Chapter 5
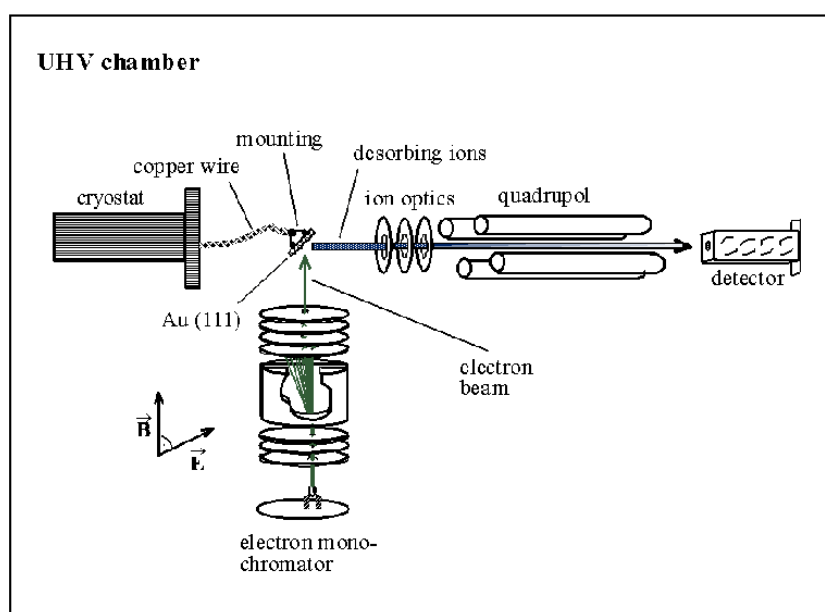
Experimental

In this part we will describe the experimental apparatus, used for investigations of electron interaction processes with cryogenic adsorbates. The apparatus was in its first stage established by Martina Meinke within her Doctoral Thesis [56]. The ultra high vacuum (UHV) apparatus enables to study ion desorption induced by collisions of low energy electrons with molecules condensed at very low temperatures ($\approx$ 25 K) onto metal substrate. Because condensation of the rest gas in the apparatus can cause serious problems in surface measurements at cryogenic temperatures, UHV conditions ($\leq 10^{-10}$ mbar) in the chamber are necessary. Preparation and calibration of the molecular films, the electron beam source, electron energy calibration and ion detection system will be described.

5.1   Experimental setup

The experimental apparatus consists of two main parts. The first part is the
collision or *main chamber* where the measurements take place and the sec-
ond one is the *inlet system*, by means of which the investigated compounds
are introduced. The inlet system is pumped using a turbomolecular pump
(Leybold, Turbovac 60) reaching a base pressure of about 10^{-8} mbar. The
inlet system is connected to the UHV chamber by a gas cell of defined volume
(40 ml) for gas quantity calibration. Inside the cell the absolute pressure is
measured with baratron (MKS 127). The molecular film deposition then pro-
ceeds by leaking the gases from the cell into the main chamber, see section
"thin film preparation".
 The schematic of the experimental setup inside the main chamber is shown

Figure 5.1: *Experimental setup inside the UHV chamber.*

in Fig. 5.1. Here ultra high vacuum (UHV) with a base pressure of 10^{-10} mbar
is achieved. UHV is maintained by parallel pumping of 360 l/sec turbomolec-
ular drag-pump (Leybold, Turbovac 360) and a 270 l/sec ion-pump (Leybold,
Trivac D8B). Ultra high vacuum (UHV) conditions in the chamber are essen-
tial to suppress condensation of impurities from the background gas within

the measurement time. The investigated compounds are condensed onto the gold crystal (Au (111)), cooled down to 25 K via a cryogenic helium refrigerator, (Leybold, RGD 510). The temperature of the Au substrate is measured by a thermocouple type E (constantan-chromel) mounted directly at the crystal.

An electron beam produced by a trochoidal electron monochromator (TEM) impinges then onto the molecular film. As already shown by earlier investigations, interactions of electrons with molecules in the condensed phase can also lead to the formation of NIRs. We are then interested in anionic fragments ejected from the surface. The desorbing ions are extracted by ion optics, selected according to their mass using the quadrupole mass filter and detected by a detector (secondary electron multiplier). The resulting ion yields as a function of electron energy, or yield functions are recorded by a computer.

5.2 Thin film preparation

As already mentioned above, the investigated compound is first admitted into the small gas cell of well known volume (40 ml). Inside the cell absolute pressure is measured using the baratron (MKS 127), with a typical pressure of about one tenth of mbar.

