

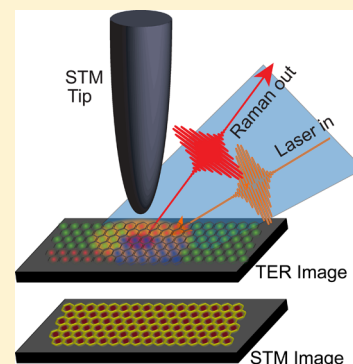
Recent Advances in Tip-Enhanced Raman Spectroscopy

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ABSTRACT: Tip-enhanced Raman spectroscopy (TERS) has experienced tremendous growth in the last 5 years. Specifically, TER imaging has provided invaluable insight into the spatial distribution and properties of chemical species on a surface with spatial resolution that is otherwise unattainable by any other analytical method. Additionally, there has been further development in coupling ultrafast spectroscopy with TERS in the hope of obtaining both ultrafast temporal and nanometer-scale spatial resolution. In this Perspective, we discuss several recent advances in TERS, specifically highlighting those in the areas of TER imaging and integrating ultrafast spectroscopy with TERS.



The characterization of surface adsorbates is of fundamental importance for describing phenomena in areas such as heterogeneous catalysis, electrochemistry, biosensing, molecular electronics, and the characterization of 2D materials. Differences on the nanometer length scale play an integral role in determining the efficiency and mechanisms of the processes and materials listed above. A variety of methods have been utilized to study both the structure and function of adsorbates; however, characterization on the sub-10 nm scale is especially difficult. Techniques such as nuclear magnetic resonance (NMR), infrared (IR), and Raman spectroscopy have high chemical information content but lack the spatial resolution required for nanoscale characterization and thus provide ensemble-averaged measurements. Scanning probe microscopy (SPM) techniques, such as scanning tunneling microscopy (STM) or atomic force microscopy (AFM), have high spatial resolution but lack the chemical specificity to uniquely identify adsorbates. Inelastic scanning tunneling spectroscopy (IETS) can obtain the vibrational spectrum of a single molecule with submolecular spatial resolution; however, the requirement for cryogenic temperatures and its low spectral resolution restrict the application of this technique to small molecules and present significant challenges for its widespread use.¹ In contrast, tip-enhanced Raman spectroscopy (TERS) has emerged as a powerful technique capable of performing such characterization as it combines the intrinsic spatial resolution of scanning probe techniques with the chemical information content of vibrational spectroscopy.^{2–5}

TERS can be utilized for point spectroscopic studies, which utilize the high sensitivity and chemical specificity of TERS but not its inherent spatial resolution. On the other hand, TER imaging provides a means to chemically characterize the heterogeneous distribution of adsorbates across a surface at the nanometer length scale. TER imaging involves measuring the

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TER signal at each pixel location of the corresponding SPM image during the raster scan of the surface. For example, a map of the integrated intensity of a particular TERS peak at each location results in a chemical image of the substrate. This method can aid in identifying surface segregation, catalytically active sites, phase domain boundaries, and chemical contamination that would be unobservable with traditional techniques. TER imaging can provide chemical maps of surfaces with spatial resolution ~ 100 times smaller than the diffraction limit of light.⁶

In addition to imaging, the spatial resolution of TERS provides an exciting opportunity for obtaining both space- and time-resolved chemical information. The ultrafast dynamics of surface adsorbates can be measured using a variety of techniques including two-dimensional sum frequency generation (2D-SFG),⁷ surface-enhanced coherent anti-Stokes Raman spectroscopy (SE-CARS),⁸ and surface-enhanced femtosecond stimulated Raman spectroscopy (SE-FSRS).⁹ However, these methods alone are limited in their achievable spatial resolution to the far-field diffraction limit. TERS has the potential to overcome this limitation.

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The use of TERS for characterizing surface adsorbates has rapidly grown in its ability to spectroscopically map surfaces with subdiffraction-limited spatial resolution and high chemical specificity. This technique has recently been applied to a variety of adsorbates including biological molecules,^{10–12} carbon nanomaterials,^{13–16} as well as many others.^{17–20} Over a decade ago, Hartschuh et al. reported TER imaging of single-walled carbon nanotubes, which exhibited spatial resolution exceeding what is possible with confocal Raman.²¹ Additionally, those authors demonstrated that additional information could be gained by imaging polarization-dependent signals. Since this seminal work, in which 25 nm spatial resolution was reported, multiple groups have systematically showed improved spatial resolution by over an order of magnitude.

