

Chapter 3

Experimental part

3.1 Set-up

The TER(R)S set-up consists of a Raman spectrograph (LabRam 1000 from DILOR) which is controlled by Labspec 4.18 software (Jobin Yvon) and coupled to a home-built STM controlled by WSxM software (Nanotec Electronic). A red He-Ne laser beam (632.8 nm) is focussed onto the STM Au-tip by a 50x long working distance objective (N.A. = 0.5) at an angle of 60° off the optical axis¹ to the surface normal with the polarization set to be parallel to the plane of incident (p-polarization). The incident power at the tip is 2 mW. If necessary, grey filters are employed to reduce the laser intensity to prevent the molecules from photobleaching. The spectral acquisition time varies between 1 and 20 s, depending on the incident laser power. All presented spectra are normalized to full power and 1 s integration time for better comparison if not indicated otherwise.

The backscattered light is collected through the same objective, led to the spectrometer (grating 600 l/mm) and read out by a CCD camera cooled with liquid nitrogen. The spectral resolution accomplished is 4 cm^{-1} . Coarse approach of the tip and focussing of the laser beam are monitored with help of an additional CCD camera. Working in constant-current mode at 1 nA, the tip is positioned approximately 1 nm

¹The 60° set-up is chosen, because the radiation pattern maximum centers around 55° to 60° , [61] in addition to the simple practical attempt to avoid steric hindrance by the STM head.

3. Experimental part

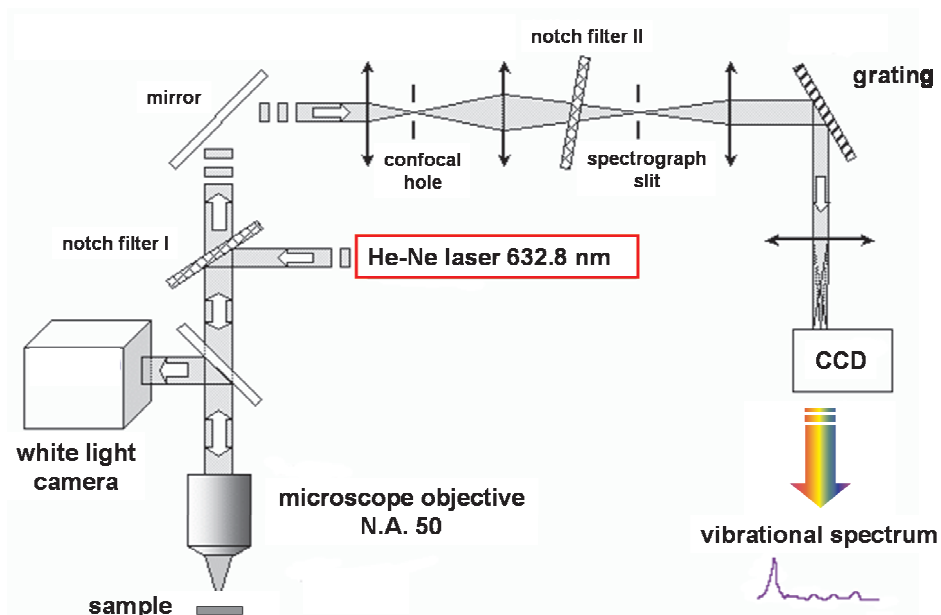


Figure 3.1: Schematic drawing of a Raman set-up for interfacial studies. The laser beam is focussed through a long working-distance objective onto the sample. The backscattered light is collected with the same objective, led through a series of optical elements, which filter out the laser line and cut off stray light, to a 600 l/mm grating and then processed with a liquid-N₂ cooled CCD camera.

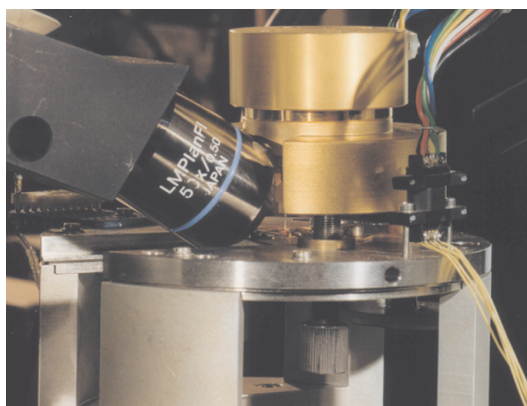


Figure 3.2: This photo shows the home-built STM head with the fine gold tip protruding underneath. The long working-distance objective that focusses the red laser light onto the tip apex is seen on the left.

