

# Tip-enhanced Raman spectroscopy on electrochemical systems

Thomas Touzalin

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### Sorbonne Université

Ecole doctorale 388 Chimie Physique et Chimie Analytique Laboratoire Interfaces et Systèmes Electrochimiques (LISE), UMR8235

## **Tip-enhanced Raman spectroscopy on electrochemical** systems

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Thèse de doctorat de chimie physique

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# Tip-enhanced Raman spectroscopy on electrochemical systems

Thomas TOUZALIN

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### Introduction

At electrochemical interfaces, complex and interlinked phenomena involving electrons and protons transfers, ions exchanges or accumulation take place. These are of major interest in a wide range of domains in biology, physics and chemistry such as energy storage and conversion, materials synthesis and transformation, corrosion science, analytical chemistry, sensors, molecular assemblies on surfaces or nanosciences.

The understanding of the mechanisms of electrochemical reactions can be achieved with advanced electrochemical techniques such as cyclic voltammetry (CV) or electrochemical impedance spectroscopy (EIS) among others that can provide information on the kinetics of the reaction and the structure of the electrochemical double layer. [1] Classical electrochemical experiments can be interpreted with the usual simple interconnected variables, namely current, potential and charge. However, these purely electrochemical approaches do not give access to the chemical structure of the material or the molecule. This is why electrochemical measurements are often coupled or at least compared to other investigation methods. Further, the electrode-electrolyte interface can be complex due to the structure of the electrode and different and intricate processes can occur at the same electrode depending on the local structure and composition of the material. Hence, it is crucial, for a deeper understanding of the electrochemical processes to be able to scrutinize directly or indirectly the electron transfer at their native spatial scale, *i.e.* the molecular or atomic scale. The development of scanning probe microscopies (SPM) in the 1980's, namely atomic force and scanning tunnelling microscopy (AFM and STM) have greatly helped to provide unobtainable information on the structure of surfaces at the nanoscale. These SPM, through mechanisms that will be further explained in the following, provide mainly topographic information. Their unique capabilities have rapidly been used to probe electrochemical interfaces and provide new insights into processes as diverse as: metal deposition, corrosion, ion adsorption or molecular layer rearrangement upon potential changes. One of the main strengths of these scanning probe techniques is that they can reach the nanoscale or even the atomic one even under electrochemical conditions.

Another SPM has been developed by Bard in the late 1980's [1,2] called scanning electrochemical microscopy (SECM). SECM uses an ultramicroelectrode (UME), *i.e.* an electrode with one of its characteristic dimensions that is micrometric. This peculiar tip measures the current caused by an electrochemical reaction triggered at the tip or at the sample. This reaction can be affected by the close proximity of a sample and the type of perturbation provides information on the nature of the substrate. Scanning this UME over a sample enables to probe the spatial (electro)chemical reactivity of the sample albeit the lateral resolution is degraded as compared to AFM or STM (typically, around a few tens of nanometres at best). SECM, depending on its mode of operation can probe the catalytic activity of a sample, its topography or can give access to specific unstable electroactive species. [3] Like AFM and STM, SECM does not enable the direct chemical identification of species adsorbed at the electrode or the chemical evolution of the electrode material. Superresolution microscopies may also in the future represent alternative possibilities, [4] but their combination with electrochemical methods is still in its infancy and chemical identification is still lacking. [5]

With the aim of obtaining structural information on the molecules or materials at these interfaces, coupling electrochemical measurements to optical spectroscopies can be of major interest. This coupling, generally called spectroelectrochemistry (SEC), can be defined as the *in situ* coupling of spectroscopic techniques to electrochemical measurements while an electrochemical process is occurring and can be carried out *in situ*. [1, 6, 7] These spectroscopic techniques can also be performed *ex situ* with the risk of compromising the properties of the surface by removing the electrode from the electrolyte and no information can be obtained on the dynamics. At the molecular level three main types of optical spectroscopies can be distinguished: absorption spectroscopies (UV-Vis, probing electronic transitions in molecules and infrared (IR) spectroscopy, probing the vibrational structure), scattering spectroscopies (Raman spectroscopy, probing vibrational structure of molecules) and emission spectroscopies such as fluorescence spectroscopy.

UV-Vis absorption and fluorescence spectroscopy can provide indirect electrochemical information such as the standard redox potential of a couple. It is particularly relevant for species, such as biological macromolecules that do not exchange electrons directly with the electrode but with smaller mediators. [1]

IR and Raman spectroscopies can probe structural changes through the appearance or the disappearance of certain vibrational modes while a reaction is occurring. They have been extensively used in electrochemistry as they can probe organic and inorganic species and then changes in the structure of the electrode material as well as molecules in solution or adsorbed onto a surface upon polarization. Raman is of special interest for electrochemical studies since it is easier to implement in electrochemical environment than IR absorption spectroscopy. Indeed, the strong IR absorption of water makes IR measurements in aqueous electrolytes more challenging.

Thus, combining all of the above-mentioned approaches would provide a complete view over electrochemical processes occurring at an electrode by acquiring simultaneously local topography, electrochemical current or potential, and vibrational information about the material or molecules at the interface under potential control. In this context, a great challenge has been to merge and couple all of these approaches, namely electrochemical measurements, SPMs and Raman spectroscopy to help gaining insights in processes occurring at electrified interfaces in electrolyte solution at the nanoscale. This coupled technique, called electrochemical tip-enhanced Raman spectroscopy (EC TERS), is still at its early stage of development so that many fundamental and technical impediments have to be overcome.

This work has started the same year as the acquisition of a nanoRaman platform in 2015 at the LISE laboratory. Therefore the developments and results described in the following chapters have pioneered TERS experiments in the laboratory. Our main motivation was to develop a TERS platform which would enable a coupled SPM and enhanced Raman analysis for a wide range of electrochemical interfaces.

In this thesis, the first chapter aims at drawing the general context in which this study can be positioned. It will describe the fundamentals of Raman spectroscopy and SPM, their common use in the analysis of electrochemical interfaces and how they can be coupled into TERS for Raman spectroscopy characterization at the nanoscale. Finally, we will describe EC TERS, its principles, the first milestones that have already been reached and the future challenges.

A second chapter will be dedicated more specifically to technical and practical requirements of TERS experiments such as the optical coupling between a conventional Raman spectrometer and a SPM platform and the fabrication of TERSefficient probes.

The third chapter will detail the first example of TERS imaging of a molecular layer in an organic solvent.

The fourth chapter is dedicated to a new spectroscopic tool developed during this thesis. The so-called EC tip-Surface-Enhanced Raman Spectroscopy (EC tip-SERS) uses a TERS probe as a microelectrode that can be functionalized with an electroactive molecular layer enabling both EC and Raman monitoring of an electrochemical transformation.

The fifth chapter will cover the development of a new setup for EC STM-TERS

imaging of an electrode under potential control. Preliminary results obtained with this configuration will be exposed.

The last chapter focuses on TERS analysis of surface grafting by aryl-based compounds from diazonium salts reduction which is a reaction of major interest for surface functionalization. [8]

### Chapter 1

# Raman spectroscopy at the nanoscale for electrochemistry: state of the art

### **1.1** Raman scattering and spectroscopy

#### 1.1.1 Light-matter interactions in the UV-Vis and IR range

Light-matter interactions are at the core of an extremely large range of physicochemical methods. With photons in the Ultra-Violet (UV) or in the Infra-Red (IR) range, two processes can occur: photons can be absorbed if their energy matches an electronic or a vibrational transition or they can be scattered. These electronic and/or vibrational transitions are summarized in the simplified Jablonski diagram displayed in Figure 1.1.

Ultra-Violet-visible (UV-vis) and visible (Vis) light (280 - 800 nm) can promote electrons from a ground electronic state to an unstable excited state. Relaxation from this excited state can occur through three processes: fluorescence (without change in the spin of the molecule), non-radiative and phosphorescence decay towards the ground state. Phosphorescence can occur if the unstable excited state (usually singlet) non-radiatively passes to a metastable triplet state (inter-crossing system) and then relaxes from this state to the singlet ground state.



Figure 1.1 – Simplified Jablonski diagram for most of the vibrational or electronic transitions in the IR to UV light range. IR: Infra-red; AS: Anti-Stokes, R: Rayleigh, S: Stokes; UV: ultra-violet, Vis: visible;  $S_i$ : singulet state,  $T_i$ , triplet state,  $\nu_i$ : vibrational state; vs: virtual state; light grey dashed arrow: vibrational relaxation, dark grey dashed arrow: intersystem crossing.

Absorption of a photon can also occur in the mid-IR region  $(2.5 - 25 \ \mu \text{m} \text{ or } 4000 - 400 \ \text{cm}^{-1})$  and promote an electron to a higher vibrational state within the same electronic sate (usually the ground sate): this energy range is commonly used in IR absorption spectroscopy which allows probing the vibrational states of a molecule. A quantum analysis of the transitions between vibrational states lead to selection rules for optical absorption: in IR, a specific mode of vibration is active only if it leads to a change in the dipolar moment of the molecule. One of the most prominent drawbacks of IR spectroscopy for its use in electrochemical studies is the very strong absorbance of water: even a very thin layer of water gives rise to broad absorption bands at 3400, 1640 and 675 cm<sup>-1</sup> with a strong background signal. [9]

If the photon energy does not match any vibrational or electronic transition it can be scattered. The majority of the photons are scattered elastically, *i.e.* with the same energy as the incident photon, the so-called Rayleigh scattering. Raman scattering is associated to photons which are inelastically scattered (with an energy different from the one of the incident photon) due to molecular vibrations. We describe below the key elements for the understanding of Raman scattering.

#### 1.1.2 Theory of Raman scattering

The scattering process was experimentally evidenced in 1928, by C.V. RÂMAN and K.S. KRISHNAN in India [10] and L. MANDELSTAM in Russia on several liquids, vapors or solids. In Raman scattering the photons can be scattered with lower energy if the molecule undergoes a transition from a lower to a higher vibrational state (referred as Stokes scattering) or with a higher energy if the molecule undergoes a transition from a higher to a lower state (referred as anti-Stokes scattering). As anti-Stokes Raman scattering requires the molecule to be in an excited vibrational state, this scattering is less likely to occur and anti-Stokes Raman scattering is much weaker than the Stokes one. Indeed, the population of an excited state is given by a Boltzmann law:

$$\frac{N_{n+1}}{N_n} = \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{1.1}$$

where  $N_n$  is the number of molecules in the *i*th vibrational state,  $\Delta E$  is the difference of energy between these states (J),  $k_B$  is the Boltzmann constant (1.38065  $\cdot$  10<sup>-23</sup> J K<sup>-1</sup>) and T the temperature (K). The theory of Raman scattering can be considered from a purely classical point of view (the molecule is viewed as an harmonic oscillator) or with quantum theory (the quantification of the vibrational states are considered). Several textbooks describe in details the Raman scattering theory. [9, 11]

Let us first consider the classical view: the molecule is an harmonic oscillator with a permanent dipolar moment  $(\overrightarrow{\mu_p})$  due to the electronic distribution in the electron cloud around the constituting atoms. Under the influence of an electric field

$$\overrightarrow{E}(t) = \overrightarrow{E_0}\cos(2\pi\nu_0 t) \tag{1.2}$$

with  $\overrightarrow{E_0}$  the magnitude of the electric field and  $\nu_0$  the frequency of the incident

photon, the molecule can vibrate with a frequency  $\nu_k$ . Because of the molecular vibrations, an instantaneous induced dipolar moment  $\overrightarrow{\mu_i}$  adds to the permanent dipolar moment so that the total dipolar moment  $\overrightarrow{\mu}$  is

$$\overrightarrow{\mu} = \overrightarrow{\mu_p} + \overrightarrow{\mu_i} \tag{1.3}$$

This induced dipolar moment depends directly on the system polarisability  $\hat{\alpha}$ . Polarisability is a second rank tensor which describes the movements of the electrons in the three dimensions of space in response to the movement of the nuclei oscillating at the normal mode frequency  $\nu_k$  such as:

$$\overrightarrow{\mu_i}(t) = \hat{\alpha} \cdot \overrightarrow{E}(t) \tag{1.4}$$

In the classical model of the harmonic oscillator, the normal vibrations are described by the normal coordinate  $q_k$  and the normal frequency  $\nu_k$ . The mass center variation relatively to its equilibrium position is:

$$q_k(t) = q_k^0 \cos(2\pi\nu_k t) \tag{1.5}$$

and the variations of the polarisability with respect to the normal coordinate can be expressed as a Taylor series:

$$\hat{\alpha_k} = \hat{\alpha_0} + \left(\frac{\partial \hat{\alpha}}{\partial q_k}\right)_0 q_k^0 \cos(2\pi\nu_k t) + \dots$$
(1.6)

The first term in this series represents the unperturbed polarizability; the second term is the first order perturbation. As for a linear polyatomic molecule, 3N-5 vibrational have to be considered (N, being the number of atoms in the molecule) or 3N-6 if the molecule is non-linear, the polarisability can be written as:

$$\hat{\alpha} = \hat{\alpha_0} + \sum_{k=1}^{3N-5(6)} \left(\frac{\partial \hat{\alpha}}{\partial q_k}\right)_0 q_k^0 \cos(2\pi\nu_k t)$$
(1.7)

if we neglect the perturbations at orders higher than one (they should be taken into account only in non-linear processes, such as multi-photons interactions). And the total dipolar moment is obtained by combining 1.2, 1.3, 1.4 and 1.7:

$$\overrightarrow{\mu} = \overrightarrow{\mu_p} + \left( \hat{\alpha_0} + \sum_{k=1}^{3N-5(6)} \left( \frac{\partial \hat{\alpha}}{\partial q_k} \right)_0 q_k^0 \cos(2\pi\nu_k t) \right) \cdot \overrightarrow{E}_0 \cos(2\pi\nu_0 t)$$
(1.8)

*i.e.*:

$$\vec{\mu} = \vec{\mu}_p$$

$$+ \left(\hat{\alpha}_0 \cdot \vec{E}_0 \cos(2\pi\nu_0 t)\right)$$

$$+ \frac{1}{2} q_k^0 \left(\sum_{k=1}^{3N-5(6)} \left(\frac{\partial \hat{\alpha}}{\partial q_k}\right)_0 \left(\cos(2\pi(\nu_0 + \nu_k)t) + \cos(2\pi(\nu_0 - \nu_k)t))\right) \cdot \vec{E}_0$$
(1.9)

The second term of 1.9 ( $\propto \cos(2\pi\nu_0 t)$ ) describes Rayleigh scattering and the third term can be decomposed into anti-Stokes ( $\propto (\cos(2\pi(\nu_0 + \nu_k)t))$ ) and Stokes ( $\propto (\cos(2\pi(\nu_0 - \nu_k)t))$ ) Raman scattering. From this term, an essential selection rule can be deduced: a vibrational mode is Raman active if there is a change in the polarizability of the molecule with respect to the normal coordinates, *i.e.* the derived polarizability:

$$\left(\frac{\partial \hat{\alpha}}{\partial q_k}\right)_0 \neq 0 \tag{1.10}$$

which can be compared to the main IR selection rule: a vibrational mode is IR active if the induced dipolar moment  $\overrightarrow{\mu}_i$  is non zero.

#### 1.1.3 Raman cross section

An important parameter in Raman scattering is the cross section ( $\sigma$ , in m<sup>2</sup>) of the material or the molecule which quantifies the efficiency of the scattering for one specific incident photon energy and one normal vibration mode. The scattering cross section determines the intensity of Raman bands in the spectra. It can be expressed as the ratio of the scattered photon intensity for the k mode ( $I_k$ ) over the incident intensity ( $I_0$ ):

$$I_k \propto \sigma_k \cdot I_0 \tag{1.11}$$

where  $I_k$  is the intensity of the scattered electrons integrated over all scattering directions and polarizations. A more accurate definition of the Raman scattering cross section is given by its absolute differential expression over the solid angle  $\Omega$ (in steradians: sr) of scattering, for a normal mode k with a frequency  $\nu_k$ :

$$I_k \propto \frac{d\sigma_k}{d\Omega} I_0 \delta \Omega \tag{1.12}$$

 $\delta\Omega$  being the solid angle of collection (related to the numerical aperture (NA) of the objective microscope, when used). Without giving the full expression of the cross section the relationship between the incoming photons frequency and the components of the polarizability can be demonstrated to be:

$$\left(\frac{d\sigma_k}{d\Omega}\right)_k^{\rm S} \propto \left(\nu_0 - \nu_k\right)^4 \left(\frac{45\alpha_k^{\prime 2} + 7\gamma_k^{\prime 2}}{45}\right) \left(1 - \exp\left(-\frac{hc\nu_k}{k_BT}\right)\right)^{-1} \tag{1.13}$$

In 1.13, the S superscript stands for Stokes; the first term highlights the  $\nu^4$  relationship between the Raman scattering intensity and the energy of the source (or  $\lambda^{-4}$ ) which is of great importance in Raman spectroscopy. Indeed, as for Raman spectroscopy visible laser sources are mostly used, Raman scattering can compete

with fluorescence (a more efficient process that can screen Raman signal). One of the solutions is to use near-IR or IR laser sources to prevent the absorption of photons by electronic transitions. The main direct drawback of this approach is to severely decrease the Raman efficiency. The second term corresponds to the Raman activity of the normal mode k where  $\alpha'_k$  and  $\gamma'_k$  are the isotropic and anistropic contributions of the polarizability changes upon a the vibration. They depend on the polarizability changes  $\left(\frac{\partial \alpha_{ij}}{\partial q}\right)_0$  allong all directions and therefore take into account the symmetry of the vibration. The last term accounts for the population of the vibrational state which is close to 1.

It has to be noticed that classical approaches are unable to estimate the intensity of the Raman lines, *i.e.* to calculate the expression of the cross section and the polarizability tensors. Semi-classical approaches (the molecule is treated as a quantum oscillator and the electric field is treated classically) or full quantum mechanics approaches can in contrast evaluate the changes in polarizability in a molecule for certain vibrations and therefore allow an estimation of the Raman bands intensity.

Taking the example of a benzene molecule, the Raman cross section of the ringbreathing mode at 992 cm<sup>-1</sup> with a 514.5 nm excitation is  $4.0 \cdot 10^{-28}$  cm<sup>2</sup>. [12] In contrast, UV absorption and then its fluorescence cross section has an order of magnitude of  $10^{-17}$  cm<sup>2</sup>. [13] These values evidence that Raman scattering is intrinsically a non-efficient process. Several strategies and mechanisms can be used to enhance the Raman intensity such as Resonance Raman (RR) or surface-enhanced Raman spectroscopy (SERS) that will be described in the following.

#### 1.1.4 Enhancement of the Raman scattering

In the so-called resonance Raman scattering (RRS) the excitation laser is set to an energy close to the one of an electronic transition and the Raman scattering intensity can increase by six orders of magnitude. The details of the theory require a semi-classical description of the polarizability [9,14] which is out of the scope of this chapter but some singularities of RRS can be though highlighted. This enhancement is not homogeneous for all vibration modes of a molecule and greatest enhancement factors are found for modes related to structural changes upon photon absorption.

In the early stages of RRS development, Hirakawa studied RRS of  $NH_3$  in the gas phase. [15] As this molecule has a pyramidal structure in its electronic ground state and a planar one in its first electronic excited state, they observed strong enhancement of the so-called umbrella vibration modes if the excitation energy was close the electronic transition energy while other vibration modes were much less affected.

RRS can then be very helpful for the attribution of Raman bands and the understanding of intramolecular charge-transfers. RRS has been widely used for the study of charge transfers in organometallic complexes where several types of transition can occur. [14]

One difficulty of RRS is the choice of the wavelength: most of Raman equipments have a set of lasers with discrete wavelengths available. Tunable laser sources cannot be used easily mainly because specific laser line rejection filters have to be used for each excitation wavelength to remove the Rayleigh contribution (see below, the instrumental part in 2.1). However, coupled to other enhancement mechanisms this RR effect can be beneficial to increase the Raman scattering intensity. The other enhancement mechanisms we will consider in the following at the origin of surface and tip-enhanced Raman (SERS, TERS). In SERS, enhancement occurs when a molecule lies on a roughened or nanostructured noble metallic surface (*e.g.* silver or gold). In TERS, enhancement is obtained with the introduction of a nanostructured metallic tip brought to the vicinity of the molecule. In both case, the enhancement mainly comes from the interaction of the electromagnetic field with the metal and the excitation of surface plasmons which are collective oscillations of the free electrons at the metal surface. The nature of these interactions and the origins of the enhancement in SERS and TERS is part of the field of plasmonics which will be described in the following section.

## 1.2 Fundamentals of plasmonics and surface-enhanced Raman scattering

#### 1.2.1 Surface Plasmons

The interaction of a metal with an electromagnetic wave can be seen as the excitation of free conduction electrons in the metal that can be considered as a plasma *i.e.* a gas of charged electrons responding collectively to an electromagnetic field. This interaction is different between bulk metal and nano-sized materials (characteristic length below the wavelength of the electromagnetic source), the latter exhibiting unique properties like signal enhancement in Raman spectroscopy among others. Before describing in details the plasmonic response of nanomaterials, we will first consider the case of bulk metals. The following description of plasmonics was mostly inspired by two textbooks by E. Le Ru [11] and L. Novotny [16] and notes from lessons by B. Palpant in 2016. [17]

#### **1.2.1.1** Optical properties of noble metals

In an homogeneous medium, the light propagation can be described using a complex refractive index:

$$\underline{n} = n + i\kappa \tag{1.14}$$

where n is the refractive index and  $\kappa$  the extinction coefficient (inversely proportional to the absorption coefficient  $\alpha$ ). Both of these parameters are wavelength-dependent. This complex index is related to the complex dielectric function of the material  $\epsilon = \epsilon_1 + i\epsilon_2$  by:

$$\epsilon = \underline{n}^2 \tag{1.15}$$

and can be defined relatively to the susceptibility of the medium,  $\chi$ :

$$\epsilon = 1 + \chi \tag{1.16}$$

The complex dielectric constant has to account for all possible light-matter interactions: the electronic transitions (and their oscillator strengths), the screening and polarization effects and finally the scattering and collisions phenomena implying electrons. In metals  $\epsilon$  has to account for two kinds of electron transitions in the Vis and near-UV range summarized in the simplified band diagram of noble metals (Cu, Au or Ag,  $((n-1)d^{10}ns^1))$  presented in Scheme 1.1:

- the *interband* (*ib*) transitions between the valence (*d* electrons) and the conduction band;
- the *intraband* transitions of the quasi-free (*sp*) electrons within the conductive band.

 $\epsilon$  can therefore be written as the sum of interband transitions contribution  $\epsilon^{ib}$ and the intraband contribution  $\epsilon^{D}$ :

$$\epsilon = \epsilon^{ib} + \epsilon^D \tag{1.17}$$

The intraband contribution has been modelled by the classical DRUDE model (D superscript): the metal is considered as a array of positively charged spheres surrounded by an electron gas (*i.e.* a plasma) that are subjected to a Lorentz force (due to the electric field) and a phenomenological friction force (due to all the possible collisions and interactions with the positively charged spheres). With this model it is possible to show that  $\epsilon^{D}$  is expressed as:

$$\epsilon^{D}(\omega) = 1 - \frac{\omega_{p}^{2}}{\omega^{2} + i\Gamma\omega}$$
(1.18)



Scheme 1.1 – Simplified electronic structure of a noble metal  $((n-1)d^{10}ns^1)$  and the band diagram of the bulk metal with electronic transisitons in the Vis and near-UV range. CB: conduction band, VB: valence band, T.: transition,  $E_F$ : Fermi energy level

where  $\omega$  is the angular frequency of the incident electromagnetic field,  $\Gamma$  a damping constant (sum of all the contributions) and  $\omega_p$  is the angular frequency of the plasma defined as:

$$\omega_p = \sqrt{\frac{n_e e^2}{m_e \epsilon_0}} \tag{1.19}$$

with  $n_e$  the density of electrons in the metal,  $m_e$  the effective mass of an electron and  $\epsilon_0$  the dielectric constant of the free space. In a metal, these oscillations are quantized and are then quasiparticles called plasmons. Under certain conditions, this plasmon can be excited by an external electric field leading to a so-called bulk plasmon resonance (PR).

Due to the Pauli principle the interband contribution concerns only photons with an energy higher than the energy gap between the Fermi level  $(E_F)$  and the highest level of the valence band which is known as the interband transition threshold. This threshold is in the UV for silver (3.9 eV or 318 nm) but in the visible for gold (2.4 eV or 518 nm) which explains that gold is colored as it can absorb the blue part of the visible spectrum. Contrary to  $\epsilon^D$ ,  $\epsilon^{ib}$  cannot be evaluated by a simple classical model as it requires to know exactly the electronic density and distribution of the valence and the conduction bands. This can be treated by the ROSEI model. [18, 19] The combination of these two models can satisfyingly explain the experimental optical properties of noble metals.

#### 1.2.1.2 Localized Surface Plasmon Resonance

The above-mentioned bulk plasmons cannot be excited by light but only by particles like electrons and cannot propagate. However, this limitation can be potentially overcome at the interface between a metal and a dielectric material. Under specific conditions (excitation with wavevector  $\vec{k}$  nearly parallel to the surface, use of corrugated surfaces or excitation with an evanescent wave or an optical near-field...) the oscillations of the electrons can be coupled to an evanescent electric field normal to the surface on each side of the metal-dielectric junction. The evanescent field is confined within 10 nm in the metal and half of the wavelength in the dielectric (called the skin depth,  $\delta$ ). This surface wave which can propagate along the interface is called a Surface Plasmon Polariton (SPP) or propagating surface plasmon. This phenomenon and the field magnitude in each material are pictured in Figure 1.2.



Figure 1.2 – Scheme of a propagating SPP at a metal-dielectric interface along the z-direction. The Electric field is normal to the interface (y-axis) and along the propagation direction (z-axis). The left part figures the charge-induced electric field magnitude at the interface in each material. From [20].

SP can also be localized or confined in metal structures of nanometre size (size be-

low the excitation wavelength). In this case the plasmon oscillates locally around the nanoparticle with a frequency called Localized Surface Plasmon Resonance (LSPR). These collective oscillations create a charge accumulation and then a local intense evanescent electric field at the surface of the particle. This is depicted in Figure 1.3.



Figure 1.3 – Scheme of a localized surface surface plasmon (LSP) in a metal nanoparticle. From [21].

For a nanoparticle (NP) of radius  $a \ll \lambda$  in an electric field  $\overrightarrow{E_0}$  the localized field can be associated to the one created by an induced dipole  $\overrightarrow{\mu}_{i,NP}$  in this field:

$$\overrightarrow{\mu}_{i,NP} = \epsilon_d \alpha(\omega) \overrightarrow{E_0} \tag{1.20}$$

 $\alpha(\omega)$  is the polarizability of the NP that can be expressed as a function of the dielectric functions of the metal and of the dielectric:

$$\alpha(\omega) = 4\pi a^3 \frac{\epsilon_m(\omega) - \epsilon_d}{\epsilon_m(\omega) + 2\epsilon_d}$$
(1.21)

where  $\epsilon_m$  and  $\epsilon_d$  are the dielectric functions of the metal and of the dielectric environment and a the NP radius. This relationship (1.21) highlights the resonance condition:  $\alpha$  is maximized when  $\epsilon_m + 2\epsilon_d \longrightarrow 0$ . Optical properties of NPs can be vizualized on optical extinction spectra (absorption and elastic scattering spectra as a function of the incident wavelength). Extinction spectrum shows a maximum at  $\lambda_{\text{max}}$  which is the plasmon resonance wavelength.

LSPR is very sensitive to the environment and  $\lambda_{\text{LSP}}$  can be shifted by several tens of nanometres by changing the dielectric constant of the surrounding medium. For example, increasing  $\epsilon_d$  shifts the LSPR towards red wavelengths. [22] An analytical solution to Maxwell's equation can be found (Mie theory, [11]) for a spherical NP and it can be demonstrated that the magnitude of the field outside the particle is enhanced in the very close proximity of the surface and decays with  $r^{-3}$  (r being the radial distance to the center of the NP).

It is noteworthy that the size and the shape of the particles also affect the LSPR. Increasing the size leads to higher absorption and scattering of the incoming light. However, the shape is also a key parameter: oblong spheroids exhibit higher enhancements than spheres while the LSPR is red-shifted. Note that the polarization of the incoming field has to be aligned with the main axis of the particle to observe the highest enhancement. [11] Some more complicated structures such as nanorods [23] or nanostars [24, 25] evidence the strong dependence of LSPR on the shape of the particle but also highlight two key aspects: the field enhancement is higher at sharp ends, edges or cones apices in nanostars and are highly sensitive to the polarization.

The last essential parameter that can affect both LSPR and field enhancement is the coupling between several nanostructures: a simple example is the LSPR of a gold NP dimer. As the gap between two NP decreases from 20 nm to 1 nm, the LSPR is red-shifted by *ca.* 200 nm and the field is highly enhanced in the gap [11] if the field polarization is along the axis of the dimer. This specific region of space where the field enhancement is maximum is called a *hot spot*. This term will be used in the following for SERS and TERS experiments. One can now understand why these properties of nano-sized metallic materials can be of tremendous interest for Raman spectroscopy: the intensity of the scattered signal can be considerably increased in presence of metallic nano-objects, opening the way to enhanced spectroscopy for the characterization of low cross section materials, molecules or nano-objects.

