# Nano- and Atomic-Scale Spectroscopy

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2020 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
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**Keywords** Atomic-Scale Optical Spectroscopy, Scanning Probe Microscopy, Nanoscale Science

An in-depth understanding of the structure and dynamics of matter at the atomic scale is crucial for designing next-generation devices and optimizing material/energy conversion processes, such as optoelectronics, solar cells, and catalysis. The rapid advancement of nanotechnology requires sophisticated measurement techniques capable of capturing phenomena with simultaneous spatiotemporal resolution at the (sub)nanometer length and pico/femtosecond time scale. Optical spectroscopy serves as a versatile tool for studying the microscopic structures, properties, and dynamics of a wide variety of materials. However, its spatial resolution is inherently limited by the diffraction limit, which restricts the ability to directly characterize nanoscale objects. Nano-spectroscopy using near-field optics offers a unique approach to overcome this physical limitation, enabling the investigation of materials at the nanoscale.

Our group has focused on the development and application of cutting-edge scanning near-field optical microscopy (SNOM) combined with various advanced spectroscopic methods, including nonlinear and ultrafast time-resolved measurements. In particular, we explore atomic-scale light–matter interactions to achieve nano-spectroscopy at the unprecedented spatiotemporal resolution. Recently, we have demonstrated the atomic-level sensitivity and spatial resolution using tip-enhanced Raman spectroscopy (TERS) based on low-temperature scanning tunneling microscopy (STM), providing novel insights into the intricate phenomena in nanoscale systems. Furthermore, by integrating ultrashort pulsed lasers, we have opened new avenues for directly observing the coherent dynamics of electrons and lattices within the STM junction. This capability is a critical step towards realizing atomic-scale ultrafast nano-spectroscopy, allowing us to probe dynamic processes that were previously inaccessible.

We are currently further pushing the boundary of nano-spectroscopy techniques with three key objectives: (1) extending the capabilities of atomic-scale spectroscopy from the visible to the infrared region to explore a broader range of materials and phenomena, (2) developing manifold nonlinear nano-spectroscopy techniques to investigate complex quantum interactions, and (3) applying these advanced methods to diverse materials, including low-dimensional materials, quantum dots, and biological molecules. These advancements will provide profound insights into the fundamental quantum properties and interactions of materials, potentially leading to the discovery of novel functionalities and the creation of innovative nanoscale devices.

## Selected Publications


- 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).
- J. Nishida *et al.*, "Sub-Tip-Radius Near-Field Interactions in Nano-FTIR Vibrational Spectroscopy on Single Proteins," *Nano Lett.* **24**, 836 (2024).

## 1. Atomic-Scale Optical Spectroscopy

Understanding and controlling of atomic-scale confinement of optical fields is a highly active area of research in light–matter interactions and their applications such as ultrasensitive spectroscopy and nano-optoelectronics. Recent studies have demonstrated that extreme confinement of near fields occurs in the presence of atomic-scale protrusions on metallic nanostructures, often referred to as "picocavity," formed by features as small as single atoms, resulting in unique optical phenomena. Yet, the underlying mechanisms remain to be elucidated, requiring highly precise experiments using atomically well-defined model systems. To address this, we investigated Raman scattering of a single Ag atom adsorbed onto the Ag(111) surface using low-temperature TERS,[1] as shown in Figure 1. The experiment demonstrated that the vibration localized at the adatom is distinctly observable in the TERS spectrum. We further explored the relationship between the gap-distance dependence and Raman scattering in the different electron transport regimes of the picocavity, specifically comparing the tunneling and quantum point contact (QPC) regimes. Notably, the TERS spectra exhibited significant changes upon the formation of the QPC. These findings highlight that atomic-level structural changes can significantly influence the plasmonic properties of the system, offering new insights into how atomic-scale features modulate optical responses.

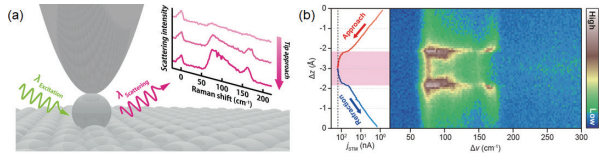


**Figure 1.** Inelastic light scattering spectroscopy for a single Ag adatom on the Ag(111) surface. (a) Schematic of the experiment. (b) Raman spectra measured as a function of the tip–adatom distance.

