TOOLS OF THE TRADE

Tip-enhanced Raman scattering for atomic-scale spectroscopy and imaging

Atomic-scale spectroscopy provides an exceptional ability to define electronic, optical, thermal, mechanical, and chemical properties of materials at the nanoscale. At these scales, dimensional confinement can lead to new and unusual properties, where the intrinsic natures and interfaces of individual atoms and molecules can result in quantum phenomena that are not exhibited in bulk materials. Realizing the full potential of these unique properties hinges upon the ability to probe them with suitable spatial resolution. Scanning tunneling microscopy (STM) uses a tunneling current between a sharp tip and the sample to yield real-space images of individual atoms and molecules. However, it lacks chemical sensitivity and therefore it is difficult to define unknown species or structures with STM alone. By contrast, complementary approaches, such as spectroscopy can provide chemical identification as well as define physical and electronic structures. However, there is a mismatch between the spatial resolution of the two techniques, as the diffraction limit of light leads to ensemble-based measurements where average properties are observed, obscuring local inhomogeneities. Instead, scanning near-field optical microscopy methods, such as tip-enhanced Raman spectroscopy (TERS), can be used to probe individual atoms and molecules with atomically confined light.

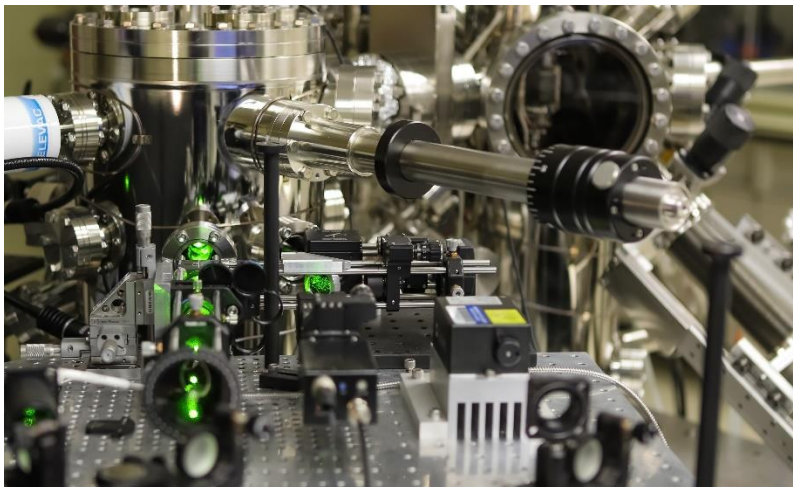
For TERS, the STM tip is composed of a plasmonically-active metal, typically silver or gold, so that incident focused, polarized, and coherent light results in a highly enhanced and confined optical field at the apex of the tip. This can generate enhanced Raman scattered photons, which define the highly sensitive vibrational fingerprint of a molecule or material. In exceptionally stable conditions, such as in ultrahigh vacuum (UHV) at cryogenic temperatures, TERS enables atomic-scale measurements. The technique has been used to capture images of vibrational modes of individual molecules with submolecular resolution, as well as to detect and identify phenomena such as the breaking or formation of a single chemical bond within a molecule or atomic lattice.

TERS requires optical coupling into and out of the STM tip–sample junction, which becomes complicated in the case of a cryogenic UHV–STM. Over time, various optical setups have seemed to converge into designs that incorporate the final excitation and collection optical elements within the UHV chamber as close to the tip–sample junction as possible, mounted on piezoelectric drivers that allow for the fine adjustment of their alignment and focus.

Although the optical setup provides the excitation and detection, the plasmonic probe is paramount to the measurement. Experimental demonstrations and new theoretical approaches suggest that beyond the micro- and nanoscale structure of the probe, an atomic-scale protrusion at the apex is necessary to confine the enhanced optical field to a “picocavity”, which is crucial for atomic-scale spectral imaging. Fabrication methods such as electrochemical etching and focused ion beam milling can be used to control the micro- and nanoscale features of the probe tip. However, atomic-scale control of the tip apex, and therefore the properties of the confined optical field, requires *in situ* tip conditioning, such as applying short pulses of the voltage bias or softly indenting the tip into the surface. These interactions can be used to tune the atomic structure of the tip.

Thus far, TERS measurements demonstrating near atomic-scale resolution have primarily been the result of carefully selected systems, limited to optimal sample and substrate selection. However,

recent demonstrations have suggested that while such selection is convenient, it is by no means essential. Recent efforts have begun to expand investigations beyond these initial demonstrations to newly discovered 2D materials, single-molecule chemistry, and industrially relevant substrates. The inclusion of ultrashort pulsed light offers the opportunity to capture and track dynamic processes with high temporal resolution. Atomic-scale spectroscopic insight into new materials and chemistry offers the means to inform our understandings of these systems in new and unexpected ways.



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Competing interests

The author declares no competing interests.