

Nanoscale chemical analysis by tip-enhanced Raman spectroscopy

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Abstract

A fine metal tip brought to within a few nanometers of a molecular film is found to give strong enhancement of Raman scattered light from the sample. This new principle can be used for molecular analysis with excellent spatial resolution, only limited by the tip apex size and shape. No special sample preparation is required, and the enhancement is identical at every sample location, allowing for quantitative surface-enhanced Raman spectroscopy measurements. When scanning the tip over the sample surface, topographic information is obtained simultaneously and can be directly correlated with the spectroscopic data. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Imaging techniques are widely used in chemical and biological research, with a spatial resolution down to a fraction of a micrometer provided either by confocal microscopy or near-field optical techniques. Fluorescence imaging is the most frequently used, but requires the sample to fluoresce strongly or to be labeled with a fluorescent dye. This is often not desirable and sometimes not possible. Chemical analysis by vibrational spectroscopy (e.g., Raman) would be superior for identifying the molecular composition of complex materials because it provides much more detailed information and can also be

used under ambient conditions. Raman, however, suffers from a very low scattering cross-section. Surface-enhanced Raman scattering (SERS) is frequently employed to improve the Raman signal intensity by several orders of magnitude [1–4]. In SERS, the sample must be deposited as a thin layer onto a rough noble metal film, an electrode, or colloids. Unfortunately, the SERS enhancement varies across the sample and depends critically on the substrate preparation. This severely limits its applicability and renders quantitative measurements almost impossible.

The effect described here eliminates most of these shortcomings and opens the way for quantitative SERS imaging with ultrahigh resolution. The rough metal film is replaced with a sharp metal tip that is scanned over the sample using scanning probe microscopy (SPM) techniques. This tip provides a large SERS signal increase without the need for depositing samples onto a special substrate.

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2. Experimental

The tip is formed by either evaporating a noble metal (e.g., 10–15 nm silver deposited at a rate of 0.05 nm/s under an argon atmosphere of 10^{-3} mbar) onto an atomic force microscopy (AFM) tip, or directly by electrochemical etching of a thin wire. A commercial scanning near-field optical microscope (SNOM; Lumina, Topometrix) was used as a scanning platform. In all experiments, the 488 nm line of an argon ion laser with an incident power of 1.5 mW was focussed onto the tip from below to excite the enhanced Raman scattering. The scattered light was collected by an oil immersion objective (NA = 1.4) of an inverted optical microscope (Diaphot 300, Nikon) and was either fed into an avalanche photodiode (Hamamatsu) for integrated reflectivity measurements, or into a spectrograph (Kaiser Holospec) coupled to a liquid-nitrogen-cooled CCD (SDS 9000, Photometrics) for spectrally resolved measurements. In this way, a conventional Raman microscopy set-up was coupled with an AFM for synchronized use.

3. Results and discussion

A Raman signal increase of more than 30 times was obtained when the metallized AFM-tip was brought into contact with a thin brilliant cresyl blue (BCB) layer (Fig. 1B) compared to measurements with the tip retracted from the sample (Fig. 1A). Since only a tiny fraction of the illuminated area provides this enhancement (see insets), we can estimate an enhancement factor of more than 2000 in this case, based on an illuminated area of 300 nm in diameter and a tip diameter of less than 50 nm, as observed by scanning electron microscopy (SEM). In an independent control experiment, normal silicon nitride AFM probes were used rather than a metallized AFM tip. No signal enhancement was observed in this case. Fig. 1C demonstrates the scanning capabilities of the set-up by cross-sectional Raman mapping of the boundary of the BCB film to correlate the chemical composition with the topographic image. As can be clearly seen in the contour plots in Fig. 1D and E, the BCB Raman signature at 1655 cm^{-1} reappears at the lateral position corresponding

to an island (lines 10–12), proving that it is also composed of BCB. The increase of signal intensity is only present if the SERS tip is in contact with the sample. The rise and fall of the BCB signal also indicates that no sample has been picked up by the tip.