#### 1.2.2 Surface-Enhanced Raman Spectroscopy

SERS makes profit of the strong electric field enhancement provided by a nanostructured substrate with plasmonic properties. This enhancement of Raman signal was first experienced by Fleischman in 1974 in his studies on the changes of Raman scattering of a monolayer of pyridine adsorbed on a silver electrode as a function of the applied electrochemical potential. [26] The enhancement mechanism of the signal was then discovered by Van Duyne and Creighton simultaneously in 1977 in works where the role of the silver substrate was pointed out. [27,28] Initially SERS was performed on electrochemically roughened substrates which displays a random distribution of hot spots on the surface. Since the 90's potentialities of SERS have been increasingly exploited and single-molecule detection could be achieved in 1997. [29,30] Top-down or bottom-up nanofabrication processes now allow the design of reproducible and tunable SERS substrates (lithography, 3D NP assembly). [31]

#### 1.2.2.1 SERS enhancement mechanism

The increase in intensity of the SER scattering is usually quantified by the enhancement factor (EF) which compares the SERS intensity to the normal Raman scattering signal. This enhancement factor can be as high as  $10^6$  to  $10^7$  or even  $10^{10}$  when SER and resonance effect are combined (surface-enhanced resonance Raman spectroscopy, SERRS). [14] It can be demonstrated that for a purely electromagnetic enhancement mechanism, the SER intensity scales with the local electric field magnitude  $(E_{loc}^4)$  as both the excitation and the scattered signals are enhanced by the substrate. In practice, this EF can be determined by comparing the intensity of the SER signal  $(I_{SER})$  to the intensity of normal Raman scattering  $(I_{NR})$  normalized by the number of molecules N probed in each case:

$$EF = \frac{I_{\rm SER}}{I_{\rm NR}} \times \frac{N_{\rm NR}}{N_{\rm SER}} \tag{1.22}$$

In most situations the number of molecules probed in SER experiments is difficult to etimate. [32]

The electromagnetic enhancement cannot account for enhancement higher than ca.  $10^5$ . In fact, another mechanism, called the chemical mechanism, is responsible for higher enhancement factors. It originates from interactions of the adsorbed molecule with the substrate. This mechanism, which is not simple as many effects interplay, is still under debate. Its nature is discussed in several reviews such as [33] and [11]. The most studied mechanisms are those involving partial charge transfer between the metal and the molecule. We briefly describe them below since they may be of importance in electrochemical SERS experiments. One mechanism considers the perturbation of the electronic structure of the molecule due to the close proximity of the metal that can affect its polarizability and then the Raman scattering intensity of some vibrational modes. Another mechanism considers the formation of "surface-complexes" with specific available electronic states which can be resonant with the incident excitation. The third one is also a resonance-based mechanism: if the energy gap between the Fermi level of the metal and the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) states of the adsorbate matches the energy of the incoming photon, RR can occur and enhance the scattering process. The latter can be important in EC-SERS experiments as the applied electrochemical potential tunes the Fermi level energy of the metal. These experiments were in fact a clear and experimental proof of the existence of such a chemical enhancement mechanism. [27,34]

#### 1.2.2.2 Electrochemical SERS

As SERS can considerably increase the Raman scattering, it appears as an ideal tool to monitor the evolution of an electrochemical interface *in situ*. In fact, SERS has often been closely associated to electrochemistry for two main reasons. The first is historical: the first SERS experimental evidences were revealed on EC-Raman

measurements. [26–28] The second one is practical since the first roughened silver SERS substrates were prepared by a process known as oxidation-reduction cycle (ORC), [35] where the silver is successively electrodissolved and electrodeposited forming a non-homogeneous surface with rough features supporting the electric field enhancement.

Since then, more advanced electrochemical deposition of metals have been developed such as the one proposed by Burgress et al. in 2016 for the electrochemical growing of dense films of "dagger-shaped" gold particles. [36]

On the other hand a recent study by Baumberg et al. explored, in an electrochemical environment, the plasmonic properties of a junction constituted of an organic layer sandwiched between a metal NP and a metal surface. The strong field enhancement at the junction (the gap) provides strong SER signal of the layer. Upon polarization, they observe variation of the SERS intensity that they explained by the potential-dependent changes in the double-layer composition and then of the local refractive index, the presence of ionic charges close to the NP inducing shifts in the plasmon resonance and in their case hydrogen evolution with a low refractive index at the surface. [37]

EC-SERS could help understanding the interactions between molecules and surfaces. As Raman spectroscopy is very sensitive to the orientation of the molecule versus the polarization of the excitation laser, SERS can exhibit more intense scattering from some vibration modes depending on the orientation of the molecule with respect to the local electric field. An example is the orientation of nicotinic acid (and its isomers, isonicotinic and picolinic acids) which can adsorb with various conformations depending on the pH and on the charge of the substrate surface. [38,39] To study these phenomena, a coupled electrochemical impedance-Raman experiment was developped at LISE and enables the variations of the Raman intensity with the potential  $(\frac{\Delta I_{\text{Raman}}(\omega)}{\Delta E(\omega)})$  [40] together with the changes in capacitance of the electrical double layer. The interpretation of EC-SERS results can be challenging because of the interferance of several parameters. The first one is the nature of the substrate which it is usually made of roughened metallic structures so that the exact environment of each molecule cannot be known. [41] The second one is that the collected SERS signal is averaged on an area defined by the optical resolution of microRaman, and therefore is diffraction-limited.

One last issue is that only molecules or compounds which can be deposited on SERS substrates can be studied. A SERS-inspired solution was proposed for the study of surfaces other than gold and silver, the so-called shell-isolated NP enhanced Raman spectroscopy (SHINERS) which will be described in the following.

#### 1.2.2.3 Shell-Isolated Nanoparticles Enhanced Raman Spectroscopy

SHINERS uses plasmonic NPs deposited on a substrate to be investigated. As the NPs enhance locally the electric field, materials in their vicinity are probed by the intense near-field generated around the particles. The "Shell-isolated" part means that the NPs are covered with an insulator dielectric layer (silica or alumina) that prevents any possible (electro)catalytic interference of the NPs with the material under scrutiny.

SHINERS has been successfully applied to the study of the conformation of molecules on flat metallic substrates, [42,43] to the study of catalytic processes, [44] and also to the study of interfacial processes on energy storage materials. [45]

If multiple SERS platforms are now available and can be selected depending on the targeted application, SERS analyses suffer from the limited spatial resolution of optical microscopies (around the micrometre in the visible range). The following section will describe how this limitation can be circumvented and how electrochemical interfaces can be characterized at the nanoscale.

# 1.3 Beyond the diffraction limit: scanning near-field optical microscopy

All the optical microscopies and spectroscopies previously described can provide multiple and complementary information about the nature, the structure and the properties of materials or molecules as well as their transformation under electrochemical potential control for example. Today, the strong trend towards nanoscale science and technologies has catalyzed the development of new fabrication, manipulation and investigation tools able to reach this scale. Electron microscopies are attractive by providing subatomic details but their implementation in situ is difficult. Moreover, the beam-induced damages to the sample may alter the mechanism under study. Another powerful approach is based on scanning probe microscopies (SPM) such as STM, AFM and their implementation in combination with optical methods. A new paradigm has emerged out of these developments: scaling down the matter investigation towards the nanoscale has revealed news borders beyond which new physical phenomena and effects were observed and even become prominent. Particularly, in optics, a new domain called nano-optics has emerged and aims at understanding optical phenomena that occur below the diffraction limit. Indeed, classically, objects observed with optical spectroscopies cannot be distinguished if they are separated by a distance smaller than roughly half of the wavelength used for their observation (200 nm in the visible range).

#### **1.3.1** Optical diffraction limit

The optical diffraction limit can be understood considering that the propagation of a photon in free space is determined by the dispersion relationship connecting its angular frequency  $\omega$  and its wavevector  $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$  via the light velocity c:

$$\hbar\omega = c \cdot \hbar k \tag{1.23}$$
Considering HEISENBERG's uncertainty relationship on the spatial position and the momentum p of a particle in a particular direction:

$$\Delta x \cdot \Delta p_x \ge \frac{\hbar}{2} \tag{1.24}$$

we can write for a photon the relationship between the spatial confinement and the spreading in magnitude of the wavevector in one particular direction:

$$\Delta x \ge \frac{1}{2\Delta k_x} \tag{1.25}$$

As for a photon the maximum spread of the wavevector is  $k = \frac{2\pi}{\lambda}$ , 1.25 can be written as:

$$\Delta x \ge \frac{\lambda}{4\pi} \tag{1.26}$$

This expression can be compared to the ABBE's diffraction limit one, formulated in 1873 (followed by a similar expression proposed by RAYLEIGH six years later) that states that the optical spatial resolution cannot be lower than half of the photon wavelength:

$$\Delta x \ge \frac{\lambda}{2 \times \mathrm{NA}} \tag{1.27}$$

where NA is the numerical aperture of the microscope objective. [46]

#### 1.3.2 Principles of near-field optics

An approach for improving spatial resolution in optical imaging is provided by Scanning Near-Field Optical Microscopy (SNOM) which allows the optical imaging of features below the diffraction limit near a surface. SNOM is usually coupled to a scanning probe microscope (SPM) allowing a topographic and optical imaging of the samples combining both the single digit nanometre scale of the SPM and the fast dynamics of optical measurements.

The optical near-field can be defined as the non-propagating electromagnetic

field surrounding an object illuminated with a propagating electromagnetic field (light, called the *optical far-field*). The optical near-field exists in a restricted region of space (generally less than 100 nm) around the irradiated object. As the optical near-field cannot propagate it cannot be directly measured with a detector but requires back-coupling to far-field through interactions with matter. [47]

The first idea of SNOM was originally proposed by SYNGE in a pioneer paper in 1928. [48] He suggested the illumination of a sub-wavelength aperture in an opaque film placed at a sub-wavelength distance on the top of a transparent substrate to be imaged: the light passing through the apperture is focused on the sample and transmitted to a detector through a non-diffraction-limited process. The implementation of this idea could be practically demonstrated with an electromagnetic radiation in 1972 by Ash and Nicholls (who actually ignored SYNGE's work) by using a microwave radiation with wavelength of 3 cm passing through a hole with an aperture diameter of 1.5 mm: a resolution of  $\frac{\lambda}{60}$  was observed on a metallic line grating with a 500  $\mu$ m periodicity. [49] These first experimental evidences opened the way to the domain of near-field microscopy.

The first experimental evidences of SNOM carried out with an excitation source in the visible range were obtained a decade later by Pohl et al. with a  $\frac{\lambda}{20}$  (25 nm) resolution [50] and Lewis et al. with a  $\frac{\lambda}{14}$  (50 nm) resolution. [51] Finally, one decade later, Betzig et al. acquired the first single molecule fluorescence imaging with a  $\frac{\lambda}{50}$ resolution. [52] All these experiments have been performed in a configuration similar to the one originally proposed by SYNGE. Other configurations have been described so that SNOM can be divided arbitrarily into three general classes, organized by the type of near-field probe employed:

- nano-aperture-based techniques called aperture SNOM (a-SNOM);
- methods using sharp tips acting as optical transducers called scattering SNOM (s-SNOM);

• and strategies based on advanced tip designs that involve sophisticated optical antenna and/or apertures, incorporating concepts from the field of plasmonics.

In the following, each of these categories will be briefly described with a few examples of applications in the analysis of solid-liquid interfaces.

#### 1.3.3 Aperture SNOM

The most commonly used SNOM approach is the one imagined by SYNGE, the aperture SNOM (a-SNOM): it makes use of conventional aperture-based probes which are usually metal-coated tapered dielectric waveguides with a sub-wavelength aperture at the apex of the structure (see Figure 1.4a). The metal-dielectric interface at the apex of the tip allows a localized evanescent wave (near-field) to leak out at the aperture creating a light nano-source in the vicinity of this aperture. It can also be used as a nano light collector (see Figure 1.4b). The size of this spot, and then the resolution is mainly defined by the size of the aperture (and not by the wavelength anymore). This approach enables background-free imaging because sample illumination occurs only within the nanoscale light spot created at the aperture.



Figure 1.4 – Scheme of the three main modes of operation in a-SNOM: a) excitation mode, b) collection mode, c) excitation and collection mode.

The optical transmission has been shown to decrease exponentially with the aperture diameter [53, 54] leading to transmission efficiency lower than  $10^{-6}$  for

apertures below 100 nm in the visible range. It has to be added that high laser powers cannot be used to compensate this drawback for the illumination as it may damage or melt the metal-coating layer. These factors prevents the use of the combined collection and excitation through the same fiber (Figure 1.4c). Hence, only collection or illumination modes can be used: the sample can be locally excited through the aperture while the emitted, scattered, or transmitted light is collected with a microscope objective, [55, 56] and reversely. [57]

It is now easily understandable that near-field Raman spectroscopy with this kind of microscope is very delicate because of the lack of efficiency of Raman scattering and because of the poor collection or excitation of aperture SNOM probes. Despite these difficulties several nano-Raman studies have been conducted using this configuration since the pioneer paper of Tsai and co-workers in 1994: they could probe the phonon mode of a diamond sample in an excitation-collection configuration with a 100 nm aperture probe. Another difficulty is due to the broadband Stokes signal of the material of the fiber which is superimposed to the Raman bands of the analyte. [57]

However, Grausem et al. published in 1997 the first near-field Raman spectroscopy results in a liquid environment (CCl<sub>4</sub>) by extracting the spectrum of the tetrachloromethane through an aperture of 50 nm (using a 514.5 nm laser excitation) with a decent signal-to-noise ratio despite the low number of probed molecules that they estimated to be 0.4 attomol (~ 240000 molecules). [58]

An a-SNOM-inspired opto-electrochemical analysis was proposed by Bard in 2002. [59] In this work, the authors propose to use a tapered optical fiber coated with a metallic layer as a scanning electrochemical microscope (SECM) probe. With these probes, an array of interdigitated electrodes was imaged in constant-height mode: simultaneously topographic (the tip was mounted on a tuning fork), optical and electrochemical current (a redox probe was in solution) could be recorded. It has to be noticed that in this work, the aperture size was estimated to be 1.3  $\mu$ m

much larger than the wavelength used (514.5 nm): the optical resolution is higher than 2  $\mu$ m, very far from the performances reached in SNOM at this time.

Moreover, as SNOM probes are usually made by gluing an optical fiber onto the prong of a tuning fork to control the probe-sample distance, it reveals difficult to operate when the tip is immersed in a liquid (see Section 1.4.5.3 below for more details). This consequently results in poor lateral resolution on topography images. These examples highlight the difficulties to use an a-SNOM approach for non-efficient optical processes such as Raman spectroscopy without any enhancement of the signal especially in a liquid environment.

#### 1.3.4 Scattering SNOM

In apertureless or scattering SNOM (s-SNOM) a sharp metallic tip with a radius of curvature smaller than the wavelength of the source light is used to locally scatter the electric field at its apex (the near-field region). [60] As such probes act as antenna, they can be used as nano-sources of light but also as nano-scatterers. The enhancement mechanism, usually referred as the lightning-rod effect, is due to the tappered profile of the illuminated probe that concentrates the surface charge density at the apex of the tip (or any sharp singularity over the surface) as depicted on Figure 1.5. [61] This enhancement is very sensitive to the polarization of the electric field relatively to the axis of the tip and is maximized when the light is linearly polarized along the main axis.

The capability of a nanoprobe to confine the electric field was for example evidenced over photosensitive polymers [62] which can imprint the electric field distribution around the tip with several illumination patterns.

s-SNOM has been successfully used with broadband IR sources to implement nanoIR spectroscopy and imaging. It was for example demonstrated on the identification of polymers thin films on silicium [63] and recently on viruses in a thin layer of water trapped between sheets of graphene using a plattinum-coated AFM



Figure 1.5 – a) Calculated surface charge density ( $\sigma$ ) at a 5 nm radius gold tip illuminated with a laser polarized linearly along the tip shaft (z); b)  $E^2$  distribution around the same tip under the same conditions of illumination. A maximum of 3000 was calculated at the apex (adapted from [60]).

tip. [64] In these works, fast single frequency nano-IR imaging was possible due to the background signal efficient filtering by demodulation of the s-SNOM signal at the oscillation frequency of the AFM probe. However recording a full nano-IR spectrum under these conditions takes at least 60 s which renders hyperspectral analysis of a sample long and delicate.

Nano-IR imaging and spectroscopy has also been performed on electrochemical materials and interfaces of interest in the field of Li-ion batteries: the phase change in positive electrode material during delithiation could be observed [65] and several products of the solid-electrolyte interphase (SEI) could be distinguished. [66] These studies are promising as they extend the range of materials that can be studied. Nevertheless, none of those were carried out *in situ*. IR s-SNOM for *in situ* analysis may be compromised as the harmonic motion of the tip is not guaranteed in liquids (poor demodulation of the scattered signal).

#### 1.3.5 Photothermal approach for nano-IR

A very different nano-IR system was developped by A. Dazzi in 2005 and commercialized by the Anasys company. It is based on the photothermal expansion of materials upon excitation by an IR laser as depicted in Figure 1.6. With this system a full local IR spectrum can be recovered by tuning the IR laser wavelength and by analyzing the cantilever response to the absorption-induced mechanical stress of the sample. It has found a wide range of applications from biology to plasmonics that are summarized in a review by Dazzi and Prater. [67] However, no nano-IR studies have been reported in liquids using this system due to strong absorption of water in the IR range.



Figure 1.6 – Principle of the photo-induced AFM-IR spectroscopy. As the material absorbs the IR incident radiation from the laser, the material expands and triggers an oscillation of the AFM cantilever. From Ref. [67].

## 1.4 Tip-enhanced Raman Spectroscopy: Raman beyond the diffraction limit

The successful combination of the Raman enhancement by SERS and of the nanoscale analysis by SNOM or SPM was achieved in 2000 simultaneously by the groups of Kawata [68], Pettinger [69], Anderson [70] and Zenobi [71] pioneering a new field in enhanced Raman spectroscopies: tip-enhanced Raman spectroscopy (TERS).

TERS can be seen as nanometric single SERS hot spot positioned at the apex of a SPM probe enabling the chemical imaging of a sample. The strength of this approach is that the sample under scrutiny is not altered and its Raman response can be extracted at each point of the sample by a strong and localized electric field (near-field) by scanning the metal tip over the sample.

A simple scheme on Figure 1.7 compares TERS to SERS and confocal Raman spectroscopy.



Figure 1.7 – Schematic of TERS, SERS and confocal Raman spectroscopy

#### **1.4.1** Pioneer experimental TERS evidences

The first reported TERS experiments by the groups of Zenobi, Kawata and Anderson were carried out in an inverted configuration on transparent samples: the illumination of the tip and the collection of the TERS signal was achieved using an inverted microscope. In all studies the molecules were Raman resonant (*e.g.* dyes) ensuring a strong and even detectable far-field signal which enabled the quantification of the enhancement due to the presence of the tip. Anderson also reported Raman enhancement from a sulfur film deposited on a glass slide using a gold-coated AFM tip. [70]

Zenobi et al. [71] used BCB (Brilliant Cresyl Blue) molecules deposited on a glass support and a silver-coated AFM tip. They could report an enhancement factor of  $10^4$ . They also reported TERS signal from a  $C_{60}$  monolayer. Kawata et al. [68] reported TERS from a thin layer of Rhodamine 6G (Rh6G) deposited on thin silver plates on glass and silver-coated AFM tip. They reported an enhancement factor of 40. However, this enhancement factor is highly underestimated as the far-field signal they observed was probably also originating from several SERS hot spots due to the presence of silver nanoplates in the focus of the laser. [72]

The same year Pettinger's group reported TERS from BCB deposited on a thin gold layer on glass with a silver STM probe. [69]

BCB and Rh6G have been widely used in TERS experiments as standard reference molecules. They provide strong Raman signal and allowed TERS to reach a breakthrough in 2008 with the detection of single BCB molecules at very low laser power in UHV. These results were reporter by Pettinger's group [73] with a  $10^6$ enhancement factor.

#### 1.4.2 About TERS enhancement

The enhancement factor quantifies the signal enhancement obtained in TERS. It is defined in a similar way to what was presented above for SERS by:

$$EF = \frac{I_{\rm NF}}{I_{\rm FF}} \times \frac{N_{\rm FF}}{N_{\rm NF}} \tag{1.28}$$

where  $I_{\rm NF}$  is the near-field intensity of a vibrational mode provided by TERS,  $I_{\rm FF}$ the intensity of the same mode in the far-field spectrum (microRaman) and  $N_{\rm NF}$ and  $N_{\rm FF}$  are the numbers of molecules probed by the near-field and the far-field respectively. Practically, the evaluation of the EF requires to be able to distinguish between the pure TER signature and the far-field signal and to assess the number of molecules probed in each case.

The discrimination between the far-field and the near-field signal is easy as a TER spectrum is the sum of  $I_{\rm NF}$  and  $I_{\rm FF}$ . The pure far-field signal is obtained usually by collecting a spectrum after pulling the tip away from the sample. When the objective and the tip are fixed and when a side or top illumination mode is used (which is our case in this work) the FF contribution is obtained after retracting the sample by a few nanometres (usually 10 to 50).

Determining the number of molecules is simple in case of a monolayer or thin layer or molecules: the number of molecules probed by TERS can be approximately estimated to be proportional to half the square of the tip radius,  $R_{\rm tip}^2/2$ . [74] The area of the surface probed by microRaman is proportional to  $R_{\rm foc}^2$ , the laser beam radius at the focus. In case of a side illumination, the shape of the focus is not circular but ellipsoidal and has to be corrected by the angle to the normal surface  $\alpha$  so that the real far-field focus area is proportional to  $R_{\rm foc}^2 \cos(\alpha)$ : [72]

$$EF = 4\left(\frac{I_{\rm NF} + I_{\rm FF}}{I_{\rm FF}} - 1\right) \times \left(\frac{R_{\rm foc}}{R_{\rm tip}}\right)^2 \cos(\alpha) \tag{1.29}$$

As an example, TER (NF) and far-field (FF) spectra of a self-assembled monolayer of thioazobenzene that forms homogeneous layers on gold is shown on Figure 1.8. The TER spectrum acquired in STM-TERS is superimposed to the FF spectrum acquired while the sample is retracted by 30 nm with the same laser power and integration time. In this case, the far-field signal does not allow one to detect any of the Raman bands of the molecule. If the FF signal cannot be detected it is assumed that its intensity is lower than the maximum of the signal noise in the FF spectrum. This value is then arbitrarily chosen as  $I_{\rm FF}$ . This assumption can lead to a large overestimate of the FF intensity. With this molecule and such a low laser power (1  $\mu$ W), obtaining a sufficient S/N ratio requires long integration times (minutes). In our configuration  $\alpha = 60^{\circ}$  and the beam radius is around 500 nm. We chose a tip radius of 30 nm which is a value commonly observed on SEM measurements. Practically, a better estimation of the tip radius can be obtained by a deconvolution procedure when a well-defined object is imaged. With the intensities reported on Fig. 1.8b, the EF can be estimated to be at least  $6 \cdot 10^5$ . This value is obviously below the real enhancement value but this method can be used to compare tips quantitatively on a reference sample.



Figure 1.8 – a) NF and FF spectra of a thioazobenzene SAM on gold. STM TERS (gold tip, 633 nm, 1 muW, bias voltage (BV): 100 mV,  $i_t$ : 100 pA) in contact with the sample (NF) and with the sample retracted by 30 nm (FF); b) Zoom onto the framed area for NF and FF spectra with intensities used for the calculation of the EF:  $6 \cdot 10^5$ .

Another possible source of EF underestimation in the previous calculation is the size of the NF region below the tip especially when the sample is a noble metal: this configuration that will be described later as the *gap mode* provides higher enhancements and lateral resolution.

The following section will discuss the enhancement mechanisms occuring at a tapered tip and the field confinement.

#### 1.4.3 Enhancement mechanisms and gap mode configuration

In TERS a gold or silver probe tapered tip is brought at the vicinity of a surface, below *ca.* 1 nm, and a laser source is focused on its apex, the polarization being linear and aligned with the shaft of the tip. The laser induces a resonant excitation of the SP at the apex of the tip creating a strong and localized hot spot such as in SERS. As visible excitation is commonly used in Raman spectroscopy, only gold and silver tips can support SPR. The enhancement mechanism is parent to the SERS enhancement *i.e.* with an electromagnetic mechanism based on the excitation of the plasmon resonance and a chemical mechanism that add to the lightening rod effect described in the s-SNOM section.

In gap mode TERS a noble metal substrate is used as substrate for the analyte. This configuration is singular as the tip and the sample can couple optically and form a new antenna with different plasmonic properties. One can see this interaction by considering the charge accumulation at the tip surface as a point dipole: by reducing the gap, a mirror dipole is formed within the sample by coulombic repulsion so that the LSP of the probe and the SPP of the surface couple to produce an hybrid plasmonic mode. [75] When the tip-sample distance increases TER signal evolution exhibits a behavior very similar to the one observed in the gap between two NPs. [76] Pettinger et al. examined the TERS enhancement and the plasmonic properties of the tip by varying the gap distance. By varying the gap between 1 and 10 nm they could observe a strong and rapid decrease in TERS and background intensity which highlights the strong effect of the optical coupling in the gap mode. They also analyzed background signal (lorentzian shape) in TER spectra and assumed its maximum to be the LSPR position of the tip-sample plasmonic antenna. They could observe a blueshift as the distance increases similarly to what is observed between two NPs. [77]

Another consequence of the gap-mode in TERS is the confinement of the nearfield below the tip. Beck et al. calculated the field enhancement and its extent in a gap between a 10 nm radius gold tip and a gold substrate. They found that as the gap is larger than the tip radius, the near-field is not affected and the enhancement can be compared to the one of a free-standing tip (apex mode regime). However below this value the near-field is increasingly confined (hybrid gap plasmon) to roughly one fourth of the initial confinement. [75] This phenomenon is shown in Figure 1.9.



Figure 1.9 - Calculated field distribution around a 10 nm radius gold TERS tip above a gold film with three different gap widths. Numbers in the lower left corners indicate multiplying factors that were applied to the color scale and below, the electric field confinement from 0.2 nm gap width to a few hundred of nm. Adapted from [75].

The gap-mode configuration has also shown to be efficient with other metal substrates that can couple to the TERS tip such as Cu, Mo, Ti, Ni or Pt [78, 79] which is interesting for experiments that cannot be performed on gold or silver substrates or for investigating catalytic reactions that can occur on such metals.

#### 1.4.4 Spatial resolution in TERS

The spatial resolution of a SPM or SNOM probe is evaluated through its ability to distinguish between two different adjacent objects. In TERS particularly, it can be experimentally determined by imaging small objects such as single molecules, [80-83] 1D (C<sub>60</sub>) or 2D (nanotubes or nanowires) materials, [84,85] an interface between two different materials [86] or molecular layers. [87]

Lateral resolution as low as 1.7 nm has been reported on single-wall carbon nanotubes (SWCNTs) imaged by gold coated AFM probes with radii of curvature ranging from 30 to 80 nm. [88] This is still to our knowledge the smallest reported lateral resolution at the ambient. Development of TERS in UHV has even allowed Dong's group to perform TERS imaging at the sub-nanometre scale reaching the submolecular imaging: distinct vibrational modes could be extracted in a single flatlying H<sub>2</sub>TBPP porphyrin deposited on Ag(111). [89] New questions have emerged about the mechanism of TERS enhancement given that such a resolution cannot be fully understood on the basis of a classical electromagnetic theory.

The spatial resolution is often assumed to be limited by the size of the tip apex but it can be increased in the gap mode due to strong field confinement. In the gap mode, the confinement was calculated to be proportional to  $\sqrt{R_{tip}d}$ (see Figure 1.9, [75]) where d is the width of the gap. This model which considers only classical electromagnetic theory can easily account for resolution below 10 nm and down to 1 nm for a tip radius around 5 nm.

Various theoretical models have been proposed to explain these results: timedependent density functional theory calculations (TDDFT) incorporating a quantum mechanics component to the system have demonstrated that the localized nearfield could be confined down to the atomic scale which cannot be interpreted with the classical plasmon theory. [90] A classical approach by Deckert et al. involving atomic-scale protrusions at the apex of the tip could theoretically provide such high enhancement factors with confinement below the nanometre scale. [91] Zhang et al. [92] recently proposed an optical model where a molecule was considered at the junction between a silver tip and a silver substrate: in such a configuration, the enhancement is so strong that the Stokes scattering has to be considered as a new source of excitation for the molecule itself. This was called the molecule self-interaction since the molecule plays an important role in the new coupled system allowing the creation of what the authors called a "super-hot spot" with a width at least 3 times lower than without the molecule.

All these theoretical views are still under debate and have to be supported by experimental proofs but greatly help to better understand the physical phenomena occurring in these very particular optical nano-cavities. From all the previous description of the physics hiden behind TERS enhancement, one can clearly understand that the control of the distance between the tip and the sample is a key parameter in TERS experiments. In the following, the probe to sample distance control will be discussed.

#### 1.4.5 Feedback Mechanisms

As explained before, it is crucial to maintain a constant and short distance between the tip and the specimen to be analyzed, within the nanometre range since the enhancement of the electric field decreases dramatically with the distance. Three main near-field microscope feedback mechanisms are used for TERS: AFM-TERS, STM-TERS and Tuning-Fork-based TERS (TF-TERS: normal or shear-force, NF or TF). They will be described in the following, highlighting their advantages and intrinsic drawbacks for TERS and their possible use in liquids for EC-TERS.

All these feedback mechanisms rely on the change of one measurable parameter reflecting the interaction between the tip and the sample: a feedback loop ensures this parameter to remain constant by moving precisely (with a piezoelectric stage) and quickly the probe or the sample in the z direction, while the tips or the sample is scanned in the xy plan. Thus, the relative motion in z is recorded and reflects the topography below the tip.

