Chapter 2. Experiment

2.1 MBI Beamline at BESSY II

Most of the experiments presented in this thesis have been performed at the MBI-User Facility at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY II). The radiation source is the U125 undulator that can deliver photon energies ranging from 15 to 600 eV. This undulator has an overall length of 4 m and a periodic length of 125 mm, with the number of periods being 32.

A schematic of the MBI-beamline is presented in Fig. 2.1-1. The radiation from the undulator is deflected by a torroidal mirror, which is the switching mirror, into the MBI beamline, U125/2, and focused onto the entrance slit of the grazing incidence monochromator [GWQ98]. The synchrotron beam enters the grating chamber through an aperture and then passes through the exit slit into the refocusing chamber. The refocusing chamber houses two interchangeable toroidal mirrors; these are denoted in Fig. 2.1-1 as toroidal refoc. mirror. Depending on which toroidal mirror is inserted into the beam path, the radiation is directed to an UHV chamber or to a water jet apparatus.

Fig. 2.1-2 illustrates the setup of the monochromator optics. The monochromator construction is based on the variable included angle (VIA) principle. The grating chamber presently contains two spherical gratings, which may be used alternatively. The first grating has 700 lines/mm and is optimized for energies between 20-50 eV; the second one, with 1666 lines/mm, covers the 50-180 eV photon energy range. They can be moved in and out of the optical path under vacuum conditions.

