Nano- and Atomic-Scale Spectroscopy

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Awards
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2016 Gerhard Ertl Young Investigator Award
2020 Gaede Prize (German Physical Society)
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A detailed understanding of atomic-scale structures, properties, and dynamics is fundamentally important for the design of next-generation devices and optimization of material and energy conversion processes, including optoelectronics, solar cells, and catalysis. The rapid advancement of nanotechnology requires measurement techniques capable of directly observing phenomena with simultaneous high spatial and temporal resolution at the (sub)nanometer scale. Optical spectroscopy is a powerful and versatile tool for characterizing materials, but its spatial resolution is fundamentally limited by diffraction, restricting its ability to directly observe nanoscale systems. Near-field optics overcomes this limitation and enables optical characterization beyond the diffraction limit.

Our group has focused on developing and applying cutting-edge tip-enhanced near-field techniques in combination with laser spectroscopy, including nonlinear and ultrafast time-resolved techniques, to investigate photophysical and photochemical phenomena. Recently, we have demonstrated atomic-level sensitivity and spatial resolution using tip-enhanced Raman spectroscopy (TERS) and scanning near-field optical microscopy (SNOM) based on low-temperature scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Furthermore, by integrating ultrashort pulsed lasers, we have shown that ultrafast coherent dynamics can be probed with atomic-scale resolution.

We are currently pushing the boundaries of atomic-scale spectroscopy with three key objectives: (1) extending its capabilities from the visible to the infrared region to investigate a broader range of materials and phenomena; (2) advancing nonlinear and time-resolved spectroscopic techniques; and (3) applying these methods to diverse low-dimensional systems to explore their unique optical properties.

Selected Publications

- B. Cirera *et al.*, "Joule Heating in Single-Molecule Point Contacts Studied by Tip-Enhanced Raman Spectroscopy," *ACS Nano* **16**, 16443 (2022).
- S. Liu *et al.*, "Nanoscale Coherent Phonon Spectroscopy," *Sci. Adv.* **8**, eabq5682 (2022).
- S. Liu *et al.*, "Inelastic Light Scattering in the Vicinity of a Single-Atom Quantum Point Contact in a Plasmonic Picocavity," *ACS Nano* **17**, 10172 (2023).
- J. Nishida *et al.*, "Sub-Tip-Radius Near-Field Interactions in Nano-FTIR Vibrational Spectroscopy on Single Proteins," *Nano Lett.* **24**, 836 (2024).
- Y. Wang *et al.*, "Ultrafast Nano-Imaging of Spatially Modulated Many-Body Dynamics in CVD-Grown Monolayer WS_2," *ACS Photonics* **12**, 207 (2024).
- A. Shiotari *et al.*, "Picocavity-Enhanced Raman Spectroscopy of Physisorbed H_2 and D_2 Molecules," *Phys. Rev. Lett.* **134**, 206901 (2025).
- A. Shiotari *et al.*, "Scattering Near-Field Optical Microscopy at 1-nm Resolution Using Ultralow Tip Oscillation Amplitudes," *Sci. Adv.* **11**, eadu1415 (2025).
- J. Nishida *et al.*, "Ultrafast Infrared Nano-Imaging of Local Electron–Hole Dynamics in CVD-Grown Single-Walled Carbon Nanotubes," *Sci. Adv.* **11**, eadv9584 (2025).

1. Atomic-Scale Optical Spectroscopy

Atomic-scale light–matter interactions are a frontier of optical nanoscience, providing opportunities not only for ultra-sensitive and ultra-high-resolution spectroscopy, but also for establishing picoscale optics and photonics. Recent studies have shown that extreme confinement of near fields occurs at atomic-scale protrusions on metal nanostructures, referred to as 'picocavity,' leading to unique optical phenomena. Using TERS, we demonstrated atomic-scale vibrational spectroscopy and revealed how picoscale structural changes affect Raman scattering.[1)]

