Chapter 7

Parabolic mirror set-up

The currently employed 60° TERS set-up exhibits several disadvantages. The lack of sufficient temperature and vibration insulation prevents from obtaining better resolution STM images. Working in air, no control of the cleanliness of the sample or the environment is given. The use of an objective as collection device, even of high numerical aperture (NA), allows only the collection of a small fraction of the Stokes photons which are scattered in all directions.

To overcome these difficulties, we have designed and built a new TERS set-up, adapted from a design by Lieb and Meixner.[192] The main difference is the exchange of the objective as focussing device by a parabolic mirror. With the much more compact new set-up, we plan to work upon electrochemical (EC) conditions and also in UHV.[1] The EC TERS allows us to work at controlled surface potentials, tuning adsorption/desorption processes or molecular orientation, which is monitored in the corresponding TER spectra. Working in electrolyte allows us to employ adsorbates in defined chemical states (e.g. protonation via pH) and, in addition, strongly improves the cleanliness of the experimental system.

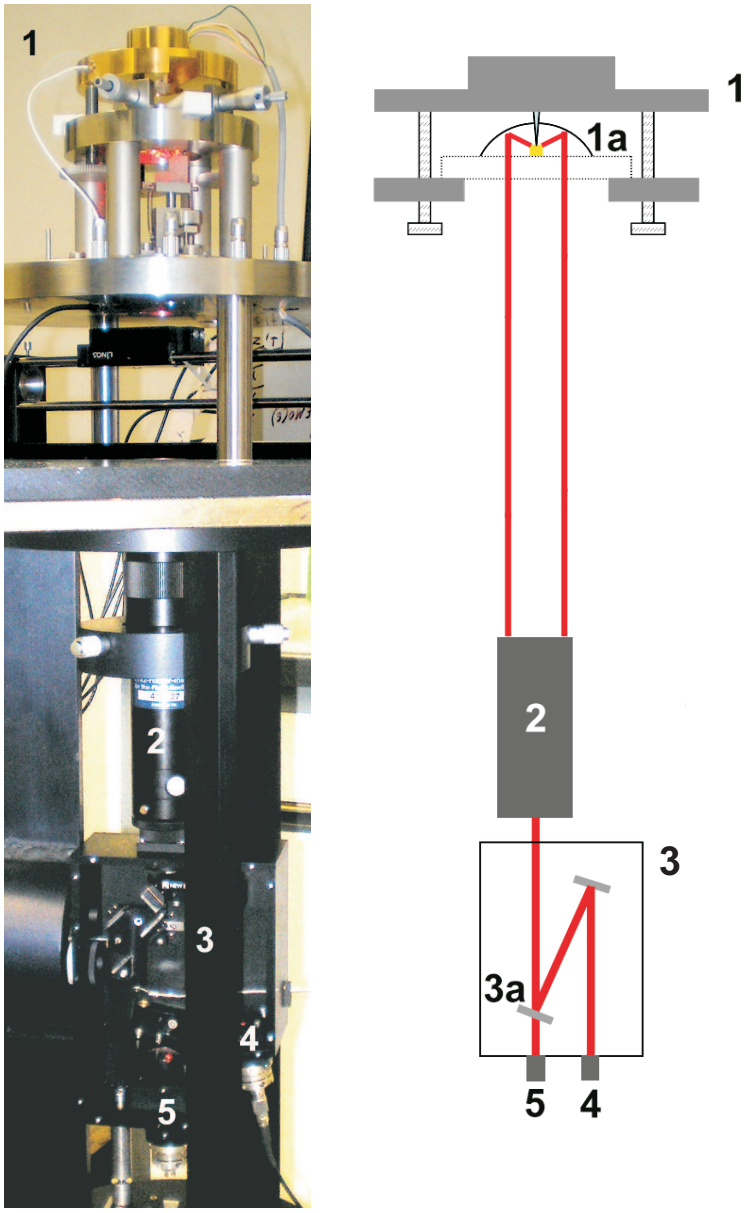

Figure 7.1: In the lower part of the photograp, the external Raman box (3) is seen that connects both, the single mode laser fiber (4) and the multi mode Raman fiber (5) to the vertical set-up. After passing the beam expander (2), the laser beam is led to the silver "heart" of the new set-up which holds glass-plate, sample, parabolic mirror (1a) and STM head (1).