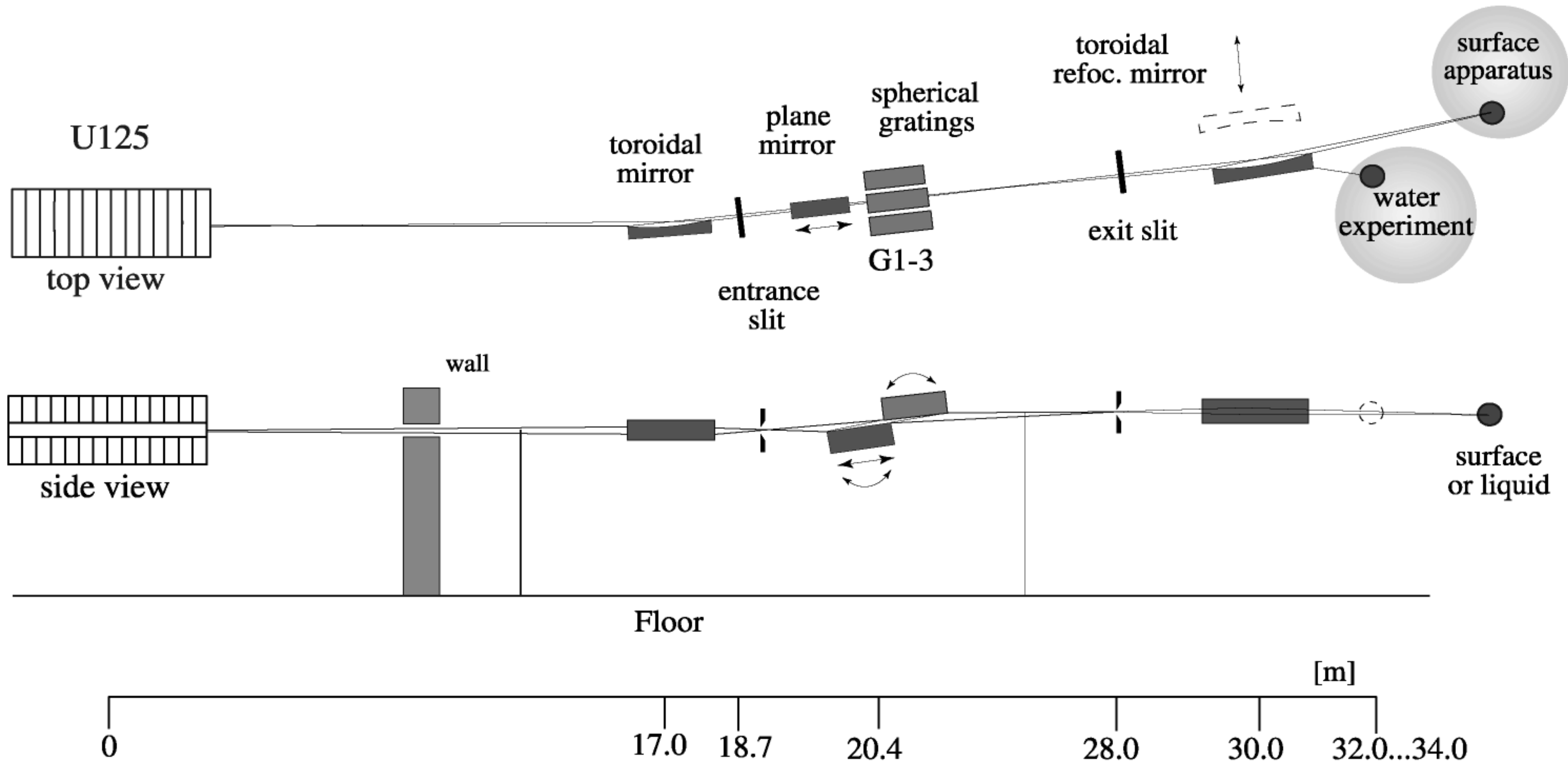

Fig. 2.1-1 Schematic of the Max-Born-Institute undulator beamline at BESSY II.

A plane mirror (PM) can be translated (between the positions A and B) and simultaneously rotated, so that the central ray always hits the center of the spherical grating (SG). The path lengths in the monochromator are thus constant over the entire energy range. The movements of the gratings and of the plane mirror are realized with computer controlled stepper gear boxes and micrometer screws. All mirrors and gratings are made of gold-coated silicon, except for the torroidal switching mirror which is made from gold coated Zerodur.

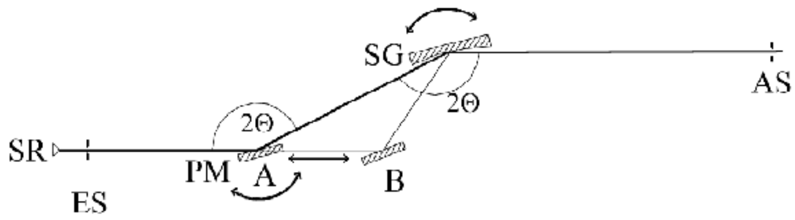

Fig. 2.1-2 Principle of the monochromator.

Using the 1666 lines/mm grating with a 200 μm entrance slit at 64 eV photon energy and 0.1 A ring current, the photon flux at the sample was determined to be approximately 4×10^{12} Photons/(s×0.1%BW) and the resolution E/ΔE of about 10 000.

The synchrotron radiation spot at the sample position was elliptical in shape with a size of about 1 mm in length and 0.3 mm in widths.

2.2 UHV Apparatus at the MBI User Facility

The sample preparation and measurements were done in a multi chamber ultrahigh-vacuum apparatus at a base pressure around 2×10^{-10} mbar. The system consists of an interconnected load-lock, preparation and analysis chamber, and a manipulator for sample transfer and handling. Each chamber is independently pumped and may be separated by valves. The scheme of the apparatus is given in Fig. 2.2-1.

The load-lock uses a magnetic transfer rod that allows parking of up to three samples. The typical working pressure in this chamber is in the low 10^{-8} mbar.

With the help of a wobble stick, the sample is taken from the transfer rod, brought into the preparation chamber, and from there placed into the main manipulator. The preparation chamber has standard surface tools: a 4-grid LEED/AES system (ErLEED

3000D, Vacuum Science Instruments), an IS 2000 ion sputter gun (Vacuum Science Instruments), and a quadrupole mass spectrometer (Balzers, QMS 421) that can be used for the analysis of molecules with masses up to 2048 amu. Two homemade evaporators (ovens), utilized for the deposition of the organic films, are mounted on a cluster flange below the quadrupole mass spectrometer. During the sample preparation the manipulator head is placed between these ovens and the quadrupole mass spectrometer; the distance between oven and sample is around 5 cm.