The surface enhancement always originates from the same metal particle at the tip apex and hence is identical at all sample positions. Quantitative SERS measurements can therefore be performed. An additional and important advantage of the SERS-active SPM probe is its small size, usually below 50 nm in diameter. The enhancement therefore stems from an interaction area that is well below the diffraction limit of the incident laser light. The lateral optical resolution of this method is consequently determined by the size of the probe in the same way as the topographic resolution. As demonstrated in Fig. 1C–E, the correlation of sample morphology and optical data is therefore straightforward. In addition, combination with the multitude of different scanning probe microscopies to obtain detailed and specific information on the sample is also possible.

Instead of metallizing an AFM cantilever, the SERS active probes can also be made directly by electrochemical etching of metal wires. Especially for gold tips, this method worked very well. To control the probe-to-sample distance, a shear-force set-up based on a quartz tuning fork was chosen in these experiments (see inset in Fig. 2). The gold tips used were generally very sharp, with a tip apex diameter below 20 nm as determined by SEM.

Such a tip was used for enhanced Raman spectroscopy on a C_{60} thin film that was drop-coated onto a glass substrate (Fig. 2). The C_{60} Raman signal was easily detected in the presence of the gold tip, whereas virtually no signal was observed without the tip. From signal-to-noise considerations, the signal increase was estimated to be at least 40. Assuming a tip diameter of 20 nm and a laser spot diameter of 300 nm, the tip-induced enhancement was estimated to be larger than 40 000 in this case. Artifacts from adsorbed C_{60} molecules on the tip itself were ruled out by repeatedly collecting data on a blank part of the substrate, where no Raman signal was detected.

The origin of the SERS effect, although still controversial, may be explained by at least two mechanisms [5,6]: electromagnetic and chemical ef-