#### 1.4.5.1 AFM-TERS

In AFM, the probe is made of an oscillating cantilever (typically made of silicon) that bears a nanometre size tip at the extremity. In AC mode of AFM, the cantilever is excited close to its resonance frequency and oscillates with an amplitude that can be modulated. Interaction forces with the sample induce a decrease of the amplitude and shifts of the oscillation phase. Usually, the feedback is ensured by tracking the amplitude of the cantilever oscillation. The cantilevers are coated with a reflective aluminium layer: a laser is focused at the extremity and reflected towards a four-quadrant photodiode that senses the laser deflection and is analyzed. The Z-deflection collected by the photodiode (converted to a voltage) is compared to a reference value chosen from the approach curve and the piezoelectric stage constantly adjusts the Z position to keep this value, *i.e.* the forces probed by the tip, constant. The feedback time constant is adjusted with integral and proportional gains to minimize the error signal (difference between the measured and the setpoint amplitude): correction of the error with the feedback loop is at the origin of the topographic information.

AFM is versatile as it can be used on any type of substrates (insulators, conductor or semiconductor materials) and allows scanning areas as large as tens of micrometres. AFM can provide atomic resolution under UHV conditions [93,94] but also in liquids. [95] As the type of substrates that can be analyzed by AFM-TERS is wide, we can find a large amount of papers using this feedback mechanisms in all the fields already explored by TERS in any configuration for the excitation/collection mode. Pioneer works by Kawata et al. [68] on Rhodamine 6-G and Zenobi et al. [71] on Brilliant Cresyl Blue (BCB) in 2000 used metal coated AFM silicon probes in a bottom illumination and collection configuration. AFM is also widely used for probing isolated biological objects. As AFM can be used on any type of sample and especially on non-conductive ones, it is particularly interesting to use this imaging mode on biological samples such as cells, viruses, lipidic membranes, etc. Cialla et al. studied for example the composition of the membrane of single viruses (300 nm in length and 20 nm in width) and could distinguish reproducibly Raman signature from the capsule proteins and from RNA. [96] Another group proposed to use TERS to distinguish two types of viruses: no far field signal could be clearly extracted but TERS revealed the chemical composition for each virus. [97] The groups of Deckert, Zenobi and Bonhommeau studied amyloid fibrils involved in neurodegenerative diseases using AFM-based TERS. [98–100]

However, one of the drawbacks of AFM-TERS is related to the probe coating. Indeed, the balance between the thickness of metal (and then the lateral resolution) and the occurrence of a field-enhancement at the apex is tedious. Moreover, as the gold or silver films are thin, their mechanical resistance is poor and it is impossible to use high laser powers without degradation of the metal coating. Another drawback may be the cost: commercial AFM-TERS tips are indeed very expensive. Using bulk metal tips is also possible but the reliability of these tips is still controversial: controlling the quality factor of the tip which is crucial to ensure a good imaging quality (for the topography) is still a challenge.

A last drawback of AC-AFM for TERS measurements is that the tip-sample distance varies continuously ranging from a few to several tens of nanometres. Therefore, in a large portion of the oscillation cycle the TERS enhancement is very weak as the tip/sample distance is too large. In order to overcome this drawback, spectra may be acquired while the oscillation is stopped and the tip maintained at a short distance corresponding to a predefined force (contact mode).

#### 1.4.5.2 **STM-TERS**

STM is a scanning probe microscopy where a bias is applied between a metallic nanometre-sized tip and a conductive or semiconductor sample. When, the tip is close to the sample (less than 1 nm), electrons can be transferred from the tip to the sample thanks to the quantum tunnel effect through a classically forbidden barrier. In this feedback mechanism the tunnelling current does not really probe the topography of the surface but the density of states of the metal or of the molecules on the metal. This assumption is crucial when it comes to interpret STM maps with atomic resolution which is not the case in our TERS experiments in air as the stability of the setup during TERS experiments is not good enough to reach this resolution due to mechanical noise.

STM-TERS is widely used at it can be implemented with probes made from electrochemically etched gold or silver wires. The method for their fabrication will be discussed in the following chapter. Moreover, STM is an appropriate and easy feedback mode for topographic surface analysis for conductive substrates. It has also been developed in liquids and in electrochemical environments for decades down to the atomic resolution. [101]

#### 1.4.5.3 **TF-TERS**

The basic principle of normal or shear-force (NF or SF) imaging is similar to AFM: a probe glued onto a quartz tuning-fork (TF) oscillates above the sample at the resonance frequency of the TF and interactions with the sample induce changes in both the amplitude and the phase of the oscillation. Commonly, microfabricated quartz TF are used as time standards in clock watches. As represented in Figure 1.10 it is made of two prongs that can oscillate at a resonance frequency ( $f_0$  with a usual  $2^{15}$  Hz = 32.8 kHz value for a non-modified TF): these oscillations induce surface charges on the quartz prongs that are collected by electrodes and measured using lock-in detection. Their oscillation can therefore be induced by applying an external voltage. If the system is considered as an effective harmonic oscillator, it can be described by a Lorentzian function with a quality factor (Q-factor) defined as:

$$Q = \frac{f_0}{\Gamma} = \frac{2\pi f_0}{\gamma\sqrt{3}}$$
(1.30)

where  $\Gamma$  is the full width at half maximum (FWHM) of the resonance peak (in Hz), and  $\gamma$  is the damping constant ( sum of both the intrinsic damping associated with the physical properties of the TF, and the one related to the interactions with the sample).



Figure 1.10 – TERS tip glued onto the prong of a TF (NF configuration).

This Q-factor is a major issue in TF-based sensing: the higher the Q factor, the higher the sensitivity but it is also a key parameter for the time response of the TF. When the probe-sample distance changes abruptly (topographic change on the sample),  $f_0$  changes and an oscillatory transient behavior is observed with a characteristic time  $\tau$  to decay to the new steady-state:

$$\tau \approx \frac{\sqrt{3}Q}{\pi f_0} \tag{1.31}$$

which highlights the intrinsic drawback of a high Q-factor and high sensitivity which means a low time response for the probe but then prevents high scanning rates in imaging. For example a free, standing TF with a typical Q factor of 25280 and  $f_0 = 27.504$  kHz has a response time of ~ 5 s while, once a tip is glued onto one prong, the system becomes asymmetric (the center of masses is no longer between the prong) and the Q factor decreases as the resonance frequency decreases ( $f_0 = 27.503$  kHz, Q = 130): the response time is now ~ 25 ms.

The targeted range of Q for NF-TERS or SNOM is between 500 and 3000 (100 <

 $\tau < 500$  ms) which enables a good sensitivity and a reasonable time constant suitable for fast scanning of the samples.

TF can be used in two configurations: if the probe is glued along the main axis of the prong, the tip probes shear forces (SF); if the tip is glued perpendicular to the long axis, the tip will oscillate as in an AFM and probe normal-force (NF). The latter is usually used in SNOM as it allows a better tip-to-sample distance control.

TF-based TERS studies are not as commonly encountered in the literature as AFM-based ones because of the difficulty to obtain suitable tip reproducibly with a Q-factor in the 500 - 3000 range.

#### **1.4.6** Fabrication of AFM and STM-TERS tips

The two major ways of producing TERS tips are based either on the physical deposition of a thin layer of gold or silver onto commercial AFM probes or on the electrochemical etching of bulk metallic wires. The latter produces tips which can be used with a STM, AFM or NF-tuning-fork feedback. Even if some companies commercialize TERS tips (AFM: Horiba, NT-MDT, Brücker (260  $\in$  per tip), TipsNano (290  $\in$  per tip); STM: Brücker (160  $\in$  per tip)), they are still expensive and as no standardized procedure has been established, it is difficult to compare the efficiency and reliability of different TERS probes. An objective comparison of TERS probes and instrumentations is thus difficult. These difficulties have been highlighted by a large inter-laboratory study (twelve groups involved) in 2013: the same samples (thiophenol, and a peptide self-assembled on gold) prepared by one group was investigated by TERS in different configurations (with top, side or bottom illumination and one equiped whith a parabolic mirror) and with different feedback mechanisms (AFM and NF, SF or STM). Even if the spectral pattern was similar on the same sample, a broad variability was observed on the intensities, on the Raman shifts of the main bands and on the signal to noise ratio in similar conditions. Even into the same research groups, variability was observed when different

feedback mechanisms or metals were used. [102] This study is a good example of the difficulties encountered in characterizing the efficiency of a TERS tip as it depends on many non-standardized experimental parameters. It also highlights the lack of reproducibility in the fabrication protocols. Between all the approaches that have been reported for the development of TERS active probes, the coating of commercial AFM probes by physical deposition of metals and the electrochemical etching of bulk metal wires (usually silver or gold) are by far the most popular. The latter are versatile as they can be used in the STM-TERS mode, but also can be glued on the prong of a tuning fork for SF or NF-TERS measurements. The etched wires can also be bent at its extremity and flattened to produce a cantilever and glued on a chip for AFM-TERS. [103, 104]

The fabrication of TERS tips mainly depends on the application and on the type of feedback mode selected for the TERS measurement. For the most commonly used configuration, AFM-TERS, many groups have used standard Si AFM tips onto which gold, silver, or both metals are deposited by physical deposition techniques. [68, 71] This process allows one to control the thickness of metal deposited and benefits from the initial nanometric sharpness of the AFM tip. This method was proposed for tuning the LSPR resonance of the tip by adjusting the thickness, the composition of the deposited layer and of the possible dielectric coatings. [105–107] Metal coated probes suffer from one major drawback: the thickness of the layer can be controlled to reach a maximum of the field enhancement but this is at the expense of the spatial resolution. [105]

More recently, Ren et al. developped an electrochemical deposition procedure for the preparation of AFM-TERS tips: Si AFM probes are coated with silver by potentiostatic electrodeposition in a silver sulfite  $(Ag_2SO_3)$  solution. A precise control of the deposition potential and time enabled them to produce TERS tips with high enhancement factors (10<sup>5</sup>) and good reproducibility. Surprisingly, they evidenced a long lifetime (around 13 days) for these probes much higher than the lifetime of probes prepared by physical deposition (a few hours). This was interpreted by the strong difference in the morphology of the tips (the tips prepared by electrochemical being smoother). [108]

#### 1.4.7 Other types of SNOM and TERS tips

Beyond the common bulk metal and metal coated tips, a lot of efforts have been engaged in designing more advanced tips especially in order to tune their LSPR and to produce probes with different profiles to match the wavelength of the excitation laser for a maximal enhancement of the signal. One route is the attachment of a single nanoparticle at the apex of an optical fiber, an AFM or STM tip. As the LSPR of a single particle can be finely tuned by controlling its size and its composition, it seems particularly suitable and has been reported several times: with a singlecrystal silver nano wire onto a tungsten STM tip, [109, 110] with Ag NPs produced by photoreduction of AgNO<sub>3</sub> directly onto Si AFM tips apex [111] or with Au NP at the apex of an optical fiber. [112]

Schuck's group studied experimentally the influence of the shape and the size of the TERS tip apex by designing it with focused ion beam (FIB) milling of AFM probes with the idea of precisely tuning the SPR. [113,114]

In the same trend, Raschke et al. proposed a gold tip onto which a grating is FIB-milled onto the tip shaft far above the tip apex so that the SPPs can be excited by the laser and propagate to the tip apex for TERS measurements. This approach enables a background-free TERS measurement as the sample is not illuminated with the laser. The space between the lines of the gratings is to be tuned to be adjusted to the laser wavelength. [115]

Another background-free and highly efficient SNOM probe was proposed by Weber-Bargioni et al. in 2012 called the Campanile probe: it is based on a metalinsulator-metal (MIM) nanogap fabricated at the apex of an etched optical fiber. This probe that can be seen as a plasmonic bowtie antenna and is capable of efficient far-field to near-field coupling (and vice-versa) with a broad bandwidth. It has been used for imaging the photoluminescence in InP nanowires with a spatial resolution below 50 nm. Due to its large optical bandwidth and signal enhancement capabilities, it was assumed that it could also be used for Raman spectroscopy but this has never been evidenced up to now. [116–118]

All of these approaches have been really important as they bring experimental evidences of the influence of geometrical parameters of TERS tips on LSPR position and enhancement factor, but are too expensive and too difficult to implement to be used routinely for TERS experiments.

# 1.5 Probing and inducing chemical reactions with TERS

Over the last two decades, TERS has appeared to be a new powerful analytical tool able to investigate complex samples such as biological objects [119,120] ranging from isolated nucleotides to RNA or DNA strands [121–127], cell membranes [128–130], or to discriminate proteins through the identification of aminoacids. [100,120,131] However none of these works could provide dynamic information on these biologic objects since it would require conducting experiments in liquids which is still a challenge in the TERS community. Dynamic TERS studies have however been carried out in the field of heterogeneous catalysis.

#### **1.5.1** Catalytic reactions monitored by TERS

As TERS can detect adsorbates on metal surfaces it is a technique of choice for scrutinizing heterogeneous catalytic reactions *operando*, *i.e.* reacting systems similarly to SERS. [132–134] The main advantage of TERS over SERS in catalysis lies in the possibility to distinguish different catalytic sites with different reactivity due to the high lateral resolution of TERS.

The first study on a catalytic system was reported by Domke and Pettinger in 2009: they studied at the ambient a cobalt *meso*-tetraphenylporphyrin (CoTPP) complex, an organometallic catalyst in STM-TERS supported on an Au (111) substrate. Topographic imaging revealed ordered and disordered areas that could be correlated with different states of complexation of CoTPP. TERS spectra from the disordered areas revealed vibrational signatures of CO and NO axially coordinated to CoTPP and generated upon the catalytic reduction of  $CO_2$  and  $NO_2$  from ambient air. [135] However, in this study, the atmosphere was not controlled and the COand NO-adducts formation mechanistic study would have required a precise control of the atmosphere gases. This was recently performed by Van Duyne's group in 2018: using a UHV-STM-TERS setup they could investigate the oxygen binding to Cobalt(II) phtalocyanine (CoPc), an important and noble metal-free catalyst for oxygen reduction reaction. As the atmosphere was controlled an isotopic study of the TER spectra by exposing the samples to  ${}^{18}O_2$  and  ${}^{16}O_2$ , Co – O and O – O vibrational modes could be observed and allowed to identify free-standing CoPc from the molecular  $O_2$  or atomic O-bound CoPc. [136]

In 2016, Ren et al. demonstrated the capability of TERS to probe the catalytic properties of a Pd(sub-monolayer)/Au(111) bimetallic surface and especially at Pd step edges where the oxidation of phenylisocyanide, Ph - NC (bound to Pd and Au via its terminal carbon atom) into phenyl-isocyanate. Ph - NCO formation is facilitated due to a weaker CN bond at step edges. In this study, the TERS resolution is demonstrated to be as low as 3 nm allowing them to assess the catalytic activity at the edge precisely. [137]

#### 1.5.2 Plasmonic tip-induced reactions

In the previously mentioned papers the catalyst is a molecule lying on a bulk material or the metallic substrate. As TERS probes are made of noble metals, the tip can be used simultaneously as a nanoscale vibrational probe and a catalyst. [133, 134] The first reported TERS study of a tip-catalyzed process was performed by the groups of Deckert and Weckhuysen in 2012. [138] They followed the laserinduced dimerization of 4-nitrothiophenol (4-NTP) into p,p'-dimercaptoazobenzene (DMAB) characterized by the formation of an azo (N = N) bond and the disappearance of the nitro group( $-NO_2$ ). This photoinduced reaction is known to be activated by a metal-to-molecule charge transfer mechanism with a green laser as already demonstrated on silver SERS substrates. In the TERS study, two lasers were focused on the apex of a silver AFM tip: a red (633 nm) laser to measure the TERS signal of the molecular layer and a green (532 nm) laser to locally induce the dimerization reaction. The characteristic band of DMAB appeared only after illumination by the green laser. A similar study was led by Xu et al. who functionalized both a gold tip and a silver substrate with 4-NTP. With a red laser illumination they could at the same time induce the coupling of 4-NTP molecules between the tip and the substrate and monitor the real-time transformation by simultaneously recording TER spectra. [139]

The azo bond can also be formed by coupling two adjacent aniline residues: this approach was used by Deckert et al. in 2017 to induce the polymerization of a thiolated molecule with two aniline functions. As for the previous works, the Ag AFM tip is at the same time the catalyst of the reaction and the TERS probe enabling the monitoring of the reaction by following the appearance of the vibrational mode of the azo bond.

These studies show the ability of TERS to monitor or even catalyze reaction at a metal interface under ambient, controlled atmosphere or UHV. Recently, TERS studies have demonstrated that TERS could also be carried out in liquids paving the way to *in situ* nanoscale analysis of electrochemical reactions, as described below.

### **1.6 Electrochemical TERS**

As mentioned earlier, a great advantage of microRaman spectroscopy is the possibility to study surfaces immersed in liquids using either long working distance air objectives or water immersion objectives. Transposition to TERS is challenging because of the delicate optical alignment through a layer of liquid, compromising both the laser focusing on the tip apex and the collection efficiency of the scattered signal. However under these conditions, improvement of the TERS signal stability has been reported and explained by the reduced photo (thermal) degradation processes (transformation, desorption) at hot spots due to greater heat dissipation and lower oxygen content as compared to measurements in the air. [41]

#### **1.6.1** Configurations proposed for TERS in liquids

First we will consider the different experimental configurations that have been used to implement TERS experiments in liquids which is the first step toward EC TERS measurements.

The different configurations are summarized in Figure 1.11. As mentioned previously, for samples deposited on transparent substrates, the tip apex is illuminated from below through the sample (through an oil immersion objective) and the laser source is therefore not deviated at any liquid-air interface and crosses only a very thin layer of liquid.

Zenobi et al. pioneered TERS in liquid in 2009 using the inverted configuration [141], followed by Fujinami et al. in 2013 [142] and finally Ren et al. [41] and Van Duyne et al. in 2015 in pioneering papers on electrochemical TERS (EC-TERS) [140]. Most of these works have been performed by using AFM-TERS (except the EC STM-TERS experiments by Ren et al.) and laser illumination from the bottom using an inverted microscope.

By contrast, implementation of TERS in liquid within an upright or side con-



Figure 1.11 – Experimental configurations for performing TERS in liquids; a) side illumination and collection trough a quartz window for EC-STM-TERS, from [41]; b) inverted AFM-TERS with a mobile AFM tip and a fixed transparent sample, from [140].

figuration is the most challenging since the optical signal is inevitably deviated and considerably attenuated by refraction at the liquid-air interface. However Ren et al. in 2015 [41] and then Domke et al. since 2016 [143,144] demonstrated its feasibility by proposing a configuration where the irradiation of a TERS-STM tip is carried out through a side window opened in the liquid cell wall. An improvement of this configuration was proposed by Ren et al. in 2017 [145] by using an immersion objective and by adding a drop of water between the objective lens and the side window diminishing strongly the signal losses at this interface as it has previously shown to be efficient for conventional microRaman spectroscopy. [146] TERS imaging within such configuration may be restricted to only small displacements of the cell-sample for which the laser focusing is not compromised since displacing the sample might degrade the required fine laser alignment.

#### 1.6.2 EC TERS

The characterization and the comprehension of electroactive systems using electrochemical techniques has been efficiently extended by TERS analyses run  $ex\ situ$  to assess the structure and the distribution of surface compositions. In 2016, Ren et al. evidenced by electrochemical impedance spectroscopy (EIS) and TERS important conformation changes during the formation of a self-assembled monolayer. [147] The aromatic C = C bond vibration was used as a marker of intermolecular pi-stacking and showed a non-monotonous evolution with the contacting time of the substrate with the precursor solution. Measurement of the charge transfer resistance by EIS confirmed this tendency.

If the potential of *ex situ* TERS analyses to help the interpretation of irreversible electrochemical processes has been already established, the real-time monitoring of an electrochemical transformation by TERS (EC-TERS) represents the most interesting challenge. So far, only three different electrochemically active systems have been studied by EC-TERS setups and reported in the literature: the potential dependent protonation of 4-PBT ((4'-(pyridine-4-yl)biphenyl-4-yl) methanethiol), [41] the potential-induced reorientation of adenine on a gold surface [148] and the reduction of Nile Blue dye (NB) [140, 149] or of a covalently bound NB derivative. [150] Although the development of EC- TERS is still at its early stages, important experimental facts have already been raised by the leaders of the fields, using the different configurations described above.

The first EC-TERS characterization was carried out by Ren et al. in 2015 on 4-PBT layer adsorbed on Au (111) using an upright configuration and a side illumination with an insulated gold tip in the EC-STM mode and a bipotentiostat to control the potential of both the tip and the substrate. Distinct and stable TERS signatures associated to different protonation state of 4-PBT at pH 10 were successfully extracted when scanning the potential applied. Interestingly the protonated form could not be observed using SERS substrates made of 4-PBT functionalized Au nanoparticles. The dominant SERS signal of the double-end bonded 4-PBT molecules connecting adjacent particles (in the gap) was interpreted to mask the signal of protonated single-end-bonded, revealing the importance to control the structure of the probed interface (number of probed molecules and their organization around multiple hot spots). This control almost impossible with SERS substrates can be achieved with TERS if the molecules are deposited on a well defined substrate. [41]

Domke et al. in 2017 using a similar EC-STM configuration also demonstrated the reversible potential-induced deprotonation and subsequent reorientation of adenine molecules adsorbed on a (111) gold surface. Strong intensity changes were observed on the collected TERS spectra upon polarization and were interpreted using DFT calculations by the induced reorientation of adenine molecules on the gold surface. Switching from tilted to vertical orientations could be observed around the point of zero charge (PZC) while a planar orientation of deprotonated adenine molecules could be triggered by the strong Au-N interactions. [148]

Using the inverted TERS setup described above, a gold coated AFM probe and a conductive ITO covered coverslip, Van Duyne et al. captured the electrochemical transformation of model dye NB adsorbates described in three papers released between 2015 and 2017. [140, 149, 151] At low NB surface coverages, individual events with different behavior (single or few molecules transformation) could be detected at the tip-sample junction, revealing a distribution of local environments, *i.e.* of the standard redox potential of the molecules  $(E^{0'})$ , an observation otherwise impossible to achieve with microRaman. They could also observe that the statistical distribution of apparent standard potentials of the anodic events is narrower than for the cathodic events: this was interpreted as a lower sensitivity of the reduced form of NB to its close environment. The close proximity of the metal tip with the polarized substrate was reported to interfere locally with the electric field, potentially affecting the electrochemical response. A potential shift in the transition from oxidized and reduced forms of NB has also been observed between the TERS signal and the electrochemical current intensity measured at the sample (> 100 mV), pointing out the influence of the tip on the effective potential experienced by the scrutinized NB molecules.

#### **1.6.3** Challenges for EC-TERS

Only a few works have been published so far on TERS combined with electrochemical measurements, mostly because of the important efforts required in instrumental developments. Despite the recent progresses, TERS imaging with high spatial resolution still have to be demonstrated under electrochemical conditions. A first AFM-based TERS imaging of a CNT has recently been reported in water (but without potential control), exhibiting a sub-30 nm lateral resolution. [152] As the spatial resolution limit under electrochemical conditions is expected to reach the single digit nanometre scale as in air, EC-TERS will probably help in pushing forward the understanding of electrochemical and electrocatalytic events at specific sites of an electrode. It is expected to reach the single molecule analysis to visualize directly the chemical consequences of an electron transfer.

Note that several fundamental questions have still to be answered such as the influence the particular environment associated to electrochemical measurements: effect of the surrounding medium, electrolyte, charges at the interface, etc. Moreover, as it has been underlined by Van Duyne et al., [140] the presence of the tip seems to affect the electrochemical behaviour of the electroactive molecules (perturbation of the electrochemical double layer). This influence has to be evaluated for further analysis of EC-TER spectra.

## Chapter 2

### **Description of TERS experiments**

In this chapter we will detail the main technical requirements and experimental details of TERS experiments. We will first describe the different micro and nano-Raman setups. Then, the fabrication process of TERS tips used in this work will be presented.

## 2.1 Description of the setup for microRaman and TERS experiments

In this part the technical characteristics of the Raman spectrometer used in LISE will be exposed as well as the optical coupling to the scanning probe microscopy (SPM: STM, AFM, TF) platform for TERS experiments.

The spectrometer we used is a LabRam HR Evolution (Horiba). It is an automated confocal Raman microscope. A simplified scheme in Figure 2.1 describes the optical path into the spectrometer and the coupling to a Smart SPM platform (Omegascope, AIST) for TERS experiments. All the abbreviations in the following refer to Figure 2.1.

An internal HeNe laser (633 nm, 10  $\mu$ W) provides a linearly polarized beam. It is first cleaned by a laser-line clean-up filter (F1) and directed to a neutral density filter wheel (ND) with 9 positions (100 %, 50 %, 25 %, 10 %, 5 %, 2.5 %, 1 %, 0.1 % and 0.01 % of the initial power). An additional polarizer can be installed before the ND filter to change the polarization angle of the beam and adjust it to the shape of the TERS tip in NF experiments. After the laser passes through a beam expander (BE), mirror (M3) directs the beam on the rejection Filter F2<sup>-1</sup> that reflects the beam towards the objective ( $\mu$ Raman part of the scheme). For microRaman measurements, M4 is removed from the path (all the mirrors symbolized with dashed-line can be manually or automatically removed depending on the application). Mirror M10 is used only to reflect a part of the signal to a side CCD camera which helps visualizing both the sample via white light illumination and the focalized laser spot. For microRaman experiments the sample is mounted onto a motorized XYZ platform designed for compositional mapping.

For TERS measurements, the laser is deviated by mirror M4 that ensures a top or side optical access to the TERS tip mounted on scanning probe microscope (SPM) (Omegascope, AIST). The Raman spectrometer and the SPM are supported by the same optical table to ensure the stability of the mechanical and optical coupling. When mirror M5 is placed on the optical path, the laser beam enters the pupil of a long working distance objective mounted on a piezo stage (XYZ(1)) with an angle of  $60^{\circ}$  to the normal to be focused on the apex of the TERS tip. Rough prealignment of the laser can be done with micrometre screws on the Omegascope module through video control using a CCD camera positioned between M7 and the objective. This CCD is manually removed before any measurements.

For top illumination and collection mirror M5 is removed. The piezo objective stage XYZ(1) is positioned vertically below mirror M6 enabling the laser beam to be focused to the apex of a slightly bent TERS tip. As for side configuration, a CCD camera can help with the alignment of the laser on the tip. M6 is replaced by a semi-reflecting mirror for this operation. During measurements, M6 is used for

 $<sup>^1\</sup>mathrm{In}$  our setup, this filter is a notch filter for the 632.8 nm laser line and an edge filter for all other wavelengths.

excitation an collection.

For all configurations, the back-scattered signal is filtered by the laser-line rejection filter F2 (a notch filter for 632.8 nm and an edge filter for other wavelengths). The role of F2 is to remove the Rayleigh scattered light from the collected signal so that only Stokes (and anti-Stokes with the notch filter) contribution is directed to the detector (CCD3 camera, EM-CCD Newton 970, Andor, cooled to -70 °C with a Peltier stage) and recorded. Before reaching the detector, the scattered signal can be filtered by a polarizer (P2) and then passes through a confocal hole (CH): its aperture size can be adjusted to control the depth of the analysis. Diminishing the size of this confocal hole in TERS experiments ensures that most of the signal originates from a thin focal plan where the tip apex is positioned, and that the far-field contribution is minimized. Finally, the Raman signal is directed to the spectrometer containing two parabolic mirrors and two diffraction gratings (Gr) which can be selected to adjust the spectral resolution (3 available: 300, 600 and 1200 grooves per mm). A shutter (Sh) is positioned before Gr and is open only during spectra acquisition. The grating finally disperses the collected scattered signal on the detector: each pixel of the CCD camera receives photons related to a range of wavelength (resolution). The spectral resolution (in  $cm^{-1}$ ) is defined by the periodicity of the grating, the excitation laser wavelength, the number and the size of pixels on the EM-CCD (1600  $\times$  400 array of 16  $\mu$ m pixels).

In this thesis, all the experiments were performed using a 300 grooves per mm grating and most of the TERS experiments were performed with a 633 nm laser. With this grating and the EM-CCD Newton (Andor), the spectral resolution is 0.065 nm (*i.e.*  $1.4 \text{ cm}^{-1}$  between 0 and 2200 cm<sup>-1</sup>). Table 2.1 gives the spectral resolution obtained with each laser wavelength available as well as the cut-off frequency of each notch (**n**) or edge (**e**) filter. This resolution can be decreased when binning of the data is used to increase the signal intensity: pixels of the spectra are then the sum of two or more pixels of the CCD which enables one to increase the

signal to noise ratio at the expense of the spectral resolution. Usually, in TERS mapping, the binning (bin) is set to 2 to reduce the acquisition time. No binning was performed on the spectra acquired in this work when precise analysis of the band shifts was necessary.

Table 2.1 - Spectral resolution and cut-off frequency of the filters for the three laser wavelengths used in this work. **n**: notch filter; **e**: edge filer.

Laser (nm)	Resolution $(cm^{-1})$	Resolution $(cm^{-1}, bin=2)$	Cut-off $(cm^{-1})$
632.8	1.4	2.7	250 <b>n</b> (and >1600) <sup><i>a</i></sup>
532	1.9	3.8	50 e
473	2.4	4.8	110 <b>e</b>

<sup>a</sup>Above 700 nm, the reponse of the back-illuminated EM-CCD camera is not reliable as oscillations appear on the spectra, compromising the detection of Raman bands in this spectral region.

The quality of the coupling of the Raman spectrometer to the SPM is crucial in TERS experiments. It relies on the stability of the mechanical coupling between the two systems and on the stability of the optical components on the optical path.

The precise alignment of the system (spectrometer, laser line, Omegascope) was verified on models samples by evaluating the signal level and the confocality.

The calibration of the spectrometer was made before each experiment with the  $520.7 \text{ cm}^{-1}$  band of silicon as reference.



Figure 2.1 – Description of the optical path in LabRam HR Evolution Raman spectrometer (Horiba) and of the coupling with the Omegascope SPM platform (AIST). See main text for abbreviations.
## 2.2 TERS tips manufacturing

As previously mentioned, one of the main impediments to TERS implementation and development is the production of efficient and robust TERS tips (mechanically and chemically) at low manufacturing cost.

