

1. INTRODUCTION

1

Single molecule spectroscopy [1–3] is a recent topic that has in the last ten years attracted considerably the interest of scientists from different fields. Biology, medical science and microengineering could all profit from new instruments working at ambient conditions with single molecule sensitivity. The possibility to avoid the averaging over an ensemble of millions or more molecules has been experimentally demonstrated, for example, by laser induced fluorescence of dye molecules in the liquid phase [4] and also by Raman spectroscopy at colloidal nanoparticles [5–8]. Scanning Tunneling Microscopy (STM) and other related local probe microscopies as Atomic Force Microscopy (AFM) and Scanning Near-field Optic Microscopy (SNOM), while able to achieve atomic imaging, do not provide enough chemical information. What is seen is not always straightforwardly identified. Not even fluorescence data yield sufficient spectral details; moreover, the excitation of fluorescence in the visible domain is limited to specific molecular systems.

On the other hand, vibrational spectroscopy (Raman, Infrared and recently Sum Frequency Generation) are powerful tools for the identification of molecules. The picture of a single molecule vibrating is mostly called to the mind by chemists, when analyzing a spectrum, almost each band being related to a particular normal mode of vibration of the molecule. For these techniques the exciting source and detecting unit are located far away from the sampled region. Far-field optics defines the resolution limit to half the wavelength of light. By the use of confocal microscopes and near-UV light, spot sizes of 0.2-0.3 μm may be obtained. Hence, millions of molecules constitute the investigated ensemble. Probing a smaller number of molecules (down to the single molecule level) is mainly demanded by surface science. For a clear insight into the huge variety of processes taking place at surfaces, from physisorption to complex catalytic reactions, it is critical to reach beyond the optical resolution limit with new techniques. The behaviour of each molecule is often dramatically influenced by its local chemical environment; as well known, molecules adsorbed at different sites can display different reactivity.

This implies that different binding energies and bond strengths are characteristic for adsorption at different sites. Therefore, when probing a disordered system, such as a catalytic surface, the chemical reactions will be correspondingly complex (with respect to reaction rates and reaction pathways). This demands analytical tools with spatial resolution in the nm region. In other words, one would like to have a technique that provides the resolution of the scanning microscopy and the rich spectral information of a vibrational spectroscopy. The objective of this thesis goes along this direction: to develop an unique spectroscopy with high spatial resolution by combining the scanning tunneling microscopy with Raman spectroscopy.

Initially, Raman spectroscopy was not considered to be a surface sensitive technique. Until no more than thirty years ago, it was mainly regarded as inadequate to study the processes taking place at solid-liquid or solid-gas interfaces. Considering the intrinsic low probability of the Raman event and the small number of Raman scatterers forming a single adsorbed layer on the surface, their signal was doomed to remain below the detection limit or buried under the signal of the bulk phase, unless highly porous systems, such as zeolites were used as substrates [9]. By applying a cyclic potential step to a silver electrode, in an attempt to increase the effective area of the surface and, thus, the number of adsorption sites available to pyridine molecules, Fleischmann and Hendra, in 1974 [10], recorded unexpectedly high intensity of the Raman scattered light. Only three years later, van Duyne [11] rediscovered this effect and offered the correct conclusion that the differential Raman cross section of molecules in the liquid or gaseous phases receive an huge enhancement upon adsorption on rough noble metal surfaces. Surface Enhanced Raman Spectroscopy (SERS) was born. The origin of this physical effect involves, on one hand, the excitation of localized plasmon modes at illuminated irregular surfaces, leading to a local electromagnetic field (more precisely, a near-field) enhancement, on the other hand, a sort of resonance Raman effect with charge transfer transitions between the metal particle and the coordinated molecule. More recently, a further, rather old concept, that is the inhomogeneity of the (catalytic) process at irregular surfaces, was carried forward to explain

the enhancement of the Raman signal, or more precisely, to the enhanced field distribution across the rough surface. For each wavelength, the enhanced electromagnetic fields localize strongly only at certain structures, bumps or cavities with sizes varying between 10 nm and several hundreds nm, denoted as *hot spots*. Though the whole group of hot spots represents a (very) small fraction of the surface, it provides a superior enhancement; therefore, molecules adsorbed at those sites produce most of the Raman signal, while the majority of molecules adsorbed within the laser focus are comparatively inactive. Thus, a much smaller ensemble of molecules than supposed just by taking in account the laser spot size is actually being monitored.

SERS may be regarded, together with SNOM, as a near-field probe technique. The exciting electromagnetic field is no longer brought to the sample by macroscopic optical elements, such as lenses or microscope objectives; instead, the exciting field is delivered by nano-objects, such as tapered fiber tips (aperture SNOM) or small illuminated metal particles (apertureless SNOM and SERS). Thus, only a small fraction of the illuminated molecules are exposed to the evanescent near-field. A major drawback of SERS is that the (more or less) randomly distributed active spots are needed for a giant field enhancement of the Raman cross section. Due to this prerequisite the SER spectroscopy can not be applied to smooth surfaces. Another limitation must be noted: strong fields are generated only at certain metals, such as silver, gold and copper. Should the studied molecules be adsorbed at an atomically flat substrate, then, in order to obtain a signal, a resonance Raman enhancement (of the adsorbate itself) and/or an external field enhancement would be necessary. The latter may be delivered by a single metal particle of suitable size with the associated enhanced field, resembling a sort of single external hot spot, approaching from above as closely as possible to the adsorbate layer. An illuminated STM metal tip actually matches with this requisite. The tip apex represents, in a way, a nano-antenna, that mediates between the external and the near-fields. Therefore, only the molecules located underneath the scanning tip are probed by this process, which is therefore denoted as *Tip Enhanced Raman Spectroscopy* (TERS).

This experimental work is divided in six main sections. The first section is this brief introduction, describing the motivation to develop the TERS approach. The first part of chapter two will deal with the fundamentals of the Raman effect and the surface enhancement of the Raman scattering. The main features of surface plasmon modes will also be introduced, together with the peculiar properties resultant from their confinement into small structures. Then a more detailed overview of the concepts and theory that moved us from SERS to TERS is given. The theory of STM-Light Emission (STM-LE)¹ makes up the second part of chapter two. It will be shown that the two sets of experiments, TERS and STM-LE, are intimately related. A confocal Raman microscope and an in house built STM facility for measurements in air were adapted in order to focus the laser on the tunneling tip and to record the Raman scattered light from the adsorbed molecules influenced by the near-field of the tip. The description of this experimental set-up is presented in chapter three.

The results on TERS and light emission are then reported in two following sections. Chapter four illustrates clearly that TERS is a new approach for locally studying molecules at surfaces, having also promise for single molecule detection. Two Raman scatterers were studied: the dye molecule Brilliant Cresyl Blue (BCB) and cyanide ions, both adsorbed at thin gold films. Both smooth and rough surfaces were tested. The external enhancement was provided by electrochemically etched silver tips illuminated, in two different configurations, from the side or from below (through a thin metal film). With the fifth chapter an attempt is made to bridge the gap between the theoretically predicted enhancement factors and the experimentally observed values by studying the optical response, *i.e.*, the light emission, of the enhancing metal unit. The STM light emission measurements yield direct informations on the energies of the plasmon modes localized at the tip-metal substrate junction and their dependence on the junction parameters. The same type of modes are excited by the laser and are responsible for the local tip enhancement.

¹Localized surface plasmon modes are not only excited by light but also by inelastically tunneling electrons at the Metal-Insulator-Metal (MIM) junction formed by the tip and the surface.

In the concluding sixth chapter, an overview of the results of this work is given and some possible future developments are proposed.

