Nano- and Atomic-Scale Spectroscopy

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Awards
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2014 Morino Award for Molecular Science
2016 Gerhard Ertl Young Investigator Award
2020 Gaede Prize (German Physical Society)
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The Young Scientists' Award
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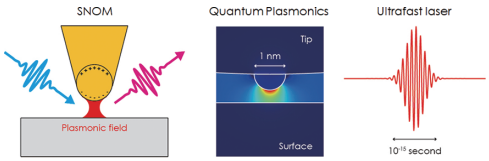
Optical spectroscopy is a potent method to study material structures and properties through light–matter interactions. As nanoscience and nanotechnology have advanced, the significance of spectroscopy at the nanoscale, and even at the atomic scale, has grown immensely. Achieving optical imaging and spectroscopy at atomic resolution stands at the forefront of nanoscience and nanotechnology, allowing for the direct investigation of atomic-scale structures, properties and dynamics in real space and real time. Using near-field optics, electromagnetic fields can be confined at the nano- and atomic-scale. In particular, the localized surface plasmons of metallic nanostructures enable exceptionally sensitive optical spectroscopy due to their significant field enhancement. To achieve nano- and atomic-scale optical spectroscopy, we integrate advanced technologies such as low-temperature scanning tunneling microscopy (STM), laser spectroscopy, and quantum plasmonics. Specifically, the use of low-temperature STM allows us to directly observe atomic-level structures and to precisely manipulate individual atoms and molecules, whereas laser spectroscopy not only facilitates precise optical measurements but also traces ultrafast dynamics using ultrashort laser pulses. Consequently, the combination of these techniques offers a promising avenue for optical spectroscopy with ultrahigh spatiotemporal resolution.

In this review, I provide a concise summary of our recent advancements in nano- and atomic-scale spectroscopy.



Cutting-edge nanospectroscopy for nano-material research

Selected Publications

- S. Liu *et al.*, "Dramatic Enhancement of Tip-Enhanced Raman Scattering Mediated by Atomic Point Contact Formation," *Nano Lett.* **20**, 5879–5884 (2020).
- S. Liu *et al.*, "Atomic Point Contact Raman Spectroscopy of a Si(111)-7×7 Surface," *Nano Lett.* **21**, 4057–4061 (2021).
- S. Liu *et al.*, "Anti-Stokes Light Scattering Mediated by Electron Transfer Across a Biased Plasmonic Nanojunction," *ACS Photonics* **8**, 2610–2617 (2021).
- B. Cirera *et al.*, "Charge Transfer-Mediated Dramatic Enhancement of Raman Scattering upon Molecular Point Contact Formation," *Nano Lett.* **22**, 2170–2176 (2022).
- S. Liu *et al.*, "Nanoscale Heating of an Ultrathin Oxide Film Studied by Tip-Enhanced Raman Spectroscopy," *Phys. Rev. Lett.* **128**, 206803 (2022).
- 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).
- K. Nishikawa, J. Nishida *et al.*, "Metastability in the Insulator Metal Transition for Individual Vanadium Dioxide Nanoparticles," *J. Phys. Chem. C* **127**, 16485–16495 (2023).

1. Atomic-Scale Optical Spectroscopy

Recent studies have demonstrated that sub-nanometer confinement of near fields arises in the presence of atomic-scale protrusions on metallic nanostructures, and extremely strong light–matter interactions occur in "picocavity." However, the specific impact of atomic-level structures on plasmonic properties still remains to be elucidated. This requires precise experiments using atomically well-defined model systems. We investigated inelastic light scattering of a single Ag atom adsorbed onto the Ag(111) surface using low-temperature tip-enhanced Raman spectroscopy (TERS), as shown in Figure 1. We discovered that the vibration mode localized at the adatom can be observed in the TERS spectrum. Furthermore, we trace how the TERS spectrum evolves as a function of the gap distance. The exceptional stability provided by the low-temperature STM enabled us to clearly examine the different electron transport regimes of the picocavity, specifically in both the tunneling and quantum point contact (QPC) regimes. Our measurements highlight a distinct vibration mode localized at the adatom. Moreover, its TERS intensity undergoes a pronounced shift upon the QPC formation. This observation underscores that the atomic-level structure has a crucial impact on the plasmonic properties. To gain microscopic insights into the intricate of picocavity optomechanics, we meticulously analyzed the structure and plasmonic field within the STM junction, employing time-dependent density functional theory. These simulations unveiled that atomic-scale structural relaxations at the single-atom QPC lead to discernible variations in the plasmonic field's strength, volume, distribution, as well as the vibration mode localized at the individual atom.