### 2.2.1 Fabrication of gold TERS tips

In this work, we mainly developed bulk gold TERS tips for three main reasons:

- they can be produced without much effort with good reproducibility following a fabrication protocol detailed hereafter;
- they do not degrade as fast as metal-coated tips and are more chemically stable than silver tips which oxidize in the air;
- EC STM-TERS measurements require the tip-sample junction to be biased but also the potential of the sample to be controlled and possibly set to oxidative values. As oxidation of gold occurs at higher potential than silver, gold tips enable the exploration of a larger potential range.

The electrochemical etching of gold wires can be achieved in solutions of hydrochloric acid (HCl) as gold metal can be oxidized into chloraurate ions (AuCl<sub>4</sub><sup>-</sup> and AuCl<sub>2</sub><sup>-</sup>). The standard potentials of the associated redox couples are given by A.J. Bard in Ref. [153]:

$$AuCl_2^- + e^- = Au + 2Cl^-$$
 (E<sup>0</sup> = 1.154 V/SHE) (2.1)

$$AuCl_4^- + 3e^- = Au + 4Cl^-$$
 (E<sup>0</sup> = 1.002 V/SHE) (2.2)

$$AuCl_4^- + 2e^- = AuCl_2^- + 2Cl^-$$
 (E<sup>0</sup> = 0.926 V/SHE) (2.3)

Usually, a gold wire anode is positioned at the center of a ring-shaped gold or platinum electrode (cathode) so that the current lines are homogeneous in the

cell, providing tapered and symmetrical tips through an homogeneous etching (Figure 2.2,a). Two main classes of etching are described depending on the type of voltage applied (AC or DC). In 2004 Ren et al. published a study using DC voltage and exploring the electrolyte composition as well as the voltage applied [154]: an electrolyte composed of a 1:1 (v:v) mixture of aqueous hydrochloride acid (37%)and absolute ethanol and a DC voltage (2.2 V) gave the desired tapered and smooth profiles for TERS application. The anode is a 250  $\mu$ m gold wire (99% purity) and the ring-shaped cathode is made of platinum. In this configuration and at such a voltage, an oscillatory behavior is observed in the current response due to the interfacial depletion in chloride ions and the accumulation at the interface of insoluble gold complexes. This depletion allows the formation of gold oxides that temporarily block the electrode causing sudden oscillations in current. This work has highlighted the importance of selecting this oscillation region of potential to obtain sharp tips. Note that the formation of oxygen and chlorine gas bubbles at the gold electrolyte interface can also induce perturbations. The presence of ethanol in the electrolyte modified the surface tension of the electroly and helps reducing the size of the bubbles and then the possible perturbations at the interface. As production of hydrogen bubbles at the cathode can also affect the etching process, a special cell (beakercell) was proposed by Kharintsev et al. in 2013: in this cell an additional beaker is introduced in solution between the cathode and the gold wire to eliminate the perturbation induced by the hydrogen production. [155] However, this configuration may increase the electrolyte resistance between both electrodes and severely affect the potential of the wire in this two-electrode configuration. But interestingly, this group also proposed to use potential pulses. Two potentials are applied alternatively, one which corresponds to the oscillatory regime for the etching, the other one corresponds to a relaxation potential below this oscillatory regime, allowing the diffusion of the corrosion products away from the electrode and of the chloride ions toward the gold wire. This procedure was further refined by varying the pulses sequence [156] and recently by using a three-electrode configuration enabling a better control of the potential applied to the wire. [157]



Figure 2.2 – Elaboration of gold TERS efficient tip by electrochemical etching: a) the gold wire (working electrode, 250  $\mu$ m diameter) is positioned at the center of a platinum ring counter electrode in etching bath composed of a mixture of HCl and EtOH. During the electroetching process when the diameter of the Au wire decreases the meniscus position progressively shifts downward until the final cutoff, producing the tapered profile; b) the bath composition and the electrochemical sequence had to be optimized to produce in a reproducible way TERS tips with a radius of curvature around 20 nm.

On the basis of these works, Alice Dauphin (a bachelor student intern) developed an etching protocol before this work started. It uses an etching bath composed of a 1:1 (v:v) HCl (37%) and absolute ethanol mixture and a pulsed sequence for the polarization.<sup>2</sup> The procedure was further improved at the beginning of this thesis by adding an analog switch in the circuit. The latter which compares the read-out etching current with a chosen threshold value opens the circuit when the current drops below this pre-set value when the immersed part of the wire falls down. This prevents over-etching that can happen if the apex of the tip is still in contact with the solution. With this fabrication procedure we could produce with a good reliability smooth and sharp tips (with radii of curvature as low as 20 nm) with a controlled cone angle in less than 10 minutes for gold wires with a 250  $\mu$ m diameter. All the tips are rinsed with bi-distilled water and absolute ethanol after fabrication and can be stored several weeks after preparation. SEM images present the typical profile obtained after etching of 250  $\mu$ m diameter gold wire (Figure 2.2,b). In order to prevent carbon contamination during SEM imaging of the tips, SEM analysis was

 $<sup>^{2}</sup>$ Further details cannot be disclosed. A Soleau envelope was filed in 2017 protecting this process as well as the fabrication of silver tips described in the following.

performed after TERS experiments if needed. In order to preselect suitable tips after their fabrication an optical microscope (40X objective) was preferred to sort and possibly discard round-shaped and non-TERS-active tips.

## 2.2.2 Fabrication of silver TERS tips

As for gold tips, several procedures have already been proposed for the electrochemical etching of silver wires for the fabrication of TERS tips. The variety of the etchants and of the type of voltage applied is wide. The etchant baths are usually based on ammonia solutions [158, 159], ammonium nitrate [160], nitric acid [161], citric acid [162] and perchloric acid [159, 163–166] with additives (methanol, ethanol). Similarly to gold tips, the range of applied potentials is wide (from a few to tens of V) as well as the type of applied voltages (AC, DC, pulsed). For this work, the etching of silver wires was explored too, during the internship of Ghizlene Zenasni (bachelor student) in 2017. We rapidly converged onto applying DC voltage in a 1:4 (v:v) perchloric acid (70%) and ethanol electrolyte. A pulsed sequence similar to the one used for gold did not lead to reproducible results. For silver, the etching mechanism is in fact more simple as no electrode passivation takes place. Using the same setup as for gold tips and a cut-off switch in the circuit, this protocol enabled the reliable and reproducible fabrication of Ag TERS tips in less than three minutes. The fabricated tips with a radius of curvature lower than 100 nm showed EF between  $1 \cdot 10^3$  and  $2 \cdot 10^4$ . A SEM-FEG image of an etched silver TERS tip is given in Figure 2.3

As for Au TERS tips, to prevent carbon contamination during SEM-FEG measurements, the tips were preselected with an optical microscope but immediately used in TERS experiments to prevent any degradation of their performances upon exposure to the air (oxidation).



Figure 2.3 – SEM-FEG image of an etched silver tip at two different magnifications with a radius of curvature of  $\sim 60$  nm

## 2.2.3 Prevention of TERS tips degradation

Among difficulties encountered during TERS implementation, tip performances degradation is by far the most detrimental. Such a degradation can originate from a contamination of the tips by organic molecules while scanning a sample or during the manipulation of the tips. The first one cannot be avoided and has to be checked after each TERS measurement by simply pulling away the sample and measuring the Raman response of the tip apex. To reproduce a gap-mode configuration, tip contamination can be evaluated by recording a TER spectrum on a clean gold substrate after any measurement.

An example of the contamination can be seen in Figure 2.4 on a spectrum acquired at the tip before any scan on a sample. The main Raman bands indicate the adsorption of probably several organic contaminants (indicated with \*).

In order to protect TERS tips from contamination a few treatments can be applied after the tip fabrication. Zenobi et al. proposed a protection method based on the functionnalization of the TERS tip with a small organic molecule (ethanethiolate) which is expected to prevent adsorption of other organic molecules but at the same time increases the tip-sample distance and causes a drop of the EF by a factor of 5. [141]



Figure 2.4 – TER spectrum at the apex of a silver tip exhibiting bands of the oxides and sulfide stretching modes (below 400 cm<sup>-1</sup>). Bands marked with asterisks are assigned to organic contaminants.  $\lambda_{\text{exc}} = 532 \text{ nm}, 220 \ \mu\text{W}, 5 \text{ s}.$ 

Ren et al. proposed a way to regenerate gold TERS tips by immersion of the contaminated tips into a concentrated sulfuric acid solution. This procedure enables the removal of organic contaminants adsorbed during previous TERS measurements or after a long storage. [167]

For silver tips, another drawback is the oxidation of silver at air. It usually can be oxidized by oxygen into  $Ag_2 - O$  and by  $H_2S$  or sulfur containing species into  $Ag_2S$ . This oxidation of the surface affects the plasmonic properties of nanostructures. For instance, the LSPR of silver NPs is quickly red shifted and their EF diminishes, resulting in drastic decrease of SERS efficiency. [168]

The formation of an oxide layer can be seen on the TER spectrum of the contaminated silver tip in Figure 2.4 as the oxidation products exhibit strong Raman bands below 300 cm<sup>-1</sup>. [169]

Laser-induced oxidation is also observed for TERS silver tips. This phenomenon could be observed after a long illumination of a silver tip at high laser power (632.8 nm, 3.3 mW) and long exposure. TER spectra were acquired with both 632.8 and 532 nm lasers before a long-time exposure for comparison(Figure 2.5). The STM-TER spectrum at 632.8 nm exhibits a clear signature from the organic SAM on the sample (thioazobenzene); a slight shoulder at low frequency can indicate the presence of an oxide layer on the tip. However, the 632.8 nm notch filter used with the 632.8 nm line truncates the spectrum below 250 cm<sup>-1</sup>. If the 532 nm laser is used, a lower signal to noise ratio is obtained for the TER signature of the azobenzene SAM (due to a lower enhancement at this wavelength) but low frequency bands exhibit clearly stretching modes of silver oxides and sulfide. After illuminating the tip during 300 s, TER spectra were acquired under similar conditions with both excitation lasers: the TER spectrum obtained with the red laser displays a clear rising of the tail of the oxide band below 400 cm<sup>-1</sup> and a strong decrease of the intensity of the Raman bands intensity of thioazobenzene. The TER spectrum acquired at 532 nm exhibits strong band intensities in the low frequency region and new ones especially below 200 cm<sup>-1</sup> which was attributed to the formation of Ag<sub>2</sub>S. Note that at this wavelength, the TERS intensity is not affected by a long illumination.

The mean lifetime of a silver TERS tip exposed to the ambient ranges from 6 to 8 hours maximum. Silver tips can be stored under inert atmosphere after their fabrication to extend their lifetime up to several weeks. [170]

Regeneration of oxidized tips was also proposed: the principle is based on the galvanic reduction of silver oxides or sulfides in presence of aluminium  $(E^0(\text{Al}^{3+}/\text{Al} = -1.68 \text{ V } vs \text{ SHE} \text{ and } E^0(\text{Ag}_2\text{S}/\text{Ag}) = -0.69 \text{ V } vs \text{ SHE})$ . Tips are electrically connected to an alluminium foil and immersed into a NaHCO<sub>3</sub> aqueous solution. This cell can also be used for long-term storage. [171]

We also investigated the protection of Ag TERS tips in this work. We used a paraffin wax (docosane,  $C_{22}H_{46}$ ) to reversibly protect them. Docosane is a low melting point wax (45 °C) in which tips can be dipped without any damage. After solidification the wax protects the tip from organic molecules, ambient oxygen or sulfur species. The tip can then be unprotected by slight heating of the tip so that



Figure 2.5 – Evolution of the TER spectra of a thioazobenzene derivative SAM on gold probed by STM TERS with a silver tip. a) TER spectra with a 632.8 nm laser exitation (1 s, 3.3 mW) before (grey) and after (purple) 300 s of exposure of the tip to the red laser. Black arrows show the evolution of the main bands intensities: global  $I_{\text{TERS}}$  diminishes while a low frequency mode (silver oxides) appears; b) TER spectra with a 532 nm laser excitation (1 s, 220  $\mu$ W) before (grey) and after the 300 s exposure to the 633 nm laser. The black arrows show the evolution of the intensity of silver oxides vibration modes, the red arrow highlights the appearance of the Ag-S stretching mode of Ag<sub>2</sub>S. No baseline correction and no y-offset were applied.

the tip apex is free of wax. This allowed the storage of the tips during more than one week with no contamination and just a slight loss in TERS efficiency. An example of two TER spectra on a reference sample (thioazobenzene) is given in Figure 2.6 just after the tip fabrication (less than 1 h) and after a one-week storage in docosane. A 25 % decrease in intensity can be observed on the 1140 cm<sup>-1</sup> band and a small raise of the background signal appears at low frequencies (due to the formation of silver oxides). Moreover, the microRaman spectrum of docosane wax is given and can be compared to the TERS spectrum obtained after one-week storage: no contamination of the tip could be observed under these conditions. This protection solution was then used for long-term storage of silver TERS tips.



(a)



(b)

Figure 2.6 – a) STM-TER spectrum of a thioazobenzene derivative SAM on gold probed by STM-TERS with a silver tip with a 632.8 nm laser exitation (5 s, 130  $\mu$ W, bias voltage (BV) = 100 mV,  $i_T = 100$  pA) acquired less than one hour after tip fabrication (red line) and TER spectrum of the same sample after a one-week storage in docosane wax (brown line); 500 unit *y*-offset for clarity; the black arrow indicates the increase of the background signal below 400 cm<sup>-1</sup>; b) microRaman spectrum of docosane wax with the main bands shifts.

## 2.3 TF-TERS experiments

During this thesis, the implementation of TF-TERS (in NF configuration) was also considered, and we therefore established a protocol for gluing gold TERS tips on TF resonators. Q-factors can be tuned by adjusting the mass and the position of the tip. Controlling the mass can be done by gluing tips etched from wires with different diameters and length. We first designed probes starting from 250  $\mu$ m diameter gold wires which imposed the use of very short and light tips difficult to manipulate and also the use of small amount of glue (cyanoacrylate) which renders them fragile. The use of thinner wires is possible as our etching process enables us to routinely etch gold wires of 30, 100 and 250  $\mu m$  to produce TERS tips. TF-probe systems with 100  $\mu$ m diameter wires (see Figure 1.10) were found to provide the highest Q-factors (several thousands). Diminishing Q to values in the 500-3000 range is achieved by successive addition of small amounts of glue. It has to be noticed that even if this kind of glue is supposed to cure within a few minutes, the system is not stabilized until several hours (24 hours was estimated to be long enough) as  $f_0$  and Q drift until the glue hardens and the tip is firmly bound to the prong. Figure 2.7 shows the evolution of Q and  $f_0$  for a TERS-TF with a 250  $\mu$ m diameter etched gold wire as a function of the hardening time: initially, the free standing TF had a 37.8 kHz resonance frequency and Q = 14660.

These NF-TERS probes were tested on several samples to evaluate their sensitivity to topography and their lateral resolution and TER activity. Here, in Figure 2.8, we could image a gold surface covered with multiwall carbon nanotubes (MWCNTs): the TER map exhibits clear Raman features of CNTs, the G band, tangential vibration mode (1590 cm<sup>-1</sup>) and the disorder mode ( $sp^3$  carbons, D mode) at 1300 cm<sup>-1</sup>. One can deduce from these maps a resolution around 20 nm; moreover, even if the topographic data are poor, Raman signature allows one to distinguish very specific parts of the CNTs such as the extremities with high D mode intensity. [172]

TF-based probes have also been developed for studies in liquids. In this con-



Figure 2.7 – Evolution of the resonance frequency  $(f_0)$  and of the quality factor (Q) of a TF onto which a 250  $\mu$ m diameter etched gold wire was glued (cyanoacrylate glue) as a function of the hardening time. Dashed lines show the values of Q and  $f_0$  after a complete hardening of the glue and stabilisation of the system (24h).



Figure 2.8 – a) TER spectrum of a MWCNT on gold recorded with a NF-TERS feedback mechanism. Red line: tip engaged (near-field); Grey: Tip retracted by 50 nm (Far-field); b) 50x50 px<sup>2</sup>, 500x500 nm<sup>2</sup> NF-TERS mapping of a MWCNT bundle on a gold substrate: the blue and red maps are obtained by integration of the D and G mode bands of the CNTs (laser: 632.8 nm,  $10\mu$ W, 100 ms/px). Simultaneous topography (height) and changes in the amplitude signal were recorded.

figuration the tip can be in the liquid without immersing the whole TF. This was achieved with SF-SNOM with a 200  $\mu$ m protruding fiber in several aqueous solutions with small degradation of the Q factor (30 % for the highest Q factor in a buffer solution used in biological experiments). [173] An alternative strategy is the encapsulation of the the TF so that only the tip apex is in contact with the solution. [142] However these strategies are difficult to implement and were not explored for TERS in liquids or EC-TERS in this work.

## 2.4 Conclusion

In this chapter, the main practical aspects of TERS experiments have been described. The description of the optical coupling between the conventional Raman spectrometer and the SPM platform has demonstrated that its robustness is a key element for reliable TERS measurements.

The manufacturing of robust and reproducible gold and silver TERS probes has been detailed. The major tip-related issue, the tip degradation, has been addressed by reporting solutions provided by other groups in the literature and a specific development we proposed for the storage of air-sensitive silver probes.

Finally, TF-TERS probes and their characteristics have been described. As these TF-based SPM are hard to be implemented in liquids, this approach has been discarded for operation in EC-TERS and will not be discussed in the following.

In the following chapters, we decided to focus only onto STM-TERS experiments.

# Chapter 3

# Tip-Enhanced Raman Spectroscopy imaging of opaque samples in organic liquids

## 3.1 Introduction

TERS implementation in liquid represents an important challenge because of the delicate optical alignment through a layer of liquid to achieve an accurate focusing of the laser beam on the tip apex and also to ensure an efficient collection of the scattered signal. Most literature reports describe transparent samples set on an inverted optical microscope; focusing of the laser beam on the TERS probe is therefore easily achieved directly through the sample. [140,142] With opaque samples that necessitate top or side illumination and collection, the optical signal is inevitably deviated and considerably attenuated by refraction at the air-liquid interface. Ren et al. [41] as well as Domke et al. [143] recently elegantly circumvented this problem by mounting the sample in a liquid cell equipped with a side thin glass window and obtained an efficient side illumination of an STM probe enabling single point TERS spectroscopy. The window was positioned about 1 mm apart from the probe.

This solution unfortunatly freezes the tip vs sample/window positioning, obliterating TERS sample imaging capabilities in liquid. We propose in this chapter a new TERS setup based on an upright illumination and collection configuration that enables TERS imaging in an organic liquid (hexadecane). We will first prove its capability to record TERS signal through a layer of liquid with a strong near-field to far-field ratio and then to investigate the structure of a molecular monolayer on a gold surface.

## **3.2** Description of the experimental setup

## 3.2.1 Optical coupling

In our setup described in Figure 3.1, a polarized excitation laser ( $\lambda_{\text{exc}} = 632.8 \text{ nm}$ ) is focused on the STM probe apex through a long distance 100 x objective (working distance: 6 mm) with high numerical aperture (NA = 0.7). Therefore, the STM tip holder can be positionned between the objective and the sample. A gold tip is bent with an angle of 30 to  $45^{\circ}$  to the normal of the sample as previously depicted by Zenobi et al. in air. [78, 165] This angle allows the apex of the tip to reach the focal point of the objective for an optimized signal collection and enables a suitable alignment of the electric field along the shaft of the tip. Within this configuration, the STM imaging capabilities of the probe are maintained. The objective is mounted onto a piezoelectric positioning system which allows an accurate screening of the optical hot spot on the gold tip, *i.e.* the position of laser on the tip giving the maximum enhancement of the Raman signal intensity.



Figure 3.1 - Upright illumination and collection setup used in STM-TERS imaging through a thin layer of organic liquid (depicted as a light blue line).

## 3.2.2 Spectroscopic characteristization of the solvent and of the molecular layer

For this study, a thioazobenzene derivative (4-[(phenylazo)phenoxy]hexan-1-thiol, named thioazobenzene, ProChimia, Poland) was chosen to form a SAM onto a gold surface. The TERS signal of the thioazobenzene derivative (see Figure 3.2) selfassembled on a gold surface was first collected in the air. It can be compared to the Raman spectrum of the powder and of the far-field micro-Raman signal collected of the SAM on gold that are displayed in Figure 3.2b. The main Raman bands in the spectrum of azobenzene are: a broad medium band at 1595 cm<sup>-1</sup> assigned to the aromatic ring breathing; a strong triplet: a band at 1443 cm<sup>-1</sup> assigned to the N = N streching mode, and the 1415 and 1465 cm<sup>-1</sup> bands assigned to ring deformations; a strong C - N streching mode band at 1143 cm<sup>-1</sup> and a medium C - C stretching band at 1184 cm<sup>-1</sup>. [174–177]

Gold samples were prepared by thermal evaporation of 100 nm of gold onto cleaved mica heated at 400 °C and flame annealed prior to use. The sample was prepared by soaking a gold substrate in a 0.2 mM ethanolic solution of thioazobenzenefor 1 h, followed by immersion in pure ethanol for 1 h in order to remove any physisorbed molecules. In comparison to literature, the SAM was prepared in more dilute solution and soaked for a shorter time. [178, 179]





Figure 3.2 – a) Raman spectrum of the powder of thioazobenzene after baseline substraction ( $\lambda_{\text{exc}} = 632.8 \text{ nm}$ ); b) Micro-Raman spectrum of the SAM of thioazobenzene on a gold surface ( $\lambda_{\text{exc}} = 632.8 \text{ nm}$ , laser power: 98  $\mu$ W, acquisition time: 10 s).

The liquid STM-TERS experiments were carried out using a non-volatile and non-conductive organic solvent, *i.e.* hexadecane (Sigma Aldrich). This latter shows very limited evaporation ensuring the stability over time of the tip-liquid interface and therefore of the optical path. Moreover, within hexadecane, no insulating of the STM tip is required since leaking currents (faradaic current) are negligible in such non-conductive solvent. The Raman spectrum of hexadecane is given in Figure 3.3: it exhibits six main Raman bands: a strong band at 1442 cm<sup>-1</sup> and a shoulder assigned to C – H scissoring in CH<sub>2</sub> groups, asymetric C – H deformation vibrations in CH<sub>3</sub> groups; a strong C – H deformation vibrations in CH<sub>2</sub> groups band at 1303 cm<sup>-1</sup>; a weak band at 1133 cm<sup>-1</sup>, a doublet at 1083 and 1066 cm<sup>-1</sup> a broad band at 900 - 830 cm<sup>-1</sup> assigned to skeletal C – C – C stretching. [180] Interestingly the most intense band at 1442 cm<sup>-1</sup> perfectly overlaps with one of the bands of the C – N modes in thioazobenzene. This point will be discussed later when analyzing the TER spectra acquired in this solvent.



Figure 3.3 – Raman spectrum of pure hexadecane ( $\lambda_{exc} = 632.8$  nm, 10X objective).

#### 3.2.3 Focusing of the laser at the apex

#### 3.2.3.1 TER in the air

Screening of the tip hot spot is achieved by performing an objective mapping, *i.e.* a raster scanning of the objective in the directions parallel (XY, Figure 3.4a) and normal (XZ, YZ) to the sample surface synchronized with the registering of the overall Raman signal intensity, while maintaining the tip at the tunnel contact with the sample. Figure 3.4b displays two TER spectra of thioazobenzene collected at the exact hot spot location and slightly away, highlighting respectively the strong



Figure 3.4 – STM-TERS hot spot in the air in top illumination and collection configuration. a) 2x2  $\mu$ m<sup>2</sup> XY ( $\lambda_{exc} = 632.8$  nm, laser power: 98  $\mu$ W, acquisition time: 10 s); b) STM-TER spectrum in the air (bias voltage (BV): 0.1 V,  $i_t$ : 100 pA,  $\lambda_{exc} = 632.8$  nm, laser power: 14.1  $\mu$ W, acquisition time: 100 ms).

near-field signal (TER) and the extremely weak far-field contribution.

Particularly, the bands at 1143, 1415 1443 and 1465 cm<sup>-1</sup> appear with a large signal/noise ratio. The Raman mapping of the spectrum intensity between 1394 and 1495 cm<sup>-1</sup> during a XY objective map is presented in Figure 3.4a and confirms the strong enhancement of the signal around the hot spot location and the abrupt drop of the signal intensity in its close proximity (600 nm). The enhancement factor can be calculated and is estimated to be  $4 \cdot 10^5$  (assuming a 15 nm radius of curvature for the tip).

#### 3.2.3.2 TERS in hexadecane

Then, a thin layer of liquid hexadecane was added onto the sample. This sample/solvent combination represents an ideal system to evaluate the possible screening of the sample signal by the surrounding solvent since the Raman spectrum of pure hexadecane presented earlier in Figure 3.3, displays several bands that overlap with those of thioazobenzene. The main limitation of this configuration lies in the tip/liquid meniscus that interferes with the optical path. The height and radius of curvature of this meniscus strongly depends on the diameter and angle of the tip. We observed that a thickness of liquid of a few micrometres  $(2 - 20 \ \mu\text{m})$  however still allowed an accurate focusing of the laser on the tip. Under such conditions, searching for the hot spot in liquid became possible as revealed by the XY objective map depicted in Figure 3.5a. The spectrum at the exact hot spot (blue) and slightly off (red) appear in Figure 3.5b. A weak contribution from the solvent is present on all collected spectra as revealed on the average spectrum collected for a large area of the Raman map outside the hot spot (black spectrum). At the hot spot however, the contribution from thioazobenzene largely dominated the Raman signature, demonstrating that TERS is effective in hexadecane. It is noteworthy that the laser power and integration time have to be slightly increased to compensate for the optical losses and to obtain a signal to noise ratio similar to the one in the air (a factor 3 on the laser power and 5 on the integration time).

Despite these losses the enhancement factor in this configuration could be evaluated to be  $4 \cdot 10^5$  which is exactly the same as the one in air highlighting that the tip-enhancement is not affected by the presence of the solvent and the change in refractive index of the dielectric medium sourrounding the tip (~ 1 in air  $vs \sim 1.43$ in hexadecane).

## 3.3 TERS imaging in organic liquid

To evidence that our setup is also suitable for TERS imaging in liquid, a 300 × 300 nm<sup>2</sup> area of the sample was scanned in STM mode in hexadecane while recording TERS spectra. With a 30 × 30 px<sup>2</sup> image and 0.107 s acquisition time per spectrum (laser power = 98  $\mu$ W), the recording of a full TERS image took only 97 s. A higher resolution STM image (256 × 256 px<sup>2</sup>) was also recorded immediately after. In Figure 3.6, the comparison between low and high resolution STM images



Figure 3.5 – STM-TERS experiment performed in a thin layer of liquid hexadecane: a) 3x3  $\mu m^2 XY$  objective map (integration of the peak intensity with baseline correction between 1125 and 1162 cm<sup>-1</sup>); b) Raman spectrum at the exact hot spot location on the tip (blue: TERS) and slightly apart (red: far-field), and averaged spectrum for the dashed rectangle area of the objective map revealing the spectrum of hexadecane ( $\lambda_{exc} = 632.8$  nm, laser power: 287  $\mu$ W, acquisition time: 500 ms, BV: 0.1 V,  $i_t$ : 1000 pA).

shows that a  $30 \times 30 \text{ px}^2$  image is sufficient to evidence topography details, like pinholes present over the gold surface. Furthermore, in the high resolution image, the topography is well-described meaning that the STM-TERS tip was sharp enough to minimize convolution effects.

A TERS map obtained by integrating the band intensity of thioazobenzene between 1125 and 1162 cm<sup>-1</sup> is presented in Figure 3.6. It reveals that signal intensity on the lower left part of the image is more intense. Such local intensity fluctuations (both in X and Y directions) would never be detected in microRaman. Figure 3.7 displays ten spectra obtained by averaging the 9 spectra around each position indicated in Figure 3.6a. The lower intensity (position 1) corresponds to 40% of the highest one (position 9). Note that the scan proceeded from left to right and from bottom to top.

To explain the drop in intensity along the vertical direction of the raster scan, a change in the laser focusing on the tip may be invoked. The latter could originate



Figure 3.6 – STM-TERS imaging in hexadecane. a)  $30 \times 30 \text{ px}^2$  TERS map in hexadecane obtained by integration of the band between 1125 and 1162 cm<sup>-1</sup> after baseline correction. ( $\lambda_{\text{exc}} = 632.8 \text{ nm}$ , laser power: 98  $\mu$ W, acquisition time: 107 ms, BV: 0.1 V,  $i_t$ : 500 pA); b) low resolution ( $30 \times 30 \text{ px}^2$ ) STM image obtained during TERS mapping; c) high resolution ( $256 \times 256 \text{ px}^2$ ) STM image obtained during TERS mapping; d) topographic profiles: 1 and 2 refer to the lines on Figure 3.6c

from thermal effect induced by the laser irradiation, altering either the refraction at the air/liquid interface or the meniscus height. Two XY objective maps recorded before and after the TERS mapping of the sample (Figure 3.8), within a 17 min interval, show however a signal loss of at most 20% but also a slight shift of the hot spot position (at most 200 nm, the TERS map was recorded with the laser focused on the black cross in Figure 3.8a). This slight progressive unfocusing cannot therefore account for signal intensity decrease during the TERS imaging. Further-



Figure 3.7 – TER spectra from Figure 3.6a. a) series of 10 averages TER spectra (9 pixels). Numbers (1-10) refer to the positions in Figure 3.6a. Spectra were offset (+100) for the sake of clarity; b) intensity of 3 raman modes as a function of the position on the sample.

more, unfocusing of the laser cannot account for variations along the horizontal (X) direction.