In 2008, Steidtner and Pettinger demonstrated the benefits of performing TER imaging in ultrahigh vacuum (UHV), achieving single-molecule detection.²² The authors observed photobleaching in UHV to be substantially suppressed compared to an oxygenated environment, which allowed for longer measurement times. Notably, TER imaging of a single molecule was reported for the first time with a lateral resolution of 15 nm. As demonstrated here, the pixel spacing required for single-molecule resolution must be on the order of the size of the molecule or smaller. Since this initial study, groups have demonstrated that an UHV environment allows for the study of atomically clean substrates as well as the capability for low-temperature operation.^{23–26}

TER imaging was utilized in conjunction with near-field photoluminescence mapping to investigate the composition of solar cell films at the nanoscale.²⁷ The authors analyzed the morphology and photophysics of an annealed poly(3-hexylthiophene) and [6,6]-phenyl-C61 butyric acid methyl ester (P3HT/PCBM) film. Clear domain boundaries can be visualized in TER images using Raman bands representative of each constituent. In this study, the authors also demonstrated that P3HT photoluminescence is quenched in areas of high local PCBM concentration due to exciton dissociation through electron transfer to PCBM. In this way, photophysical phenomena directly relevant to solar energy technology were analyzed with unprecedented spatial resolution.

Published in *Nature* in 2013, Zhang et al. utilized UHV sample preparation and measurement to improve surface cleanliness and tip stability, reporting an astonishing spatial resolution below 1 nm in the detected Raman signal of a porphyrin, as shown in Figure 1.²³ The obtained TER images allow for visualization of the inner structure of a single molecule. Also demonstrated in this work was the ability to correlate the observed Raman signal with a molecule's local environment using TER imaging. Importantly, the authors laid the groundwork for future single-molecule, high-resolution chemical imaging studies, which will have far-reaching utility.

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In a similar vein, earlier this year, the Kawata group demonstrated sub-2 nm resolution using STM operated in ambient, suggesting that UHV systems are not required to observe high spatial resolution.²⁸ In this report, the chemical specificity of TER imaging is exploited, whereby images constructed using intensities of different carbon nanotube

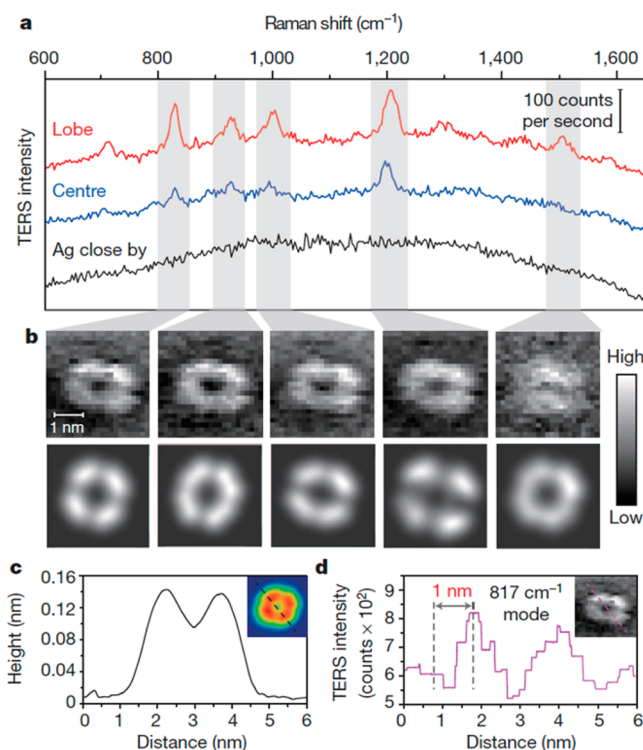


Figure 1. TERS mapping of a single H₂TBPP molecule on Ag(111). (a) Representative single-molecule (SM)-TERS spectra on the lobe (red) and center (blue) of a flat-lying molecule on Ag(111). The TERS spectrum on the bare Ag is shown in black. (b) The top panels show experimental TERS mapping of a single molecule for different Raman peaks. The bottom panels show the theoretical simulation of the TERS mapping. (c) Height profile of a line trace in the inset STM topograph. (d) TERS intensity profile of the same line trace for the inset Raman map associated with the 817 cm⁻¹ Raman peak. Reproduced with permission from ref 23. Copyright 2014, Macmillan Publishers Limited.

