Angewandte Highlights

Single-Molecule Spectroscopy

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Where Does It Vibrate? Raman Spectromicroscopy on a Single Molecule**

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Acquiring information on individual molecules, for example identity, orientation, and conformation on a sub-nanometer length scale is arguably one of the ultimate goals of chemical analysis. In the case of solid surfaces and adsorbates, which play an important role in catalysis, the chemical composition is typically probed with surface sensitive, laterally integrating spectroscopic techniques such as X-ray photoelectron spectroscopy. Lateral integration ensures sufficient signal intensity, but necessitates model systems with many identical repeat units. This is achieved by using surfaces of single crystals, which, however, are often not representative as model systems for the—structurally much more complex—real catalysts. Complementary topographic information is obtained with scanning probe techniques of limited sensitivity to chemical composition. Such combinations of nonlocal spectroscopic and chemically insensitive microscopic techniques make it difficult to obtain both chemical and topographic information on the atomic or molecular level, for example from a single adsorbed molecule. Apparently, there is a need for local spectromicroscopic techniques which provide parallel chemical and topographic data with sub-nanometer resolution and which can be applied to chemically and structurally complex samples under a wide range of experimental conditions.

Scanning probe techniques, in particular scanning tunneling microscopy (STM) and atomic force microscopy (AFM), have developed rapidly since their invention in the 1980s. Atomic resolution is routinely possible with crystalline metal or insulator surfaces. For adsorbed molecules, however, atomic resolution was achieved only during the past five years[1] with tip-functionalized noncontact AFM (NC-AFM)[2] and with scanning tunneling hydrogen microscopy (STHM).[3] Spectroscopy on single molecules with an STM is possible, but has limited scope as far as chemical analysis is concerned: Scanning tunneling spectroscopy (STS) probes the valence electronic structure in a narrow energy range and does not provide element-specific information. Inelastic tunneling spectroscopy with the STM (STM-IETS) can probe the molecular vibrations of adsorbed molecules, but has limited potential for characterizing species using the vibrational fingerprint and requires cryogenic temperatures.[4]

An especially powerful technique for chemical analysis is tip-enhanced Raman spectroscopy (TERS), which combines scanning probe microscopy (STM or AFM) with Raman spectroscopy. In a TERS experiment, the nanometer-sized gap between an STM or AFM tip and the surface is illuminated with a laser beam (Figure 1 a). The metallic tip acts as an antenna that enhances, in its vicinity, the fields of both the incident and the emitted light. As a result, the intensities of the vibrational Raman lines are increased by factors of typically 10^4 to 10^7 compared to the intensity without tip (considering the same probed volume).[5] The polarization of the enhanced field along the tip shaft leads to special selection rules, which can be used to determine the orientation of an adsorbed molecule.

TERS was proposed by Wessel[6] in 1985 to overcome the limitations of surface-enhanced Raman spectroscopy (SERS), a nonlocal method that works only on rough coinage metal surfaces. Wessel's suggestion was first adopted by Zenobi and co-workers,[7] who used a Ag-coated AFM cantilever for TERS on adsorbed C_{60}. The lateral spatial resolution was below 50 nm. Refinement of TERS during the past ten years led to improved sensitivity and resolution below 10 nm, such that Raman spectra from isolated adsorbed molecules could be recorded.[5,8] However, the probed area was still larger than a molecule, and therefore no submolecular resolution was achieved. Another drawback of TERS is radiation damage of the sample by the tip-enhanced field under ambient conditions and to a lesser extent also in ultrahigh vacuum (UHV).[9]

Only with these limitations of classical TERS in mind can one appreciate the recent progress made by the group led by J. G. Hou and Z. C. Dong. As they reported in *Nature*,[10] isolated porphyrin molecules on a Ag surface were investigated by TERS with an unprecedented resolution of approximately 0.5 nm. In this way, it was possible to create a series of Raman images of a single molecule for different wavenumbers. The image contrast arises from the different intensities with which a certain Raman line is emitted from different parts of the molecule (Figure 1 b,c). In addition, the overall sensitivity was raised to a level that the incident

