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Techniques and Application of Electron Spectroscopy Based on Novel X-ray Sources

STEFAN PLOGMAKER

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Abstract

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The curiosity of researchers to find novel characteristics and properties of matter constantly pushes for the development of instrumentation based on X-radiation. I present in this thesis techniques for electron spectroscopy based on developments of X-ray sources both in time structure and energy. One part describes a laser driven High-Harmonic Generation source and the application of an off-plane grating monochromator with additional beamlines and spectrometers. In initial experiments, the source is capable of producing harmonics between the 13th and 23rd of the fundamental laser 800 nm wavelength. The intensity in the 19th harmonic, after monochromatization, was measured to be above $1.2 \cdot 10^{10}$ photons/second with a repetition rate of 5 kHz.

The development of a chopper system synchronized to the bunch clock of an electron storage ring is also presented. The system can be used to adjust the repetition rate of a synchrotron radiation beam to values between 10 and 120 kHz, or for the modulation of continuous sources. The application of the system to both time of flight spectroscopy and laser pump X-ray probe spectroscopy is shown. It was possible to measure triple ionization of Kr and in applied studies the valence band of a laser excited dye-sensitized solar cell interface. The combination of the latter technique with transient absorption measurements is proposed.

The organic molecule maleic anhydride (MA) and its binding configuration to the three anatase TiO_2 crystals (101), (100), (001) has been investigated by means of Xray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine structure Spectroscopy (NEXAFS). The results provide information on the binding configuration to the 101 crystal. High Kinetic Energy Photoelectron Spectroscopy was used to investigate multilayers of complexes of iron, ruthenium and osmium. The benefit of hard X-rays for ex-situ prepared samples is demonstrated together with the application of resonant valence band measurements to these molecules.

Keywords: High Harmonic Generation HHG, HELIOS, X-ray Beam Chopper, Dye-sensitized Solar Cell, Ultra High Vacuum UHV, Photoelectron Spectroscopy, Pump-Probe, XUV

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till Nina, meine Eltern und meine Schwester

List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I **Develpoment of HELIOS – A Laboratory Based on High-order Harmonic Generation of XUV Photons for Time-resolved Spectroscopy**
Stefan Plogmaker, Joachim Rausch, Mattias Svanquist, Johan Forsberg, Jan-Erik Rubensson, Hans Siegbahn and Johan Söderström
Manuscript

II **Versatile high-repetition-rate phase-locked chopper system for fast timing experiments in the vacuum ultraviolet and X-ray spectral region**
Stefan Plogmaker, Per Linusson, John Eland, Neville Baker, Erik M. J. Johansson, Håkan Rensmo, Raimund Feifel, and Hans Siegbahn
REVIEW OF SCIENTIFIC INSTRUMENTS **83** 013115 (2012)

III **Comparing Surface Binding of the Maleic Anhydride Anchor Group on Single Crystalline Anatase TiO_2 (101) (100) and (001) Surfaces**
E. M. J. Johansson, S. Plogmaker, L. E. Walle, R. Scholin, A. Borg, A. Sandell, H. Rensmo
JOURNAL OF PHYSICAL CHEMISTRY C **114** 35 (2010)

IV **Spin-Orbit Coupling and Metal-Ligand Interactions in Fe(II), Ru(II), and Os(II) Complexes**
E. M. J. Johansson, M. Odelius, S. Plogmaker, M. Gorgoi, S. Svensson, H. Siegbahn, H. Rensmo
JOURNAL OF PHYSICAL CHEMISTRY C **114** 22 (2010)

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The following papers have been omitted from this thesis due to the character of the material, or due to the limited extent of my contribution.

