6. CONCLUSIONS

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In this thesis two topics have been treated: the Tip Enhanced Raman Spectroscopy (TERS) and the Light Emission (LE) from tunneling junctions. TERS promises to overcome a number of limitations inherent to the Surface Enhanced Raman Spectroscopy (SERS), offering also the perspective of single molecule sensitivity. LE can deliver further information that is directly connected to TERS, *i.e.,* the optical properties of the tip-metal substrate junction and their dependence on the junction parameters. Both TERS and LE experiments are based on a Raman microscope coupled to a scanning tunneling microscope. The illumination of the junction leads to the excitation of localized surface plasmon modes and, consequently, to a field enhancement. Therefore, a huge enhancement of the Raman process occurs, which is highly localized below the tip. The LSP can be also excited by tunneling electrons with suitable energies; their radiative decay can be monitored and analysed.

Stoeckle *et al.* first reported in 2000 the tip enhancement for the Brilliant Cresyl Blue dye using a silver coated AFM tip over a glass side. The STM tip-metal substrate configuration adopted by us has a number of advantages: i) quenching of the fluorescence for the adsorbate, ii) better distance control, iii) a stronger confinement of the excited LSP compared with that produced by the tip alone.

The focus of this work was not only to develop further the TERS approach but also to assess how generally applicable it is and to what extent single molecule detection is a realistic perspective. Two experimental realizations have been tested, differing in the way of illumination, a) by an inverted microscope illuminating the tip from underneath through a thin metal film and b) by a microscope oriented 60° to the surface normal, permitting side illumination of the tip. Smooth and rough gold surfaces were used. In the former case, only TERS is operative; in the second, TERS combines with SERS. At smooth surfaces the TERS enhancement is too weak, thus adsorbates such as dyes (BCB) exhibiting resonant Raman

scattering at the excitation wavelength are needed. At rough surfaces, also small, transparent molecules, such as cyanide ions can be studied because of the giant combined TERS and SERS enhancement.

The effective enhancement of the Raman signal provided by the tip amounts to up to roughly four orders of magnitude. Similar values have been reported by different groups. Theoretically estimated enhancements factors (up to 10^{12}) are many orders of magnitude larger, if the exciting source is located in the Near-IR region. On the other hand, an estimation of the number of the dye molecules providing most of the TERS signal gives an ensemble of ~ 1000 molecules. These are located in the central zone below the tip, where the field enhancement is largest. At the present stage of TERS, the gap to single molecule spectroscopy is only 3–4 orders of magnitude. The other system studied by TERS is CN^- adsorbed at roughened gold films. A striking result is a frequency shift of the cyanide ion stretch vibration under tip enhancing conditions. This is related to a different sampling between TERS and SERS of the adsorbate covered rough surface, where TERS has a superior spatial resolution, proved in this case, by the lower inhomogeneous broadening of the band.

STM light emission spectra show that the excitation of the LSP modes inside the gap takes place more easily at energies much below the surface plasma frequency. The detection of multiple peaks in the emission spectra may be interpreted considering that the tip and the metal film form a resonant cavity into which electromagnetic modes of increasing order may be confined. A shift in the LSP resonances is observed upon changing the tunneling parameters (current and bias voltage) since these directly define the cavity size. A theoretical model developed by Rendell and Scalapino where the tip apex is approximated by a sphere was used to reproduce the emission pattern. The same model predicts that very intense emission should take place in the NIR. Unfortunately, this region is, at the moment, not accessible to us, mainly due to the inadequacy of the detector.

Outlook

The parameters that mostly influence the enhancement factors are the distance of the metal tip from the surface, the tip radius size, the direction of illumination and the exciting laser frequency. According to the model of Demming *et al.*, the smaller the gap, the higher is the field intensity. Moreover, as for SERS, these enhanced electromagnetic fields should decay evanescently with increasing distance of the scatterer from the particle. The influence of the tip height from the surface, in other words, the distance dependence of the tip enhancement has still to be properly investigated over a region of several nm. Also, a better control of the tip fabrication procedure, in terms of reproducibility of a (smooth) tip shape and smaller apex sizes (as considered in the models) may lead to higher enhancement factors.

A further valuable application of TERS, that is actually already feasible, is to record the topography of a SERS active substrate in the Raman scattered light. The localized field at the tip may be exploited to enhance the rate of other optical processes. Recently, enhanced Second Harmonic Generation (SHG) at the apex of a gold tip has been reported [139]. Regarding the goal of approaching the level of single molecule Raman spectroscopy, the predicted maximal enhancement factors are required, but these will be obtained only when properly exciting the optical resonances of tips with radii as small as 20 nm or even less. Therefore, STM-light emission and TERS studies should be also extended into the (near) IR region.