## 2. Nanoscale Coherent Phonon Spectroscopy

Coherent phonon spectroscopy is a valuable technique for gaining microscopic insights into ultrafast lattice dynamics, especially under nonequilibrium conditions. Understanding these dynamics is crucial for advancing our knowledge of fundamental material properties and for the development of ultrafast electronic and photonic devices. However, the conventional method cannot directly observe phonon dynamics at the nanoscale. To overcome these limitations, recently we have successfully demonstrated nanoscale coherent phonon spectroscopy using an ultrafast laser-induced STM within a plasmonic junction, as shown in Figure 2.[2] This approach uniquely leverages the highly confined plasmonic field to locally excite coherent phonons in ultrathin zinc oxide films, which are then probed via the photoinduced tunneling current through an electronic resonance of the zinc oxide film. Unlike the Raman spectra, the phonon dynamics detected in coherent phonon spectroscopy display pronounced nanoscale spatial variations that correlate with the distribution of the electronic local density of states. We plan to further extend this technique to investigate various low-dimensional systems.

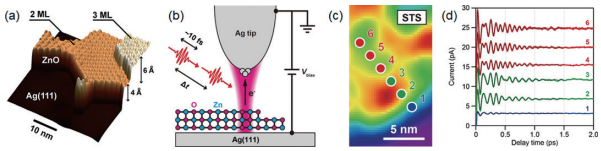


**Figure 2.** Nanoscale coherent phonon spectroscopy. (a) STM image of the ZnO ultrathin film grown on the Ag(111) surface. (b) Schematic of the experiment. (c) STS map of the ZnO ultrathin film. (d) Interferometric autocorrelation of the tunneling current recorded over the ZnO ultrathin film.

## 3. Nanoscale Infrared Nano-Spectroscopy of Nanomaterials

We have developed an advanced SNOM system based on atomic force microscopy (AFM), equipped with a wavelength-tunable pulsed laser that spans from the visible to the mid-infrared (MIR) region. This system allows us to perform nanoscale infrared (nano-IR) spectroscopy with exceptional sensitivity and resolution. The sensitivity of our nano-IR spectroscopy was demonstrated by successfully measuring the MIR response of a single protein molecule isolated on a gold (Au) surface, as shown in Figure 3.[3] By implementing a unique detection scheme that extracts highly localized near-field MIR scattering down to a spatial resolution of just a few nanometers, we have achieved world-record sensitivity.

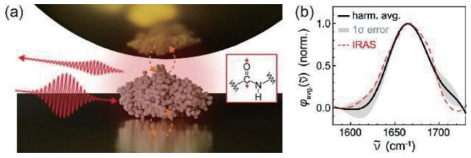


**Figure 3.** MIR vibrational spectroscopy of a single protein. (a) Schematic of the experiment. (b) MIR spectrum around the vibrational resonance of the amid group.

Figure 4 illustrates the application of the ultrafast visible-pump–MIR-probe nano-spectroscopy to visualize the spatially modulated many-body photo-carrier dynamics within a monolayer $WS_2$. By capturing these dynamics, we can directly observe how photo-carriers behave and interact in response to optical excitation, revealing intricate details of the material's electronic properties.

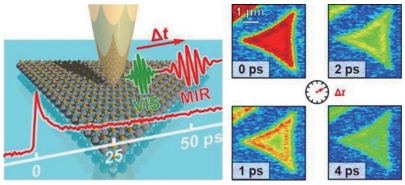


**Figure 4.** Ultrafast nano-imaging of spatially modulated many-body dynamics in monolayer $WS_2$.

### References

1) S. Liu *et al.*, *ACS Nano* **17**, 10172 (2023).
2) S. Liu *et al.*, *Sci. Adv.* **8**, eabq5682 (2022).
3) J. Nishida *et al.*, *Nano Lett.* **24**, 836 (2024).