

## TIP-ENHANCED RAMAN SPECTROSCOPY: TOPOGRAPHIC AND CHEMICAL INFORMATION ON THE NANOSCALE

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Tip-enhanced Raman spectroscopy (TERS) is based on the excitation of collective electron oscillations in a metal SPM tip: By focussing a laser onto the very end of the tip apex, localized surface plasmons (LSPs), or gap modes, are excited, which create a very strong near-field between tip and metal sample, a 'hot spot'. Only the molecules located in this hot spot contribute to the strong Raman signal. In this way, the usually very low normal Raman scattering cross section is overcome and vibrational analyses of a small amount of species, like an adsorbate monolayer, can be carried out. In addition to the Raman chemical fingerprint of the target species, SPM images can be simultaneously obtained, which show the topography of the sample (Fig. 1).

A tip-substrate cavity as present in TERS experiments can be considered as a quite simple, but effective photonic unit with a tunable LSP resonance providing huge enhancements for optical processes. We have investigated the dependence of the scattering signal on the tip-sample distance.<sup>[1,2]</sup> The gap is formed by a conical Au STM-tip of 20 nm radius located at piezo-controlled distance above an atomically smooth Au(111) substrate. For increasing tip-sample separation, we observe a remarkable blue-shift of the spectral background maximum that is ascribed to an energy shift of the LSP resonance. In addition, we report on a steep background and Raman intensity decrease within 5-10 nm tip retraction that highlights the underlying near-field enhancement mechanisms of TER spectroscopy.

Our group recently demonstrated the sensitivity of TERS for the detection of smallest sample amounts both, in air and in UHV.<sup>[3,4]</sup> TER spectra obtained from dye samples in resonance with the laser excitation energy, like malachite green isothiocyanate or brilliant cresyl blue, allow the straightforward identification of the target species down to the single-molecule level. In order to determine the detection limit for nonresonant species, picomolar quantities of the DNA base adenine adsorbed at Au(111) were probed. We find an approximately 100 times lower Raman enhancement and detection limit, which is attributed to the absence of a resonance contribution to the overall enhancement.<sup>[5]</sup>

### Referencias:

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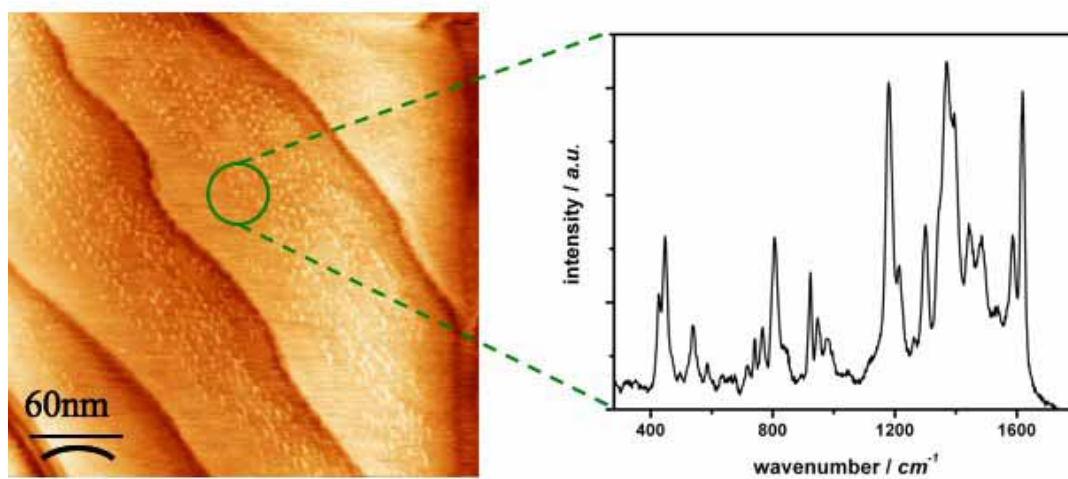


Fig. 1: Topographic and chemical information of the sample can be obtained simultaneously with TERS (left: STM image of a Au(111) surface covered with adsorbate molecules; right: TER spectrum of the small number of molecules located in the hot spot).