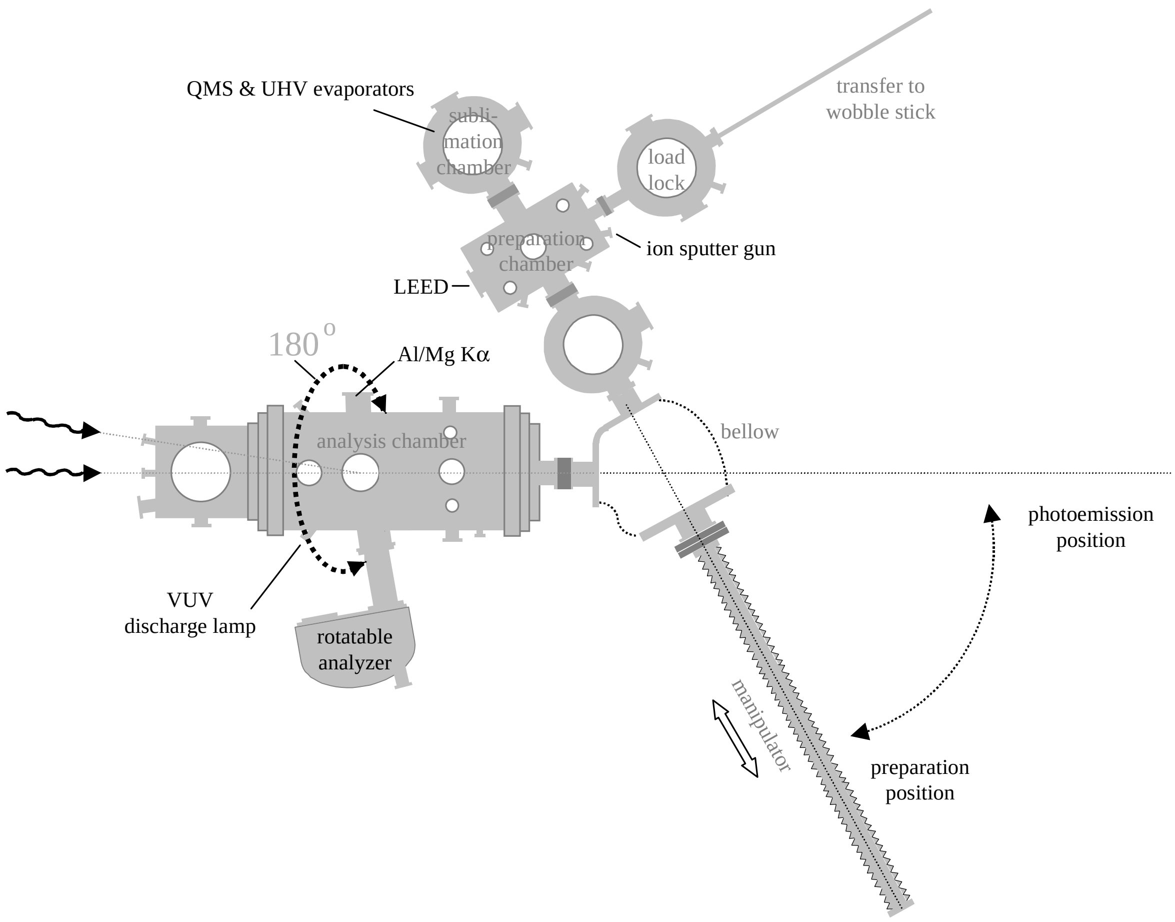

Fig. 2.2-1 Schematic layout of the MBI UHV surface apparatus.

Such an evaporator consists of a quartz crucible surrounded by a spiral from a heating element with 1 mm diameter (1NcI THERMOCOAX-nickel-chromium 80/20 as core part and Inconel alloy as outer sheath) and two thermocouples attached to the crucible, the whole assembly being mounted on an electrical feedthrough. To prevent possible future contamination to the molecular films, the ovens were cleaned in the ultrasound bath and empty heated to 750°C, prior to each fill. The setup also includes a quartz microbalance, STM-100/MF from Sycon Instruments, mounted on a retractable bellow. During evaporation of organic molecules the quartz monitor is placed nearby the substrate and thus the thickness of the films can be evaluated. In addition to these components, user ports of different sizes, and at various positions, are available in the preparation chamber.

