

Chapter 8

Summary

Tip-enhanced Raman spectroscopy (TERS) is a young surface science technique that makes use of the excitation of localized surface plasmons in a Au STM tip in tunneling contact above a sample surface and of the strong near-field created thereupon in the tip-sample gap. In this thesis, physical, chemical and technical aspects of TERS have been treated in order to improve the understanding of the underlying plasmon resonance phenomenon and to highlight the wide variety of application possibilities.

Tip-sample distance dependence In order to determine the vertical extension of the near-field underneath the tip apex in the tip-sample cavity, the dependence of the TER band and background spectral features on the distance between tip and substrate is analyzed. Guanine and perchlorate are coadsorbed at Au(111). We monitor the perchlorate ring breathing band at 930 cm^{-1} because of its greater stability in comparison to the initially weaker and less stable guanine peaks. For typically employed tips of 20 nm radius, we find an intensity drop of the Raman band to nearly zero within 15 nm retraction length. This highlights the short-ranged nature of the plasmon-created electromagnetic near-field responsible for the strong scattering enhancement.

TER (and also SER) spectra are often presented after background-correction in the literature, because the background is of no importance for the Raman band analysis

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and its origin is still under discussion. As the omnipresent spectral background represents the major part of the collected scattering intensity, it is worth investigating it. The background decreases proportionally to the band intensity up to 5 nm tip-sample distance and then levels off to about 10 % of the integrated intensity recorded with tip in tunneling distance. It exhibits a pronounced energy maximum attributed to the gap resonance. The blue-shift of the plasmon resonance with increasing tip-sample distance, long since predicted by theory, was observed for the first time experimentally.

Species in optical resonance: MGITC The practicability of single-molecule detection with TERS is demonstrated. Enhanced Raman spectroscopy prevails over usually employed fluorescence spectroscopy as a SM analytical tool, because no chemical modification (labelling) of the target species is needed and Raman spectra provide much richer information than fluorescent spectra, at similar photon count rates. The investigation of dye molecules in resonance with the excitation laser line adsorbed in different concentrations at Au(111) is carried out. Malachite green isothiocyanate gives rise to an unambiguous TER spectral fingerprint in the whole tested concentration range, even at surface concentrations lower than 0.7 pmol/cm². Single dye molecules can be recognized as nanometer-sized dots in the corresponding STM images. The correlation of these images with the recorded TER spectra strongly supports the conclusion that we are indeed detecting single dye molecules with TERS. In contrast to SM SER studies published in the literature, where statistics are employed to "prove" SM detection and no images of surface morphology are presented, we can rely on the combination of spectral and topographic information.

Species off optical resonance: DNA bases In order to demonstrate the versatility of TERS and its applicability for monitoring biochemically relevant species, the four DNA bases (adenine, cytosine, guanine, thymine), which are not in resonance with the incident laser line, are tested. The characteristic vibrational spectral fingerprint of each DNA base obtained with TERS allows the straightforward identification of the molecules at concentrations down to 0.8 nmol/cm². This elementary study opens up routes towards the label-free investigation of nucleosides or whole DNA strands. First conclusions regarding the adsorption behaviour of the bases at Au(111) are drawn: Adenine-Au interactions seem to be quite strong upon our experimental

conditions, in contrast to cytosine, which seems to be more weakly bound, likely in its enol form. Guanine TER spectra exhibit features that can be assigned to deprotonated and protonated species, as well as to nanocrystals, displaying the difficulties and uncertainties in the sample preparation for this nucleobase. In agreement with the literature, our thymine TER spectra suggest that, upon our working conditions, the molecule binds to gold with its oxygen atoms rather horizontally at the surface.

New set-up design A new TERS set-up to overcome several disadvantages of the old set-up has been designed. Using a parabolic mirror instead of an objective lens as focussing device, the central part of the new apparatus is much more compact than the old one. The main aim of reconstructing the TERS set-up was to enable TERS measurements upon electrochemical conditions and in UHV to overcome the problem of working upon ill-defined ambient conditions, where problems of contamination and degradation of the species by oxidation are inherent. Regarding the electrochemical TERS project, potential control of the substrate is reached with help of a three-electrode set-up in electrolyte as usually employed in electrochemical H-cell or STM measurements. Controlled precise variation of the surface potential allows to deliberately influence adsorption/desorption processes or adsorbate-metal interaction and molecular orientation with respect to the surface, which can be directly monitored by TERS. In addition, the new TERS set-up was designed to be, with some adaptations, also suitable for a UHV TERS set-up (PhD project of Jens Steidtner, Fritz Haber Institute).