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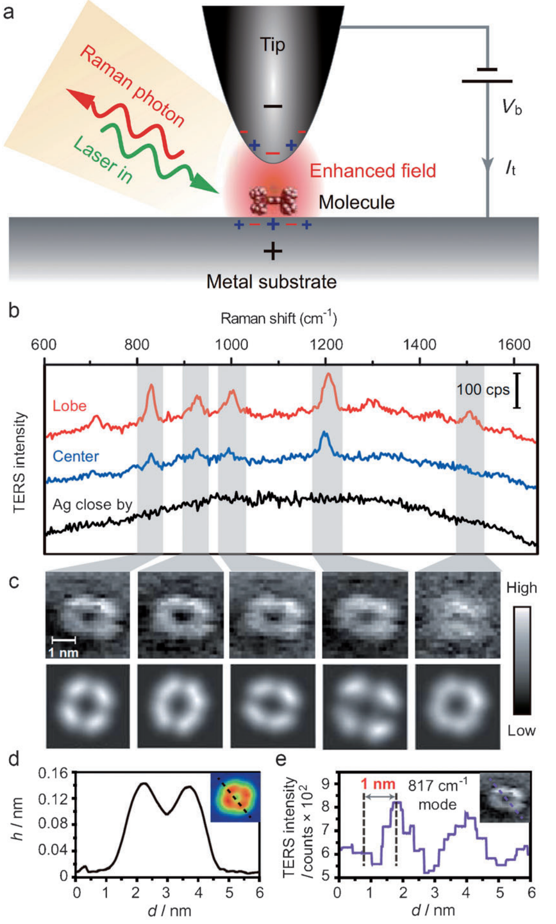

Figure 1. a) Tip-enhanced Raman spectroscopy (TERS). Laser light is focused on the tip–sample nanocavity with the adsorbed molecule. The near field created in the vicinity of the tip causes the enhanced Raman scattering from the area around the tip. b) TER spectra from a single tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (H_2TBPP) molecule on a Ag(111) surface, recorded in the center (blue) and at the periphery ("lobe", red) of the molecule at 80 K. The TER spectrum of the clean Ag(111) surface is shown in black. c) Top: TERS mapping of a single H_2TBPP molecule for different Raman wavenumbers as indicated. Bottom: Theoretical simulations of the TERS mapping. d) STM height profile of the H_2TBPP molecule shown in the inset. e) TERS intensity profile of the same line trace for the Raman map (inset) in the range 800–852 cm^{-1}. Adapted from Ref. [10].

photon fluxes are lower by 1–2 orders of magnitude compared to previous work. This means that the molecules can be observed for a longer time without damage. This success is partly based on the highly controlled conditions of the UHV-STM: Both tip and sample are ultraclean and well defined, resulting in a high stability of the tip–sample junction. UHV in combination with the low sample temperature also reduces radiation-induced reactions.

Decisive for the drastically improved TERS performance achieved by Hou, Dong, and co-workers[10] appears to be the fact that their experiment was done under the conditions of a double-resonance Raman enhancement for both excitation and emission: Efficient Raman excitation requires spectral overlap between the nanocavity plasmon shoulder, the laser line, and the upwards vibronic transition of the adsorbed porphyrin molecule in the tip–sample nanocavity. In addition, and this is the particular novelty, there is also a resonant enhancement of the emission process. This is achieved by spectral matching of the nanocavity plasmon to the deexcitation transition, that is, to the downwards vibronic transition of the molecule. The spectral matching is obtained by careful tuning of the status of the STM tip. As a result of the more efficient emission, the photon flux can be reduced such that photodegradation is minimized.

The TER spectra of a single porphyrin molecule (Figure 1 b) and their comparison with bulk data permit the unambiguous chemical identification of the species.[10] In addition, it was possible to distinguish a horizontally oriented molecule adsorbed on a terrace site from a tilted molecule on a step edge by making use of the TERS-specific selection rules: For a given geometry, in-plane vibrational modes of the porphyrin core become Raman active if the molecular plane is inclined relative to the surface.

Perhaps the most impressive recent development in TERS is the spectromicroscopic mapping of an individual porphyrin molecule with sub-nanometer lateral resolution (Figure 1 c).[10] When imaged at low wavenumbers around 800 cm^{-1}, the molecule appears darker in the center than at the periphery, which means that the respective low-frequency modes are preferentially localized at the periphery. Imaging at higher wavenumbers makes the center appear brighter, because the porphyrin core contributes more to the higher-frequency vibrational modes. The lateral resolution is similar to that of a topographic STM image of the same molecule (Figure 1 d,e), but the TERS images contain additional spectral information.

To shed light on the physical background of the unprecedented spatial resolution and sensitivity, analogies to broadband femtosecond stimulated Raman scattering, which has a similar spectral profile, and the nonlinear relationship between the incident laser power and the TERS response were discussed.[10] The combination of linear and third-order components in the TERS response suggests that stimulated Raman emission occurs besides spontaneous emission. It is proposed that the field of the nanocavity plasmon induces the stimulated Raman emission.

Whether tip-enhanced Raman spectromicroscopy with sub-nanometer resolution will develop into a standard surface analytical technique that is applicable under less well-controlled ambient conditions remains to be seen. There is certainly great demand for a surface analytical tool for chemical identification with molecular resolution, especially in fields like surface science, catalysis, biochemistry, electrochemistry, molecular electronics, and nanophotonics. But even if the recent improvements[10] in resolution and sensitivity remain limited to low-temperature UHV experiments, they represent an extraordinary breakthrough that is likely to trigger exciting activity in surface science and related areas.

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