- **Solid state dye-sensitized solar cells prepared by infiltrating a molten hole conductor into a mesoporous film at a temperature below 150 degrees C**
  Fredin, K; Johansson, EMJ; Hahlin, M; Scholin, R; Plogmaker, S; Gabrielsson, E; Sun, LC; Rensmo, H
  SYNTHETIC METALS **161** 21-22 (2011)

- **Triple ionization of CO_2 by valence and inner shell photoionization**
  Eland, JHD; Andric, L; Linusson, P; Hedin, L; Plogmaker, S; Palaudoux, J; Penent, F; Lablanquie, P; Feifel, R
  JOURNAL OF CHEMICAL PHYSICS **135** 13 (2011)

- **Mixed Dissociative and Molecular Water Adsorption on Anatase TiO_2(101)**
  Walle, LE; Borg, A; Johansson, EMJ; Plogmaker, S; Rensmo, H; Uvdal, P; Sandell, A
  JOURNAL OF PHYSICAL CHEMISTRY C **115** 19 (2011)

- **Characterization of the Interface Properties and Processes in Solid State Dye-Sensitized Solar Cells Employing a Perylene Sensitizer**
  Cappel, UB; Smeigh, AL; Plogmaker, S; Johansson, EMJ; Rensmo, H; Hammarstrom, L; Hagfeldt, A; Boschloo, G
  JOURNAL OF PHYSICAL CHEMISTRY C **115** 10 (2011)

- **Mapping the frontier electronic structures of triphenylamine based organic dyes at TiO_2 interfaces**
  Hahlin, M; Odelius, M; Magnuson, M; Johansson, EMJ; Plogmaker, S; Hagberg, DP; Sun, LC; Siegbahn, H; Rensmo, H
  PHYSICAL CHEMISTRY CHEMICAL PHYSICS **13** 8 (2011)

- **Energy alignment and surface dipoles of rylene dyes adsorbed to TiO_2 nanoparticles**
  Cappel, UB; Plogmaker, S; Johansson, EMJ; Hagfeldt, A; Boschloo, G; Rensmo, H
  PHYSICAL CHEMISTRY CHEMICAL PHYSICS **13** 32 (2011)

- **Single and multiple photoionisation of H(2)S by 40-250 eV photons**
  Eland, JHD; Fink, RF; Linusson, P; Hedin, L; Plogmaker, S; Feifel, R
  PHYSICAL CHEMISTRY CHEMICAL PHYSICS **13** 41 (2011)

- **Surface Molecular Quantification and Photoelectrochemical Characterization of Mixed Organic Dye and Coadsorbent Layers on TiO_2 for Dye-Sensitized Solar Cells**
  Marinado, T; Hahlin, M; Jiang, XA; Quintana, M; Johansson, EMJ; Gabrielsson, E; Plogmaker, S; Hagberg, DP; Boschloo, G; Zakeeruddin, SM; Gratzel, M; Siegbahn, H; Sun, LC; Hagfeldt, A; Rensmo, H

JOURNAL OF PHYSICAL CHEMISTRY C **114** 27 (2010)

- **Electronic and molecular structures of organic dye/TiO_2 interfaces for solar cell applications: a core level photoelectron spectroscopy study**
  Hahlin, M; Johansson, EMJ; Plogmaker, S; Odelius, M; Hagberg, DP; Sun, LC; Siegbahn, H; Rensmo, H
  PHYSICAL CHEMISTRY CHEMICAL PHYSICS **12** 7 (2010)

- **Using a molten organic conducting material to infiltrate a nanoporous semiconductor film and its use in solid-state dye-sensitized solar cells**
  Fredin, K; Johansson, EMJ; Blom, T; Hedlund, M; Plogmaker, S; Siegbahn, H; Leifer, K; Rensmo, H
  SYNTHETIC METALS **159** 1-2 (2009)

- **Probing and modifying the empty-state threshold of anatase TiO_2: Experiments and ab initio theory**
  Sandell, A; Sanyal, B; Walle, LE; Richter, JH; Plogmaker, S; Karlsson, PG; Borg, A; Uvdal, P
  PHYSICAL REVIEW B **78** 7 (2008)

Comments on my participation

My participation in the case of the HELIOS laboratory (paper I) was the design, construction drawings, commissioning, first experiments and data analyses.