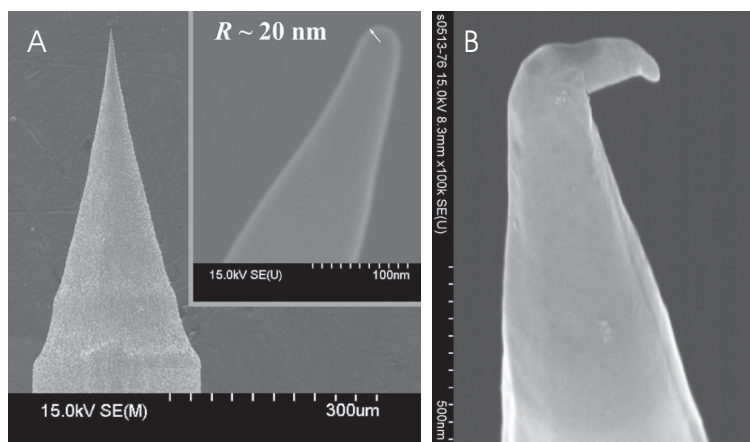


Figure 3.3: A) The smooth, pencil-shaped Au STM tip produced by electrochemical etching is shown in this SEM image. B) This SEM image shows a crashed tip. The bending of the tip end might have occurred during rinsing of the tip with water, or when approaching it to the surface. Such a tip produces only weak or no Raman signal enhancement and is disposed of (recorded by G. Weinberg).

above the sample. The bias voltage between tip and sample is set to -100 mV. All experiments are carried out in ambient conditions at room temperature. Spectral analyses were performed with Origin®7G software.

3.2 Tip preparation

Pencil-shaped STM tips (Fig. 3.3A) are produced from gold wire of 0.25 mm diameter by electrochemical etching in a 1:1 mixture of ethanol and fuming HCl.[62] The tips are rinsed with Millipore-QTM ultrapure water (MilliQ) to avoid contamination. We reproducibly obtain tip curvatures of 20 nm and, for these tips, assume the radius of the enhanced field to $r_{ef} = 20$ nm following a Heaviside step function approximation. However, it may occur that the tip is damaged during rinsing or approach to the sample. Bent tips, like the one shown in Fig. 3.3B, do not lead to intense Raman scattering due to difficult focussing and are discarded.

3. Experimental part

3.3 Sample preparation

The Au(111) single crystal (MaTeck) is flame-annealed according to the method of Clavilier [63] prior to adsorption of the target molecule in order to remove contaminations and obtain large, atomically smooth (111) terraces. After 1 hour adsorption from a continuously stirred 5 mL adsorption volume, the crystal is rinsed with 10 mL ethanol to remove multilayers, and allowed to dry in air. All glassware is cleaned in Piranha solution (concentrated H_2SO_4 : H_2O_2 (30%) = 3:1), followed by extensive rinsing with MilliQ prior to use.

To rule out undesired contribution of SE(R)R scattering to the spectra, the tip is verified to be free of adsorbate after each TE(R)R experiment. Even slight traces of contamination attached to an (atomically rough) tip can be easily observed due to intense SE(R)R scattering from a retracted tip or a tip in tunneling contact with an adsorbate-free Au substrate. A spectrum of a clean (or negligibly contaminated) tip does not show any Raman bands. To verify reproducibility, several TE(R)R spectra are recorded at different tip positions above the substrate to always guarantee a fresh, unbleached sample.

Any special experimental procedure will be described in the corresponding chapter.

3.4 Difficulties

In general, the main difficulty of the TE(R)R experiment is the focussing of the laser beam onto the tip apex. The focussing procedure is roughly monitored by a white-light camera that shows a symmetric bright spot at the tip apex if well-focussed. Of course, it is impossible to view the finetuning of the focus, and the only possibility to know whether the focus is sufficiently good is to record a TER spectrum. Even the slightest movement of the micrometer screws with which the objective (z-direction) and the STM table (x-, y-directions) are adjusted can lead to a sudden increase or decrease of the signal. Employing an objective to collect the Stokes scattering allows to collect the scattered light in one direction only, a large fraction of signal intensity is lost. One way to overcome this problem is the alteration of the set-up to a vertical

alignment with a parabolic mirror as collecting device. This new approach is described in Chapter 7.

The missing vibration and temperature insulation of the instrument causes experimental difficulties. The stability of the tip position is essential for STM as well as for TERS measurements. As drift is unavoidable with the current set-up, the resolution of the STM images is suboptimal, which complicates, for example, single-molecule analysis as presented in Chapter 5. In addition, precise control of the tip location, as often available with commercial STM set-ups, is not possible. Positioning of the tip above a certain structure or at a step edge, for example, that would allow to relate TER spectral characteristics to such features cannot be achieved so far. We hope that the new set-up currently being built for UHV experiments will largely improve the precision with which the STM tip can be manipulated. Contamination problems, as extensively discussed in Chapter 5.4, should also be avoided with the new set-up.