peaks display differing signal distributions, as shown in Figure 2. In particular, effects from bundling, defects, and nanotube diameter were discerned, clarifying physical phenomena that cannot be interrogated on the ensemble level.

TERS has experienced significant growth over the past several years particularly in the area of TER imaging. The increased sensitivity of these instruments has allowed TER images as large as 256 × 256 pixels to be obtained without a commensurate increase in acquisition time.

Even more challenging has been the integration of pulsed excitation sources with TERS for time-resolved and nonlinear spectroscopy. While spontaneous TERS has received much attention, stimulated spectroscopies have been less developed. One current limitation of TERS lies in its inability to obtain time-resolved data. Recently, several groups have published results that indicate that pump–probe experiments should be obtainable.^{29,30}

The Kawata group has demonstrated both single-frequency and broad-band tip-enhanced coherent anti-Stokes Raman spectroscopy (TE-CARS). In the initial report, both on-resonant and off-resonant TE-CAR images of a DNA network were obtained.³¹ No damage to either the tip or DNA sample was observed. The broad-band TE-CARS work allowed multiplexed TE-CAR imaging of semiconducting carbon nanotubes, and the spatial resolution was demonstrated to be of order 50 nm.³² Furthermore, they found that the transient

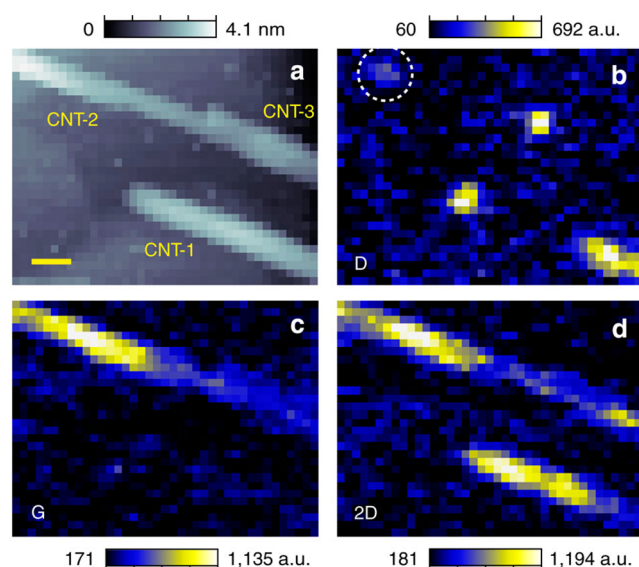


Figure 2. (a) STM topography taken simultaneously with TERS images. The image size is $39 \times 30 \text{ nm}^2$ (39×30 pixels). Scale bar, 5 nm. (b–d) Spectrally resolved TERS images for three Raman peaks, for D (b), G (c), and 2D (d) bands with color palettes corresponding to the integrated peak area. The scale is offset by the averaged far-field background. Note that there is a weak D-band signal at the upper left region of CNT-2, as indicated by a dashed circle in (b). At each pixel, one full spectrum with 0.1 s integration was recorded, and then, each Raman band was fitted to compose the images. Reproduced with permission from ref 28. Copyright 2014, Macmillan Publishers Limited.

G-band signal possessed a different decay constant than the far-field response, which was attributed to an Auger process induced by the high field intensities generated at the tip–sample junction.

The field of TERS is now rapidly advancing past technique development toward answering important scientific questions in surface spectroscopy, materials science, physics, and chemistry.