In paper II I did the design, construction drawings and commissioning of the X-ray beam chopper system. I was responsible for the pump-probe experiments on dye-sensitized solar cells and I was involved in the experimental part of the time of flight experiments.

In paper III and IV I performed the experiments and was strongly involved in the data analyses and discussions.

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1. Introduction

Investigating and understanding matter is one of the basics for the development of new materials and products. Such investigation can be made with various different methods depending on the question asked and the tested material. Methods used in industry on a daily basis range from the simplest pull-out test to determine the tensile strength of steels down to microscopy and interferometric methods to measure surface qualities.

Not so common in industry but widely used in research are spectroscopic techniques applied to various materials reaching from condensed matter to molecules and atoms in gases and liquids. Here infrared spectroscopy can be used to measure vibrations of molecules, visible light spectroscopy to determine optical properties of e.g. crystal structures, ultra violet light to probe the outer shell electrons of molecules and X-rays to eject electrons from the so called core levels in order to get information about the atomic structure in materials.

What all the above named spectroscopic techniques have in common is the need of a special photon source providing the experiment with exciting photons of a certain energy and a detector which measures the effect of the interaction between the sample and those photons. Developing such photon sources and spectrometers to extend the range of possible experiments, our department has a strong tradition which continues in this work.

An overriding aim of these efforts is to be able to combine the atomic resolution inherent in X-ray excited core level spectroscopy with time resolution down to the femtosecond regime. This is of particular importance in studying processes at functional interfaces, such as solar cell structures. In terms of time resolved measurements, the main focus in this thesis is the design work on the High Harmonic Generation (HHG) laboratory HELIOS including first measurements of the performance of this source. This development also includes the design, construction and application of a versatile X-ray beam chopper. Furthermore, in order to refine conditions for well-defined studies of functional interfaces the deposition procedure of an organic molecule (maleic anhydride) on to anatase TiO_2 under ultra high vacuum is investigated. Finally, the implications are presented of using the new possibilities of hard X-ray photoelectron spectroscopy to dye-sensitized solar cell compounds in terms of elemental specificity and bulk sensitivity.

2. Historical background to this thesis

The work within the scope of this thesis is centered on the development of new techniques in electron spectroscopy using radiation sources for excitation. Therefore I would like to give a brief background of the history of such instrument development in our department.

The experiments of Hertz in 1887, when he observed sparks initiated by ultraviolet light on a negative electrode, were the basics for Einsteins formulation of the photoelectric effect in 1905 [1]. In the following years a lot of effort was put into the development of spectroscopic techniques to make use of this effect. However, it took until the 1950s when Siegbahn and coworkers developed the first electron spectrometer with magnetic double-focussing and improved electron detection. A resolution of 10^4 was reached for electrons in the keV region with a instrument especially designed for low energy electrons ejected by the absorption of soft X-ray radiation from Al ($h\nu = 1486.6eV$) and Mg ($h\nu = 1253.6eV$). One very important observation done with this instrument was the shift of core electron lines due to the chemical state of the atom [2, 3].

In about the same time period valence band electron spectroscopy with ultraviolet light form helium discharge processes was developed. This technique was in the beginning limited to photon energies below 11.8 eV due to the use of LiF as a vacuum window material. This could be extended to the use of 21.2 eV (HeI) and 40.8 eV (HeII) in ultra high vacuum experiments after the introduction of a differentially pumped helium lamp [4].

A next step in terms of resolution and intensity was the implementation of spherically shaped crystals in X-ray monochromators. This made it possible to narrow the line width of AlKα radiation to about 160 meV and to focus it in both directions at the same time [4].

During the early seventies synchrotron radiation sources became an additional source for both valence band and core level electron spectroscopy. Furthermore the possibility to tune the photon energy opened up for the combination of electron spectroscopy with other methods like for example X-ray absorption spectroscopy.

AlKα sources consist usually of a fixed water cooled anode bombarded with electrons by means of an electron gun. These sources however are limited by the efficiency of the water cooling applied. A major step was the implementation of the rotating anode which made it possible to increase the applied power density by two orders of magnitude. I would like to mention here that the very first commercial system of this kind (SCIENTA ESCA 300) which was taken into operation in 1991 in our department still works well and delivers a substantially higher photon flux than today's other commercially available sources.