We therefore rather incriminate a local variation in the surface coverage of thioazobenzenedue to non-homogenous SAM formation on gold, possibly combined with a modification of the molecular orientation of thioazobenzene on the surface. This change in the molecular orientation cannot be clearly extracted from TER spectra, however a close look at the 1595 cm<sup>-1</sup> band reveals some slight changes: in spectra 1 an 2 (low surface coverage), the peak is broad and unique (26 cm<sup>-1</sup> width) while in spectrum 3, the peak could be deconvoluted into two peaks 1593 and 1602 cm<sup>-1</sup>. These two modes have previously been theoretically predicted as in-plane ring deformation [174, 175] but have never been evidenced to our knowledge. Considering they originate from two similar vibration modes, they cannot easily be interpreted as molecular orientation differences. This intensity variation was then only interpreted as a molecular surface concentration gradient and was assumed to be due to the SAM preparation and especially the low immersion time in the ethanolic solution of thioazobenzene. [178, 179] As a consequence of this surface concentration change, no relation between the topography and the Raman intensity could be clearly established. [181, 182]



Figure 3.8 – 2x2  $\mu$ m<sup>2</sup> XY hotspot imaging a) before and b) after TERS imaging (Figure 3.6) obtained by integration of the peak intensity with baseline correction between 1125 and 1162 cm<sup>-1</sup>; c) Raman spectra corresponding to the markers in (a) and (b) maps ( $\lambda_{exc} = 632.8$  nm, laser power: 98  $\mu$ W, 107 ms acquisition, BV: 0.1 V,  $i_t$ : 500 pA); +x below each spectrum: y-offset for clarity.

This set of results illustrates that TERS imaging is operational in organic solvent using an upright configuration. The next stage will be to precisely determine the spatial resolution of TERS in liquid by imaging small nano objects in a similar way to what was recently performed by Chen et al. in air with carbon nanotubes (CNTs): they could demonstrate a lateral resolution down to 1.7 nm. [88] More recently, imaging of CNTs was performed in water on an inverted microscope with an AFM TERS probe revealing a sub-30 nm lateral resolution which is still far from the single digit nanometre scale reachable at ambiant. [152]

## 3.4 Conclusion

In this chapter we have demonstrated that it is possible, using an upright optical configuration, to implement TERS imaging of an opaque sample in an organic liquid which the Raman signature overlaps with the one of the SAM under scrutiny, with fast acquisition time and minimal laser power. With this set-up, the efficient excitation and collection of the scattered Raman signal allows the extraction of the chemical signature of a molecular monolayer from the one of the surrounding solvent. To achieve such performances, the liquid thickness has to be optimized (around 20  $\mu m$  at most here), in order to reduce the distortion of the optical path and the loss of signal at the tip-liquid interface (meniscus). These promising results pave the road to TERS imaging in other solvents or electrolytes. Moreover, the thin layer of liquid deposited over the sample is also an interesting and easy way of protecting oxygen sensitive samples. It can also prevent the sample from being contaminated by organics present in the air. Moreover, it has already been demonstrated that less fluctuation of the TER spectra intensity are observed in liquids as compared to the air, it could be interesting using this set-up to determinate if this effect relates to the local temperature stabilization due to the presence of the solvent which acts locally as a heat sink. [183]

# Chapter 4

# Electrochemical Tip Surface-Enhanced Raman Spectroscopy

## 4.1 Context

In TERS, among previously mentionned difficulties due to liquid environement, signal fluctuations can be observed when scrutinizing only a few molecules with the tip and challenge the real-time quantification of surface processes, although these variations can also provide important information regarding the local microenvironment of individual molecules. [140] Besides, in an electro-chemical TERS setup, other complications may arise from ohmic losses across large polarized substrates. These latter drastically affect the temporal resolution of the electrochemical processes [184] and minimize the benefits of time-resolved TERS experiments. Similar questions may arise in electrochemical Surface Enhanced Raman Spectroscopy (EC SERS) for which the signal is collected and averaged on a square micrometer area possibly on an inhomogeneous substrate. [140] Finally, the close proximity of the tip with the polarized substrate may interfere locally with the electric field, potentially affecting the electrochemical response. In some cases, these drawbacks may hinder detection and identification of reaction intermediates by TERS and thus the comprehension of complex reaction schemes involving multi-electron transfer to molecular species.

In this chapter we introduce a novel spectroscopic analytical tool for the study of electrochemical mechanisms based on the Raman enhancement provided by TERS tips. We will demonstrate that a partially insulated TERS tip can be functionalized by an electroactive molecule and used both as a microelectrode and as a single hot spot surface-enhanced Raman (SERS) platform.

This configuration has previously been proposed by Pienpinijtham et al. to probe the local pH by functionalizing a gold TERS tip with p-aminothiophenol and p-mercaptobenzoic acid whose Raman vibrations are sensitive to the pH. [185] Even if in this configuration the spatial resolution is lost (no surface is scanned), as well as the enhancement due to the possible tip-substrate junction between the tip and a gold or silver substrate, [186, 187] the number of probed molecules is higher than in usual TERS measurements providing intense Raman signal with no fluctuations. Functionalized tips have also been used to probe inhomogeneities of plasmons enhanced field distribution on SERS substrates at the nanoscale [188, 189] or to evidence higher electric field enhancement on the edges of Au(111) substrates [190] by scanning the functionalized TERS tip over the substrate. However, to the best of our knowledge no work has been conducted on electrochemical systems using such a configuration.

This chapter will be dedicated to the study of the electrochemichal reduction mechanism of a monolayer of 4-nitrothiophenol self-assembled on TERS active microelectrode that was chosen as a reference system to test and validate our approach. This approach which combines the advantages of measurements onto microelectrodes to those provided by SERS is denominated as tip SERS (EC tip SERS) in the following.

## 4.2 Description of the studied system: 4-NTP

## 4.2.1 Electrochemical study of the reduction mechanism of a 4-NTP monolayer

#### 4.2.1.1 Description of the studied system

To test and validate our approach, we selected an electroactive system that could be immobilized on a metallic surface and which shows distinct Raman signatures depending on its oxidation state. Organic compounds bearing a thiol group which can chemisorb onto a gold surface by making a bond between the sulfur and the gold atoms (Au-S bond) as depicted on Figure 4.1 are good candidates. [191, 192]



Figure 4.1 – Chemical adsorption of thiols on gold. An Au-S bond is formed; the radical R can be any functional group.

The thiol derivatives can immobilize onto the substrate and form an organized self-assembled monolayer (SAM). For this work we chose an aromatic thiol compound carrying a redox active functional group: the 4-nitrothiophenol. The thiophenol part ensures the anchoring of the molecule onto gold while the nitro group  $(-NO_2)$  can undergo a complete six-electron and proton reduction (see equation 4.1) into aniline  $(-NH_2, 4\text{-aminothiophenol} (4\text{-ATP}))$ :

$$R - NO_2 + 6e^- + 6H^+ \to R - NH_2 + 2H_2O \tag{4.1}$$

The literature on the EC transformation of 4-NTP using either advanced electrochemical techniques [193–196] or EC-SERS [197, 198] abounds, but still the mechanism of its transformation remains poorly understood. The mechanism of this electroreduction has been investigated since the pioneer works of Haber in 1898 on nitrobenzene. [199] This reduction can occur following a direct path: the nitro group is first reduced to nitroso (4-NSTP, 4-nitrosothiophenol) and then to an hydroxylamine group (4-HATP, 4-hydroxylaminothiophenol). The latter can finally be reduced to the aniline derivative (see top part of Scheme 4.1). A condensation path has also to be considered in alkaline medium: the nucleophilic 4-HATP can condense with 4-NSTP to form p,p'-dimercaptoazoxybenzene (DMAOB) which is reduced to p,p'-dimercaptoazobenzene (DMAB), then into p,p'-dimercaptohydrazobenzene (DMHAB); this latter can be reduced into two 4-ATP molecules (see the second line on Scheme 4.1).



Scheme 4.1 – Possible reaction paths for the electroreduction of 4-NTP into 4-ATP (Haber mechanism)

The electrochemical behavior of 4-NTP was first studied on a model gold sphere electrode (no contaminants and well defined electroactive surface).

#### 4.2.1.2 Gold sphere electrode functionalization and experimental details

For accurate electrochemical studies, gold sphere electrodes which can be flame annealed prior functionalization to provide a contaminant free surface compared to standard microelectrodes are preferred. [200, 201] The self-assembled monolayer was made from an ethanolic solution (3 h at  $10^{-4}$  M) to ensure a compact packing of the molecules on the surface. Physisorbed species were removed by a thorough rinsing of the surface with absolute ethanol and three 30 minute baths in absolute ethanol. All the cyclic voltammetry (CV) experiments were performed in a three electrode configuration in an argon-purged cell to prevent the reduction of dissolved oxygen. The reference electrode was a saturated calomel electrode (SCE), the counter-electrode was a platinum grid and the solution was a 50 mM sulfuric acid solution (pH  $\simeq 1.1$ ).

#### 4.2.1.3 Gold sphere electrode characterization

In order to correlate the number of events (number of molecules involved in the redox processes) to the electrochemical response (current intensity), the surface of the model gold electrode has to be first determined by recording cyclic voltammograms of ferrocene (Fc) (5.4 mM + 0.2 M tetrabutylammonium perchlorate in acetonitrile) which can be oxidized into ferricinium (Fc<sup>+</sup>) through a one-electron process:

$$Fc \leftrightarrows Fc^+ + e^- \tag{4.2}$$

According to the Randles-Sevcik equation (equation 4.3) the anodic peak current can be expressed, for a fast electron transfer as:

$$i_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} v^{1/2}$$
(4.3)

where  $i_p$  is the peak current in A, n is the number of electrons involved in the transfer (one electron for the ferrocene), A is the area of the electrode in m<sup>2</sup>, C is

the concentration in ferrocene in mol m<sup>-3</sup>, D is the diffusion coefficient in m<sup>2</sup> s<sup>-1</sup> (2.43 × 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup> for the ferrocene under these conditions [202]) and v is the sweep rate in V s<sup>-1</sup>. [1] Figure 4.2 shows the linear relationship between the anodic peak current ( $i_{pa}$ ) and the square root of the sweep rate. A linear regression provides an area of 0.87 mm<sup>2</sup>



Figure 4.2 – Anodic peak current as a function of the square root of the sweep rate ( $\blacksquare$ ) and linear regression (red line) (slope=  $2.76 \times 10^{-5}$  A V<sup>-1/2</sup> s<sup>1/2</sup>).

#### 4.2.1.4 Irreversible reduction of 4-NTP

A first CV experiment was performed to fully reduce the 4-NTP SAM into 4-ATP. The potential was swept from +450 mV to -550 mV vs SCE over two cycles: a broad irreversible cathodic peak appeared during the first cycle at -265 mV and disappeared at the second cycle (see Figure 4.3). Assuming a six electron and proton exchange (reduction of the nitro group into aniline) the surface coverage could be estimated by the charge integration of the irreversible peak between -90 and -475 mV:

$$\Gamma_{\rm NTP} = \frac{Q}{nFA} = \frac{\int_{-475}^{-90} \frac{i_f(E)}{v} dE}{nFA}$$
(4.4)

where Q is the charge of the irreversible peak at -265 mV obtained after baseline subtraction, n is the number of electrons involved in the reduction (6), F is the Faraday constant, A is the area of the electrode and  $i_f$  is the faradaic current. We found a coverage of  $7.73 \times 10^{-6}$  mol m<sup>-2</sup>. This value is slightly higher but consistent with values reported in the literature under such conditions. [193, 203]



Figure 4.3 – Cyclic voltammetry response of a 4-NTP functionalized gold sphere electrode in a 50 mM  $H_2SO_4$  solution (scan rate: 100 mV s<sup>-1</sup>); irreversible reduction into 4-ATP involving 6 electrons and 6 protons during the first cycle (black line) with a -550 mV vs SCE vertex potential.

#### 4.2.1.5 Electrochemical characterization of 4-ATP

To confirm the formation of 4-ATP at the electrode, the reduced SAM was oxidized under the same conditions: a functionalized electrode was reduced by two successive CVs from +400 to -800 mV vs SCE. The potential range was then increased to oxidize the SAM within the -500 to +1000 mV vs SCE range: the CV is comparable to the ones observed in previous studies by other groups. [204, 205] During the first cycle an oxidation irreversible peak (A) appears at +730 mV vs SCE followed by two peaks at +443 (B) and +197 mV vs SCE (C) in the second cyle (Figure 4.4). During the second scan, the irreversible peak (A) disappears while a new reversible peak appears centered at +478 mV vs SCE (peak B) and the irreversible reduction peak at +197 mV vs SCE (peak C) disappears. These peaks have been attributed to: (A), the formation of the 4-ATP radical cation followed by a dimerization towards 4,4'-thiophenylquinone diimine (4-TPQDI) involving the breaking of one C-S bond concerted with a N to C bonding; this head-to-tail coupling product can be reversibly reduced into 4,4'-thioaminodiphenylamine (4-TADPA) (peak B). The origin of the peak C is uncertain but was attributed to the reduction of the sulfide species attached to the gold surface after the scission of the C-S bond. [204] Even if this electrochemical oxidation of 4-ATP could be interesting for evaluating the ratio of 4-ATP transformed out of 4-NTP on the electrode, the reaction was not quantitative. However it was a first qualitative investigation of the nature of the reduction product.



Figure 4.4 – Cyclic voltammogram (100 mV s<sup>-1</sup>) of a 4-ATP electrode in 50 mM  $H_2SO_4$  prepared by three successive CVs on a 4-NTP functionalized gold sphere electrode between +400 mV and -800 mVvs SCE (100 mV s<sup>-1</sup>). Black line: first cycle; red line: second cycle. A, B, C: see main text for attribution.



Scheme 4.2 – Simplified scheme of the chemical and electrochemical reactions of a 4-ATP SAM on a gold electrode (**A**, and **B** reactions refer to the peak assignement on Figure 4.4). Adapted from [204].



Figure 4.5 – Cyclic voltammetry response of a 4-NTP functionalized gold sphere electrode in a 50 mM  $H_2SO_4$  solution (scan rate: 100 mV s<sup>-1</sup>) with a -250 mV vs SCE vertex potential. 4-NTP is partially reducted to 4-HATP below -100 mV vs SCE. 4-HATP is reversibly oxidized into 4-NSTP at +241 mV vs SCE.

#### 4.2.1.6 Study of the conversion of 4-NTP into 4-HATP

In comparison, if the vertex potential is set to a less cathodic value, a reversible peak at +241 mV vs SCE appears after the first cycle. Figure 4.5 shows an example of this behavior: the cathodic vertex potential was set to -250 mV vs SCE. The reversible peak appears during the reverse scan of the first cycle. This is consistent with previous results from other groups who studied this system: this peak was attributed to the oxidation of the 4-electron and proton reduction product (4-HATP) into 4-nitrosothiophenol (4-NSTP) through a 2-electron and 2-proton exchange.

These results suggest a complex mixed reduction process involving either 6 electrons and 6 protons or 4 electrons and 4 protons potentially followed by 2 electrons and 2 protons within the same broad irreversible peak. We studied the conversion ratio of 4-NTP into 4-HATP as a function of the cathodic vertex potential as well as the number of cycles for each vertex potential (from 5 to 10 cycles). The coverage



Figure 4.6 – Three first CV cycles of a gold sphere electrode functionalized with 4-NTP in 50 mM  $H_2SO_4$  (scan rate: 100 mV s<sup>-1</sup>) with various cathodic vertices. a)-150 mV vs SCE; b)-200 mV vs SCE; c)-300 mV vs SCE

was estimated by integrating the reversible peak at +241 mV vs SCE assuming a 2 electron and proton transfer and then the conversion ratio was calculated as:

$$\frac{\Gamma_{\text{HATP}}}{\Gamma_{\text{NTP}}} \times 100 = 3 \times \frac{Q_{-265}}{Q_{+241}} \times 100$$
 (4.5)

where  $Q_i$  is the charge associated to the peak centered on a specific potential value i mV after baseline subtraction.

Within the first CV and for a vertex potential of -150 mV vs SCE (Figure 4.6a), the conversion takes place as the reversible peak appears and increases during the four first cycles until it reaches a plateau at around 10%. This indicates either that only a fraction of the 4-NTP SAM can be reduced to 4-HATP without further reduction to 4-ATP or that the competition between the 4 and 6 electron processes is balanced. During the next CV series on a freshly functionalized electrode, the vertex potential was set to -200 mV vs SCE (Figure 4.6b). The conversion ratio reaches its maximum during the second CV at 23.5% and decreases afterwards indicating that the 4-HATP or remaining 4-NTP are reduced to 4-ATP. The last two CV series (-250 and -300 mV vertex potentials, Figure 4.5 and 4.6c) exhibit a similar behavior: the maximum of conversion is reached during the first cycle and decreases abruptly. The higher conversion ratio (27.5%) was observed for the first CV of the series with a -250 mV vertex potential.

This series of data, summarized in Figure 4.7, led us to a first set of conclusions about this system: the reduction of 4-NTP under acidic conditions allows the formation of 4-ATP preferentially over 4-HATP. More than 72.5% of the 4-NTP SAM was not converted into 4-HATP, the latter being reduced to 4-ATP since it is formed.



Figure 4.7 – Calculated conversion ratio of 4-NTP to 4-HATP extracted from the charge of the reversible peak at +241 mV vs SCE on successive CVs with different vertex potentials ( $E_{vertex}$ ) presented in Figure 4.6 and Figure 4.5.

To further support this conclusion, the conversion ratio of 4-NTP into 4-HATP


Figure 4.8 – Evolution of the +241 mV vs SCE reversible peak charge (Q: right vertical axis) and estimated 4-NTP to 4-HATP conversion ratio (left vertical axis) as function of time (s) during a reduction sequence on the same gold sphere electrode in 50 mM  $H_2SO_4$ . Each data point corresponds to a 15 second chronoamperometry at different potentials (E<sub>chrono</sub> ranges from +50 to -350 mV vs SCE); reference electrode: SCE.

was also evaluated after a chronoamperometric reduction sequence: this latter is composed of successive 15 second chronoamperometric steps at more and more cathodic potentials ( $E_{chrono}$  ranging from +50 to -350 mV vs SCE). After each polarization at  $E_{chrono}$  a CV was recorded at 100 mV s<sup>-1</sup> around the 4-HATP/4-NSTP reversible peak. The peak at +241 mV was integrated and the conversion ratio was calculated for each step. These data are reported in Figure 4.8. In this experiment the highest conversion ratio was 5.8% and obtained after 5 steps at 50, 0, -50, -100 mV followed by three steps ( $3 \times 15$  s) at -150 mV vs SCE. The low conversion ratios are explained by the progressive transformation of 4-HATP or remaining 4-NTP into 4-ATP at potentials as high as -50 mV vs SCE during long polarization steps (15 s). The ratios are much lower than in CV experiments as the polarization time scale is larger in the chronoamperometric experiments. These observations support the conclusion drawn from CV experiments.

#### 4.2.2 Spectroscopic characteristics of the system

The 4-NTP/4-ATP system shows intense and distinct Raman signatures as seen on Figure 4.9: the 4-NTP spectrum exhibits a very strong band at 1335 cm<sup>-1</sup> (attributed to the NO<sub>2</sub> symmetric stretching) and one at 1570 cm<sup>-1</sup> (attributed to the C = C stretching mode of the aromatic ring). The 4-ATP can be characterized by the absence of the 1335 cm<sup>-1</sup> band and by a blue shift of the C-C stretching mode up to 1588 cm<sup>-1</sup>.

The Raman spectra of ATP and NTP were acquired using first microRaman on powders of the two compounds (Figure 4.9) and then STM-TERS on SAMs developed on a gold functionalized sample (from ethanolic solution of 4-ATP and 4-NTP). The Au-S bond formation is confirmed by the disappearance of the S-H bond vibration at *ca.* 2700 cm<sup>-1</sup>.

Possible products from the reduction of 4-NTP such as 4-NSTP and 4-HATP are expected to show particular bands such as a N = O stretching mode for the nitroso compounds in the 1488-1523 cm<sup>-1</sup> region or a band at 1230 cm<sup>-1</sup> for 4-HATP. [206] These vibrational modes could not be detected during our experiments. Moreover, these products are not stable (oxidation or dimerization in air) and difficult to obtain in the powder form for a microRaman measurement. We then used a compound with a similar structure as 4-NSTP, N,N-dimethylnitrosoaniline, which is reported to dimerize easily into azodioxides ((O - N) = (N - O) bond, see Annex A.1). The dimerization was confirmed by three Raman bands in the 1300-1400 cm<sup>-1</sup> region. The characteristic Raman bands of the different systems are presented in table Table 4.1 and in Figure 4.9 (Raman spectra of the powders of 4-ATP and 4-NTP).



Figure 4.9 - Raman spectra of a) 4-NTP, b) 4-ATP (powders, 632.8 nm)

# 4.3 Spectroelectrochemical analysis of 4-NTP reduction reaction

## 4.3.1 Electrochemical reduction of 4-NTP monitored by *ex situ* TERS

To get a deeper understanding of the reduction process of the 4-NTP, *ex situ* TERS measurements were performed on a 4-NTP monolayer self-assembled onto a large gold-coated electrode. In order to ensure that the functionalization is homogeneous, a TERS map was realized prior to its polarization. Figure 4.10a shows a  $300 \times 300 \text{ nm}^2$  STM-TERS map on a freshly derivatized electrode. The STM map (Figures 4.10b and 4.10c) reveals the typical structure of a flame-annealed gold film

Table 4.1 – Main characteristic Raman bands for 4-NTP and the expected reduction products (4-ATP, 4-HATP, 4-NSTP) with band assignation and shift from literature. the values in parentheses correspond to the Raman shifts observed during EC tip SERS experiments on a TERS-active gold tip. Intensities: vs, very strong; s, strong; m, medium; w, weak.

Molecule	Vibration	Raman shift $(cm^{-1})$ (experimental)	Reference
4-NTP	C-H bending	1079 m (1080,m)	
	C-H bending	1100  s  (1100,  s)	
	C-H bendind	$1181 \ m \ (1180, \ w)$	[207]
	NO <sub>2</sub> symmetric stretching	$1335 \ vs \ (1335, \ vs)$	
	C-C stretching	1577  s  (1570,  s)	
4-ATP	C-S stretching	$1089 \ vs \ (1087, \ s)$	
	C-H stretching	1173 m (1180,m)	[208]
	C-C stretching	1593  s  (1588,  s)	
4-NSTP	N=O stretching	1488-1523  (not observed)	[206]
	C-N	$1318+1342~({ m not~observed})$	
4-HATP	(not atributed)	1230 (not observed)	[197]
DMAOB	ON = N stretching	1450-1490 (not observed)	[206]
DMAB	N = N stretching	1380-1463 (not observed)	[206]

deposited on mica *i.e.* large and flat terraces with atomic steps (~ 0.24 - 0.27 nm for a monoatomic step). [137, 209] The TERS map was produced by integration of the NO<sub>2</sub> stretching mode at 1335 cm<sup>-1</sup>. This map reveals the uniform coverage of the pristine 4-NTP surface. Some area display more intense spectral features: this has already been attributed to higher enhancement on particularly rough parts of the substrate (such as sharp edges or corners). [210]



Figure 4.10 – Characterization of a 4-NTP SAM on a gold substrate before electrochemical reduction. The scale bar is 50 nm on each map - a) TERS map  $(300\times300 \text{ nm}^2, 100\times100 \text{ px}^2, 10 \ \mu\text{W}$  laser power, 50 ms integration time per pixel) by integration of the NO<sub>2</sub> stretching mode band at 1335 cm<sup>-1</sup> revealing a uniform coverage of the 4-NTP layer on a pristine electrode. b) STM topography obtained during TERS mapping  $(300\times300 \text{ nm}^2, 100\times100 \text{ px}^2, 100 \text{ mV})$  bias, 100 pA setpoint current). c) Subsequent high resolution STM topography (400×400 nm<sup>2</sup>, 512×256 px<sup>2</sup>, 100 mV bias, 100 pA setpoint current). The dashed square highlights the area where the TERS map was recorded.

A 4-NTP SAM was then electrochemically reduced by chronoamperometry at -300 mV vs SCE in a 50 mM  $H_2SO_4$  solution during 30 s. According to the previous CV and chronoamperometric results, considering this polarization time at this potential, the whole layer should be fully reduced into 4-ATP. A seen on Figure 4.11, a 300×300 nm<sup>2</sup> TERS map (integration of the 1080 cm<sup>-1</sup> and 1588 cm<sup>-1</sup> bands) exhibits a rather homogeneous distribution of the 4-ATP spectrum. Concomitantly, the NO<sub>2</sub> stretching band at 1335 cm<sup>-1</sup> has completely disappeared as expected.



Figure 4.11 – Characterization of the 4-NTP functionalized gold electrode after a uniform electrochemical reduction. a) STM topography obtained during TERS mapping  $(300 \times 300 \text{ nm}^2, 100 \times 100 \text{ px}^2, 100 \text{ mV}$  bias, 500 pA setpoint current); b) TERS map  $(300 \times 300 \text{ nm}^2, 100 \times 100 \text{ px}^2, 250 \ \mu\text{W}$  laser power, 50 ms integration time per pixel) by integration of the band at 1590 cm<sup>-1</sup> revealing a uniform coverage of the 4-ATP. c) Point spectra associated to points on the TERS map (b).

On a second sample polarized this time at -300 mV vs SCE during 5 min in

the same electrolyte the collected TERS map (Figure 4.12) confirms the presence of 4-ATP (spectra  $a_1$  and  $a_2$ ) but also shows the signature of 4-NTP. A 400 × 400 nm<sup>2</sup> TERS mapping of the 1335 cm<sup>-1</sup> NO<sub>2</sub> stretching mode of 4-NTP reveals the presence of many residues of nonreduced 4-NTP.



Figure 4.12 – Ex situ STM-TERS map of an inhomogeously reduced 4-NTP functionalized flat electrode (300 s at -300 mV vs SCE) obtained by integration of the band at 1335 cm<sup>-1</sup> (400 × 400 nm<sup>2</sup>, 80 × 80 pixels, laser power:  $500\mu$ W, acquisition time: 200 ms per pixel, tunneling current: 200 pA, bias: 100 mV). Four selected spectra (averaged over 9 pixels) are presented:  $n_1$  and  $n_2$  are dominated by the bands of 4-NTP,  $a_1$  and  $a_2$  by the one of 4-ATP.

In these experiments several parameters can explain the discrepancy of the results:

- sans.
  - The substrate preparation: the large and flat gold electrodes were produced by thermal evaporation of gold on mica. The structure of the gold deposited across such large surface may not be homogeneous and may display various contact resistance between gold grains. The resulting ohmic losses may affect the distribution of surface potential and the effectiveness of the reduction process. This stresses that the preparation of high quality EC TERS substrates (homogeneity and conductivity across the whole sample) is crucial for a proper interpretation of the produced data.
  - The nature of the SAM: this system (4-NTP, 4-ATP) has already been studied by electrochemical STM (EC STM) by Kolb *et al.* [203] They found out that

only 50 % of the 4-NTP SAM organizes in ordered domains on Au(111). When the potential is set below the reduction potential (20 mV vs SCE in 50 mM  $H_2SO_4$ ) the formation of disorganized islands could be observed over 40 % of the surface. These authors could however not conclude on the nature of these disorganized islands (no correlation with the 4-HATP formation quantified by the reversible peak at 250 mV vs SCE in a 50 mM  $H_2SO_4$  solution); an EC STM study after reductive desorption of the SAM in a  $Na_2SO_4$  solution also revealed the formation of small gold triangular islands (4-5 % of the surface) all over the sample. These observations revealed two important characteristics of this reduction reaction: first, it seems to be very dependent on the chemical nano-environment of the molecule (formation of disorganized islands) and then the reaction seems to directly impact the structure of the underlying gold (appearance of the gold islands).

## 4.3.2 Electrochemical reduction of 4-NTP monitored by *in situ* EC tip SERS

#### 4.3.2.1 Description of the setup and experimental conditions

To circumvent the above-mentionned difficulties associated to EC TERS on large flat electrodes, we designed a TERS-inspired platform for *in situ* Raman analysis by functionalizing and partially insulating a TERS-active gold tip to be used a microelectrode. In this configuration the TERS tip acts as a single hot spot SERS platform of which the potential can be modulated. The setup, described in Scheme 4.3, is based on an upright configuration with top illumination and collection including a 40X water immersion objective with high numerical aperture (NA = 0.8) mounted on a XYZ piezoelectric stage.

The use of an immersion objective has already been reported for EC SERS [211, 212] or EC microRaman [213, 214] as it prevents losses and distortion of the



Scheme 4.3 – Scheme of the electrochemical tip SERS setup including a three-electrode cell: a TERS active gold working microelectrode (WE) functionalized by 4-NTP, a platinum counter electrode (CE), a silver wire pseudo-reference electrode (RE), and a 40X immersion objective with high numerical aperture (0.8), all immersed in a 50 mM  $H_2SO_4$  solution.

optical path at the air/liquid (or air and glass or quartz if a window is used to close the electrochemical cell) interface (mainly due to the refractive index mismatch: ca. 1.33 for the electrolyte and 1.00 for air). Moreover the long working distance (3.3 mm) of the 40X immersion objective allows a gold TERS tip mounted on a side holder to reach the focal point with an angle between 10 and 30°. In this setup, we use a three-electrode configuration where the tip stands as the working electrode (WE), a platinum wire as counter electrode (CE) and a silver wire as pseudo-reference electrode (RE). The potential of the silver wire was measured to be  $+208 \pm 20$  mV vs SCE in 50 mM H<sub>2</sub>SO<sub>4</sub>. All the potential values reported in this chapter will be shifted by this value and given relative to the SCE in order to facilitate the comparison with values from the literature. The TERS tip was partially insulated with polyethylene wax to reduce the size of the electroactive area. In this configuration, ohmic losses and the RC charging time constant of the electrode are minimized.