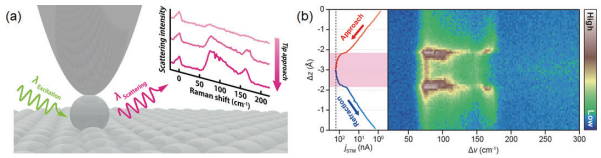


Figure 1. Inelastic light scattering spectroscopy for a single Ag adatom on the Ag(111) surface. (a) Schematic of the experiment. (b) ILS spectra measured as a function of the tip–adatom distance.

2. Nanoscale Coherent Phonon Spectroscopy

Coherent phonon spectroscopy offers microscopic insights into ultrafast lattice dynamics, especially when considering its interaction with other degrees of freedom in nonequilibrium conditions. While ultrafast optical spectroscopy is an established method for studying coherent phonons, the restrictions imposed by the diffraction limit have made direct observations of their nanoscale dynamics elusive. We successfully showcased nanoscale coherent phonon spectroscopy using an ultrafast laser-induced STM within a plasmonic junction (Figure 2). Coherent phonons are locally excited in ultrathin zinc oxide films by the highly confined plasmonic field and are probed via the photoinduced tunneling current through an electronic resonance of the zinc oxide film. Using concurrently performed TERS, we revealed the specific phonon modes involved. Unlike the Raman spectra, the phonon dynamics detected in coherent phonon spectroscopy display pronounced nanoscale spatial variations. These variations correlate with the distribution of the electronic local density of states, as discerned by scanning tunneling spectroscopy..

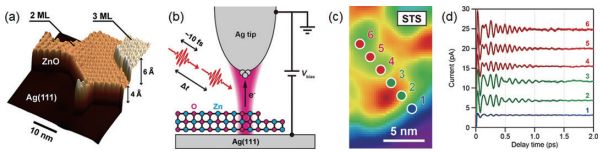


Figure 2. Nanoscale coherent phonon spectroscopy. (a) STM image of the ZnO ultrathin film expitaxially grown on the Ag(111) surface. (b) Schematic of the experiment. (c) Scanning tunneling spectroscopy image of the ZnO ultrathin film. (d) Interferometric autocorrelation of the tunneling current recorded over the ZnO ultrathin film.

3. Nanoscale Infrared Imaging of Nanomaterials

We have also developed advanced mid-infrared (MIR) spectroscopy and imaging techniques based on scattering-type scanning near-field optical microscopy (s-SNOM). We have successfully set up s-SNOM equipped with a MIR tunable broadband laser for investigation of nanomaterials. Figure 3 presents a direct observation of the insulator–metal transition in individual vanadium dioxide (VO_2) nanoparticles. Using temperature-dependent mid-IR nanoimaging, we were able to discern the phase transition of these individual VO_2 nanoparticles. Particles of smaller volumes generally transition to metal at elevated temperatures. This is attributed to fewer nucleation sites within each particle. Using mid-IR nanoimaging, we observed that the phase transition displays a stochastic behavior: The same particle shows varying transition temperatures across different heating cycles. Our findings suggest that the phase transition in VO_2 nanoparticles is prone to superheating and supercooling, and these transitions are limited by nucleation.

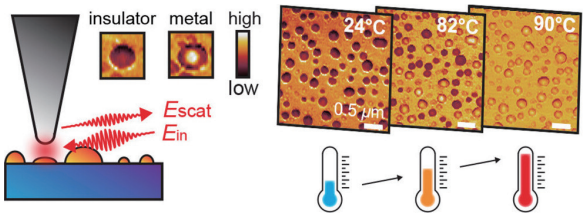


Figure 3. Nanoscale MIR imaging of VO_2 nanoparticles at different temperatures.

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1) S. Liu *et al.*, *ACS Nano* **17**, 10172 (2023).
2) S. Liu *et al.*, *Sci. Adv.* **8**, eabq5682 (2022).
3) K. Nishikawa, J. Nishida *et al.*, *J. Phys. Chem. C* **127**, 16485 (2023).