There are inherent limits to using ultrafast pulses in TERS, specifically regarding damage to either the adsorbate or tip. Klingsporn et al. performed TERS experiments under picosecond irradiation and observed significant signal decay, as depicted in Figure 3.²⁹ It was determined that the plasmonic tip was undamaged and the decay followed first-order kinetics. The signal decay was attributed to either photothermal desorption or reactive decay chemistry. This work suggests that similar experiments performed in a more controlled environment could help mitigate these degradation mechanisms. Along these lines, Pozzi et al. performed a TERS experiment on rhodamine 6G in UHV with picosecond pulses and did not observe any irreversible degradation of the signal. SERS experiments with picosecond pulses suggest that the exact mechanism of signal loss (diffusion or reactive decay chemistry) depends on the adsorption properties of the target analyte; however, both effects are minimized by conducting the experiments in UHV.³³

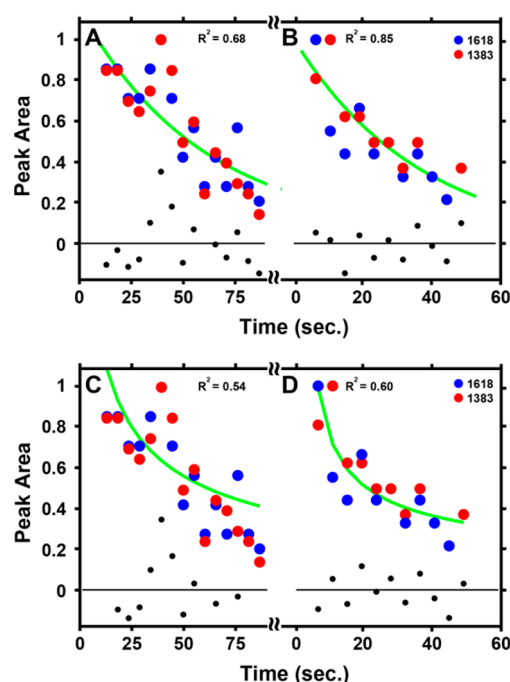


Figure 3. Plot of the time dependence of the integrated intensity of the 1618 (blue) and 1383 (red) cm^{-1} bands of MGITC. The areas are normalized to the highest value, and only those above the noise are plotted. The break indicates moving the tip to a new position within the laser focus. The fits to the data in (A,B) exponential ($e^{-t/\tau}$) and (C,D) inverse square root ($t^{-1/2}$) are plotted in green, while the residuals are plotted in gray, and R^2 values are shown for each case. Reprinted with permission from ref 29. Copyright 2014, American Chemical Society.

One other area in which TERS has the capacity to grow is gaining insight into chemical processes on surfaces. The Weckhuysen group was able to monitor the reduction of *p*-nitrothiophenol on a surface by using two laser wavelengths, one to initiate the chemistry and the other to probe the photochemical response.³⁴ After the reduction occurred, significant intensity fluctuations were observed in the TERS spectrum, which the authors attributed to a disruption of the monolayer as a result of the photoreduction process. Given the inherent spatial resolution of TERS, this provides a pathway to examine how different surface sites may modify the chemical activity of molecules on surfaces.

At ambient temperature and pressure, the ability to distinguish molecules on independent surface sites is extremely difficult. To circumvent this issue, the Van Duyne group performed low-temperature (19 K) UHV-TERS to gain insight into the adsorption properties of rhodamine 6G adsorbed on Ag(111).²⁵ The low temperature immobilized the molecules on the surface and modified the Raman spectrum compared to room-temperature (RT)-TERS as well as low-temperature (LT)- and room-temperature (RT)-SERS measurements. These results are shown in Figure 4. These authors demonstrated that the frequency shifts are the result of the adsorbate–substrate interactions, specifically the ethylamine moieties with the silver surface. Although these interactions are present in all four measurements, the combination of low copy number detection and R6G immobilization in LT-TSERS reduces inhomogeneous broadening in the TERS signal and allows for the interrogation of a subensemble of molecules in a low-energy configuration on the surface. These low-temper-

