

# Chapter 1

## Introduction

Tip-enhanced Raman spectroscopy (TERS) is an elegant combination of two Nobel-prize winning discoveries in the natural sciences:

In 1922, the Indian physicist Sir Chandrasekhara Venkata Raman published his work on the "Molecular diffraction of light". Only eight years later, he was awarded the Nobel prize for his discovery of inelastic scattering of photons,[1–3] called after him the Raman effect. When light is scattered by a molecule, most photons are elastically scattered, i.e. they have the same energy as the incident photons (Rayleigh scattering). Only a very small fraction is scattered at optical frequencies different from the incident photon energy (Stokes and anti-Stokes scattering), where the difference in energy is used for rotational or vibrational (de-)excitation of the molecule. As the measured energy differences are characteristic for the molecule, Raman spectroscopy has become one of the most important tools in analytical chemistry and physics.

Gerd Binnig and Heinrich Rohrer were awarded the 1986 Nobel prize in physics for their invention of the scanning tunneling microscope (STM).[4–7] To probe the electron density of a (semi)conductive surface and visualize its topography, an atomically sharp metal tip is brought into close proximity ( $\sim 1$  nm) to the sample. A voltage applied between tip and sample allows electrons to "tunnel" between the two metal contacts, the resulting current being exponentially proportional to the tip-sample distance. The movement of the piezo-crystal which maneuvers the tip is correlated to the surface topography if the tunneling current is kept as a constant value and allows

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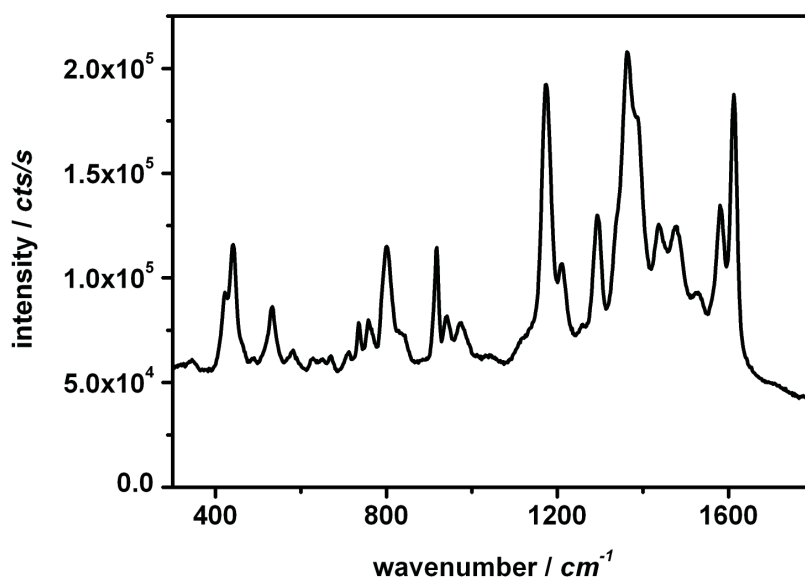
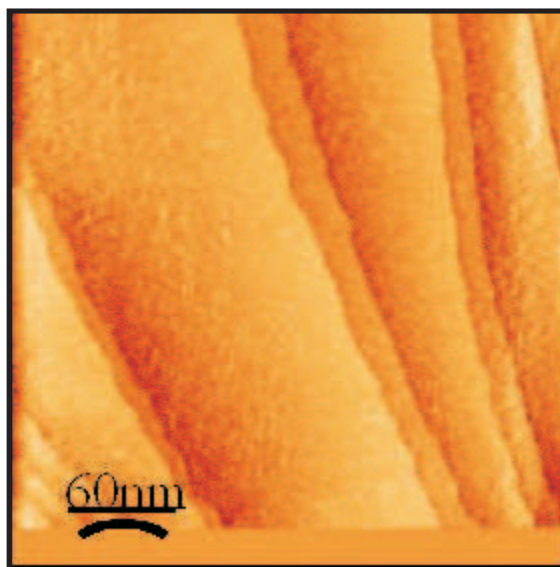
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the imaging of the surface structure with molecular or even atomic resolution.

