



Tip-enhanced Raman scattering: Influence of the tip-surface geometry on optical resonance and enhancement

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ABSTRACT

The tip-sample distance (z) dependence of tip-enhanced Raman scattering (TERS) has been investigated. The intensities of both, the Raman lines and the broad TERS background, exhibit strong decays with increasing z , which are nearly complete within 10 nm withdrawal of the STM tip in z direction. Interestingly, the maximum of the broad Lorentzian-shaped TER background is substantially blue shifted in energy with z . This effect is ascribed to a corresponding blue shift of the energies of localized plasmon modes upon tip retraction. Both experimental results fit very well data of a simple theoretical near-field model.

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1. Introduction

Tip-enhanced Raman spectroscopy (TERS) belongs to the most intriguing recent developments in optical spectroscopy [1–15]. This approach combines optical vibrational spectroscopy with scanning probe microscopy by using an illuminated fine end of a tip as a near-field probe that enhances the sensitivity and spatial resolution of optical processes to unprecedented levels. If, for example, the Au tip of a scanning tunneling microscope in tunneling position over a Au substrate is sideways illuminated by p-polarized light of a He–Ne laser, localized surface plasmons (LSP) are strongly excited in the nano-cavity formed between tip and substrate. The corresponding electromagnetic (EM) near-field in the tip-substrate cavity is highly enhanced in comparison to the EM field of the incident laser. This increases the Raman scattering of an adsorbate by many orders of magnitude and, thus, enables to detect and spectroscopically identify even a small number of molecules adsorbed on atomically smooth single-crystalline metal surfaces. Due to the strong localization of the electromagnetic near-field around the tip apex, the Raman signal stems from a small region with its size defined by the size of the tip apex. Thus, TERS combines excellent spectroscopic sensitivity with high spatial resolution in the nanometer range. Experimental results for many

different kinds of optically resonant and non-resonant adsorbates on different surfaces indicate that TERS is a generally applicable spectroscopical tool [10,11,13,15,18–20]. In contrast, conventional surface-enhanced Raman spectroscopy (SERS) depends strongly on the kind of adsorbate and the nature of the substrate. It is mainly restricted to roughened surfaces of Ag, Au and Cu. Weak SERS is also found for rough Pt, Rh or Ni surfaces [21–25].

Although several theoretical concepts study the evolution of the LSP with optical and geometrical properties of the tip-surface gap [5,26–30], experimental evidence for the amplification mechanism and the importance of the LSP for the enhancement process is rather scarce. Therefore, in this communication, we revisit the tip-sample distance dependence of TERS with the emphasis to correlate experimental data with theoretical results. Experimental results concern the TERS distance dependence of guanine and ClO_4^- ions coadsorbed on a monoatomically flat Au(111) surface [16]. The intensities of the discrete Raman bands of the adsorbates decrease steeply by almost two orders of magnitude upon retracting the tip only about 20 nm. Together with the lateral resolution, which was estimated to about 20 nm [11], this elucidates the high spatial resolution of TERS not only parallel but also perpendicular to the surface [16]. The measurement of the TER intensity over a range of more than 20 nm of tip-surface distances (in sub-nm steps) enables the quantitative comparison with recent calculations [17]. In addition, we complement these calculations, which are based on finite element methods, with a simple model of the

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distance dependence based on classical electrodynamics, as used for the interpretation of surface-enhanced Raman scattering. To a very good approximation, the tip-sample distance dependences of both the TER intensity and of TER background are governed by a power law of the type $I_{TERS} \propto z^{-10}$, where z is the tip-sample distance.

The concept of LSP for the explanation of TERS is further substantiated by the behavior of the background of the TERS spectra during tip retraction. This exhibits a Lorentzian band shape and a remarkable blue shift of its band energy with increasing gap width. This broadband luminescence of the background has been reported to arise from luminescence of the adsorbate enhanced by surface plasmon modes of the tip-metal cavity [31–33]. The emphasis of this paper is to support this concept by showing that the experimentally observed energy shift of the background maps very well the energy shift of localized surface plasmons predicted theoretically by Rendell and Scalapino [34,35]. Further support in this direction is given by light emission experiments performed on a Au-tip Au-substrate tunnel junction, showing an LSP-mode structure that can also be analyzed following the approach of Rendell and Scalapino [34,35].

Our results provide direct experimental evidence for the near-field character of the electromagnetic field excited in the tip-surface cavity and, therefore, strongly underlines the electromagnetic nature of the tip-enhancement mechanism.