3. Instrumentation

The following description of different instrumentations and experimental setups is related to the work carried out and publications included in this thesis. However the various sections are meant to be more of an overview than a detailed description and closer insight to the topics can be found in the given references.

3.1 Electron spectroscopy

The measurements in paper III and IV were carried out by means photoelectron spectroscopy and near edge x-ray absorption fine structure spectroscopy (NEXAFS). The principle of both techniques are described in the following part.

3.1.1 Photoelectron spectroscopy

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi) \tag{3.1}$$

This formula describes the principle of Photoelectron Spectroscopy (PES) (also called X-ray Photoelectron Spectroscopy (XPS)) where E_{photon} is the energy of the photons irradiating the sample, $E_{kinetic}$ the energy of the electron measured by the analyzer and ϕ the work function of the analyzer. The above equation yields $E_{binding}$, the binding energy of the ejected electron referenced to the Fermi level.

In a PES measurement the sample is illuminated with light of well known energy and the number of ejected electrons as a function of their kinetic energy is recorded. Those two values plotted against each other result in the photoelectron spectrum which gives insight to different properties of the sample. It is useful for the discussion to divide the spectrum into two different parts , the core levels and the valence levels.

In the core levels the electrons are strongly bound to its nuclei and hardly participate in the formation of bonds in molecules. Therefore the distribution of core level binding energies is very characteristic for every atom. This part of the spectra can not only be used to identify the various atoms in the sample but also to determine the relative amount between them [3].

In contrast to the core levels the valence part is more difficult to interpret. The valence electrons are involved in the formation of molecules and form the molecular orbitals. Usually many atoms are involved and valence bands extending over many electron volts are the result. However in combination with theoretical data these spectra are powerful tools in delineating the electronic structure of molecules and surfaces.

In the interpretation of a PES spectrum one has to take different aspects into account.

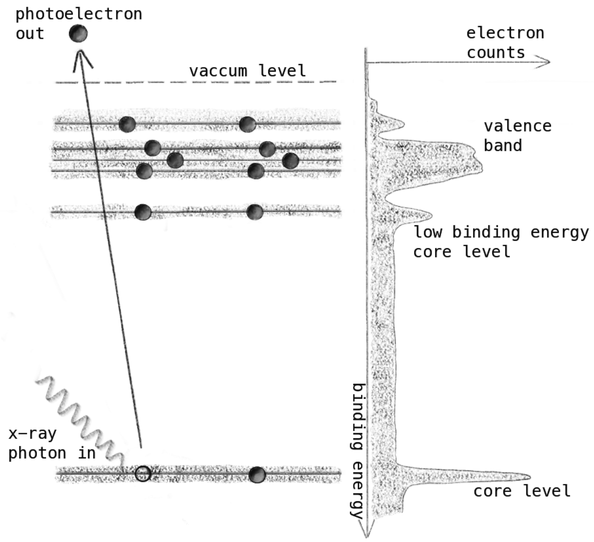


Figure 3.1: The process of photoelectron ejection and the resulting photoelectron spectrum.

First it should be realized that the measured binding energy refers to the total binding energy difference between the system in its initial unperturbed state and the system with one electron removed. The total energy of the latter state is affected by the relaxation of the remaining electrons and therefore the binding energy also reflects this final state effect.

Furthermore, especially in case of solid samples, the intensities of the peaks have to be corrected in order to get values for the amount of a certain substance present in the sample. The measured intensity depends on a set of parameters and can be written as

$$I = I(\sigma, \rho, \Lambda, S) \tag{3.2}$$

where the differential cross section σ depends on the photon energy and the angle between the incident light and the direction of the escaping electron, ρ is the number of atoms per unit volume, S a spectrometer function and Λ the inelastic mean free path of electrons in the sample [5].