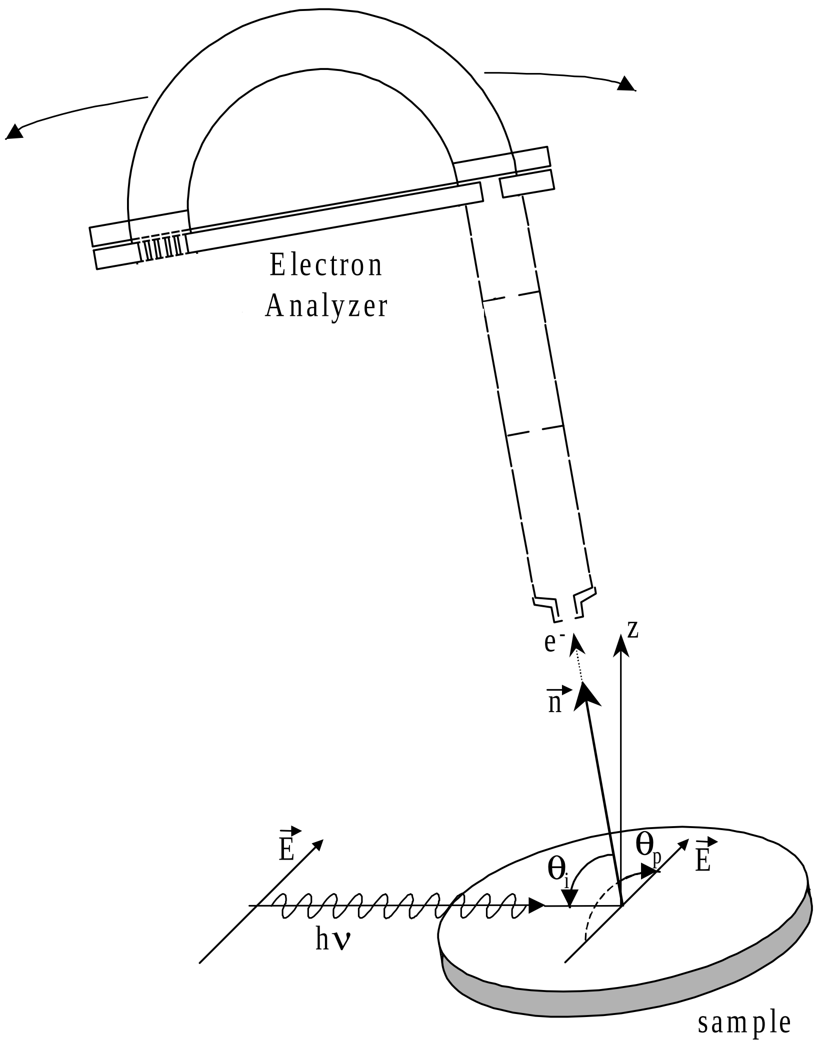

Fig. 2.2-2 Sketch of the measurement geometry used in the present experiments. θ_i represents the incidence angle, which was 83º, and θ_p represents the angle between the synchrotron light electric vector and the sample normal (θ_p was 80º or 90º). The detection of the photoelectrons was normal to the sample surface.

The main part of the UHV apparatus is the analysis chamber, which provides the option to perform angular-resolved photoelectron spectroscopy and two-color two-photon photoemission (2C-2PPE) experiments using both laser and synchrotron radiation. The whole chamber can be rotated around the axis of the synchrotron beam by a servomotor, so that optimal use of the polarization of the synchrotron light can be made. Since the films investigated in the present work contained randomly oriented molecules, the measurements were not performed for series of different orientations of the sample relative to the light polarization.

In the analysis chamber various ports and windows allow for user specific inserts into the apparatus and give flexibility for introducing the laser radiation. The entire analysis chamber has a 1 mm μ-metal shielding that compensates for the earth's magnetic field to less then 0.1 μT at the sample position. The chamber is equipped with a hemispherical electron energy analyzer (Omicron EA 125 U5) having a 125 mm mean radius and a 5-channeltron detector. During the present experiments, the usual sample take-off angle was ±1° and the Fixed Analyzer Transmission Scan Mode was used, typically with 10 eV pass energy. This leads to a resolution around 0.15 eV. The photoelectron detection was normal to the sample surface, the sample and analyzer being always rotated together. Fig. 2.2-2 shows a sketch of the measurement geometry used in the experiments described in the thesis. The experimental setup also contains an X-ray source (Omicron, DAR 15) with Al and Mg twin-anode, and a high-intensity VUV discharge lamp (Omicron, HIS 13); thus permitting additional XPS and UPS measurements. A CCD camera attached to one of the windows provides an image of the sample and manipulator inside the analysis chamber.