#### 4.3.2.2 Ex situ tip SERS

In order to reveal the signal enhancement capabilities of the produced tips, an XY objective mapping was first implemented in the air on a non-insulated gold TERS tip ( $r_c$ : 35 nm;  $\theta_t$ : 55° tapper angle) functionalized with 4-NTP through a high magnification, high NA and long working distance objective (Mitutoyo; 100X; N.A.= 0.7; 6 mm working distance) in a side illumination and collection configuration (Figure 4.13).



Figure 4.13 – SEM micrographs at different magnifications of a TERS-active gold tip obtained from electrochemical etching of gold wires, used for *ex situ* tip TERS and revealing the typical tapered profile whith the following characteristics:  $r_c = 35$  nm and  $\theta_t = 55^{\circ}$ .

The tip apex was imaged by XY scanning of the microscope objective: the hot spot position is revealed by integration of the 1335 cm<sup>-1</sup> Raman band (between 1325 and 1345 cm<sup>-1</sup>) and by classical least square (CLS) analysis of the spectra on the 1.6 × 1.5  $\mu$ m<sup>2</sup> XY map (Figure 4.10c). Its width can be estimated to 500 nm (Figure 4.10b). The position of this hot spot at the apex and the shape of the tip can also be revealed by integration of the entire spectrum (gold luminescence and TER spectra of 4-NTP, see Figure 4.10c). Furthermore, the SER origin of the signal at the tip was also evidenced by illuminating the tip apex with a green (532 nm) laser, *i.e.* out of the surface plasmon resonance for a gold tip, at a similar power (218  $\mu$ W at 532 nm and 250  $\mu$ W at 633 nm): only a very weak signal (compared to the 632.8 nm excitation) of the 4-NTP could be extracted since the conditions for the plasmon resonance are not achieved with green illumination of the gold tip as it can be seen on Figure 4.15 where two spectra are overlaid and normalized by the respective laser powers.



Figure 4.14 – Characteristics of a functionalized TERS tip. For a) b) and c) the scale bar is 1  $\mu$ m a) SEM image of the tip; b) 3 × 8  $\mu$ m<sup>2</sup> XY objective map of a 4-NTP functionalized tip obtained by integration of the peak intensity (with baseline correction) at 1335 cm<sup>-1</sup> revealing the location of the hot spot at the tip apex (blue) and c) map of the same area obtained by integration of the luminescence (whole spectrum between 250 and 1800 cm<sup>-1</sup>) revealing the shape of the tip (gold luminescence) and the position of the hot spot (gold luminescence and SER signal); d) 1.5 × 1.5  $\mu$ m<sup>2</sup> XY objective map of the apex of the functionalized tip analyzed by a classical least squares (CLS) analysis: the spectrum at each pixel is fitted with a combination of three reference spectra shown below. The color scale refers to the colors of each spectrum. Red: 4-NTP, green: gold luminescence, grey: noise out of the tip (each one is the mean of 4 spectra). The laser wavelength was 632.8 nm (290  $\mu$ W laser power and 500 ms integration time per pixel).

#### 4.3.3 Potential dependent tip SERS measurements

A set of tip SERS measurements was performed on a functionalized TERS-active tip under the same conditions as the EC analysis on gold sphere electrodes to access vibrational information on the SAM during the electroreduction sequence. The tip SERS signature of the 4-NTP SAM was recorded after one CV cycle starting from +250 mV vs Ag (*i.e.* +458  $\pm$  20 mV vs SCE) down to a vertex potential (E<sub>vertex</sub>) ranging from -200 to -500 mV vs Ag. In order to reproduce exactly the conditions of the EC measurements on gold sphere electrode, the same scan rate



Figure 4.15 – Tip SER spectra at the hot spot of a 4-NTP functionalized gold tip: the red spectrum was acquired by illuminating the tip with a 632.8 nm laser (250  $\mu$ W, 3 s) and a green 532 nm laser (218  $\mu$ W, 3s). The spectra are normalized relatively to the laser power at the sample.

was set (100 mV.s<sup>-1</sup>). All spectra were acquired at a relaxation potential, -200 mVvs Ag, where no electron transfer is expected to occur.

The Raman signal collection at a unique and same potential after all polarization steps ensures the possible intercomparison of the produced spectra: it is well-known from previous works on EC SERS that the vibrational spectra of a molecule can dramatically change with the applied potential. This can be explained by:

- changes in the molecular orientation and conformation; [40, 148, 215, 216] or the protonation state of the molecule [148, 217]
- possible laser induced charge-transfers under certain potential conditions (potentialdependent RR, see Section 1.1.4); [218–220]
- changes in the surface state of the substrate (such as oxidation of the underlying gold or silver). [40].

As it has been mentioned in Section 1.5.2, 4-NTP is known to dimerize into



Figure 4.16 – Tip SER spectra of a 4-NTP monolayer acquired at -200 mV vs Ag (+8 mV vs SCE) after successive CVs ranging from +250 mV vs Ag to  $E_{vertex}$  (50 mM  $H_2SO_4$ , scan rate: 100 mV s<sup>-1</sup>

DMAB upon intense laser illumination or by plasmon-induced reactions. Thus, to prevent this dimerization, the laser power was set to a minimal value (100  $\mu$ W).

In order to compare all the spectra acquired throughout the experiment, they were normalized by the intensity of the 1078 cm<sup>-1</sup> peak which is common to both 4-ATP and 4-NTP ( $I_{\omega}^{norm} = \frac{I_{\omega}}{I_{1078}}$ ). To build diagrams of the evolution of the characteristic vibration modes the area of the main bands ( $A_i$ ) of the two main species were compared to the area of the 1078 cm<sup>-1</sup> band ( $\frac{A_i}{A_{1078}}$ ). These diagrams are reported in Figure 4.17 and discussed in the following.

The first CV down to -200 mV vs Ag exhibits only the vibration modes of 4-NTP and was used as a reference spectrum for this molecule at this potential (Figure 4.16). The next CV (n<sup>o</sup> 2) down to -400 mV vs Ag and the associated spectrum did not show significant differences with the 4-NTP spectrum except a slight decrease in the ratio of the area of the major bands (1110, 1335 and 1570 cm<sup>-1</sup>) of 4-NTP.



Figure 4.17 – Evolution of the characteristic bands of 4-NTP (1110, 1335 and 1570 cm<sup>-1</sup>) and of 4-ATP (386, 628 and 1588 cm<sup>-1</sup>) depending on the cycle number (see Figure 4.16). The areas are normalized by the area of the band that is common to the two molecules (1080 cm<sup>-1</sup>), these ratios being then normalized.

However, no spectral features from 4-HATP, such as a band at  $1230 \text{ cm}^{-1}$ , could be observed whereas, according to the previous electrochemical study, this first CV must have generated around 22,5% of 4-HATP. During the next cycles (3, 4 and)5), where the vertex potential was lowered to -450 mV vs Ag, the same general behavior was observed for the 4-NTP bands: their intensity decreases, especially the  $NO_2$  stretching mode indicating the disappearance of the nitro group. Moreover, characteristic bands from 4-ATP appear from the third CV (386, 628  $\rm cm^{-1}$ , not attributed, and the C-C stretching mode shifted from 1570 to 1588  $\rm cm^{-1}$ ) while no band from the 4-HATP appears. After this measurement the potential was set to +100 mV vs Ag, where the 4-HATP is oxidized to 4-NSTP and a spectrum was acquired (Figure 4.18): we could not observe any new Raman bands but only a change in the band intensities that could not be attributed to the nitroso compound. The relative intensities of the bands attributed to 4-NTP are higher in the spectrum acquired at +100 mV vs Ag than at -200 mV vs Ag. This highlights the possible influence of the potential on the Raman signal enhancement factor that might differ from one molecule to another. A final CV with a vertex potential set at -500 mV vs Ag exhibits a spectrum characteristic of a 4-ATP SAM: all the bands



Figure 4.18 – Comparison of the EC tip SER spectrum acquired at -200 mV vs Ag (spectrum 5 exctracted from Figure 4.16) with the spectrum acquired immediatly afterwards at +100 mV vs Ag.

attributed to 4-NTP disappeared. Figure 4.19 shows EC tip SERS obtained from a pristine 4-ATP functionalized tip at the same potential in the same electrolyte: the perfect resemblance confirms the complete reduction of the 4-NTP SAM into 4-ATP.

We noticed that no spectral signature of 4-HATP or 4-NSTP could be detected throughout the experiment, even under the conditions of maximum conversion observed in electrochemical measurements on gold sphere electrode (see Figure 4.7). This could be explained by the low conversion ratio of 4-NTP into 4-HATP (27.5% at maximum) and/or by a Raman cross section lower than 4-ATP and 4-NTP. Then, a further analysis of the spectra revealed that the tip SER spectra (2-5) can be fairly reproduced by a linear combination of the spectra of 4-ATP and 4-NTP as shown in Figure 4.20 where the spectrum 5 is reproduced by:

$$I_5 = 0.30I_1 + 0.70I_6 \tag{4.6}$$



Figure 4.19 – EC tip SER spectrum of a pristine 4-ATP functionalized electrode (E= -200 mV vs Ag, laser power =  $10 \mu$ W, 30 s integration, 633 nm)



Figure 4.20 – EC tip SERS spectra 1 (blue, 4-NTP), 6 (4-ATP), 5 from Figure 4.16 and the spectrum obtained by linear combinaison of 1 and 6 (70% 4-ATP + 30% 4-NTP) in black.

Even if this linear combinations cannot be quantitatively interpreted, it suggests that 4-ATP is formed as early as the second cycle and also that the reduction of 4-NTP leads concomitantly to 4-HATP and 4-ATP. This was recently suggested by Zhao et al. [221] in a study of p-NTP electroreduction at gold and silver electrodes using density functional theory (DFT) calculations. They calculated that standard reduction potentials decrease as p-HATP > p-NSTP > p-NTP, which means that p-NTP is directly reduced to p-ATP since the electrode potential reaches the potential reduction of p-NTP, explaining then the broad reduction peak observed in CV experiments. Kinetic considerations may explain the observations on the reversible peak attributed to the 4-HATP/4-NSTP couple: the 4-NTP to 4-HATP reduction must be faster than the 4-NTP to 4-ATP one. This kinetics issue can be highlighted by the comparison of the chronoamperometry results with the one observed in CV experiments on a gold sphere electrode: the maximum conversion ratio is observed in the CV experiments *i.e.* in the experiment where the time scale is the smallest (of the order of 1 s in CVs, 15 s in chronoamperometry).

#### 4.4 Conclusion

In this chapter we demonstrated the capability of a functionalized TERS tip to act as a powerful single hot spot SERS platform to probe *in situ* electrochemical transformation of a 4-NTP monolayer assembled on a tapered gold microelectrode. In this non-gap mode configuration the volume of the enhanced near-field is larger than in the gap mode so that SER signal arises from more molecules: tip SERS averages signal from possibly different molecular environments and then prevents signal fluctuation. The use of an immersion objective allowed us to overcome airliquid interface issues such as reflection, laser path distortion and to increase the signal collection efficiency (higher NA than air objectives). We could therefore use minimal laser powers that prevented the photochemical degradation of the organic layer (e.g. dimerization of the 4-NTP layer). The electrochemical 4-NTP reduction into 4-ATP was studied both by classical CV experiments and EC tip SERS. The Raman signature extracted during EC tip SERS measurements revealed that 4-ATP is formed simultaneously to 4-HATP which has never been reported in any electrochemical studies. Lowering the reduction potential makes the 6-electron and 6-proton transfer (4-ATP) to dominate over the 4-electron and 4-proton one (4-HATP). However, even in the maximum conversion ratio conditions, neither the 4-HATP or 4-NSTP Raman signatures could be observed: this can be explained both by a low Raman cross-section of these two molecules and/or by the somehow low conversion ratio (27.5% maximum) determined from CV experiments. The EC Tip SERS experiment which proved its effectiveness to solve the reduction process of 4-NTP is expected to be applied to the study of many redox processes for which the mechanism of electron transfer is still unknown and also to complicated molecular architectures as long as they can be immobilized on a gold or silver surfaces. The hybrid tips developed herein, *i.e.* TERS ready UMEs, also pave the way to timeresolved EC TERS experiments. [222]

# Chapter 5

# Electrochemical TERS imaging of functionalized gold surfaces

#### 5.1 Introduction

As it has already been mentionned in the previous chapters, implementation of TERS imaging under electrochemical conditions is still a challenge as many technical difficulties remain to be overcome (for more details, see Section 1.6.3). Up to now, TERS imaging has only been performed in organic liquids (see Chapter 3 and [223]) or more recently in water with a sub-30 nm lateral resolution. [152]

This chapter aims at describing an EC STM-TERS setup inspired by the development of the one used for EC tip SERS and introduced in Chapter 4. The proposed design couples then a conventional EC-STM cell (in a four-electrode configuration) with the optical configuration used in EC tip SERS experiments, *i.e.* a top illumination and collection configuration with a water immersion objective for an optimal illumination and collection efficiency.

We will first demonstrate the possibility to record efficiently EC STM-TER spectra. Then, preliminary results on EC TERS imaging will be presented. To the best of our knowledge, this set of results is the first demonstration of TERS imaging under electrochemical conditions.

#### 5.2 Description of the setup

Several important modifications were introduced to the commercial (AIST-Horiba) setup in order to run EC STM-TERS:

- both tip and sample potentials (working electrodes,  $WE_1$  and  $WE_2$ ) have to be controlled and defined vs a reference electrode (RE), so that a 4-electrode potentiostat also including a counter electrode (CE) should be implemented;
- the cell design used for the EC Tip-SERS method developed in this work (see Chapter 4) needs to be revised to allow introduction of the sample to be imaged;
- electrical insulation of the tip should be improved to minimize leakage currents vs tunnelling current  $(i_t)$ .

#### 5.2.1 Electronic implementation

Implementation of EC STM requires to introduce 4 electrodes into the cell. Indeed, in addition to the traditional counter and reference electrodes (CE and RE) that allow a precise control of the sample potential (WE<sub>2</sub>), the tip potential (WE<sub>1</sub>) needs also to be accurately defined. Therefore, while in Chapter 4 we simply relied onto a commercial potentiostat, a dedicated electronic setup was elaborated to run EC-TERS experiments since it was not directly available onto the SMART-SPM system. The challenge is here to maintain accurate potentials at the tip and sample (versus the reference electrode) and a precise measure of the tip current with a noise level below 30 pA because typical setpoint currents for STM imaging are in the 200-1000 pA range. This may be performed currently by commercial or home-made bipotentiostats but some specific adjustments need to be made for implementation onto our system.

In a first attempt, we thus tried to use only a home-made bipotentiostat made by our electronic engineer Daniel Rose. However, while the potentials of the two working electrodes (WE<sub>1</sub> and WE<sub>2</sub>) could be accurately controlled, we noticed that the electronic noise at the tip was far too important to allow regulation of the feedback STM loop. This may be a consequence of a too long and unshielded connection to the tip, or to the noise introduced via the signal access module that was used to reinject the current into the STM feedback loop.

Consequently, we focused onto an intermediate solution where the current at the tip was still measured by the SMART-SPM current amplifier that shows a very low noise level, the other electrodes being connected to the bipotentiostat. The setup is described in Figure 5.1.

It is beyond the scope of this chapter to fully describe the operation of the bipotentiostat, and we only underline below some important features:

- in the configuration we used, the tip potential  $(V_{tip})$  is in fact at 0 V vs ground (virtual ground of the current amplifier);
- the bias voltage (BV = V<sub>tip</sub> V<sub>sample</sub>) is applied thanks to two potentiometers (tension dividers);
- an external tension, provided by an external generator (Agilent Technologies, 33521A, USA), can be added to both WE<sub>1</sub> and WE<sub>2</sub> channels (offset) to conduct cyclic voltammetry while maintaining a constant bias.

A large gold ring counter electrode and an Ag wire as reference electrode were used. This configuration provided noise levels below 30 pA provided that the tip was correctly insulated (see Section 5.2.3 below for details). The interested reader may refer to Chapter 15 of [1] for a complete electronic scheme of a bipotentiostat.



Figure 5.1 - EC STM setup: a) simplified scheme of the electronics required for EC STM measurements; b) picture of the coupling between the SPM (Omegascope, AIST) and a home-made bipotentiostat.

#### 5.2.2 Cell design for EC STM-TERS measurements

The EC-cell, depicted in Figure 5.2 is composed of a flat PEEK (Polyether Ether Ketone) support onto which the sample (WE<sub>2</sub>) is immobilized. An O-ring is glued (with an epoxy resin) to form the walls of the cell. A ring-shaped gold wire (CE), attached to the PEEK support is placed into the cell as well as a silver wire (pseudo RE). These three electrodes are connected to the bipotentiostat, the cell is mounted on the STM piezostage and finally filled with *ca.* 1 mL of electrolyte.

When the tip is just a few millimetres away from the sample surface, the ob-



Figure 5.2 – Top-view of an EC STM-TERS cell with a gold-coated mica substrate as  $WE_2$ , a gold ring as CE and a silver wire pseudo RE.

jective contacts with the surface of the liquid to form a meniscus. Any mechanical contact between the tip and the objective would dramatically alter the STM performance and therefore should be avoided. This setup uses the same water immersion objective (Olympus, 40X, NA: 0.8, working distance: 3.3 mm) as in the EC tip SERS experiments previously described in Chapter 4. As for tip SERS, the tip is brought in the focus of the objective using the micrometre stage of the Omegascope platform holding the STM microscope.

#### 5.2.3 Tip insulation and characterization

In EC-STM, the faradaic current at the tip should be kept minimal, *i.e.* much lower than the tunneling current, for a proper control of the tip-sample distance. In most of our STM experiments the tunneling current setpoint was usually 1 nA at the most. Therefore, a threshold of 50 to 100 pA for was considered as the maximal acceptable value for the leakage current (the noise level with our current amplifier being around 30 pA). In the better conditions the leakage current could be lower than the noise level of the measured signal.

The tip has then to be insulated so that only a few micrometres of metal is in contact with the solution. In conventional EC STM experiments, tips are insulated either with a layer of Apiezon wax (Wax W, M&I Materials Ltd., England) or with



Figure 5.3 – EC STM-TERS setup : a) photo of an EC STM-TERS cell mounted on the SPM platform with the water immersion objective; b) scheme of the EC STM-TERS cell including an insulated STM-TERS tip, a flat conductive sample (WE<sub>2</sub>) onto which an O-ring is glued, a gold ring as CE and a silver wire as pseudo-RE.

polyethylene. In both cases, the polymer is heated and melted: the tip briefly contacts a drop of the melted insulating material and is let to cool down. While cooling down, the polymer layer retracts leaving only the tip apex unprotected. Unfortunately, these two materials turned to be unsuitable for EC STM-TERS. Indeed, Apiezon (black wax) produced a strong fluorescence background on TER spectra and polyethylene releases contaminants in solution which could be detected in TERS measurements. We finally chose Zapon varnish (Laverdure & fils, Paris), as previously proposed by Domke et al. for EC STM-TERS. [143] The insulating was achieved by immersing the tip up to four times in the liquid varnish. The tip was then left to the ambient for at least 24 hours so that the entire coating layer hardens.

Coated tips were investigated by SEM to evaluate the surface of the non-coated part. Figure 5.4 shows an example SEM image of a typical well-coated tip and an optical image of the insulated tip as it is seen through the 40X immersion objective in the EC cell. On SEM micrographs the border between the coated and non-coated parts are difficult to evaluate as charge accumulate at the polymer surface during the imaging. The surface could though be estimated to be *ca.*  $3.5 \ \mu m^2$  with an exposed length of the gold electrode of  $3.75 \ \mu m$ . This length allows a proper focusing of the  $\sim 1 \ \mu m$  laser spot at the apex of the tip for TERS measurements.



Figure 5.4 – Left: SEM micrograph gold TERS tip coated with Zapon varnish revealing the exposed surface at the apex of the tip (white part); Right: optical image of the coated tip using a 40X immersion objective in an EC cell.

Prior to any experiment, the extremity of the partially insulated tip was immersed in the solution to measure the intensity of the leakage current without being in tunneling conditions. The leakage current was then compared to the electronic noise recorded when the tip is in the air (open circuit).

Two extreme cases are presented in Figure 5.5. A first tip (Figure 5.5a), suitable for EC STM, shows a leakage current close to 0 pA (-5 pA) while immersed in the solution. A second tip (Figure 5.5b) shows a drastic jump of the current after the tip

contacts the solution (-4 nA) meaning that the insulating coating is not optimal. In case the tip is not properly coated, it is reprocessed by repeating the above-described procedure until the leakage current reaches a value lower than 100 pA.



Figure 5.5 – Leakage currents measured on partially insulated gold tips recorded in a 50 mM  $Na_2SO_4$  solution ( $E_{tip} = 200$  mV vs Ag) a) on a well-coated tip, current measured in the air (dash black line) and in solution (red line), the current is below 30 pA; b) on a second tip, with non-suitable coating, when the tip is immersed in the solution the measured current jumps to -4 nA.

#### 5.3 Evaluation of the system stability

We first verified that the coupled system presents mechanical noise low enough to enable STM imaging with a good spatial resolution in liquids and also under potential control in an electrolyte solution.

For this purpose we prepared samples of a thioazobenzene derivative that forms SAMs on gold on mica sample (their preparation is described in details in Chapter 3). On such samples, monoatomic steps can be found between large gold terraces and allow the evaluation of the Z resolution.

A first large scale  $(500 \times 500 \text{ nm}^2)$  STM image of this gold surface is presented in Figure 5.6a.



Figure 5.6 – EC STM imaging  $(500 \times 500 \text{ nm}^2)$  of a gold surface functionalized with thioazobenzene in a 50 mM Na<sub>2</sub>SO<sub>4</sub> solution;  $E_{sample} = 0 \text{ V} vs \text{ Ag}$ , BV = 200 mV,  $i_t = 400 \text{ pA}$ , scan rate: 1 Hz per line; a) STM image b) height profile along the white line.

This EC STM image exhibits the typical characteristics of such surfaces with monoatomic steps of 0.3 nm on Au(111) surfaces as revealed by the height profile (Figure 5.6b).

A second image performed on a smaller area  $(200 \times 200 \text{ nm}^2)$ , depicted in Figure 5.7) exhibits the characteristic gold vacancy islands ("pits"), with heights of one or several gold atoms (~ 0.3, 0.6 or 0.9 nm) created by the Au atom removal from terraces to form thiolate-gold complexes upon sulfur species adsorption. [224, 225] The width of these vacancies can be measured to be as low as 5 nm providing an estimation of the minimal lateral resolution that can be achieved by our EC STM setup.

These results are comparable to those obtained in the air on similar samples and evidence the good mechanical stability of the STM/Raman coupled system in liquid, prerequisite for EC STM-TERS experiments.



Figure 5.7 – EC STM imaging  $(200 \times 200 \text{ nm}^2)$  of a gold surface functionalized with thioazobenzene in a 50 mM Na<sub>2</sub>SO<sub>4</sub> solution;  $E_{sample} = 0 \text{ V} vs \text{ Ag}$ , BV = 200 mV,  $i_t = 400 \text{ pA}$ , scan rate: 1 Hz per line; a) STM image b) height profile along the white line.

### 5.4 EC TERS imaging

#### 5.4.1 Laser focusing on the tip

As previously mentioned, the EC STM-TERS experiments using a water immersion objective can be carried out in the exact same way as in air because the liquid/air interface is no longer a problem.

This can be evidenced by the ease to bring the tip in the focus of the objective and at the position of the laser spot. A picture of the partially insulated tip as seen through the 40X water immersion objective is presented in Figure 5.8a with the laser pointed at the apex of the tip. The precise laser focusing is realized by scanning the piezo objective scanner in the three directions XYZ. The map presented in Figure 5.8b is built by integration of the triplet between 1380 and 1510 cm<sup>-1</sup> of the azobenzene derivative. The intensity of the Raman signal decreases to zero from the hot spot within 1  $\mu$ m as observed in the air, attesting of the quality of the coupling and of the efficiency of the enhancement at the tip (see spectra in Figure 5.8c and Figure 3.4 for comparison). An averaged spectrum over 100 pixels provides a clear far-field (FF) Raman signature, composed of a single band at 982 cm<sup>-1</sup> which can be assigned to the symmetric stretching mode of the sulfate ions of the electrolyte (Na<sub>2</sub>SO<sub>4</sub>). [226]



Figure 5.8 – Hot spot imaging in EC TERS in 50 mM Na<sub>2</sub>SO<sub>4</sub> solution; a) image of the tip in contact with the sample and when the laser is focused at the apex; b)  $6 \times 6 \ \mu m^2 XY$  objective map revealing the position of the hot spot (1) obtained by integration of the triplet between 1380 and 1510 cm<sup>-1</sup> c) selected spectra from b) 1 at the exact hot spot position, 2: 1  $\mu$ m away, 3: FF signal; d) FF signal obtained by averaging the spectra in the white rectangle in b).  $\lambda_{exc} = 632.8$  nm, laser power: 250  $\mu$ W, acquisition time: 307 ms/px; E<sub>sample</sub> = 0 V vs Ag, BV = 200mV,  $i_t = 400$  pA.

To reinforce the evidence that the measured signal was TERS and not SERS from the gold substrate, the tip-sample distance was increased to 100 nm so that the laser is still focused on the sample but the gap mode is no longer effective. The spectrum with the sample retracted (grey line in Figure 5.9) exhibits only the Raman band of the sulfate ion confirming that the enhancement is due to the presence of the tip.



Figure 5.9 – EC STM-TERS spectrum (red line) recorded at  $E_{sample} = 0$  V vs Ag, BV: 100 mV  $i_t$ : 1 nA and far-field signal (grey line) recorded with the sample retracted by 100 nm from the tip;  $\lambda_{\text{exc}} = 632.8$  nm, laser power: 250  $\mu$ W, acquisition time: 300 ms

Note that all the spectra are recorded at  $E_{sample} = 0$  V vs Ag which was chosen because it is below the potential at which gold is oxidized and above the one at which dissolved oxygen is reduced, preventing any electrochemical reaction to interfere.

#### 5.4.2 Preliminary results on EC-TERS imaging

As our setup allows TER spectra to be collected in the STM mode in liquid, we demonstrate in the following the possibility to run STM-TERS imaging while polarizing the substrate.

Hyperspectral TERS imaging of a thioazobenzene functionalized gold surface was performed over a large area ( $365 \times 120 \text{ nm}^2$ ). The EC TERS map presented in Figure 5.10 was obtained by integration of the peak at 1143 cm<sup>-1</sup>. It clearly exhibits a stripe from the top left to the bottom right part of the image for which the intensity is higher: both along the X and Y directions, the signal reaches its maximal value within two pixels. This stripe is correlated with to a step on the topography image (Figure 5.10a).



Figure 5.10 –  $365 \times 120 \text{ nm}^2$  EC STM TERS imaging of a gold surface functionalized with thioazobenzene in a 50 mM Na<sub>2</sub>SO<sub>4</sub> solution; a) EC STM image recorded during the TERS imaging; b) EC TERS topography image obtained by integration af the band at 1143 cm<sup>-1</sup>.  $\lambda_{\text{exc}} = 632.8 \text{ nm}$ , laser power: 130  $\mu$ W, acquisition time: 507 ms/px; E<sub>sample</sub> = 0 V vs Ag, BV = 200 mV,  $i_t = 400 \text{ pA}$ .

In order to demonstrate the correlation between topographic and vibrational information, a line profile (white line in Figure 5.10) was drawn across the STM map and the Raman signal. For the Raman signal, the area of the band at 1143 cm<sup>-1</sup>  $(A_{1143})$  and that of the triplet between 1380 and 1510 cm<sup>-1</sup>  $(A_T)$  are reported as function of the distance along the line. These three profiles are reported in Figure 5.11.

It clearly appears that the most intense Raman signal is measured at the edge of the gold steps. The highest increase appears in position 2 (Figure 5.11) but is also observed on positions 1 and 3 of the profile line where steps are observed on the topographic profile. The transition between lower TERS intensity region towards the stronger one occurs at minimum on a one-pixel distance, *i.e.* 8 nm on this TERS mapping. This increase in intensity is often observed on gold steps in air and was interpreted as an increase of a local electric field enhancement. [227] This first preliminary results demonstrate the ability of our setup to probe variations of the electromagnetic field intensity in the gap between the tip and the sample with a resolution as low as 8 nm under electrochemical environment.

The variation of the intensity can be seen on spectra presented in Figure 5.11b: the 1143  $\text{cm}^{-1}$  band is 2.2 times more intense in spectrum 2 than in spectrum 5 which indicates variations of the enhancement factor of the same value in this case.



Figure 5.11 – EC TERS and STM profile along the white line in Figure 5.10. a) Integration of the band intensity at 1143 cm<sup>-1</sup> ( $A_{1143}$ ) and of the triplet between 1380 and 1510 cm<sup>-1</sup> ( $A_T$ ) as function of the distance along the profile line compared to the STM topography (dashed line): b) selected EC TER spectra at different positions of the sample marked in Figure 5.11a.

The enhancement factors can be calculated to be at minimum 7.2  $10^5$  at point 2 and 3.3  $10^5$  at point 4 (see Section 1.4.2 for the calculation method).

As it had already been observed for the same molecule in liquid hexadecane (see Chapter 3), the presence of the surrounding electrolyte or of the polarization does not affect the energy of the vibration mode of this molecule since the observed Raman bands are found to be at the exact same Raman shift as in air. Further experiments have to be carried out to investigate the influence of electrochemical polarization on TERS mechanism, *i.e.* on the plasmonic properties of the tip under such conditions.

#### 5.5 Conclusion

In this chapter we described a new setup and configuration for EC TERS imaging that overcomes the major drawbacks of previously reported experimental setups for EC TERS. This was made possible through the use of an immersion objective that prevents optical distortions and signal losses at the interface between air and liquid (or glass and liquid).