7.1 Set-up design

In Fig. 7.1, a photograph and a schematic sketch of the main features of the new design are presented. A 35 mW He-Ne laser (632.8 nm, Melles Griot) is coupled into the external Raman box (3) via a single-mode optical fibre and coupler (single-mode fibre PMC and fibre coupler 60SMS, Schäfter + Kirchhoff). The Raman box contains a reflective mirror (plane mirror, *lambda*/10, Linos) and an edge filter (3a, RazorEdge^{TM}, Semrock). The latter reflects the 632.8 nm incoming laser beam, but transmits the outgoing Stokes-shifted radiation. This arrangement permits the alignment of the incoming and the scattered beam paths and their separation before detection and analysis of the scattered radiation.

The laser beam is led through a pinhole to a beam expander (2) before approaching the sample stage, where the parabolic mirror is resting on a plane-parallel polished glass plate ($\lambda/10$, Halle). The mirror is made of an aluminium alloy (Al6061) by Linos. Its base is polished to $\lambda/10$ so that it sits tightly on the glass, and the mirror inner surface is polished to $\lambda/2$. It has an outer diameter of 20 mm and is 6.25 mm high. The focal length of the parabolic mirror is 4 mm. If the optical axis is aligned perfectly perpendicular to the glass plate (and thus the base of the mirror), the expanded light beam (16 mm diameter) is reflected by the mirror inner surface and focussed tightly to a spot of 500-1000 nm radius.

The small gold sample (a Au(111) bead single crystal of 2-3 mm diameter[2] on a 8 cm long Au wire) is placed in a thin Teflon tube in the center of the glass plate underneath the hole in the mirror roof (3 mm diameter) through which the STM tip is inserted. The position of the Teflon tube is adjusted in z-direction with a micrometer screw allowing to move the sample surface into the focus. This is monitored with an auxiliary white light source and an additional CCD camera installed in the Raman box.

The new STM head was constructed essentially like the old one (design by Rolf Schuster). It had to be extended in size to fit around the parabolic mirror located between the STM head and the sample. Because of the increased distance between

[1]The UHV TERS set-up is the PhD project of Jens Steidtner (Fritz Haber Institute).

[2]The bead single crystals were kindly provided by Prof. Dr. Juan M. Feliu from the University of Alicante, Spain.