A horizontally mounted manipulator forms the connection between the preparation and analysis chambers. Fig. 2.2-3 and Fig. 2.2-4 illustrate the two extreme positions of the manipulator: the position for bringing the sample into the preparation chamber and that necessary for bringing it into the analysis chamber. The translation of the sample along the main axis of the chamber is achieved with the help of an electrical motor. The movements in the vertical and horizontal directions perpendicular to the main axis of the chambers are controlled with two screws. The manipulator is constructed such that the sample has a large number of degrees of freedom. The sample can also be rotated around its surface normal, azimutal rotation, and can be tilted up to 90°. The manipulator can additionally rotate 360° around its main axis. Such flexibility ensures that practically every desired position and orientation of the sample with respect to the incident synchrotron radiation can be attained.

The 10 mm diameter sample has a thermocouple attached on its side and is mounted on a sapphire plate with four connection points. Two of these connections are for the thermocouple and the other two can be used for resistive heating, grounding, or application of a bias to the sample. In addition to resistive heating, electron impact heating of the sample can be realized up to 1200°C, with the help of a tungsten filament mounted on the manipulator and located behind the sample.

To obtain a base pressure of 2×10^{-10} mbar, the whole surface apparatus is baked for a minimum of 24 h at 150-180° C.

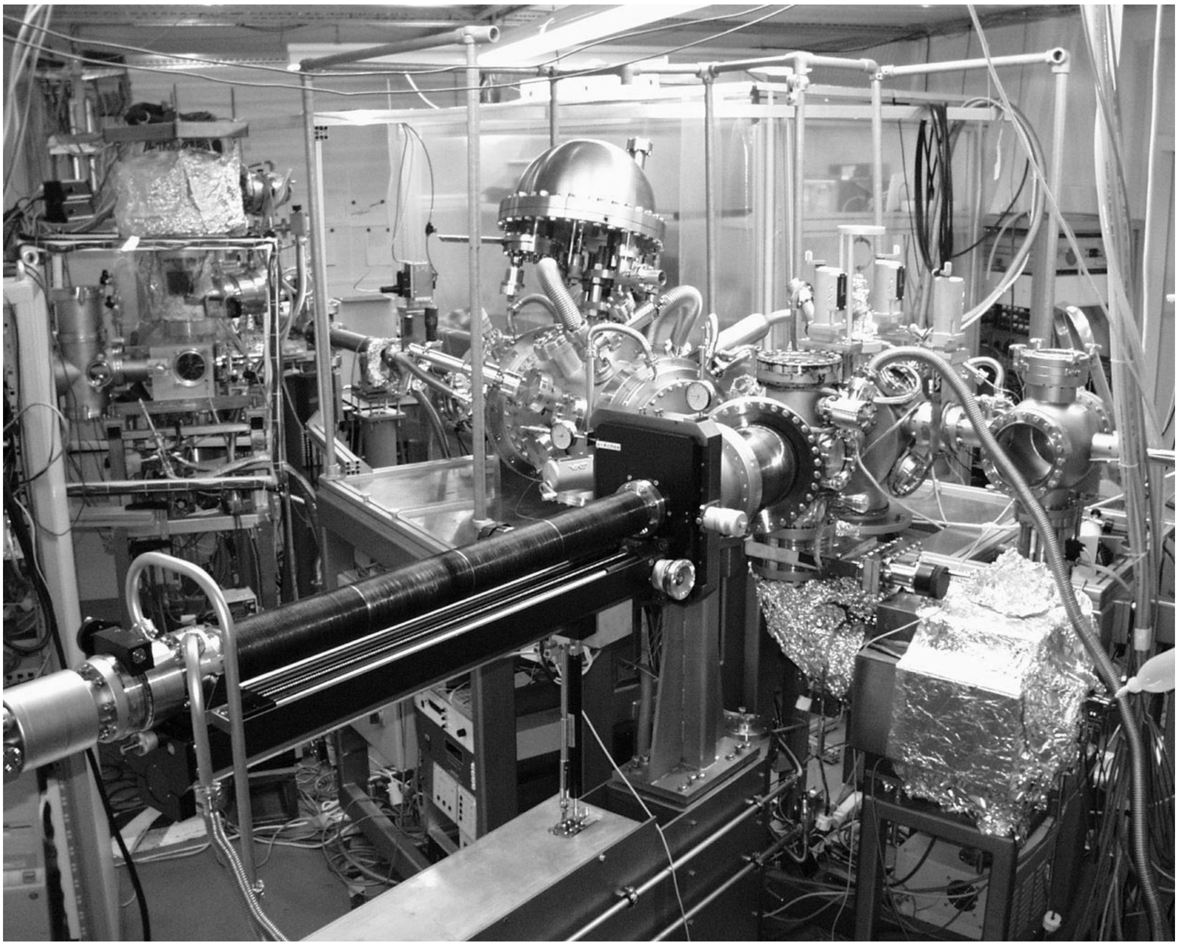

Fig. 2.2-3 View of the UHV apparatus at MBI User facility at BESSY II. In the photography the manipulator is set to serve the preparation chamber.

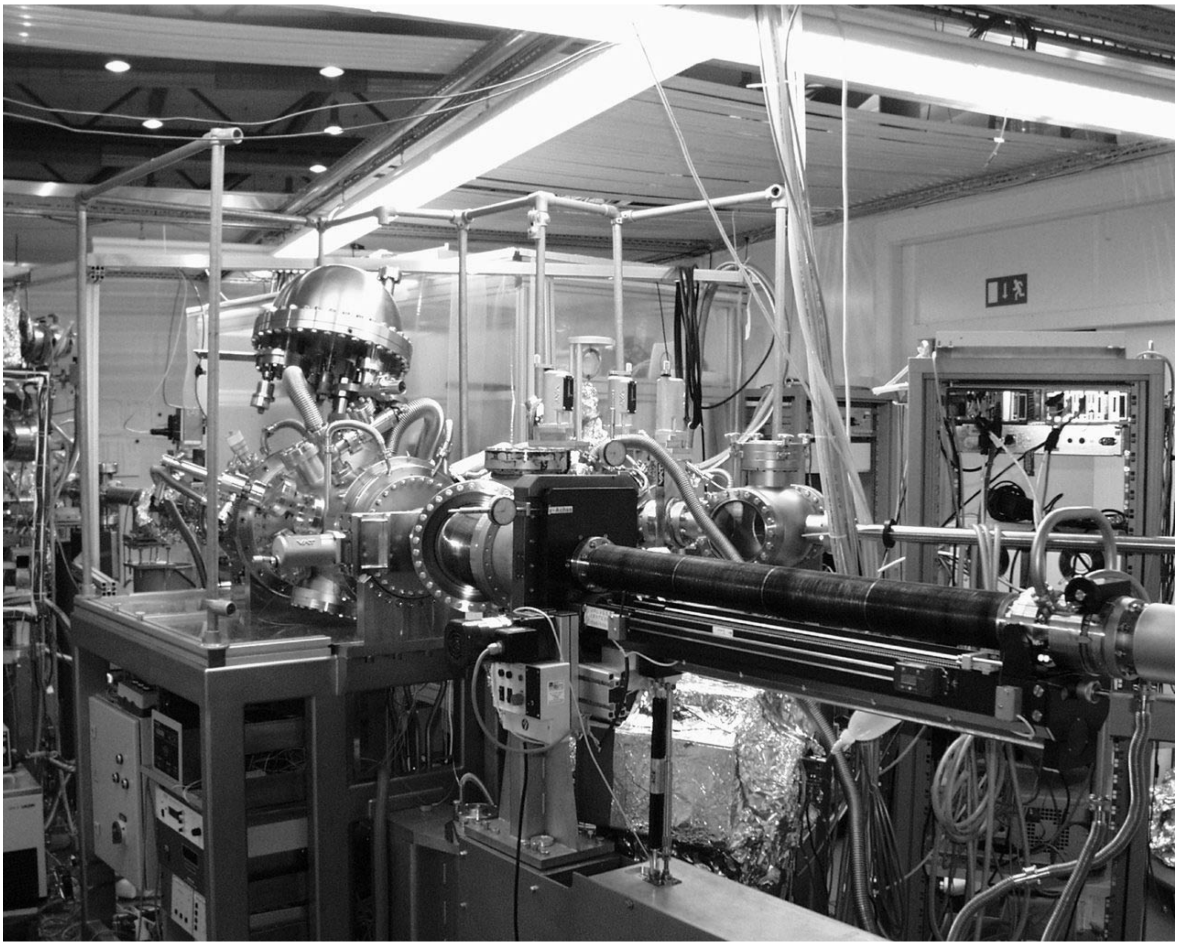

Fig. 2.2-4 View of the UHV chamber at MBI User facility at BESSY II. The manipulator was rotated for bringing the sample into the analysis chamber.