The gold crystal $(Au(111), S = 1cm^2)$ is mounted on an UHV manipulator, by which it can be moved along three axis (x, y, z) and rotated around the z axis. The molecular film is prepared by vapor deposition at constant pressure inside the main chamber. Within the time of film growth, the molecules are leaked into the main chamber through the stainless steel capillary tube (2 mm diameter). The deposition proceeds by positioning of the gold substrate of about 0.7 cm in front of the capillary tube. Under this condition, almost 90% of the introduced molecules hit the crystal. The sticking coefficient for most of the compounds is near one at cryogenic temperatures. Therefore, most of the molecules leaked into the chamber contribute to film formation. The remaining 10% of molecules which do not adsorb at the cold surface give rise to pressure. The gold surface is repetitively cleaned by

means of resistive heating up to $800 - 900$ K and no further cleaning proce-
dure (ion sputtering) is needed as already shown in earlier investigations by
Meinke [56].

The number of deposited layers or the film thickness is calibrated by
temperature programmed desorption (TPD). Here the fact that the adsorp-
tion energy between the first monolayer (ML) and the metal substrate (gold
crystal) is higher than that between the upper layers is used. In favorable
cases, one can observe two separate peaks in the TPD spectrum due to multi-
layer and monolayer desorption, respectively. The first increase in pressure at
lower temperature is due to the desorption of weakly bound layers (*multilayer
peak*). The second increase in pressure at higher temperature is due to the
first layer (*monolayer peak*) bound directly to the gold substrate. While the
multilayer peak increases with increasing the number of layers (2,3,...), the
intensity of second one is constant. TPD measurements are used to correlate
the amount of molecules introduced from the gas cell in order to form one
monolayer. On this basis, the thickness of the molecular film can directly be
controlled by using the fact that the number of monolayers is directly propor-
tional to the gas amount leaked from the cell into the chamber. Multilayer
films at an error of about 30% are prepared, if the deposition conditions are
kept constant (position of crystal, pressure in the UHV chamber ...). We also
assume, that the sticking coeficient remains close to unity with increasing the
number of layers (which may be reasonable at cryogenic temperatures).

5.3   Trochoidal electron monochromator (TEM)

A trochoidal electron monochromator (TEM), first established by Stamatovic
and Schulz [57,58] is used to generate a monochromatic electron beam. Here,
the perpendicular electric and magnetic filed is used to separate the electrons
according to their energies. The advantage of the trochoidal monochromator
is the possible use of electrons at energies ranging from 0 to 20 eV without
considerable loss of intensity at the very low energy region (< 2 eV). The
schematic of the TEM is pictured on Fig. 5.2. All the monochromator parts
are made from molybdenum, because it diminishes the problem of molecule
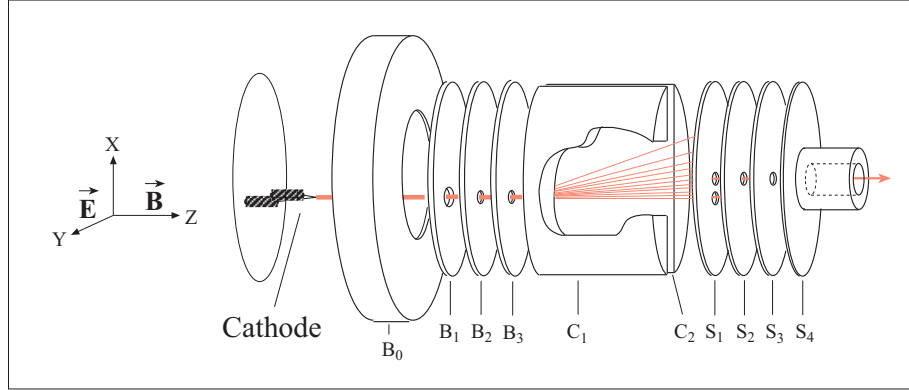
Figure 5.2: *Trochoidal electron monochromator.*

deposition onto surface during the measurements. The free electrons are generated via thermal heating of the tungsten cathode. The role of the monochromator lens B_0 is to protect emitted electrons from external electric fields generated in different parts of the apparatus. The next three lenses B_1, B_2 and B_3 are then used to collect and focus electrons to the *selection region* where the electric and magnetic fields cross each other perpendicularly. The homogeneous magnetic field with a strength of about 30 Gauss is formed using two Helmholtz coils positioned outside the chamber. The magnetic field $\vec{B}$ acts along the $\vec{z}$ axis of the monochromator as it can be seen from Fig. 5.2. In general the movement of electrons, when under the influence of electric and magnetic fields $\vec{E}$, $\vec{B}$ is determined by the Lorentz force expressed as