Considering the mean free path (figure 3.2) it is evident that PES/XPS is a very surface sensitive technique. Even electrons with several hundred *eV* energy will not be able to travel more that 25-30Å through the bulk of the sample and make it to the surface. This might sound rather negative but is of huge advantage in order to study surface effects or to follow the formation of interfaces.

3.1.2 Resonant spectroscopy

Synchrotron radiation sources (see further section 3.2) have some advantages compared to conventional X-ray sources. One is the possibility of scanning the photon

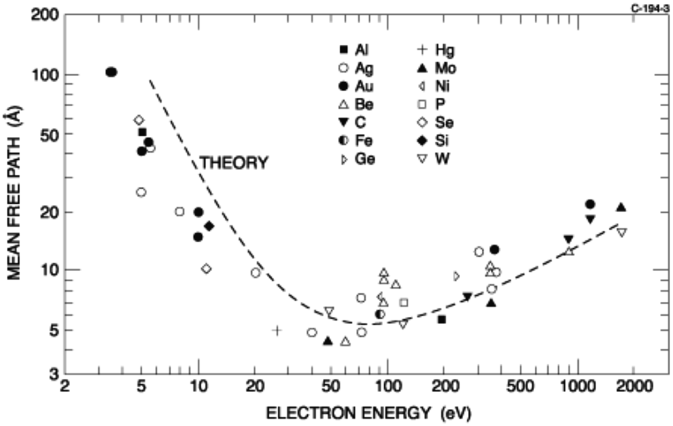


Figure 3.2: The mean free path for different elements. [5]

energy of the radiation by means of a monochromator. By tuning the photon energy to the energy difference between a core level and an unoccupied orbital, electrons can be excited into the latter. The core hole site is subsequently filled by an electron from an outer shell and the energy of this process is released by either a photon or transferred to a secondary electron (termed Auger electron). Figure 3.3 illustrates two different processes with an Auger electron as an outcome. By measuring the number of Auger electrons as a function of the X-ray photon energy the structure of the unoccupied states can be studied, referred to as Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy.

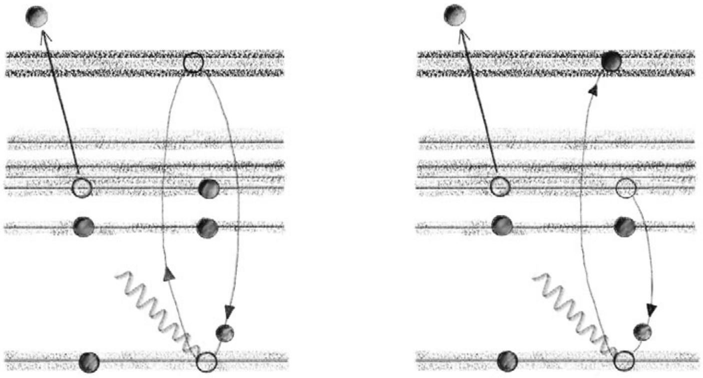


Figure 3.3: Different processes in NEXAFS spectroscopy. Participator (left), spectator (right).

3.2 Synchrotron radiation

Synchrotron radiation sources make use of the fundamental law that electrons traveling at velocities close to the speed of light emit electromagnetic radiation when they undergo any kind of acceleration process. This quite simple principle however becomes a major challenge if one wants to use it for the generation of X-rays in a large scale facility on a daily bases. A short description of the main parts is given here since synchrotron radiation was the X-ray source of choice in papers III and IV.

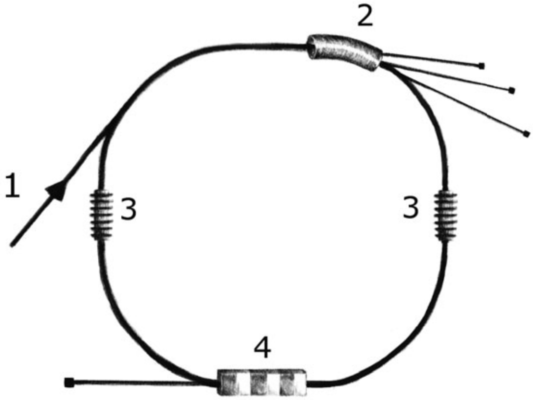


Figure 3.4: The main parts of a synchrotron radiation source are indicated in this sketch. The electron injector (1), a bending magnet (2), RF cavities (3) and an undulator (4).