2.3 NEXAFS Experiments

The NEXAFS measurements have also been performed at BESSY II, but at the U49/2 BTUC PGM beamline. The optical layout of this beamline is given in Fig. 2.3-1.

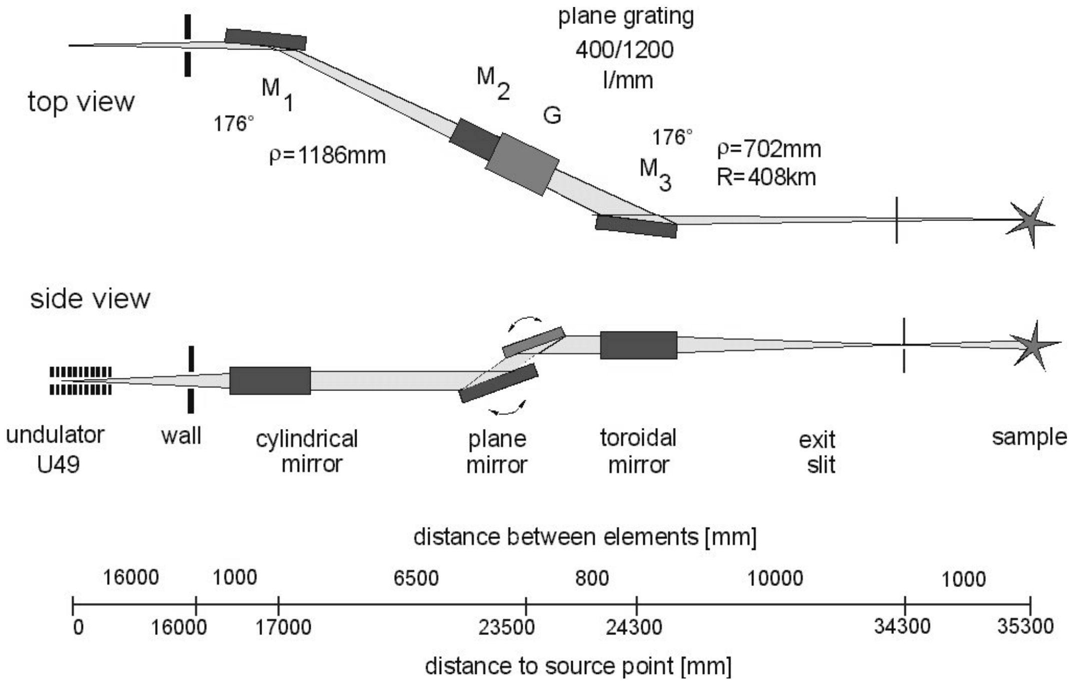

Fig. 2.3-1 Optical layout of the U49/2 BTUC PGM beamline.

The monochromator utilizes two plane gratings, a high density 1000 lines/mm and a low density 300 lines/mm grating. The first, third and fifth harmonics of the undulator cover the 800-1500 eV energy region and are accessed by the high density grating which has an energy range between 70 and 2000 eV. The 300 lines/mm grating provides higher flux at the cost of energy resolution, but it extends the energy range of the beamline to lower energies [BFS2000].

The NEXAFS spectra were measured using a channeltron partial yield detector with the sample at 45° angle with respect to the synchrotron light in the horizontal plane. The detector was placed at 45 degrees above in the vertical plane containing the surface normal and was moved to within circa 4 cm of the sample. The samples were transferred via a fast entry lock and preparation chamber directly into the analysis chamber, where the vacuum remained in the low 10^{-10} mbar range. The spectra were taken having the monochromator in synchronous mode (monochromator and undulator driven together) and employing the third harmonic of the undulator. Using an exit slit of 80μm, the resolving power of the monochromator at the Cu2p edge (where the measurements have been done) was approximately 3000.