. The spatial variation of such coherent phonon spectroscopy further reveals that one of the two excited modes are enhanced by the surface defects.

[1] Cocker, et al. Nat. Photon. 7, 620-625 (2013)
[2] Yoshida et al. ACS Photonics 6, 6, 1356-1364 (2019)
[3] Liu et al. Sci. Adv. 8, eabq5682 (2022)
[4] Roelcke et al. Nat. Photon. 18, 595-602 (2024)

O 5.6 Mon 11:45 H6

Charge Transfer in Lightwave-Driven Scanning Tunneling Microscopy — •Nils Krane, Jonas Allerbeck, Laric Bobzien, S. Eve Ammerman, and Bruno Schuler — Empa - nanotech@surfaces Laboratory, 8600 Dübendorf, Switzerland

Lightwave-driven STM is a promising technique for exploring ultrafast charge-state dynamics at nanoscale. The tip electrode of the STM provides spatial resolution at the single-atom level, while single-cycle lightwave pulses supply an ultrafast voltage source at GHz to multi-THz frequencies that injects charge carriers to the system. In contrast to optical far-field measurements, the STM tip interacts with the investigated system also between the pulses where the applied voltage is low. This allows for ultrafast back tunneling of electrons from an excited charge state via discharging to the tip electrode, resulting in zero net current. Equal magnitude of forward and backward tunneling hence quenches the time-integrated charge rectification and imposes a major

challenge on investigating ultrafast nanoscale charge dynamics. In this talk, I discuss the consequences of back tunneling for lightwave-driven STM and time-domain pump-probe techniques, at the example of picosecond charge-state lifetimes related to selenium vacancies in WSe_2 studied with THz-STM. I outline pathways to overcome this challenge by utilizing effects such as the Franck-Condon blockade or spin multiplicity for the promotion of unidirectional charge transport. A theoretical model based on the master equation, accurately reproduces the time-dependent tunneling processes observed in the experiments.

O 5.7 Mon 12:00 H6

Ultrafast Coulomb blockade in an atomic-scale quantum dot — Jonas Allerbeck[1], •Laric Bobzien[1], Nils Krane[1], S. Eve Ammerman[1], Daniel E. Cintron Figueroa[2], Joshua Robinson[2,3], and Bruno Schuler[1] — [1]Empa - nanotech@surfaces Laboratory, 8600 Dübendorf, Switzerland — [2]Department of Chemistry, The Pennsylvania State University, University Park, 16802, PA, USA — [3]Department of Physics and Department of Materials Science and Engineering, The Pennsylvania State University, University Park, 16802, PA, USA.

Controlling electron dynamics at optical clock rates is a fundamental challenge in lightwave-driven nanoelectronics. At the example of individual selenium vacancies (Vac_{Se}) in few-layer tungsten diselenide (WSe_2), which are prototypical atomic-scale quantum dots with localized defect states, I present ultrafast charge transfer in the time domain using lightwave-driven scanning tunneling microscopy (LW-STM). Layer-dependent decoupling of Vac_{Se} in WSe_2 varies the average charge-state lifetime of defect states from 1.2 ps (1L) to 3 ns (4L), showing an unexpected sub-exponential. Picosecond terahertz (THz) source pulses, focused onto the picocavity of the STM, control and read the charge state of individual Vac_{Se} quantum dots. THz pump-THz probe time-domain sampling of the defect charge population captures atomic-scale snapshots of the transient Coulomb blockade, a signature of charge transport via quantized defect states. These results open new avenues for exploring charge dynamics and lightwave-driven electronics at the space-time limit.

O 5.8 Mon 12:15 H6

THz Pulse induced Luminescence in a Scanning Tunneling Microscope — •Kurt Lichtenberg, Johannes Schust, Felix Huber, Ines Hartkopf, Susanne Baumann, and Sebastian Loth — University of Stuttgart, Institute for Functional Matter and Quantum Technologies, Stuttgart, Germany

Light-matter interaction at the atomic scale lies at the heart of many processes in nature and technology, ranging from light harvesting to quantum communication applications. But experimental tools to access the respective dynamics at this scale with sufficient time resolution are rare.