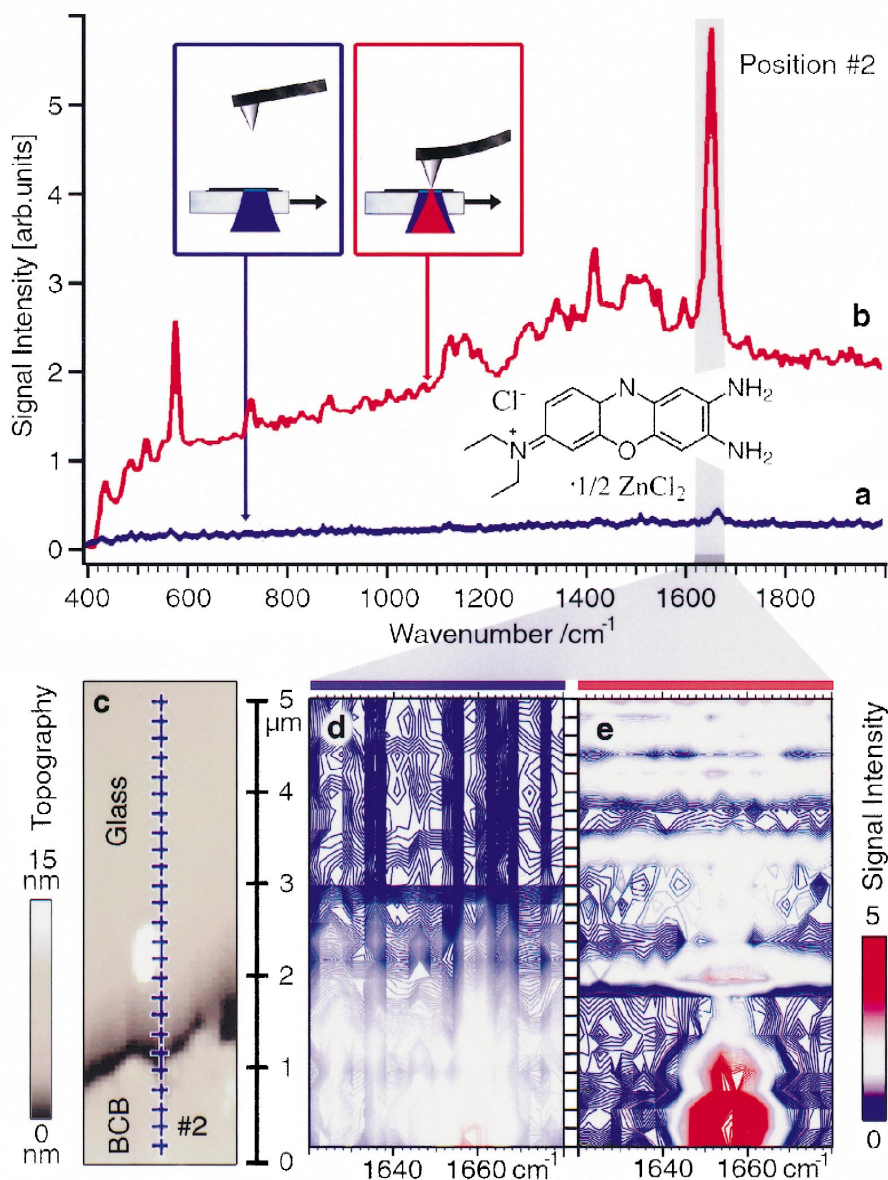


Fig. 1. Tip-enhanced Raman spectra of brilliant cresyl blue (BCB) dispersed on a glass support measured with a silver-coated AFM probe. The two Raman spectra in the upper part were measured with the tip retracted from the sample (a) and with the tip in contact with the sample (b) at the position marked #2 in the topography image (c). Contour plots of 25 Raman spectra (d, e), measured across a sample boundary recorded at the positions marked in (c). Red denotes high intensity, blue denotes low intensity. (d) Corresponds to the Raman signal with tip retracted from the sample. In (d) even very small background signals (i.e., glass, immersion oil) lead to many contour lines, resulting in stripes in the contour plot. (e) Raman signal with the tip in contact with the sample. (Acquisition time: 60 s per spectrum.)

fects. The electromagnetic effect is either due to the increase of the electrostatic field in the vicinity of large curvatures or edges (lightning rod effect) or

due to the excitation of surface plasmon–polaritons by the incoming electromagnetic waves. These electrodynamic resonances are coupled modes of electro-

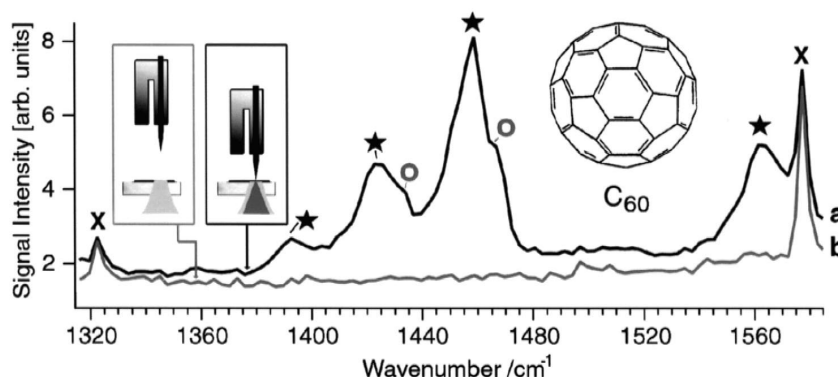


Fig. 2. Raman spectra of C_{60} measured with a tuning fork set-up. Trace (a), gold tip in contact with the sample, trace (b), tip retracted. Circles mark C_{60} normal modes, stars mark C_{60} modes due to charge transfer with the gold tip. The crosses mark Raman bands of the immersion oil. (Acquisition time: 200 s per spectrum.)

magnetic waves and collective electron density fluctuations that are bound to the surface. Both effects significantly increase the surface electromagnetic field compared to that of the incoming radiation field. The chemical effect can result from an increased polarizability of the adsorbate due to charge-transfer or bond formation with the metal.