The combination of these two nowadays routinely employed techniques to tip-enhanced Raman spectroscopy has created a new tool that meets a long-awaited goal in surface science, namely, it enables the correlation of topographic and chemical information of the same sample region at nanometer scale (Fig. 1.1).

The first approach to scanning near-field optical microscopy (SNOM) followed the theory of diffraction of light at small holes. With apertures significantly smaller than the wavelength of the incident light, the Abbe barrier limiting the optical resolution to approximately  $\lambda/2$  is penetrable: The creation of evanescent waves at a very narrow aperture lowers the optical resolution capability tremendously to several tens of  $\lambda$ . [8–11] The fabrication of smaller and smaller apertures in order to increase the optical resolution, however, suffers technical limitations. An elegant solution to further improve the optical resolution of SNOM was to employ an apertureless metal probe instead. Already in 1985, Wessel made use of a Ag particle that was scanned across a surface – apertureless SNOM (aSNOM) was born. [12] He predicted that the difficulties he encountered in controlling the particle-sample distance should be overcome by employing a metal STM-tip in tunneling distance as a field enhancer. Zenhausern *et al.* presented the first enhanced fluorescence SNOM study employing an atomic force microscope (AFM) tip in 1994, claiming atomic optical resolution, [13, 14] and in 2000, Zenobi and coworkers introduced the combination of a Raman spectrometer and an atomic force microscope (AFM). [15]

The use of an illuminated scanning probe tip to greatly enhance Raman scattering from the sample underneath the tip is one of the most intriguing developments in optical spectroscopy, and the increasing number of publications per year shows that the importance of this technique is recognized among chemists, physicists and biologists alike. Nevertheless, the enhancement processes allowing for tip- and surface enhanced Raman spectroscopy are still not fundamentally understood. The spatial near-field distribution at the scattering particle is not ascertained, and pushing the detection limit towards the single molecule level is an important target. The currently employed experimental set-up leaves space for improvement, too: Up to now, due to the difficult optical alignment, TERS has always been carried out in air, not yet in ultrahigh vacuum (UHV) or in electrochemical environment.



**Figure 1.1:** The combination of scanning probe microscopy and Raman spectroscopy to TERS provides topographic and chemical information of the investigated sample region at the same time.

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In this thesis, we treat some of the above-mentioned problems and add another piece to the TERS puzzle. Problems and difficulties encountered are presented, together with possible solution routes. An introduction to the development and the underlying phenomena of TERS is found in Chapter 2. The basic principles of interfacial Raman studies are illustrated and a brief discussion on the origin of the enhancement and the nature of localized surface plasmons is presented. In addition, theoretical approaches to the lateral and vertical near-field distributions are summarized, which are referred to in the discussion of the tip-retraction experiments in Chapter 4. The main body of the thesis is divided into three parts:

The first part (Chapter 4) deals with the physical properties of the TER experiment. Carrying out tip-retraction studies, the behaviour of Raman bands and spectral background with varying tip-sample distance and their different nature are analyzed. The changes in the localized surface plasmon (LSP) or gap resonances are visualized and discussed according to theory.

Studies on the chemistry of species in and off optical resonance with the excitation laser line adsorbed at atomically smooth single crystals are presented in the second part (Chapter 5 and 6). The triaryl dye malachite green isothiocyanate (MGITC), whose absorption resonance coincides with the excitation laser frequency, is investigated at different surface concentrations. It is remarkable that we have indeed reached the single-molecule detection limit with Raman spectroscopy, whereas only forty years ago, Raman spectroscopy of (sub)monolayer adsorbates was thought impossible because of the extremely low normal Raman cross section. The TER spectra of the four DNA bases adenine, cytosine, guanine and thymine (all off resonance) adsorbed at Au(111) are investigated. The assignment of their Raman fingerprint according to normal and surface-enhanced Raman spectra taken from the literature allows the unequivocal identification of the nucleobases and gives first insights on their adsorption behaviour at Au(111).

In the third part (Chapter 7), technical aspects of TERS are discussed and an outlook on interesting TERS research routes is given by presenting a newly designed and built experimental set-up. Its much more compact design is expected to largely facilitate working upon much better defined conditions in electrolyte under potential control or in UHV.