Here we show a proof-of-concept combination of the ultrafast time resolution of THz scanning tunneling microscopy (THz STM) with tunneling-induced light emission at the atomic scale (Scanning Tunneling Luminescence).

We use intense sub-cycle THz pulses to excite plasmons in the tunnel junction consisting of a gold tip and a bare silver sample. We find that THz-induced voltage transients ignite luminescence in ultrashort time intervals within a fraction of a single period of the THz pulse that was used for the excitation. These ultrafast luminescence bursts can be used to sample the waveform of a second THz pulse with femtosecond time resolution.

This work contributes to a new line of methodology, that can probe the rich dynamics of light emission from single atoms and molecules.

O 5.9 Mon 12:30 H6

Ultrafast manipulation of charge-density wave order with THz-STM — Shaoxiang Sheng[1,2], Kurt Lichtenberg[1], Susanne Baumann[1], and •Sebastian Loth[1,3] — [1]University of Stuttgart, Institute for Functional Matter and Quantum Technologies, Stuttgart, Germany — [2]Max Planck Institute for Solid State Research, Stuttgart, Germany — [3]Center for Integrated Quantum Science and Technology (IQST), University of Stuttgart, Stuttgart, Germany

Charge-density wave (CDW) materials present unique opportunities for exploring the interplay between structural distortions and the collective dynamics of complex electronic phases at the atomic scale. We use terahertz spectroscopy in the scanning tunneling microscope (THz-STM) to investigate charge-order dynamics in the prototypical CDW materials 2H-$NbSe_2$ and 1T-TaS_2. By employing tip-enhanced terahertz electric fields, we directly excite phase dynamics of the charge order and probe their local electronic response by terahertz-induced electron tunneling. Our measurements show that the incommensurate CDW of $NbSe_2$ features slow phase dynamics in the proximity of defects [1], whereas the commensurate CDW of TaS_2 exhibits fast reconfigurations within individual domains. The presented spatially resolved dynamics of CDWs demonstrate how atomically localized THz excitation can be leveraged to manipulate electronic states with femtosecond temporal precision, offering insights into the fundamental mechanisms of electronic or structural phase transitions in different materials.

[1] S. Sheng, et al., Nat. Phys. 20, 1603 (2024).

O 5.10 Mon 12:45 H6

Tracking phonon-induced electronic dynamics on atomic scale with ultrafast tunnelling spectroscopy — Carmen Roelcke, Lukas Kastner, Maximilian Graml, Jan Wilhelm, Jascha Repp, Rupert Huber, and •Yaroslav Gerasimenko — Department of Physics and Regensburg Centre for Ultrafast Nanoscopy, University of Regensburg, 93040 Regensburg, Germany

Atomic-defect-based quantum systems in monolayers and moiré heterostructures of 2D materials have attracted huge interest for their qubit and single-photon emission functionalities, but directly observing the interplay of their electronic structure with elementary excitations remained a long-held dream.

We directly resolve in space, time and energy how spin-orbit-split bound states of an individual Se vacancy – an atomic single-photon emitter – evolve under coherent lattice vibrations in moiré-distorted WSe_2 using lightwave-driven scanning tunnelling spectroscopy [1]. We selectively launch a drum phonon mode with a THz pulse coupled to the tip and take ultrafast snapshots of electronic spectrum on atomic scales faster than a vibration period. Such ultrafast tunnelling spectra reaching ∼300 fs temporal resolution reveal transient energy shifts of the lower vacancy state by up to 40 meV, depending on the amplitude and phase of the coherent lattice vibration. We discuss how THz fields can couple via the Coulomb interactions to the drum mode, and how the interplay of Se-W bonds distortion and image charge renormalization affect the energy levels of the vacancy.

[1] C. Roelcke et al., Nat. Photon. 18, 595-602 (2024)