$$\vec{F} = Q(\vec{E} - \vec{v} \times \vec{B}) \qquad (5.1)$$

with $\vec{v}$ and Q the velocity and charge of the electron respectively. In the *selection region* between the electrodes B_3 and S_1 two parallel plates C_1 and C_2 generate a homogeneous electric field $\vec{E}$ perpendicular to the $\vec{B}$ field. In the cross-field region, the electrons move in trochoidal paths with the center of rotation moving at constant velocity in $\vec{x}$ direction,

$$\vec{v}_x = \frac{[\vec{E} \times \vec{B}]}{|\vec{B}|^2} \qquad (5.2)$$

Since the holes of the electrodes following the selection region $(S_1 - S_4)$ are displaced by Δx with respect to those before $(B_1 - B_2)$, only electrons which are dispersed by Δx within the selection region will be transmitted trough the monochromator. The electrons to be transmitted must therefore satisfy the following condition: the time T_z the electrons need to move in **z** direction from the electrode B_3 to S_1 must equal the time T_x the electrons need to travel the distance Δx in $\vec{x}$ direction,

$$T_z = \frac{L}{v_z} = \frac{\Delta x}{v_x} = T_x \qquad (5.3)$$

Here L is the distance between B_3 and S_1 and v_z, v_x are the components of the electron velocity $\vec{v}$. The electrons are thus dispersed according to their translational energy in $\vec{z}$ direction. The kinetic energy of the electrons leaving the selection region is then determined as follows

$$E_{kin,z} = \frac{1}{2} m_e \left(\frac{EL}{B \Delta x} \right)^2 \qquad (5.4)$$

The electrodes S_2, S_3 and S_4 are used to extract and focus the monochromatized electron beam to the gold substrate. Because the magnetic field $\vec{B}$ is designed in the way that it acts along the electron path to the reaction zone, it enables to investigate electron-molecule interactions down to very low electron energies. Here the magnetic field prevents from beam spreading induced by repulsive Coulombic forces between the electrons. The spreading is more pronounced at the very low energy region (< 1 eV) and at higher current intensities (> 1 μA), due to the increasing charge density in the beam.