This setup has demonstrated to be robust both for EC STM imaging of functionalized surfaces (with lateral resolution better than 5 nm in STM imaging) and for EC STM-TERS measurements in an electrochemical environment.

Finally we evidenced the ability of our coupled EC STM-TERS system to image an electrochemical interface under potential control, which is to the best of our knowledge the first ever reported EC TERS image in an electrochemical environment. Moreover we could probe the local variations of the electric field in the gap between the TERS probe and the substrate with a lateral resolution as low as 8 nm.

We expect that this configuration will soon demonstrate EC TERS lateral resolution down to the single nanometre as it has already been demonstrated in the air. [88] For this purpose, non-homogeneous surfaces or nano-objects have to be probed.

These preliminary results pave the road for TERS analysis of more complex electrochemical interfaces and reactivity at the nanoscale under potential control.

# Chapter 6

# TERS characterization of surfaces derivatized with diazonium salts

#### 6.1 Introduction

Electrochemical grafting of diazonium is a simple and well-established method to functionalize carbon, metal or semiconductor surfaces with organic films. The grafted organic layers are strongly attached to the surface via covalent bonding which is rare in the field of surface modification. [228]

Surface modifications by such diazonium salts has shown to be a very efficient mean of grafting covalently organic moieties onto an electrode. The initial studies were carried out onto glassy carbon electrodes. [229, 230] But since the grafting process relies on radicalar reactions, it was quickly extended to many other materials. Highly Oriented Pyrolytic Graphite (HOPG), [231] is also reactive as well as metals (Fe [232], Co, Ni, Cu, Zn, Pt, and Au [233]) and semiconductors. [234] Graphene has also been reported to be functionalized in order to tune its electronic properties. [235–237]

Even if the mechanism of electrochemical reduction of diazonium salts is wellknown, the structure of the grafted layers is not always clear and can be difficult to ascertain. TERS offers the possibility of nanoscale analysis of the chemical structure of these layers but has never been used for the investigation of such functionalized surfaces, to the best of our knowledge.

This chapter will expose preliminary results on the use of STM-TERS to investigate the structure of gold surfaces functionalized using diazonium salts.

# 6.2 Chemistry and electrochemistry of diazonium salts

A diazonium compound is an aliphatic, aromatic or heterocyclic compound in which a  $-N_2^+$  group is attached to a carbon atom. In aromatic diazonium compounds (aryl diazonium salts) the conjugation with the aromatic cycle makes aryl diazonium ions much more stable than their aliphatic counterparts.

The reactivity of diazonium salts is known since the pioneer work of Pinson et al. in 1992. [229] These authors modified a glassy carbon electrode to further immobilize glucose oxidase. Upon reduction,  $N_2$  is released and the aryl radical may attack the surface as shown on Figure 6.1. It was later demonstrated that electron transfer is concerted with C – N bond rupture. [230]

The tight covalent binding of the aryl layers with the substates can be evidenced by the strong resistance of these films to aggressive treatments such as ultrasonication in a variety of solvents, heating of the substrate up to 700 K in UHV, [230] or even polarization at high potential. [238] They can only be removed by mechanical abrasion, *i.e.* electrode polishing or by AFM lithography. [239]

Due to its high reactivity, the aryl radical formed by electrochemical reduction of the diazonium salt can attack the C-H bonds of the first aryl-grafted layer via an aromatic homolytic substitution. This reaction can lead to the formation of polyarylene multilayers through the formation of new C-C bonds as depicted on the top part of Figure 6.1. [228,240] Some other side reactions have been suggested such



Figure 6.1 – Electrochemical reduction of an aryl diazonium (top) for the formation of monoor multilayers and partial alternative path for the spontaneous grafting (bottom). **R** can be any chemical group; the dashed area can represent any electrode material.

as azo bonding (-N=N-) in multilayer films as shown on Figure 6.1. [241]

Characterization of the layer structure and composition can be achieved by various and complementary methods. As the reduction of diazonium salts is irreversible, the electrochemical response of the electrode to be functionalized can be a first indication of the grafting process. If the grafting is performed using CV, a broad irreversible peak due to the one-electron transfer can be observed at the first cycle and disappears during the subsequent cycles since the grafted layer blocks the surface of the electrode. The blocking properties of the organic layer are usual proofs of the efficiency of the grafting. For example, on a functionalized electrode, reversible redox probes such as ferrocenemethanol, [242] ferrocene, dopamine [243] or  $Fe(CN)_6^{4-}$  can become irreversible or even not be detected. [244]

When the diazonium salt carries a redox-active chemical group, the electrochemical signature of the functionalized electrode allows the direct quantification of the grafted entities. For example, the reversible one-electron reduction of the nitrophenyl groups in the layer grafted from nitrobenzene diazonium has been used for
the determination of the surface coverage of the electrode. [230]

For structural characterisation SPMs have been used on electrochemically grafted surfaces. STM has for example revealed the possibility to control the surface organization by precisely adjusting the grafting parameters (charge, concentration, polarization time and potential) by imaging at the molecular scale the self-organized grafted layer of bromophenyl groups on Si surface modified by bromobenzenediazonium reduction. [234] The formation of multilayers with important surface roughness as well as inhomogeneities have been demonstrated by AFM. [245, 246] Such multilayers are not conductive enough to be imaged by STM.

The presence of grafted layers can also be revealed by vibrational spectroscopies such as Raman or Fourier Transform IR Reflection Spectroscopy (FTIRRAS) through the chemical identification of functional groups. FTIRRAS is very sensitive to vibrational modes perpendicular to the surface and is a tool of choice for determining the orientation of surface-bounded molecules. [247, 248] Raman spectroscopy and especially SERS could evidence the formation of an Au-C bond upon reaction of diazonium salts with gold nanoparticles. [249] Grafting-induced defects in graphene layers could also be observed by Raman after spontaneous grafting of nitrobenzene diazonium. [250] X-ray photoelectron spectroscopy (XPS) is also a popular technique for chemical characterization of organic layers as it generally allows a non-destructive and quantitative analysis of chemical groups. [251]

As previously mentioned, diazonium salts can spontaneously react with surfaces (see the bottom part of Figure 6.1). This has in particular been demonstrated on non-noble metals such as iron that can provide the required electrons for the reduction without potential control. [252] This spontaneous grafting has also been demonstrated on other substrates such as Au, [249] or carbon. [252] Spontaneous grafting may occur following a different mechanism than the one obtained under polarization of the surface. XPS studies have for example revealed the existence of Au-N bonds at the surface of spontaneously derivatized gold surfaces (bottom line of Figure 6.1). [253]

All of these reports suggest varied structures for electrochemically and spontaneously grafted layers from diazonium salts. They strongly depend on the substrate and on the experimental conditions.

One challenge in diazonium chemistry is to obtain well-defined monolayers. The simplest structures are provided by diazonium salts that cannot form multilayers. Among all the possible strategies employed for grafting only monolayers of aryl groups on surfaces, the most common are the addition of radical scavengers to the solution [254, 255] or the use of sterically hindered aryldiazonium derivatives (such as bis-*tert*-butylbenzene diazonium). [256, 257] The previously mentioned organized self-assembly of bromophenyl groups on Si substrate is a rare example of organized structures formed from diazonium precursors by electrochemical reduction. [234] Another alternative, described in the following section, is to rely on a system for which radicalar addition is prevented.

# 6.3 Electrochemical grafting of a monolayer of a diazonium salt

In this section we first relied on compounds for which multilayer formation is impossible. Indeed, a way for preventing multilayer formation is the use of aryl derivatives without C-H bonds where the aromatic homolytic substitution usually takes place. We describe in this section the results obtained with the penfluorobenzenediazonium salt (PFBD) presented in Figure 6.2.

As for the work described in Chapter 4, we first conducted an electrochemical study onto gold sphere electrodes and then onto flat gold-coated mica substrates for STM and STM-TERS analyses.



Figure 6.2 – Pentafluorobenzene diazonium molecule (PFBD) and pentafluorobenzene moity (PFB) grafted onto a surface.

## 6.3.1 Electrochemical grafting and characterization of a monolayer of penfluorobenzene

PFBD was synthesized from pentafluoroaniline by Laure Fillaud in LISE following a synthesis procedure described in Annex B.3.1. The electrochemical reduction of PFBD on a gold sphere electrode was performed by CV in acetonitrile (ACN, CH<sub>3</sub>CN) (1.1 mM + 0.1 M Et<sub>4</sub>NPF<sub>6</sub>, TEAPF<sub>6</sub>). The CV presented in Figure 6.3 exhibits a single irreversible peak as expected for the monoelectronic reduction of a diazonium salt. The reduction is initiated at a potential of ~0.41 V and the peak is observed at +0.075 V vs SCE. These rather high values are consistent with what is observed for other diazonium salts bearing electronegative groupments such as bromide (0.02 V vs SCE) or nitro functional groups (0.20 V vs SCE on glassy carbon). [230] It can be compared to values found in literature for the same PFBD salt:  $E_p = 0.15$  vs SCE on glassy carbon or 0.14 on Pt. [258] It has also surprisingly been reported at -0.39 V vs SCE on glassy carbon and was recorded at too positive potential on iron to be reliably measured by Chaussé et al. This last study does however not display the CV for this molecule. [259]

The variability of the results found for different electrode materials could be explained by a mechanism involving preadsorption of the diazonium salt onto the surface prior to its reduction which can explain different kinetics and thermodynamics for the same reaction.



Figure 6.3 – Functionalization of a gold sphere electrode by PFBD; a) CV on a 0.24 mm<sup>2</sup> gold sphere electrode in a PFBD solution (1.1 mM in ACN, 0.1 M TEAPF<sub>6</sub>), scan rate: 500 mV s<sup>-1</sup>

Moreover, we noticed a very poor stability of this diazonium salt in solution. This would induce a strong diminution of the concentration of the starting PFBD salt and the appearance of other products in solution. We could indeed observe that the color of the solution evolves from pale yellow (color of the PFBDBF<sub>4</sub> salt) to dark yellow within a few minutes. This can be explained by the conversion to an azo coupling product (*bis*(pentafluorophenyl)diazene). This change in the composition of the precursor solution may explain the very poor reproducibility in the CV results probably due to different grafting mechanisms. This could be observed on CVs performed in a freshly prepared solution (Figure 6.6a) and in an older solution (5 minutes after the first CV). In the freshly prepared solution an irreversible peak is observed during the first cycle at +0.084 V vs SCE while in the oldest solution the most intense peak is measured at -0.240 V vs SCE (Figure 6.6b).

Another observation can be made on these CVs: in the second cycle, the CVs do not show faradaic current and are identical (see cycle 2 and 3 on Figures 6.6a and 6.6b) which indicates that the reduction reaction occurring during the first cycle



Figure 6.4 – Comparison of the the functionalization of a gold sphere electrode by PFBD (1.1 mM in ACN, 0.1 M TEAPF<sub>6</sub>) by CV ; a) in a freshly prepared solution, b) on the same flame-annealed electrode, 5 minutes later. Scan rate: 100 mV s<sup>-1</sup>.

blocks the surface of the electrode for further reduction of PFBD. Finally, a small irreversible peak at 0.70-0.71 V vs SCE is also observed: this peak cannot clearly be attributed but could be due to the reduction of pre-adsorbed species as it has been previously observed for other diazonium salts on gold. [260]

The charge associated with the irreversible peak in the CV presented in Figure 6.3 corresponds to a maximum coverage of  $ca. 2.8 \cdot 10^{-9}$  mol cm<sup>-2</sup> which is smaller but consistent with what can be estimated from ref [258] ( $ca. 6 \cdot 10^{-9}$  mol cm<sup>-2</sup>). These values are however still higher than those determined from geometrical models ( $ca. 1 \cdot 10^{-9}$  mol cm<sup>-2</sup>). The electrochemical properties of the layer were characterized by comparing the CV of a ferrocene solution before and after the grafting (Figure 6.5): the current does not significantly decrease from one CV to the other which is consistent whith a thin and non-blocking monolayer. Electron transfer from the ferrocene to the metal is still efficient which is for example not the case in the well-known blocking layers formed by polymerization of nitrobenzenediazonium. [245] It is then suggested that the larger charge observed reflects that only a fraction of the radical

produced by electrochemical reduction is grafted. The other radicals probably react in solution.



Figure 6.5 – CV of a gold sphere electrode in a Ferrocene solution (4.6 mM in ACN, 0.1 M TEAPF<sub>6</sub>) before (green line) and after (grey line) electrochemical grafting of PFBD presented in Figure 6.3; scan rate: 100 mV s<sup>-1</sup>.

#### 6.3.2 STM imaging of PFBD-grafted gold surfaces

The covalent grafting of PFB moities onto gold was investigated by STM. The EC reduction of PFBD  $(7 \cdot 10^{-5} \text{ M in ACN}, 0.1 \text{ M TEAPF}_6)$  was performed on a large (~ 0.7 cm<sup>2</sup>) flat flame-annealed gold surface by CV (from 1 to -0.5 V vs SCE, 500 mV s<sup>-1</sup>).

The STM map is characteristic of a functionalized gold surface: a non homogeneous distribution of small pits with depths ranging from 0.5 to 1 nm appears over the surface. This depth is consistent with the height of a benzene molecule. Larger depletions observed in the structure are due to holes on gold terraces that are usually observed on our flame-annealed Au(111) surfaces. This observation is consistent with an organic layer formed from diazonium salts reduction that usually do not self-organize as thiol derivatives do. These results also confirm that the PFBD does not polymerize to form a multilayer since randomly dispersed extrusions would be observed.



Figure 6.6 – STM imaging of a PFB grafted gold surface. a)  $256 \times 256 \text{ nm}^2$ ,  $256 \times 512 \text{ px}^2 \text{ STM}$  map,  $i_t = 100 \text{ pA}$ , BV = 0.1 V, 1 Hz per line; b) height profile along the white line on the STM map.

#### 6.3.3 TERS analysis of the PFBD-grafted surface

STM experiments were performed on several samples prepared by EC reduction of PFBD on gold substrates. Unfortunately no clear TER spectrum could be recorded with this molecule. Whatever the incident laser power or the tunneling feedback conditions, no reproducible Raman signature could be extracted and compared to the Raman spectrum of PFBD powder (see Annex B.2.1).

We suggest that the random behaviour of the Raman signal can be explained by the photodecomposition of the organic layer upon illumination. Lowering the laser power to the minimal value and increasing the acquisition time up to several minutes did not prove to be successful either. We concluded on a too high photosensitivity of this molecule and did not pursue further investigations on this systems by TERS

# 6.4 Electrochemical and TERS investigation of an electroactive diazonium salt

Another diazonium salt was studied to investigate the structure of the grafted layer onto a gold surface. We chose an electroactive diazonium salt composed of an organometallic core: the bis(phenylterpyridyl)iron. This type of redox diazonium salt has in fact already been used in molecular junctions for molecular electronics. [261] As an example, in a recent work by Tefashe et. al., the efficiency of a molecular film containing  $\operatorname{Ru}(\operatorname{bipyridine})_3^{2+}$  to act as an emitting diode was demonstrated. In this study, a 7 nm thick layer was grafted and light emission was assigned to the existence of change in the redox state of the organometallic compound. [262] The properties of these molecular layers are strongly dependent on the mechanism of the electron transfers in the layer. For this purpose electrochemical experiments can provide a rich set of information which should be correlated with the structure of the molecular layer produced by electrochemical reduction of the diazonium salt.

In this part we mainly focused on the structure of the molecular layer produced from the reduction of a bis(phenylterpyridyl)iron diazonium derivative.

## 6.4.1 Electrochemical characterization of a gold electrode functionalized by FeBTPD

The structure of bis(phenylterpyridyl)iron diazonium derivative used in this study ([Fe(4'-(phenyl)-2,2:6',2"-terpyridine)(4-([-2,2':6',2"-terpyridin]-4';-yl)benzenediazo $nium)(PF_6)_2(BF_4)])$  is presented in Figure 6.7. It will be abbreviated FeBTPD in the following. FeBTPD was synthetized from its aniline-derivatized parent compound by Laure Fillaud at the LISE laboratory. Details about its synthesis and the synthesis of other parent compounds used in this section can be found in Annex B.3.

The grafting of FeBTPD was performed on a gold sphere electrode in ACN  $(10^{-5} \text{ M}, 0.1 \text{ M TEAPF}_6)$  during one CV from 0.9 to -1 V vs SCE. Surprisingly the



Figure 6.7 – Structure of FeBTPD

recorded CVs do not show any reduction peak that could be attributed to the oneelectron reduction of the diazonium. This may originate from the low concentration of the initial solution due to the poor solubility of FeBTPD in ACN.

To attest the effectiveness of the functionalization, the electrochemical behaviour of the electrode was tested in an electrolyte solution without any precursor (ACN +0.1 M TEAPF<sub>6</sub>). A reversible peak centered at 1.13 V vs SCE could be observed as shown on Figure 6.10. The scan rate was varied between 100 and 2000 V s<sup>-1</sup>: a linear relationship between the peak current and the scan rate (Figure 6.8c) was found up to 2000 V s<sup>-1</sup>, which is consistent with the presence of a redox system immobilized onto the surface of the electrode. [1]

Below a scan rate of 100 V s<sup>-1</sup> the faradaic current could not be distinguished from the capacitive one because of a too important noise level. This peak is assigned to the reversible Fe(III)/Fe(II) couple. Its integration can provide an estimation of a surface coverage of  $2 \cdot 10^{-8}$  mol m<sup>-2</sup> which is very low. It is *ca.* one order of magnitude lower than what is expected for a densely packed monolayer of this molecule. [263]<sup>1</sup>

The electrochemical signature of this layer can be compared to the one of the corresponding molecule with a thiol group instead of the diazonium function (FeBTPSH) depicted in Figure 6.9.

FeBTPSH was self-assembled onto a gold sphere electrode and a CV was recorded

<sup>&</sup>lt;sup>1</sup>Further experiments involving different reduction potentials, solvent and scan rates could not be explored because of time constraints. This will be performed in the future.



Figure 6.8 – Electrochemical characterization of a FeBTP grafted layer onto a gold sphere electrode. a) scheme of a FeBTP grafted onto a gold surface; b) CV of a FeBTP layer at 1000 V s<sup>-1</sup>, in ACN +0.1 M TEAPF<sub>6</sub>, centered on the reversible peak of the Fe(III)/Fe(II) at 1.13 V; c) cathodic peak current reported as a function of the scan rate.

at 20000 V s<sup>-1</sup>.<sup>2</sup> A peak centered at 1.15 V vs SCE could be observed. A surface concentration of  $1 \cdot 10^{-7}$  mol m<sup>-2</sup> was calculated from the integration of the reversible peak (which is consistent with what is expected from a monolayer of this molecule).

 $<sup>^2{\</sup>rm This}~{\rm CV}$  was recorded with a home-made potentio stat whith ohmic drop compensation. We thank Mr. Gabriel Boitel-Aullen who ran this experiment.



Figure 6.9 – Structure of FeBTPSH

These observations support the conclusion that FeBTP is anchored onto the gold surface.



Figure 6.10 – a) FeBTPSH anchored onto a gold surface; b) CV of a FeBTPSH SAM assembled onto a gold electrode in ACN (0.1 M TEAPF<sub>6</sub>), scan rate: 20000 V s<sup>-1</sup>.

## 6.4.2 STM-TERS analysis of a FeBTP grafted surface

In order to investigate the structure of the layer grafted onto gold, STM and TERS measurements were performed. For this purpose, a flame-annealed gold electrode ( $\sim 1 \text{ mm}^2$ ) was functionalized by electrochemical reduction of FeBTPD ( $10^{-5}$  M in ACN, 0.1 M TEAPF<sub>6</sub>, CV at 100 mV s<sup>-1</sup> from 0.9 to -1 V vs SCE). As for gold sphere electrodes, no reduction peak could be observed during the CV.

The FeBTP functionnalized surface was then investigated by STM-TERS. TERS spectra displayed in Figure 6.12 were recorded at several points on the sample. They are all characterized by common strong Raman bands that can be compared to the main Raman bands of the bisphenylterpyridine iron (Figure 6.11). Table 6.1 presents a summary of the main bands observed in TER spectra and the corresponding bands in FeBTP. Assignment was based on published data referring to a Ruthenium parent compound (Ru(bis-terpyridine)). [264] For comparison, the Raman spectrum of the ligand (4'-(phenyl)-2,2':6',2"-terpyridine (BTP)) and of FeBTPD can be found in Annex B.2.2 and B.2.3.



Figure 6.11 – Raman spectrum of FeBTP (powder);  $\lambda_{\text{exc}} = 632.8$  nm, laser power: 10.8  $\mu$ W, acquisition time: 100 s, 50X objective).

The most intense bands of FeBTP are found in all TER spectra recorded at three different points of the sample which confirms that the reduction of the diazonium salt produced effectively a grafted molecular layer. Most of the bands are broad, some of them being shifted (see the bands at 1294 and 1485  $\text{cm}^{-1}$  in the spectrum 2



Figure 6.12 – STM-TER spectra at three different positions of a FeBTP layer grafted onto gold by EC reduction of FeBTPD in ACN ;  $\lambda_{\text{exc}} = 632.8$  nm, laser power: 130  $\mu$ W, acquisition time: 10 s, BV: -100 mV,  $i_t = 200$  pA.

of Figure 6.12). New bands appear especially in the 1100 - 1600 cm<sup>-1</sup> region (such as the strong one at 1557 cm<sup>-1</sup> in spectrum 1). This kind of spectral characteristics may indicate a non-homogeneous and non-organized organic layer under the tip.

These observations should be further correlated with topographic information of the layer. On this sample STM imaging could however not be performed which can indicate a thick non-organized layer on gold that makes STM imaging complicated or impossible.

In order to ensure that the structure is a non-organized multilayer, we assembled the thiol derivative of FeBTP (FeBTPSH) on a gold sample from a 0.1 mM solution in ACN and recorded its TER spectrum for comparison. As a thiol compound, FeBTPSH is expected to form an organized SAM and then the same TER spectrum should be recorded at different positions of the sample to attest the homogeneity of the SAM. Three STM-TER spectra taken from different positions on the surface are

Table 6.1 – Main bands of Raman spectra of FeBTP (powder, microRaman), of the TER spectra recorded on a gold sample electrochemically grafted by FeBTPD (TER) and their assignation from [264]. The Raman shifts are in  $\text{cm}^{-1}$ ; the shift values marked with a star are found in only one spectrum. "bend.": bending; "str.": stretching.

FeBTP (Raman)	FeBTP (TER)	Assignation [264]
654	651	ring bend.
1009	997	ring str.
1024	1023	ring str.
-	1075	ring str. $+$ C-H bend.
1166	1157	C-H bend.
1287	$1285~(1294^{\star})$	ring str. $+$ C-H bend.
1361	1362	C-H bend. $+ \operatorname{ring  str.}$
1466	$1470~(1485^{\star})$	ring str.
1563	$1557^{\star}$	ring str.
1612	1598	ring str.

presented in Figure 6.13. It has first to be noticed that collected spectra are similar across the surface (both for the position and relative intensity of the bands) which is a first clear indication of an homogeneous molecular assembly. Moreover, the spectra all exhibit the same main Raman bands as the spectrum of the FeBTPSH powder.

TERS results support therefore the hypothesis of a non-organized multilayer formation upon electrochemical reduction of FeBTPD on gold. Further important information on the exact structure of the layer should be provided by AFM-TERS experiments as imaging is easier in AFM on samples with high roughness and potentially insulating areas. In order to favour formation of a monolayer that can be analyzed by STM-TERS, we further discuss the results obtained on samples onto which spontaneous grafting was explored.



Figure 6.13 – STM-TER spectra of a FeBTPSH SAM on gold at different positions on the sample (black, red and blue lines) compared with the microRaman spectrum of the FeBTPSH powder. TER spectra:  $\lambda_{\text{exc}} = 632.8$  nm, laser power: 10.8  $\mu$ W, acquisition time: 30 s, BV: 100 mV,  $i_t = 200$  pA; microRaman:  $\lambda_{\text{exc}} = 632.8$  nm, laser power: 10.8  $\mu$ W, acquisition time: 30 s, intensity divided by a factor of 3 for comparison. All spectra are offset for clarity.

# 6.5 Spontaneous grafting of diazonium salts investigated by STM-TERS

The spontaneous grafting of diazonium salts, as the result of simple immersion of the surface in a diazonium salt solution, is known to lead to thiner organic layers (from a monolayer to a bilayer) as compared to the electrochemically grafted ones that can grow up to 15 nm. [265] It has previously been demonstrated with nitrobenzenediazonium that alternative routes my be followed involving for example the formation of Au-N bonds besides the expected Au-C ones (see bottom part of Figure 6.1). [253]

Herein, we propose to investigate the spontaneous grafting of FeBTPD in ACN on a gold surface.

### 6.5.1 Sample preparation and characterization

The samples were prepared by immersing flame-annealed gold surfaces in a  $4 \cdot 10^{-5}$  M solution of FeBTPD in ACN for 30 min at 22 °C. The surface was then thoroughly rinsed with ACN and ethanol to remove any physisorbed species from the surface and dried under a nitrogen flow.

The surface was then investigated by STM. A STM image of the surface on a  $300 \times 300 \text{ nm}^2$  area is presented in Figure 6.14.



Figure 6.14 – STM imaging of a gold surface spontaneously grafted by FeBTPD. BV: 0.20 V,  $i_t$ : 200 pA; 300 × 300 nm<sup>2</sup>, 512 × 128 px<sup>2</sup>; scan rate: 1 Hz per line.

First, contrary to the samples grafted by electrochemical reduction of the same diazonium salt, the imaging in STM mode is here possible indicating that either the grafted layer is thinner in the case of a spontaneous grafting or that no grafting occurs under such conditions. Some dispersed protrusions are observed all over the scanned area with heights ranging from 0.5 to several nanometres: as most of them are found along the X axis, they may be STM artefacts. STM imaging onto a restricted area will be performed in the future to try to visualize molecules individually within the layer.

#### 6.5.2 STM-TERS analysis of the spontaneously grafted layer

As no topographical details could clearly evidence the grafting of FeBTP by STM, compositional analyses by STM-TERS were performed on the same sample.

A STM TER spectrum is given in Figure 6.15. It exhibits all of the main spectral features of FeBTP. Compared to the spectra of the FeBTP layer grafted by EC reduction of FeBTPD (Figure 6.12), the bands are thinner and no extra bands appear in this spectrum. The collected spectra compared to the TER spectrum of the FeBTPSH SAM indicating then a much more organized molecular layer than the one formed upon electrochemical reduction of FeBTPD.



Figure 6.15 – STM-TER spectra of a gold surface immersed in a FeBTPD ACN solution (blue line). The orange line is a spectrum recorded with the same STM parameters and Raman acquisition conditions on a clean gold sample as a control for tip contamination.  $\lambda_{\text{exc}} = 632.8$  nm, laser power: 10.8  $\mu$ W, acquisition time: 30 s, BV = 200 mV,  $i_t = 200$  pA; the spectra are the average of 5 aquisitions.

A TERS map was recorded over the same area as the STM map in Figure 6.14 to corroborate the hypothesis of a more organized structure. This STM-TERS map is presented in Figure 6.16.





<sup>(</sup>c)

Figure 6.16 – STM TERS imaging of a gold on mica surface spontaneously grafted by FeBTPD. a) TERS map obtained by integration of the peak at 1021 cm<sup>-1</sup>. b) low resolution STM image obtained during TERS measurement (the high resolution image can be found in Figure 6.14); c) selected TER spectra (averaged over 9 spectra in each square) extracted from a); spectra were offset for the sake of clarity. BV: 0.2 V,  $i_t$ : 200 pA; 300 × 300 nm<sup>2</sup>, 30 × 30 px<sup>2</sup>;  $\lambda_{exc} = 632.8$  nm, laser power: 130  $\mu$ W, acquisition time: 507 ms/px.

The TERS map obtained by integration of the band at  $1021 \text{ cm}^{-1}$  displays heterogeneities in intensity that can be related to the topography of the substrate: the most intense area is located (middle left part of the map) over a specific gold terrace while the less intense part is found in a valley between two terraces. On other parts of the sample, the intensity is mainly homogeneous.

A selection of 5 spectra were extracted from this map on 5 different positions of the sample and are displayed in Figure 6.16c.

The main difference between all of these spectra concerns the overall intensity of the bands. A close look to spectra 2 and 5 recorded on gold terraces suggest that the surface concentration is different between both areas. Indeed, the overall TER intensity is 1.3 higher on position 2 than on position 5. This suggests that the spontaneous grafting does not occur completely homogeneously over the sample. These slight differences cannot be explained at the moment.

Note that a spectrum was collected on a clean gold substrate after all the TERS measurements: it does not exhibit Raman bands from FeBTP or any other organics which discards contamination of the tip by FeBTP during previously described experiments (see orange line in Figure 6.15).

TERS imaging therefore supports the hypothesis of the formation of a monolayer of FeBTP on gold.

A more spatially resolved TERS mapping (down to the molecular scale) on this surface could help correlating these intensity variations with specific sites on the sample. However, in the ambient, TERS mapping at the molecular scale has not been achieved yet and might be very difficult because of the thermal drift of the sample at the timescale of TER experiments (500 ms per spectrum in this example).

## 6.6 Conclusion

In this chapter, we have investigated the structure of a molecular layer grafted onto gold surfaces from electrochemical reduction of diazonium salts. The first diazonium derivative, PFBD, was studied as a model compound for the formation of monolayers. STM images revealed the non-compact structure of these layers but also confirmed their ability to form only monolayers. This system could unfortunately not be investigated by TERS probably due to its high photosensitivity. In this case no spectroscopic information could be correlated to the structure determined by STM.