The main peaks in Fig. 2 (marked with stars) correspond to bands known from SERS spectra of C_{60} on gold [7]. The enhancement and the line shift compared to bulk measurements can be attributed to a chemical effect caused by a charge-transfer interaction between the sample and the gold. In our case we assume the C_{60} molecules to chemically interact with the tip in a similar way. Interestingly, the two peaks near 1440 cm^{-1} have shoulders to the blue (marked with circles in Fig. 2). These shoulders coincide with bands known from bulk C_{60} Raman spectra [8]. We assign them to purely electromagnetically enhanced signals of underlying or neighboring molecules, further away from the probe. The co-existence of both shifted and unaltered bands indicates that both electromagnetic and chemical effects are present in the tip-enhanced Raman spectra of C_{60} . Since the electromagnetic and chemical effects have different interaction ranges, appropriate experiments will allow distinguishing between the two classes of enhancement.

To confirm the lateral resolution, an additional imaging mode of the instrument was used. Instead of scanning the sample, the metallized AFM tip was

scanned while leaving the laser focus and the sample, a homogeneous thin layer of BCB, aligned (see inset in Fig. 3). Because no sample inhomogeneities were detectable by AFM measurements, the observed signal variations can only be caused by the SERS tip. If the integrated reflectivity is measured, such a scan yields an optical map of the AFM cantilever itself (Fig. 3A). For the Raman experiments, only the tip apex (Fig. 3B) is relevant. The Raman active region of the tip can be measured by deconvoluting the laser spot from the observed spot size using a Raman line scan (Fig. 3C). The selected Raman spectra shown in Fig. 3D represent data collected at various positions of the tip either inside or outside of the laser spot. The full width at half maximum of the intensity distributions for the Raman scattered light was measured to be 435 nm . The dimension of the laser spot at the sample surface was 300 nm in diameter, as determined by fluorescence imaging of dye labeled latex spheres in independent experiments. By deconvoluting the intensity distributions for the Raman scattered light and the laser spot, we found that the enhanced Raman signal originates from an area of only $\sim 55\text{ nm}$ in diameter, in good agreement with the 50 nm tip diameter determined by SEM.

This is the best lateral resolution ever obtained in Raman microscopy. There have been several reports on Raman imaging at a lateral resolution around 100 nm using apertured near-field optical tips [9,10]. However, there are a number of limitations with the

aperture SNOM approach. The main limitation for Raman spectroscopy is the low transmission of

SNOM tips, often combined with a low damage threshold ($\sim 5\text{--}10\text{ mW}$). For so-called apertureless