Figure 3.4 shows a schematic view of a typical synchrotron consisting of a linear accelerator, an electron storage ring and its beamlines. It should be mentioned that the linear accelerator sometimes is connected to the storage ring by a small booster synchrotron but that will not be described here. Starting from an electron source, groups of electrons are accelerated in a linear accelerator and injected into the storage ring. Different schemes are used, either the accelerator is capable of providing relativistic speeds to the electrons or low energy electrons are injected into the storage ring and then accelerated. The main function of the storage ring however is to maintain the kinetic energy of the electrons at a constant level after their injection. The word "ring" is actually a little misleading in this context since the electrons travel on straight lines until they are forced to leave this path by a so called bending magnet. Thus the storage ring itself consists rather more of a couple of straight sections and an equal number of bending magnets and not a real circle.

Already in this bending process the relativistic electrons emit electromagnetic radiation over a broad spectral range which is one mode of producing synchrotron radiation for various types of measurements. However, the much brighter radiation is produced by a periodic array of magnets inserted into the straight sections of the synchrotron. Here the electrons are forced to follow an undulating path which gives this device the name undulator. In every turn of the electrons, electromagnetic radiation is emitted which sums up to a very bright beam with low divergence. The emitted light covers a broad band of energies in terms of undulator peaks and the intensity of a certain range can be enhanced by adjusting the gap between the magnets rows (figure 3.5).

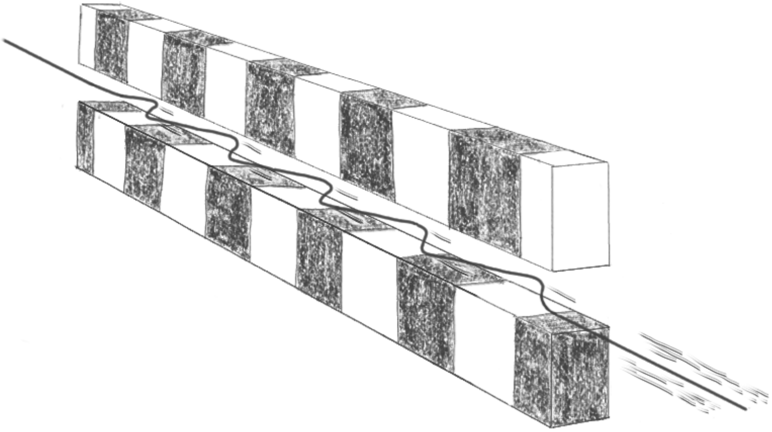


Figure 3.5: The oscillating electron beam in an undulator is shown with just a couple of magnets for simplicity, but it should be mentioned that an undulator usually consist of some tens of pole pairs.

The radiation emitted from both bending magnets and undulators is distributed over a wide range of energies. But since most spectroscopic techniques need a monochromatic source a certain ΔE part of the emitted energies have to be separated from the rest by means of a monochromator. This is described in more detail in section 3.3.3 in the context of HHG X-ray sources.

3.3 High harmonic generation

High harmonic generation in gases is a technique to generate XUV and X-ray pulses. This is possible due to the rapid development of very high power pulsed laser sources in the last two decades.

If a laser beam with a power density of more than $1 \cdot 10^{14}\ W/cm^2$ is focused into a gas like for example argon, higher harmonics of the fundamental laser pulse can be generated [6, 7]. The emitted harmonics follow the propagation direction of the fundamental and with a divergence lower than that of the focused laser beam. Both the divergence and the pulse length of the generated high harmonics are lower than those of the fundamental pulse which is due to the spatial intensity distribution in the focus and the temporal intensity distribution in the traveling laser pulse. The figure below shows a sketch of a typical high harmonic spectrum where harmonics up to a certain cutoff are generated.