In Fig. 5.3 a typical profile of the transmitted current (black curve) with its established resolution (red curve) is shown. Here the vacuum level is defined as the *zero energy reference* (ZER), determined by the onset of the transmitted current. The current is measured directly on the gold substrate. Since some reflection may occur at the interfaces vacuum/film and film/substrate the transmitted current represents a lower limit of the electrons impinging the surface. The energy resolution of the beam is in the range from $200 - 300$ meV for transmitted currents in the range between
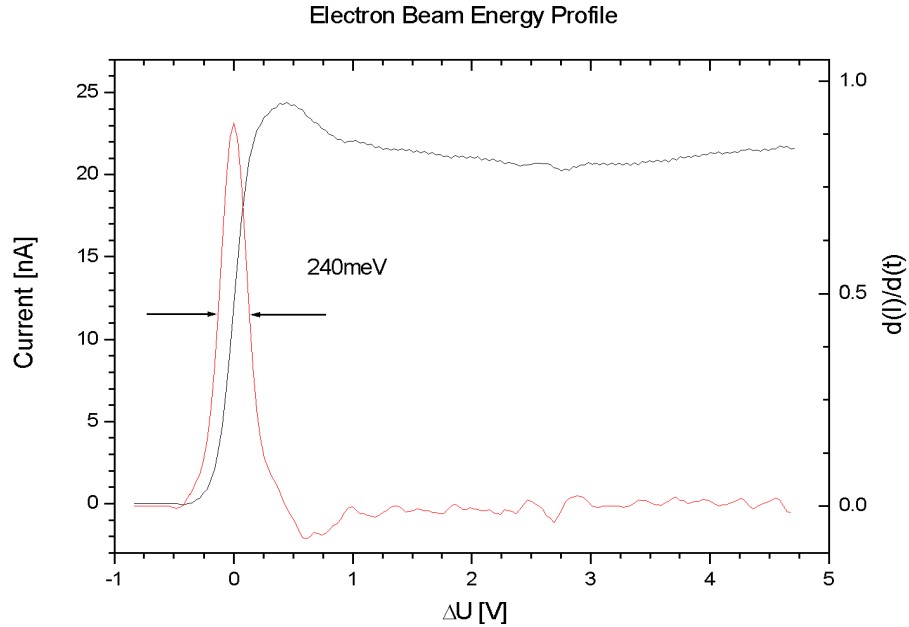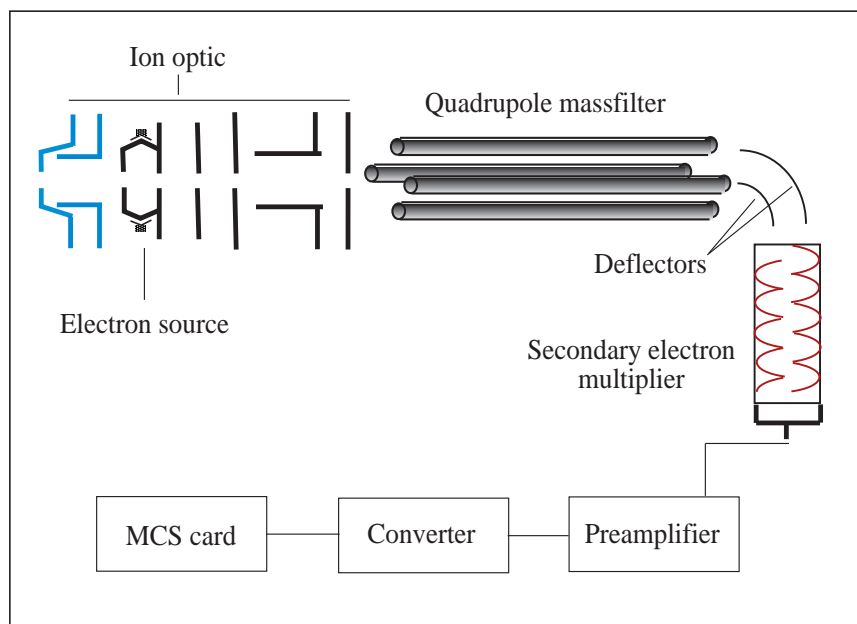
Figure 5.3:
Transmitted current (black curve) and energy resolution of the electron beam (red curve).

$20 - 120$ nA. The approximate energy resolution can be established from the steepness of the current onset or its derivation. Because of accumulating charge at the surface, a shift of the onset as well as some degradation of the energy resolution after irradiation may be observed. The electron energy can be determined using the calibration method with current onsets at an accuracy of ± 0.3 eV. During the measurements the electron energy is controlled by varying the potential difference between the middle point of the cathode and the gold substrate.

5.4   Desorption analysis

For the collection of desorbed negative ions a commercial quadrupole mass spectrometer (Balzers, QMG 422) is used. Parts of the spectrometer are schematically pictured on Fig. 5.4. It consists of the ion optics, the quadrupole mass filter, ion deflectors and the secondary electron multiplier.

Figure 5.4: *Quadrupole mass spectrometer.*

The desorbing negative ions are first extracted and then accelerated and focused to the mass filter by a system of cylindrical lenses. The quadrupole mass filter consists of four rods on which a high frequency voltage together with a constant voltage is applied. Opposite rods are electrically connected pairwise. The ions entering the mass filter move then in different paths depending on their mass/charge ratio. Theoretically, for a specific frequency only ions with particular m/q ratio pass trough the filter while all other ions strike the rods because of their increasing oscillation amplitude. Transmitted ions are afterwards deflected by two cylinder plates and directed to the first dynode of the secondary electron multiplier (channeltron). The multiplier consists of series of dynodes with secondary electron emission greater than one. An ion which impinges the first (conversion) dynode induces the emission of the secondary electron, which are then accelerated to the following dynode until an electron pulse arrives at the last dynode, called the anode. The electrons within the multiplier are accelerated by applying the voltage between two adjacent dynodes ($\approx$ 200 V). The generated current pulse on the anode is finally amplified and electronically converted to the appropriate

(TTL) voltage pulse. The obtained pulses are counted via a MCS (National Instruments E-series) computer plug in.

The quadrupole spectrometer can be used to analyze both the anions and cations. Positive ions are generated by ionizing the background molecules using the internal electron source, see Fig.5.4. Here the electrons emitted from the tungsten filament are accelerated towards the central axis of the ion optic gaining thus $\approx 75 - 85$ eV energy. The detection of positive ions is usually used to analyze the background gas or by TPD measurements, where the increase in pressure (caused by film evaporation) is converted to the detection of appropriate positive ions.