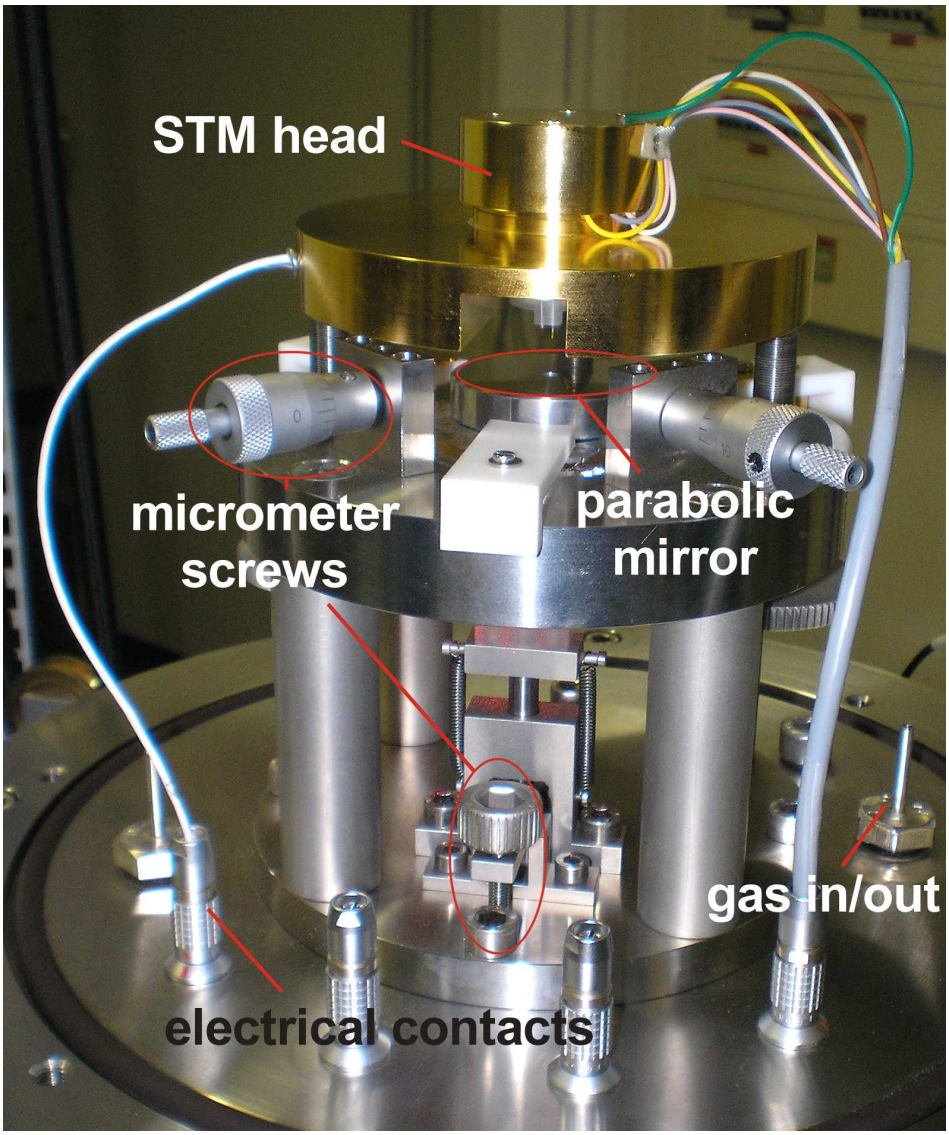

Figure 7.2: The "heart" of the new set-up: STM head, parabolic mirror as well as the high-precision alignment screws are seen in this photograph. Electrical contacts and gas in/outlets are installed in the base platform.

STM head and sample, the tips have to be longer (around 8 mm). Therefore, we employ 0.5 mm diameter Au wire to improve the tip stability. Sample stage and mirror are depicted in Fig. 7.2. When the tip is in tunneling contact with the substrate, the focus is positioned laterally onto the tip by two x-, y-micrometer screws (specifications) that move the parabolic mirror. In order to guarantee a more precise movement, we have girded the mirror with an iron belt and added magnetic caps to the screws.

The scattered light is collected by the mirror from all directions (2π sr) and led back through the beam expander into the Raman box. The edge filter (3a) separates Rayleigh and Stokes scattering. While radiation that has the same energy as the incident beam is reflected by the filter, the Stokes-shifted photons can travel on through the filter and are focussed into the multimode fibre with a second fibre coupler (Schäfter und Kirchhoff). The multimode fibre (inner diameter 50 μm, Schäfter und Kirchhoff) is connected to a third fibre coupler at the original Raman spectrometer (Jobin Yvon), which leads the light to the nitrogen-cooled CCD camera for read-out.

The hole sample stage can be covered with a tightly fitting metal cap that allows to work in defined gas environment. Inert gases to reduce the oxidation-bleaching rate but also reactive gases like CO can be employed. All necessary gas in- and outlets as well as the electric contacts are built into the base plate of the sample stage. A hole (or plane-parallel glass window) is inserted in the plate, where the beam passes through.

In order to perform TERS measurements under potential control in solution (electrochemical conditions), we have added two Pt electrodes (counter and pseudo reference) onto the glass plate. The thin Pt film (100 nm thickness) is sputtered onto the glass in two semicircles, sparing a clean glass circle of about 18 mm diameter in the center for the beam. These two electrodes can be contacted with two clamps, which additionally stabilize the glass plate. The mirror inner surface is covered with a Au protection layer to increase chemical resistivity of the mirror surface exposed to the electrolyte, but maintaining its high reflectivity in the red regime. The volume of the mirror can be filled with electrolyte through the hole in its roof, and an insulated tip is employed to prevent from flow of Faradayic current. Jens Steidtner (Fritz Haber Institute) is adapting the new TERS set-up design to UHV conditions.

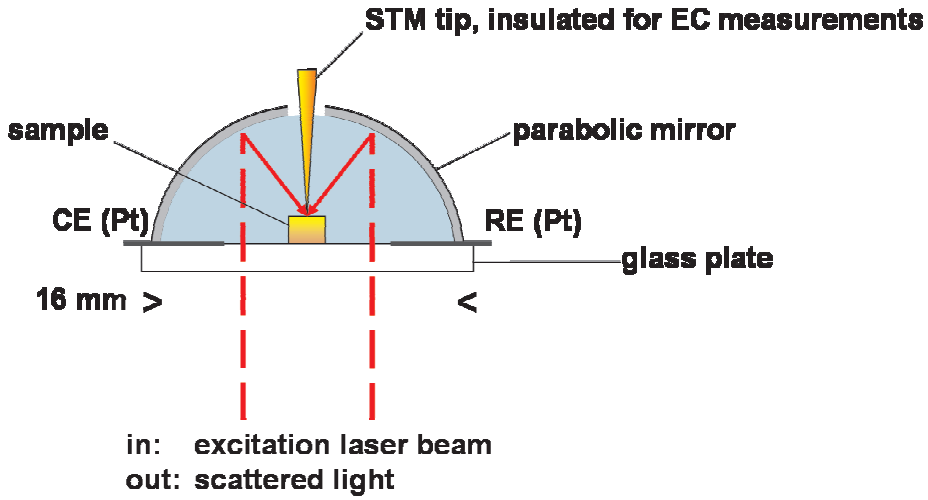

Figure 7.3: The "heart" of the new set-up consists of a parabolic mirror sitting on a glass plate on which the small sample bead crystal is placed. The expanded laser beam (16 mm diameter) is led through the glass plate, focussed onto the tip apex/sample cavity, and the backscattered light is collected from 2π sr. The volume of the mirror is designed to be filled with electrolyte, which enables to work under potential control when connecting the counter and reference Pt electrodes. RE: reference electrode, CE: counter electrode.