2. Experimental

A detailed description of the TERS principles and the experimental set-up is given elsewhere [9–12]. The experiments are performed on flat Au(111) single crystal surfaces prepared by flame-annealing [36]. To coadsorb guanine/perchlorate at a Au(111) surface, the Au crystal is immersed into an ethanolic solution of 10^{-3} M guanine and 10^{-1} M HClO_4 for 1 hr. Afterwards, the sample is rinsed with ethanol to remove multiple adlayers. The coadsorption of ClO_4^- and guanine leads to a layer of coadsorbed molecules with (sub-)monolayer coverage. A He-Ne laser beam (632.8 nm, 3 mW, indicated lower power is reduced with gray filters) is focused to a spot of about 2 μm diameter and the STM tip is placed into its center. During tunneling at 1 nA current and 150 mV bias voltage, the tip rests at about 1 nm distance above the sample surface. Tip radii of approximately 20 nm are reproducibly obtained by etching a 0.25 mm diameter gold wire in a 1:1 mixture of EtOH and HCl_{fume} [12]. To measure the tip-sample distance dependence of the TER signal, the feedback loop of the STM is gated and the vertical position of the tip is controlled by a programmable ramp generator. Tip retraction with a constant speed is started 5–10 s after gating the feedback loop. From the small intensity fluctuations of the TER signal during the initial holding time without tip retraction, the vertical stability of the tip is estimated to be about 0.3 nm. During the retraction of the STM tip (using retraction speeds from 0.16 to 1.6 nm/s), a series of Raman spectra (1 s integration time) is taken at intervals of about 1.5 s (see Fig. 1).

3. Results and discussion

3.1. Experimental tip-surface distance behavior of TERS

Both adsorbed species under study, the guanine molecules and the ClO_4^- ions, show TER scattering. With the tip in tunneling position, for guanine a number of weak characteristic bands are measured, while perchlorate shows a characteristic intense band at 930 cm^{-1} , assigned to its A1 breathing mode (Fig. 2, curve (a)). In contrast to the guanine bands, which decrease slowly with pro-

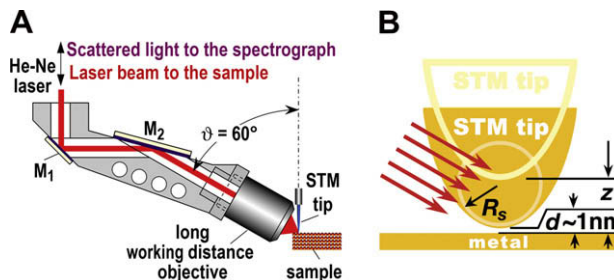


Fig. 1. Scheme for tip-enhanced Raman spectroscopy. Left: Side-illumination approach; right: illuminated STM tip at various distances z . Minimum distance: $d \sim 1$ nm.

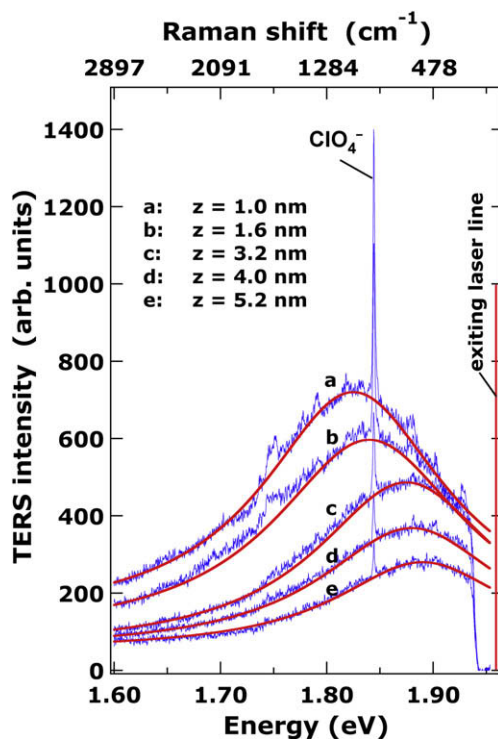


Fig. 2. TER spectra for ClO_4^- and guanine coadsorbed at Au(111) for different distances z of the STM tip to the surface: Five spectra from a series of 15; (a–e): $z = 1$ to ~ 5.2 nm, $\Delta z \sim 1$ nm. Solid red curves: fit to the background using a Lorentzian profile. Retraction speed: 0.16 nm/s. Smooth red lines: background curves from a Lorentzian fit. Red vertical line at 1.9592 eV (15803 cm^{-1}) is the energy of the laser line. After Ref. [16].

ceeding illumination due to progressive photodegradation or photodesorption, the ClO_4^- band intensity remains constant during the illumination. Therefore, in the following the recording of quantitative TER intensity vs z distance profiles are based on the intensity measurement of the perchlorate band. (Note that the bands of coadsorbed guanine molecules decrease similarly with increasing z distance.) In the absence of the STM tip, at flat, adsorbate-covered Au(111) surfaces, no characteristic Raman bands could be identified with integration times up to 100 s. In addition to discrete Raman bands characteristic for either adsorbate, the TER spectra exhibit a strong, very broad Lorentzian-shaped background (bg) (see red fitting curves in Fig. 2). At $z = 1$ nm, the bg maximum is located at an energy of 1.836 eV (corresponding to a Raman shift of about 1075 cm^{-1}) and has a half width of about 0.19 eV (650 cm^{-1}). Evidently, the inelastic bg contains by far more integral intensity than the sum of all other discrete Raman lines. The intensity of the broad bg also depends on the adsorbate coverage; thus,

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