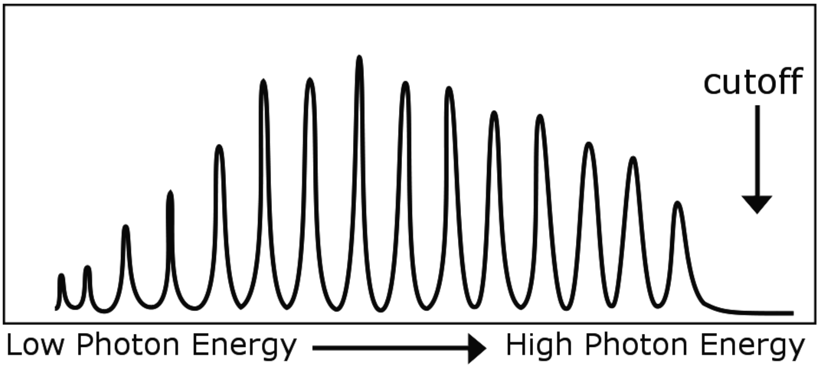


Figure 3.6: Sketch of the discrete high harmonic spectrum up to a certain cutoff.

3.3.1 The generation process

One way of describing the generation process of high harmonics in more detail is the three step model of tunnel ionization, acceleration and recombination (figure 3.7). The coulomb barrier which traps the electron is bent by the strong electric field of the fundamental laser pulse which makes a tunnel ionization of a valence electron possible. Thereafter the electron is accelerated away from its parent ion in the electric field of the laser pulse and gains momentum. The direction of the electric field changes after half an optical cycle and accelerates the electron towards its parent ion [8, 9]. In this cycle the electron has gained kinetic energy which sums up with the ionization potential I_p to the energy of the emitted photon. The highest emitted photon energy, the so called cutoff, is given by $E_{max} = I_P + 3.17 \cdot U_P$ where U_p is the ponderomotive potential of the laser pulse.

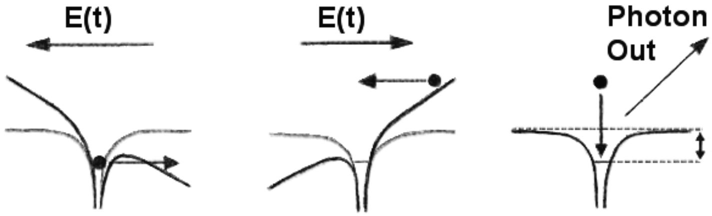


Figure 3.7: The three step model of high harmonic generation. (left) tunnel ionization, (middle) acceleration, (right) recombination

3.3.2 Generation schemes

The generation of high harmonics in the XUV usually takes place in a gas target. Since the emitted radiation is strongly absorbed in air, the gas target has to be placed in vacuum. Most of the systems today use gas jets, capillaries or gas cells but also more exotic solutions like semi infinite gas cells which will not be described here.

Gas jets are usually as simple as a gas nozzle with a small aperture pointing into the vacuum chamber and the system is mounted on a manipulator to align the nozzle to the focus of the fundamental laser beam. The gas has a constant flow by means of an adjustable leak valve to optimize the generation process, which to a substantial portion is dependent on the gas pressure. The maximum gas pressure is simply limited by the capacity of the vacuum pumps used in the system. Advanced systems are therefore equipped with pulsed gas valves which are synchronized to the driving laser system [10]. By opening the valve with a defined delay before the arriving laser pulse, the pressure in the gas jet can be maximized while a low gas flow is kept between the pulses in oder to minimize the total gas load on the pumps. To my knowledge these systems are limited to about 1 kHz at the moment.

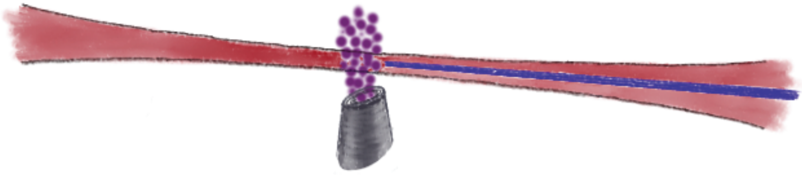


Figure 3.8: High harmonic generation in a gas jet.