The second system, based on a diazonium salt with a redox core, was studied by cyclic voltammetry. Its anchoring onto the gold surface could be demonstrated. Two grafting paths were investigated: the electrochemical reduction and the spontaneous grafting. STM and TERS measurements revealed different molecular organizations depending on the grafting origin. In electrochemical grafting, we concluded on the formation of a thick multilayer. TERS results corroborated this hypothesis by providing spectra that could be associated to a disorganized organic layer. Comparatively, the STM and TERS experiments conducted on a sample functionalized by spontaneous grafting suggested the anchoring of a less densely packed monolayer. The STM and TERS results were in this case complementary since STM images did not provide clear evidences of the grafting.

This is to the best of our knowledge the first set of TERS results provided on the grafting of diazonium salts. These preliminary results should be completed by deeper electrochemical analysis, especially to measure the electron transfer rate in these redox layers and correlate them to the structure that can be investigated by STM and TERS. This work demonstrated that TERS can be a powerful tool for the understanding of the mechanism of both the grafting of diazonium salts and of electron transfer in such organic layers, which are of major importance for molecular electronics.

## General conclusion and outlook

The work described in this thesis has demonstrated that the implementation of TERS for the analysis of electrochemical systems can be realized under a wide range of conditions for various applications. In this work, several instrumental challenges had to be overcome due to difficulties related to the coupling of electrochemical measurements with SPM and Raman investigations.

In chapter 2, the experimental prerequisites of conventional STM-TERS measurements have been developed. In particular, we have described the manufacturing process of reliable and robust bulk gold and silver TERS probes for STM-based TERS. These probes are a key element in any TERS experiment since both lateral resolution and sensitivity for nanoRaman imaging strongly depend on tip geometry and on the structure of the probe apex.

Chapter 3 covered the possibility of TERS to image samples immersed in an organic liquid in an upright illumination and collection configuration. These results were the first demonstration of TERS imaging in liquid and revealed the ability of our setup to probe inhomogeneities in the coverage density of a molecular self-assembled monolayer (SAM) on a gold surface. It may be of major interest for the protection and investigation of air-sensitive samples or to prevent surface contamination and signal fluctuation usually observed in the air. Implementation of this configuration in electrochemical conditions is potentially possible, but would require handling a very thin layer of electrolyte.

We introduced in Chapter 4 a TERS-inspired analytical tool, the so-called tip

SERS, to monitor electrochemical reactions. A partially insulated and functionalized TERS tip was used as a single hot spot SERS and microelectrode to probe the electrochemical transformation of a 4-nitrothiophenol SAM. We introduced in this chapter the high excitation and signal collection efficiency provided by the use of a water immersion objective for *in situ* TERS en SERS experiments. The hybrid tips developed are expected to be applied to the investigation of more complicated electrochemical transformation in immobilized molecular systems.

In Chapter 5, TERS imaging in electrochemical environment was evidenced. The EC tip-SERS configuration was promoted in order to enable STM-TERS imaging of a surface under potential control. The presented preliminary results demonstrate the ability of the proposed setup to probe variations of the local electromagnetic field enhancement under the tip with a lateral sensitivity down to 8 nm. This is to the best of our knowledge the first demonstration of TERS imaging under electrochemical conditions.

The last chapter was dedicated to the TERS analysis of surfaces functionalized by electrochemical reduction and spontaneous grafting of aryldiazonium salts. STM and TERS results evidenced the different molecular structures obtained from a diazonium salt with an electroactive core depending on the grafting route and revealed that layers formed upon spontaneous grafting are less densely packed monolayers whereas electrochemical reduction led to disorganized multilayers. These preliminary results have to be completed by deeper electrochemical analyses and to be corroborated by more accurate topographic information which could be provided by AFM-TERS.

During this work several approaches have demonstrated the strengths of TERS to investigate electrochemical interfaces both *in situ* and *ex situ*. The reliable setup developed for EC STM-TERS imaging was a first important milestone to reach for further investigations of electrode/electrolyte interfaces. Even if TERS lateral resolution is still to be demonstrated, we expect this configuration to enable Raman analysis at the nanoscale of more complicated electrochemical systems and pave the road for the *operando* investigation of catalytic reactions, energy storage materials under the conditions of their operation or organic layers for molecular electronics. Implementation of AFM-TERS in electrochemical conditions is also to be explored and requires further instrumental developments. It would enable to probe a more varied range of samples especially for energy storage and conversion for which STM imaging would be difficult to implement because of the poor conductivity of the substrate.

# Appendix A

# Supplementary materials to Chapter 4

## A.1 Raman signature of N,N-dimethylnitrosoaniline

As 4-nitrosothiophenol (4-NSTP) is not commercial, we used N,N-dimethylnitrosoaniline (Aldrich, 97% purity) as a reference compound for nitroso compounds. The spectrum, acquired with a 632.8 nm laser line through a 50X objective, exhibits mainly bands that can be assigned to the *cis* nitroso dimer: the strong band at 1391 cm<sup>-1</sup> (N = N stretching for *cis* dimer) and the 1358 and 1331 cm<sup>-1</sup> bands (C – N stretching). The medium band at 1298 cm<sup>-1</sup> can be assigned to N – O stretching. [206]



# Appendix B

# Supplementary materials to Chapter 6

# B.1 Electrochemical characterization of a FeBTP functionalized gold sphere electrode

A gold sphere electrode  $(A = 0.250 \text{ mm}^2)$  was functionalized by electrochemical reduction of FeBTPD  $(5 \cdot 10^{-4} \text{ M})$  in ACN  $(0.2 \text{ M TBAPF}_6)$  under nitrogen by CV  $(200 \text{ mV s}^{-1}, 1 \text{ cycle}, \text{ from } +1 \text{ to } -1.5 \text{ V} vs \text{ SCE}$ . The electrode was then thoroughly rinced with ACN and CVs were recorded in ACN + 0.2 M TBAPF<sub>6</sub> under nitrogen at scan rates ranging from 100 to 2000 V s<sup>-1</sup> between 0.6 and 1.7 V vs SCE centered on the reversible peak of the Fe at 1.13 V vs SCE. Below 100 V s<sup>-1</sup>, the noise was too large so that no faradaic current could be separated from the capacitive signal. Above 2000 V s<sup>-1</sup>, the electrode time constant and ohmic drop were far too important to allow a proper CV aquisition (undistorded signal). [266]



Figure B.1 – CVs recorded on a gold sphere electrode grafted with FeBTPD at a) 100 V s<sup>-1</sup>, b) 300 V s<sup>-1</sup>, c) 500 V s<sup>-1</sup>, d) 1000 V s<sup>-1</sup>, e) 1500 V s<sup>-1</sup>, f) 2000 V s<sup>-1</sup>.

## **B.2** Raman Spectra of reference products

The Raman spectra were recorded on products powders through a 50X objective with a Labram HR Evolution Raman Spectrometer (Horiba, Japan) with a 632.8 nm laser excitation.

# B.2.1 Raman signature of 2,3,4,5,6-pentafluorobenzenediazonium tetrafluoroborate (PFBD)



-500 Raman shift (cm<sup>-1</sup>)

B.2.2 Raman signature of 4'-(phenyl)-2,2':6',2"-terpyridine (BTP)

B.2.3 Raman signature of [Fe (4'-(phenyl)-2,2':6',2"-terpyridine) (4-([2,2':6',2"-terpyridin]-4'-yl)benzenediazonium)( $PF_6^-$ )<sub>2</sub>-( $BF_4^-$ )<sub>2</sub>] (FeBTPD)



# B.3 Synthesis and characterization of organic compounds

B.3.1 Synthesis of 2,3,4,5,6-pentafluorobenzenediazonium tetrafluoroborate (PFBD)



At  $-40^{\circ}$ C under argon atmosphere, to a solution of 2,3,4,5,6-pentafluoroaniline (2.7 mmol, 0.5 g) in cold acetonitrile (4 mL), nitrosium tetrafluoroborate (4.9 mmol, 0.57 g) was added dropwise. The mixture was stirred for 45 min. Cold diethyl ether (40 mL) was added. A white powder appears; which was filtered and washed with diethyl ether. Yield: 94.7%, (0.72 mg). **IR**:  $\nu_{max} = 2306 \text{ cm}^{-1}$ ,  $\nu_{(N\equiv N)}$ ; **Raman**:  $\nu_{(N\equiv N)} = 2310 \text{ cm}^{-1}$ .

## B.3.2 Synthesis of 4'-(phenyl)-2,2':6',2"-terpyridine (BTP)



To a solution of benzenaldehyde (18.8 mmol, 2 g, 1.92 mL) in ethanol (50 mL), 2acetylpyridine (38.29 mmol, 4.64 g, 4.29 mL) and potassium hydroxyde (38.29 mmol, 2.15 g) were added. The solution became orange. The reaction mixture was stirred overnight at room temperature. A yellow precipitate appeared which was filtered, washed three times with diethyl ether and dried under vacuum. A light yellow powder was obtained. Yield: 46 % (2.7 g). <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$  (ppm)): 8.76 (ddd, J = 4.8 Hz, J = 2 Hz, J = 1 Hz, 2H), 8.70 (s, 2H), 8.63 (s, 2H, H<sub>7</sub>), 8.67 (d, J = 8 Hz; 2 Hz, 2H), 8.04 (td, J = 7.8 Hz, J = 1.9 Hz, 2H), 7.92 (d, J = 8 Hz, 2), 7.60 (d, J = 8 Hz, 2H), 7.54 (t, J = 1.7 Hz, 1H), 7.52 (ddd, J = 7.8 Hz, J = 4.8 Hz, J = 1.2 Hz, 2H).

#### B.3.3 Synthesis of 4-aminobenzaldehyde



To a solution of 4-nitrobenzaldehyde (6.62 mmol, 1 g) in ethanol, tin powder (66.2 mmol, 7.9 g) was added. Hydrochloric acid (12 N, 50 mL) is added dropwise to the reaction mixture maintained at 0°C. The reaction mixture became red. The reaction mixture was stirred at room temperature for twelve hours, then filtered through Celite pad and washed with ethyl acetate. The reaction mixture was neutralized with sodium hydroxide (4 M). The organic phase was extracted, dried with magnesium sulfate and dried under vacuum. An orange powder was obtained. Yield: 38 % (0.3 g). <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$  (ppm)) : 9.6 (s, 1H), 7.54 (d, J =8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 4.03 (brd, 2H).

## B.3.4 Synthesis of 4'-(4-aminophenyl)-2,2':6',2"-terpyridine



To a solution of 4-aminobenzenaldehyde (2.48 mmol, 0.3 g) in hot ethanol (50 mL), the 2-acetylpyridine (7.43 mmol, 0.9 g, 0.83 mL) and potassium hydroxyde (7.43 mmol, 0.41 g) were added. The solution became orange. The reaction mixture

was kept under reflux and stirred overnight at room temperature. A yellow precipitate appeared which was filtered, washed three times with diethyl ether and dried under vacuum. A light yellow powder was obtained. Yield: 25 % (0.2 g). <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$  (ppm)): 8.74 (ddd, J = 4.8 Hz, J = 2 Hz, J = 0.9 Hz, 2H), 8.63 (dt, J = 7.8 Hz, J = 1.2 Hz, 2H), 8.59 (s, 2H), 7.98 (td, J = 7.6 Hz, J = 2 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.48 (ddd, J = 7.8 Hz, J = 4.8 Hz, J = 1.2 Hz, 2H), 6.68 (d, J = 8.1 Hz, 2H), 5.59 (brd, 2H).

### B.3.5 Synthesis of 4'-(4-bromophenyl)-2,2':6',2"-terpyridine



To a solution of 4-bromobenzenaldehyde (10.9 mmol, 2 g) in ethanol (50 mL), 2acetylpyridine (43.38 mmol, 5.25 g, 4.86 mL) and potassium hydroxyde (42.84 mmol, 2.40 g) were added. The solution became dark yellow. The reaction mixture was kept under reflux and stirred overnight at room temperature. A light green precipitate appeared which was filtered, washed three times with diethyl ether and dried under vacuum. A light green powder was obtained. Yield: 59.6 % (2.49 g). <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$  (ppm)): 8.77 (ddd, J = 4.8 Hz, J = 1.9 Hz, J = 1 Hz, 2H), 8.76 (s, 2H), 8.67 (d, J = 7.8 Hz, 2H), 8.04 (td, J = 8 Hz, J = 1.8 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.58 (ddd, J = 7.8 Hz, J = 4.8 Hz, J = 1.1 Hz, 2H).

## B.3.6 Synthesis of 4-([2,2':6',2"-terpyridin]-4'-yl)benzenethiol



To a solution of copper (II) sulfate pentahydrate (0.14 mmol, 0.035 g) and potassium hydroxide (13.5 mmol, 0.75 g) in DMSO:H2O (1:0.1; 20:2 mL), 1,2ethanedithiol (5.4 mmol, 0.49 mL) was added. The solution became brown. The reaction mixture was heated at 110°C during 1 h and stirred overnight at room temperature. The organic phase was extracted by (ethyl acetate: H<sub>2</sub>O:HCl) (1:1:0.05), dried with magnesium sulfate and dried under vacuum. The crude product was further purified by column chromatography to provide light yellow crystals. Yield: 91.3 % (0.84 g). <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$  (ppm)): 8.75 (ddd, J = 4.8 Hz, J =2 Hz, J = 0.8 Hz, 2H), 8.69 (s, 2H), 8.67 (dd, J = 7.8 Hz, J = 0.8 Hz, 2H), 8.03 (td, J = 7.8 Hz, J = 1.0 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.52 (ddd, J = 7.8 Hz, J = 4.0 Hz, J = 1.1 Hz, 2H), 3.00 (s, 1H). [267]

## B.3.7 Synthesis of [Fe (4'-(phenyl)-2,2':6',2"-terpyridine) $_2(PF_6^-)_2$ ] (FeBTP) derivatives

The syntheses of FeBTP asymmetric derivatives were carried out according to procedures described by Kurita et al. [268]


#### **B.3.7.1** Synthesis of [Fe (4'-(phenyl)-2,2':6',2"-terpyridine)<sub>2</sub>( $PF_6^-$ )<sub>2</sub>] (FeBTP)

To a solution of 4'-(phenyl)-2,2':6',2"-terpyridine (X g, X mmol) in methanol (20 mL), FeSO<sub>4</sub>.7H<sub>2</sub>O(0.0384 g, 0.138 mmol) suspended in methanol (20 mL) was added. The reaction mixture immediately became violet, and was stirred overnight. A saturated aqueous solution of  $NH_4PF_6$  (2.5 g, 15 mmol) was then added. A purple precipitate formed immediately. After 24 hours, the violet solid was filtered and washed with diethyl ether.

The UV spectrum of FeBTP in ACN exhibits an absorption band at 566 nm. This band is characteristic of the metal-to-ligand charge transfer (MLCT) in these compounds.



B.3.7.2 Synthesis of [Fe (4'-(phenyl)-2,2':6',2"-terpyridine)(4'-(4-amino-phenyl)-2,2':6',2"-terpyridine)( $PF_6^-$ )<sub>2</sub>]

To a solution of  $\text{FeCl}_2.4\text{H}_2\text{O}$  (0.323 mmol) in ethanol (15 mL), 4'-(phenyl)-2,2':6',2"terpyridine (100 mg, 0.323 mmol) in solution in ethanol (15 mL) was added. The reaction mixture immediately became violet. The reaction mixture was stirred at room temperature for 30 minutes. The 4'-(4-aminophenyl)-2,2':6',2"-terpyridine (120 mg) was solubilized in hot ethanol (15 mL) and then added to the reaction mixture which was refluxed overnight. The reaction mixture was precipitated by slow addition of a saturated  $NH_4PF_6$  solution and then filtered. The violet residue was dissolved in  $CH_3CN$  and diethyl ether was slowly diffused. Small purple crystals appeared and were washed with diethyl ether. <sup>1</sup>H NMR ( $CD_3CN$ ,  $\delta$  (ppm)): 9.20 (s, 4H), 8.61 (d, J = 8.68 Hz, 4H), 8.31 (d, J = 7.89 Hz, 4H), 7.88 (td, J = 7.8 Hz, J = 1.3 Hz, 4H), 7.83 (t, J = 7.1 Hz, 4H), 7.80 (d, J = 7.3 Hz, 1H), 7.19 (d, J = 5.4 Hz, 4H), 7.08 (t, J = 6.3 Hz, 4H), 5.90 (brd, 2H).

To a solution of [Fe(4'-(phenyl)-2,2':6',2"-terpyridine) (4'-(4-aminophenyl)-2,2':6',2"terpyridine)  $(PF_6^-)_2]$  in cold acetonitrile (3 mL) under argon atmosphere, nitrosium tetrafluoroborate was added. The reaction mixture was stirred at  $-40^{\circ}C$  (15 min). Cold diethylether (20 mL) was added and a purple-blue crystalline precipitate appeared. Crystals were filtered and washed with diethyl ether and slightly dried under vacuum. **Raman**:  $\nu_{(N\equiv N)} = 2297 \text{ cm}^{-1}$ . UV-Vis: 283 and 321 nm (tpy), 565 nm (MLCT).

# Abbreviations and symbols

#### Abbreviations

AC	Alternating current
AFM	Atomic Force Microscopy
BCB	Brilliant Cresyl Blue
BE	Beam Expander
BV	Bias Voltage (STM)
CCD	Charge-Coupled Device
CE	Counter Electrode (auxiliary electrode)
CH	Confocal Pinhole
CLS	Classical Least Square
CV	Cyclic Voltammetry
DC	Direct Current
DFT	Density Functional Theory
e	Edge filter
EC	Electrochemical
$\mathrm{EF}$	Enhancement Factor
EIS	Electrochemical Impedance Spectroscopy
EM-CCD	Electron-multiplying CCD

F	Filter
FIB	Focused Ion Beam
$\mathbf{FF}$	Far-Field
FTIRRAS	Fourier Transform IR Reflection Spectroscopy
Gr	Diffraction Grating
НОМО	Highest Occupied Molecular Orbital
HOPG	Highly-Orientated Pyrogenic Graphite
IR	Infrared
ITO	Indium-Tin Oxide
LSP	Localized Surface Plasmon
LSPR	Localized Surface Plasmon resonance
LUMO	Lowest Unoccupied Molecular Orbital
М	Mirror
MIM	Metal-Insulator-Metal
n	Notch Filter
NA	Numerical Aperture
ND	Neutral Density Filter
NF	Near-Field
NF	Normal Force (TF)
NFM	Normal-Force Microscopy
NP	Nanoparticle
ORC	Oxidation-Reduction Cycle
PR	Plasmon Resonance
PZC	Potential of Zero Charge
RC	Resistor-Capacitor

RE	Reference Electrode
RR	Resonance Raman
RRS	Resonance Raman Spectroscopy
SAM	Self-Assembled Monolayer
SCE	Saturated Calomel Electrode
SEC	Spectroelectrochemistry
SECM	Scanning Electrochemical Microscopy
SECCM	Scanning Electrochemical Cell Microscopy
SEI	Solide-Electrolyte Interphase
SEM	Scanning Electrons Microscopy
SERS	Surface-Enhanced Raman Spectroscopy
SERRS	Surface-Enhanced Resonance Raman Spectroscopy
$\mathbf{SF}$	Shear-Force
$\mathrm{SFM}$	Shear-Force Microscopy
$\mathbf{Sh}$	Shutter
SHE	Standard Hydrogen Electrode
SHINERS	Shell-Isolated Nanoparticles Enhanced Raman Microscopy
SNOM	Scanning Near-Field Optical Microscopy
a-SNOM	Aperture SNOM
s-SNOM	Scattering SNOM
$\mathrm{SPM}$	Scanning Probe Microscopy
SP	Surface Plasmon
SPP	Surface Plasmon Polariton
SRS	Stimulated Raman Spectroscopy
SPR	Surface plasmon Resonance

STM	Scanning Tunneling Microscopy
TDDFT	Time-Dependent DFT
TERS	Tip-Enhanced Raman Spectroscopy
TF	Tuning fork
UHV	Ultra-High Vacuum
UME	Ultra-Microelectrode
UV	Ultraviolet
Vis	Visible
WE	Working Electrode
XPS	X-ray Photoelectron Spectroscopy

### Abbreviations and acronyms of chemical compounds

4-ATP	4-aminothiophenol
4-HATP	$4 ext{-hydroxylaminothiophenol}$
4-NSTP	4-nitrosothiophenol
4-NTP	4-nitrothiophenol
4-PBT	((4'-(pyridine-4-yl)biphenyl-4-yl) methanethiol)
4-TADPA	4-4'-thioaminodiphenylamine
4-TPQDI	4,4'-thiophenylquinone
ACN	Acetonitrile ( $CH_3CN$ )
CoTPP	meso-tetraphenylporphyrin cobalt
CNT	Carbon Nanotube
DMAB	p- $p$ '-dimercaptoazobenzene
DMAOB	p- $p$ '-dimercaptoazoxybenzene
DMHAB	p- $p$ '-dimercaptohydrazobenzene
DNA	Desoxyribonucleic Acid

$\mathrm{Fc}$	Ferrocene
FeBTP	[Fe (4'-(phenyl)-2,2':6',2"-terpyridine) <sub>2</sub> ( $PF_{6}^{-}$ ) <sub>2</sub> ]
FeBTPD	$[{\rm Fe}(4'-({\rm phenyl})-{\rm terpyridine})~(4-({\rm terpyridin-4'};-~{\rm yl}){\rm benzenediazonium})({\rm PF}_6^-)_2({\rm BF}_4^-)]$
FeBTPSH	$[{\rm Fe}(4'-({\rm phenyl})-{\rm terpyridine})~(4-({\rm terpyridin-4'};-~{\rm yl}){\rm benzenethiol})({\rm PF}_6^-)_2]$
PFBD	2,3,4,5,6-pentafluor obenzene dia zonium
$H_2TBPP$	meso-tetrakis (3,5-di-tetrary butyl-phenyl-porphyrin)
MWCNT	Multiwall Carbone Nanotube
NB	Nile Blue
m Rh6G	Rhodamine 6G
RNA	Ribonucleic Acid
SWCNT	Single-Wall Carbone Nanotube
TBAP	Tetrabutylammonium perchlorate $(Bu_4NClO_4)$
TBPP	(tert-butyl-phenyl)-porphyrin
$\mathrm{TEAPF}_6$	Tetraethylammonium Hexafluorophosphate $({\rm Et}_4{\rm NPF}_6)$

## Symbols (and units)

$\alpha$	Angle to the normal surface of the sample	degree
$\hat{\alpha}$	Polarisability	$C m^2 V^{-1}$
Г	Surface coverage	mol $m^{-2}$
$\Delta E$	Difference of energy between two states in eq. $1.1$	J
$\epsilon$	Complex dielectric function	-
$\epsilon_0$	Dielectric constant of the free space	${\rm F}~{\rm m}^{-1}$
$\epsilon_d$	Dielectric function of the dielectric medium	-
$\epsilon^{ib}$	Interband transition contribution to $\epsilon$	-
$\epsilon^D$	Intraband transition contribution to $\epsilon$ (Drude model)	-
$\gamma$	Damping constant (harmonic oscillator)	Hz

Г	Molecular surface coverage	mol m $^{-2}$
Г	Damping constant in the expression of $\epsilon^D$	-
Г	Resonance peak FWHM (harmonic oscillator)	Hz
$ heta_t$	Tapper angle	degrees
$\kappa$	Extinction coeficient	-
λ	Wavelength	nm
$\overrightarrow{\mu}$	Total dipolar moment	C m
$\overrightarrow{\mu_i}$	Induced dipolar moment	C m
$\overrightarrow{\mu_p}$	Permanent dipolar moment	C m
$\overrightarrow{\mu_p}$	Induced dipolar moment	C m
$ u_0$	Frequency of an incident photon	$s^{-1}$
$ u_k$	Frequency of the normal mode $k$	$s^{-1}$
$\sigma_k$	Cross section for the $k$ mode	$m^2$
au	Characteristic time constant (harmonic oscillator)	S
ω	Angular frequency of an EM field	rad $s^{-1}$
$\omega_p$	Angular frequency of a plasma	rad $s^{-1}$
ω	Raman shift	$\mathrm{cm}^{-1}$
$\Omega$	Solid angle	sr
a	NP radius	m
A	Electrode area	$m^2$
$A_i$	Raman peak area	$\rm cnts~s^{-1}~cm^{-1}$
c	Light velocity	${\rm m~s^{-1}}$
C	Concentration	mol $m^{-3}$
d	Tip-sample distance (TERS)	m
D	Diffusion coefficient	$\mathrm{m}^2~\mathrm{s}^{-1}$

E	Electrode potential	V
$E^0$	Standard redox potential	V
$\mathrm{E}_{\mathrm{vertex}}$	Cathodic vertex potential in CVs	V
$E_{loc}$	Local electric field magnitude in TERS and SERS	$V m^{-1}$
$\overrightarrow{E}$	Electric field	$V m^{-1}$
$E_F$	Fermi energy level of a metal	J
$f_0$	Resonance frequency (TF)	Hz
F	Faraday constant	$96,485.3 \text{ A mol}^{-1}$
ħ	Reduced Planck constant	$6.582 \ 119 \cdot 10^{-16} \ \mathrm{eV} \ \mathrm{s} \ \mathrm{rad}^{-1}$
$i_f$	Faradaic current	А
$i_p$	Peak current in CV	А
$i_{pa}$	Anodic peak current in CV	А
$i_{pc}$	Cathodic peak current in CV	А
$I_k$	Scattering intensity of the $k$ mode	-
$I_{\omega}$	Raman intensity at a $\omega \ {\rm cm}^{-1}$ shift	cnts $s^{-1}$
$I_{NR}$	Intensity of confocal Raman signal	a.u.
$I_{SER}$	Intensity of SER signal	a.u.
$i_t$	Tunneling current (STM)	А
$I_{TER}$	Intensity of TER signal	a.u.
$\overrightarrow{k}$	Wavevector	$\mathrm{m}^{-1}$
$k_B$	Boltzmann constant	$\rm J~K^{-1}$
$m_e$	Effective mass of an electron	$9.11 \cdot 10^{-31} \text{ kg}$
n	Number of electrons	-
$n_e$	Density of electrons in a metal	$\mathrm{m}^{-3}$
<u>n</u>	Complex refractive index	-

N	Number of atoms in a molecule	-
$N_n$	Population of vibrational state	-
$N_{NR}$	Number of molecules probed in confocal Raman	-
$N_{SER}$	Number of molecules probed in SERS	-
$N_{TER}$	Number of molecules probed in TERS	-
p	Momentum of a particle	$\rm kg~m~s^{-1}$
$q_k^0$	Normal coordinate at equilibrium (harmonic oscillator)	-
$q_k$	Normal coordinate (harmonic oscillator)	-
Q	Charge	С
Q	Quality factor (TF)	-
r	Radial distance to the center of a NP	m
$r_c$	Radius of curvature (TERS tip)	nm
$R_{foc}$	Focused laser beam radius	m
$R_{tip}$	TERS tip radius	m
t	Time	S
T	Temperature	Κ
v	Sweep rate in CV	$\rm V~s^{-1}$
x	Position of a particle	m

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Abstract - The *in situ* investigation of electrochemical interfaces structures at the nanoscale is a key element in the understanding of charge and electron transfer mechanisms e.g. in the fields of energy storage or electrocatalysis. This thesis introduces the implementation of tip-enhanced Raman spectroscopy (TERS) in liquid and in electrochemical conditions enabling the nanoscale analysis of electrified solid/liquid interfaces through the strong and local electric field enhancement at gold or silver scanning tunneling microscopy (STM) probes. The ability of TERS to image inhomogeneities in the coverage density of a self-assembled monolayer (SAM) through a layer of organic solvent on gold was demonstrated. A TERS-inspired analytical tool was also developed, based on a TERS tip used simultaneously as a single-hot spot surface-enhanced Raman spectroscopy (SERS) platform and as a microelectrode (EC tip SERS). The reduction of an electroactive SAM could then be monitored by electrochemical and in situ SERS measurements. In situ electrochemical STM-TERS was also evidenced through the imaging of local variations of the electric field enhancement on peculiar sites of a gold electrode with a lateral resolution lower than 8 nm. Finally TERS also demonstrated to be efficient in investigating the structure of organic layers grafted either by electrochemical reduction or spontaneously. This work is therefore a major advance for the analysis of functionalized surfaces.

Résumé - L'analyse in situ d'interfaces électrochimiques à l'échelle nanométriques est un enjeu majeur pour la compréhension des mécanismes de transferts de charges et d'électrons dans les domaines du stockage d'énergie ou de l'électrocatalyse. Ce travail a permis le développement de la spectroscopie Raman exaltée de pointe (TERS) en milieu liquide et en conditions électrochimiques. Le TERS permet l'analyse de la structure de molécules ou de matériaux à l'échelle nanométrique du fait de l'exaltation localisée du champ électrique à l'extrémité d'une sonde de microscope à effet tunnel (STM) en or ou en argent. Un dispositif reposant sur l'illumination d'une pointe au travers d'un solvant organique a démontré la possibilité d'imager les inhomogénéités d'une monocouche auto-assemblée sur or. Une seconde approche reposant sur l'exaltation du signal Raman à l'apex d'une pointe de taille nanométrique utilisée comme microélectrode (spectroscopie Raman exaltée de surface de pointe, tip SERS) a permis de suivre la réduction d'une monocouche auto-assemblée et d'améliorer la compréhension de son mécanisme. Afin d'imager la surface d'une électrode polarisée, le couplage d'un STM utilisant une pointe TERS en conditions électrochimiques a montré une résolution latérale de moins de 8 nm pour sonder de variations locales de l'exaltation du champ électromagnétique induites par des singularités géométriques de surface. Par ailleurs, l'analyse TERS de couches organiques formées à partir de sels d'aryldiazoniums a permis de montrer des différences de structures selon type de greffage. Ce travail constitue donc une avancée majeure pour l'analyse locale de surfaces modifiées.