While TERS has been applied to the study of organic molecules and atomically thin films, it has not yet been used to investigate small molecules such as hydrogen, oxygen, and water. Recently, we reported on TERS of H_2 and D_2 molecules physisorbed within a plasmonic picocavity at 10 K.[2)] The intense Raman peaks resulting from the rotational and vibrational transitions are observed at picoscale gap distances of the junction formed by an Ag tip and an Ag(111) surface, where a picocavity-enhanced field plays a crucial role. A significant redshift of the H–H stretch frequency is observed as the gap distance decreases, while the D–D stretch frequency is unaffected. Density functional theory, path-integral molecular dynamics, and quantum anharmonic vibrational energy calculations suggest that this non-trivial isotope effect is explained by a different molecular density between H_2 and D_2 on the surface. The capability to measure such small molecules holds great promise as a method for probing local structures and reactions that are involved in the elementary processes of heterogeneous catalysis.

In addition, single-molecule TERS has generally been limited to measurements on plasmonic substrates such as Au, Ag, or Cu surfaces. Recently, we have demonstrated that single-molecule TERS measurements are also feasible on a bulk silicon surface.[3)] This represents an important step toward expanding the applicability of TERS-based chemical analysis to a broader range of material systems and holds promise as a method for investigating atomic-scale structures in nanodevices.

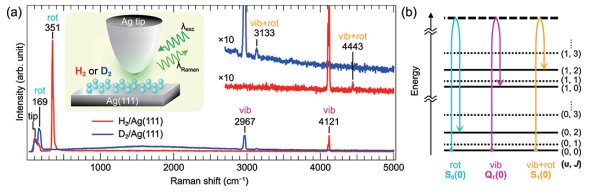

Figure 1. (a) TERS spectra of H_2 and D_2 confined within a picocavity. Raman peaks corresponding to rotational (rot), vibrational (vib), and combined vibrational–rotational (vib + rot) modes are clearly observed in each spectrum. (b) Schematic illustration of the rotational and vibrational energy level transitions of a hydrogen molecule, corresponding to the Raman peaks observed in (a).

2. Ultrafast Nano-Spectroscopy of Atomically-Confined Materials

Atomically confined materials, such as transition metal dichalcogenides (TMDs) and carbon nanotubes (CNTs), exhibit unique optoelectronic properties due to strong quantum confinement effects and are regarded as promising candidates for next-generation semiconductor materials. However, their properties are highly sensitive to local structures, such as defects, and interactions with the surrounding environment, owing to their extremely large surface-to-volume ratio. Recently, there has been growing interest in controlling their properties by stacking atomically thin layers to create moiré superlattices—nanoscale structural modulations that offer new degrees of freedom. These developments highlight the increasing importance of experimental techniques capable of simultaneously probing local structures and optical properties.

We have recently developed a highly sensitive ultrafast infrared SNOM, enabling real-time and real-space visualization of photoinduced dynamics in TMDs and CNTs.[4,5)] Figure 2 shows an example of photoexcited carrier dynamics in monolayer WS_2 grown by chemical vapor deposition (CVD) on a sapphire substrate. The near-field signal is stronger at the edges of the triangular domains, reflecting local variations in defect density within the WS_2. We also applied ultrafast nano-spectroscopy to directly observe exciton dynamics in CNTs grown on a sapphire substrate, capturing the generation and relaxation of electron–hole pairs confined within the one-dimensional structure at the nanoscale. These results demonstrate the capability of our technique to directly visualize spatial heterogeneity in ultrafast dynamics, arising from underlying local structures, which would otherwise be obscured in conventional, spatially averaged spectroscopic measurements. We are currently investigating ultrafast electron–phonon interactions in heterostructures composed of TMDs and hexagonal boron nitride, where ultrafast modulation of the photo-carrier and phonon polariton is observed.

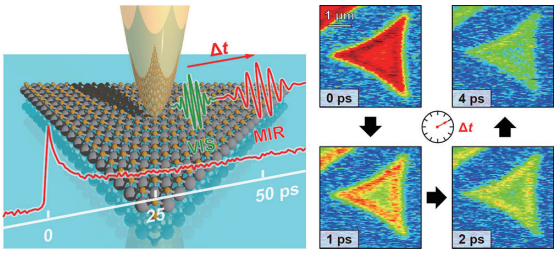

Figure 2. Ultrafast IR-SNOM imaging that visualizes spatially modulated photo-carrier dynamics within monolayer WS_2.

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