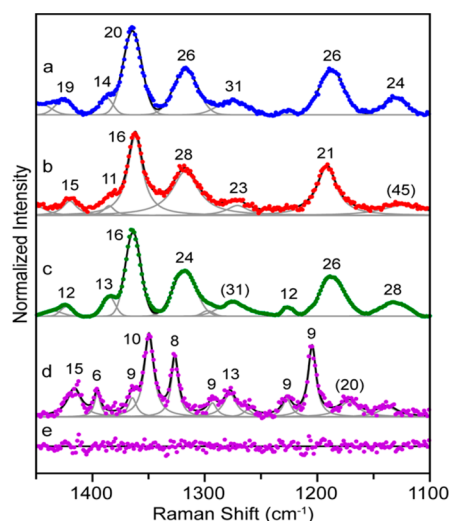


Figure 4. (a) RT-SER, (b) RT-TER, (c) LT-SER, and (d) LT-TER spectra of R6G. The displayed values are full widths at half-maximum (fwhms) for the corresponding peaks. Spectra were background-subtracted and fit with Gaussians (SERS) or Lorentzians (TERS) using a least-squares approach. Data are represented by colored circles, individual peak fits by gray lines, and composite fits by black lines. (e) Residuals after fitting for LT-TERS. All of the spectra were normalized by the maximum intensity in their respective composite fits. The fwhm values in parentheses designate peaks either marginally above $3\times$ noise and/or largely influenced by background uncertainty. Reprinted with permission from ref 25. Copyright 2014, American Chemical Society.

ature measurements provide access to chemical information regarding adsorbate–substrate interactions that is otherwise inaccessible.

Spectral fluctuations have long been observed in single-molecule Raman spectroscopy and have often been attributed to molecular diffusion, reorientation, and hot-spot heterogeneity.^{35–39} Sonntag et al. examined the relative intensity fluctuations in SMTERS of R6G and found no correlation in the intensity and/or frequency fluctuations of multiple modes throughout the spectrum.⁴⁰ Theoretical calculations revealed that allowing for small changes in the excited-state bond lengths and lifetime of the adsorbate reproduced the experimentally observed spectral changes. Single-molecule experiments can thus provide a measurement of the excited-state properties of molecules via analysis of the spectral fluctuations.

Signal fluctuations were also discussed in a recent report by Shiotari et al. In this study, the authors applied UHV-TERS to graphene nanoribbons on Au(111) and observed significant blinking of the TER signal and an asymmetric distribution of both the D- and G-band intensities.²⁴ Imaging of the surfaces via STM revealed that the nanoribbon adsorption structure remained stable under laser illumination. The intensity fluctuations were attributed to thermal fluctuation of the radius of the TERS probe. The experimentally observed intensity distribution was reproduced by modeling the probe radius as a sphere.

The Wickramasinghe group published a report integrating both the imaging capabilities of TERS along with a stimulating pulse in a technique they term stimulated TER (sTER) imaging. Simultaneous topographic and sTER images of a printed thiol monolayer were obtained on a Au(111) surface. The sTER image can clearly distinguish the molecular species from the Au surface, while the topographic image cannot

resolve the molecular pattern. Additionally, the authors experimentally determined the stimulated gain of the experiment to be 1.0×10^9 , in line with the theoretically predicted value.³⁰

Imaging particular Raman bands to expose nanoscale chemical inhomogeneity exploits the chemical mapping capabilities possible in TER imaging and will provide unprecedented insight into phenomena relevant to a broad array of technologies.

The field of TERS is now rapidly advancing past technique development toward answering important scientific questions in surface spectroscopy, materials science, physics, and chemistry. Recent papers have utilized the spatially resolved chemical information gained to describe subensemble-averaged phenomena, and this capability makes TER imaging extremely powerful. Imaging particular Raman bands to expose nanoscale chemical inhomogeneity exploits the chemical mapping capabilities possible in TER imaging and will provide unprecedented insight into phenomena relevant to a broad array of technologies. The integration of ultrafast pulses into the traditional TERS experiment will lead to probing the nonlinear response of chemical systems and investigations of damage mechanisms when exposed to high peak powers. Finally, the combination of high temporal resolution present in ultrafast spectroscopy with the inherent spatial resolution of TERS should provide site-specific information about the dynamics of surface-adsorbed molecules.

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Nan Jiang is currently a postdoctoral fellow with Prof. Richard Van Duyne at Northwestern University. He received his Ph.D. in Condensed Matter Physics from Chinese Academy of Sciences in

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