7.2 Difficulties & outlook

During the installation of the new TERS set-up, we have encountered several difficulties, especially with the laser beam adjustment. Work to improve the optical alignment of the EC as well as the UHV set-up is still in progress.

A parabolic mirror only produces the desired sharp focus if the light beam is aligned perfectly parallel with its optical axis.[192] Slightest deviations produce large, smeared-out foci, causing great losses in the enhancement process and thus in the photon count rates. We assume that the base of the mirror is perpendicular to the optical axis for our adjustment procedure. The direction of the optical axis is only very roughly controlled by screws that fix the position of the beam expander.

Imaging the tip in order to place the focus correctly at its apex is far more complicated for illumination via a parabolic mirror than via an objective. Currently, we are watching the tip with only one quadrant of the laser beam. The resulting image is not well-understood yet and requires further testing.

The parabolic mirror allows the collection of light from all scattering directions. The gain in photon counts might be compensated by the fact that the Au crystal (hole in the mirror) cuts out the center of the incoming Gaussian laser beam, i.e. its maximum intensity, leading to an intensity decrease of around 15 %. In order to increase the field enhancement and, thus, the scattering intensity, we plan to employ pseudo radially polarized instead of p-polarized light. This will notably enhance the near-field created at the tip-sample gap by focussing the light with a parabolic mirror.[192, 193]

In addition, there are high losses of laser intensity on the way to the sample. Of the 35 mW laser source power, only around 10 mW arrive at the mirror (measured intensity after the glass plate). The losses at the mirror are expected to be negligible due to the high reflectivity at the polished Al or Au surface. The highest losses of the scattered radiation are expected to occur at the third fibre coupler that leads the light to the CCD camera. According to Jobin Yvon, only 1/10 of the intensity is transmitted at this point due to difficult adjustment. Possibly, an exchange of this Jobin Yvon fibre coupler for a Schäfter and Kirchhoff one (as the ones used at the Raman box) that allows much more precise adjustment may lead to a better throughput.

The new STM head is much larger in diameter than the old one. The embedding of the mirror causes a much longer electrical path from tip to sample, likely decreasing the resolution of the instrument. Larger tips will contribute to this effect. On the other hand, the large volume and weight of the new head might counteract and better stabilize the system.

In contrast to the 60° set-up, the new design does not permit to monitor the approach of the tip to the sample with an external camera as the mirror is blocking the sight. This greatly complicates the approach procedure, and the chance of crashing the tip into the surface is greatly enhanced. The only way to monitor the approach lies in watching the tunneling current display needle.

Regarding the electrochemical TERS measurements, insulation of the tip is necessary. It is essential that the coating material does not fluoresce, so that the Raman signal can still be detected. So far, tested paints and lacquers that are usually employed for electrochemical STM experiments have resulted in an unsatisfyingly high spectral background that exceeds the capacity of the CCD camera. An optimal coating would be a thin glass layer, as sometimes employed for the coating of tungsten tips. Due to its low melting point, gold cannot be easily covered by molten glass. It might be feasible to chemically adsorb thin glass layers, but this results in a variety of different problems such as tip apex protection (the tip apex must not be covered) and preparation time. In addition, it is still unclear how stable the electrolyte is kept in the mirror volume, i.e. how quickly it will leak or be contaminated.

In summary, we are working on the alignment of the optical path in the new set-up, monitored by the Raman signal of a Si sample. When the adjustment is good enough to obtain a sufficiently high Si signal, the approach of the tip will be tested and the signals with/without tip compared. Distance dependence measurements similar to the ones described in Chapter 4 could be carried out in order to gain insight on the influence of the substrate material on the enhanced-field distribution. To approach EC TERS, first, structured samples will be tested for SER scattering in air and in electrolyte. This will identify problems with electrolyte leakage and the three-electrode set-up. Differently coated tips will be examined with respect to their scattering properties, and tip approach will be trained. First EC TERS experiments will possibly be carried out with DNA bases on Au(111).