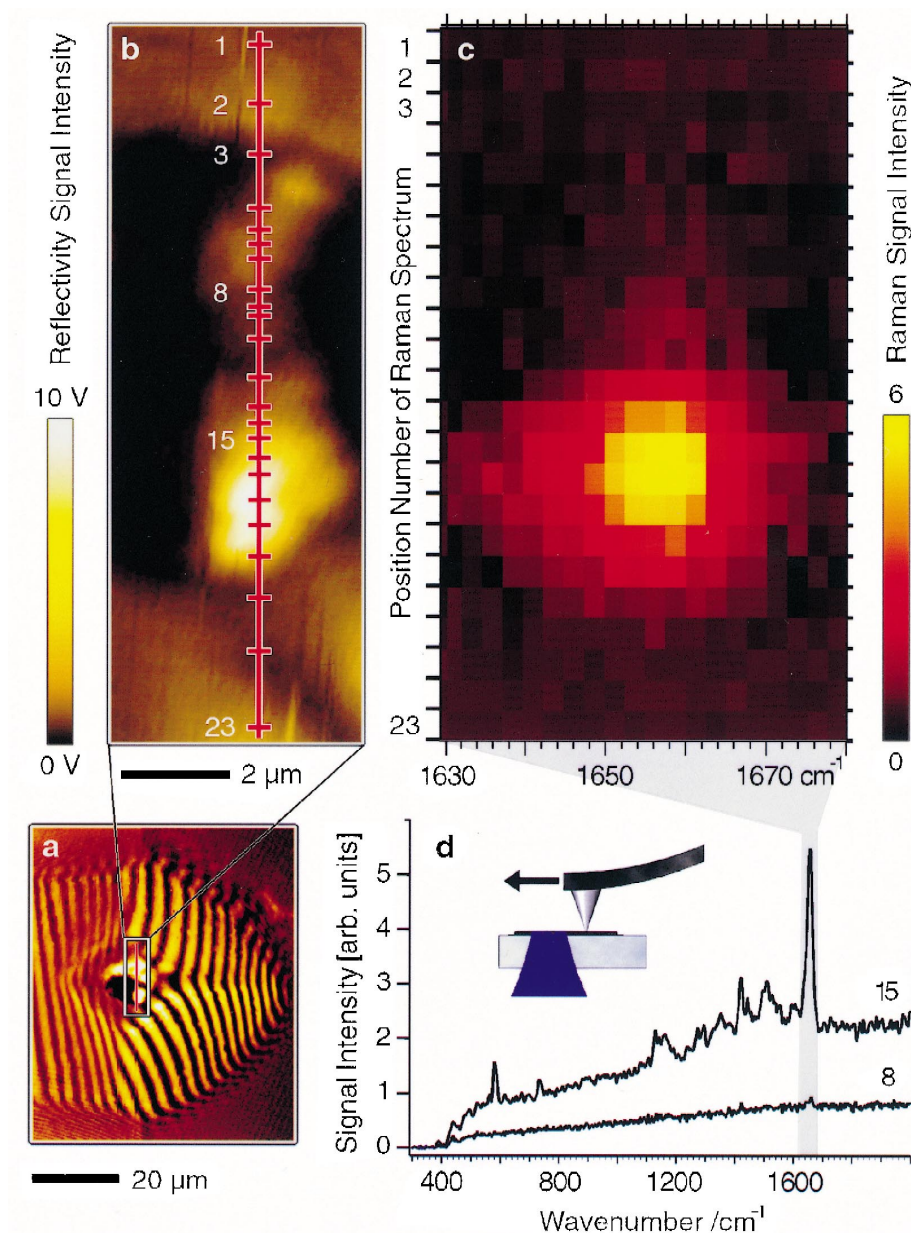


Fig. 3. Ultraflat homogeneous BCB sample measured in tip-scan mode: In contrast to Fig. 1, the same sample spot remains in the laser focus while the tip is scanned (see schematic in inset of (d)). (a) Reflectivity image. The fringes are due to an optical interference between the cantilever and sample surface (the cantilever is not parallel to the sample surface). (b) Zoomed reflectivity image of tip region. Raman spectra were measured along the line in figure (b) at the marked positions; the intensity of the main Raman band between 1630 and 1680 cm^{-1} is displayed color coded in (c). Note that the tip locations in (b) are not equidistant. (d) Two selected overview Raman spectra measured with tip inside (position #15) and outside (position #8) of the laser focus. (Acquisition time: 60 s per spectrum.)

[11–13] near-field techniques like the method described here, this limitation is overcome. In principle, the laser power is only limited by the damage threshold of the sample. This allows much shorter data acquisition times, which is crucial to avoid problems with stability and thermal drifts. By reducing the tip size or when making use of short-range chemical effects, a further improvement in resolution down to few nanometers [14] can be expected.

An interesting perspective for tip-enhanced Raman scattering might be to study the origin of the SERS effect. Because only a single particle is used for the enhancement, the laser wavelength can be tuned to exactly match the corresponding plasmon frequency. Further, there have been efforts to separate the electromagnetic and chemical effects in SERS using specially prepared SERS substrates [15,16]. With the method described here, it is possible to measure the Raman enhancement as a function of tip-to-sample distance ranging from a few ångströms to several nanometers directly. Hence, the tip-enhanced Raman scattering mechanism can be varied between long-range (electromagnetic) and short-range (chemical) enhancement regimes under otherwise identical experimental conditions.

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