Capillaries consist of a glass tube with an entrance and exit hole and additionally a hole for the supply of the generation gas. The fundamental is focused into one side of the capillary and is guided through it by means of low angle reflexion at the wall of the so called wave guide. The advantages of such systems are the possibility of high pressures in the tube and a long interaction region between the gas and the fundamental laser pulse. However, this is only an advantage in the case of low order harmonic generation up to the 45th harmonic (about 70 eV) [11].

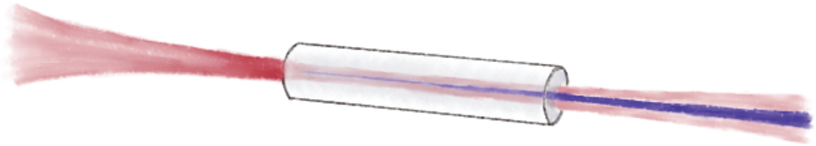


Figure 3.9: High harmonic generation in a straight waveguide.

To generate higher order harmonics with a decent intensity, modulated waveguides have to be used. The inner diameter of the gas transporting tube is modulated which leads to a periodically focussing and refocussing of the fundamental laser beam. In this way, high degrees of ionization occur only in short sections and the fundamental as well as very high order harmonics can stay in phase. Thereby so called quasi phase matching is achieved and an increase in photon flux with a factor of 2-5 for photon energies over 60 eV is reported [12] [13]

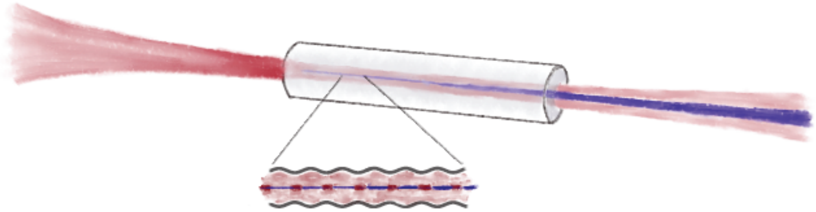


Figure 3.10: High harmonic generation in a modulated waveguide. The periodically focussing and defocussing is indicated by red dots.

Gas cells can be designed in such a way that the interaction region between gas and fundamental is optimized. By using metal plates as entrance and exit "window" the laser drills perfect sized holes, typically about 100 micrometer, on its path through the gas cell and is thereby self aligning. Even in these systems phase matching can be achieved by carefully tuning the the gas pressure, the length of the gas cell and the position of the focus in the propagation direction [14].

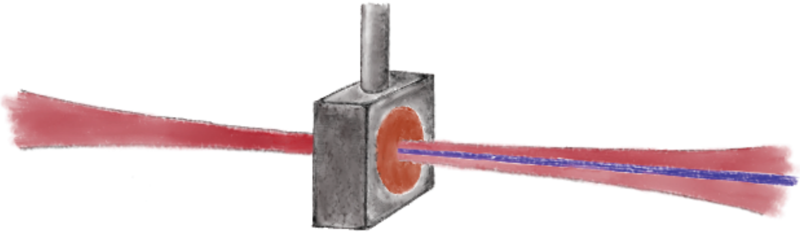


Figure 3.11: High harmonic generation in gas cell. The laser machines a perfectly sized hole through the copper plate.

3.3.3 Monochromatization of HHG XUV pulses

Monochromatization in general means that a narrow energy range ΔE centered around a certain energy E is selected from a broad energy distribution of the incident radiation. This can be done with various different techniques like for example multi layer mirrors, zone plates or gratings. The latter is the main technique used in this thesis and is briefly described here.

Gratings used for monochromatization can have different shapes, surface structures and coatings but all of them have one thing in common. The surface structure is periodically modulated in order to diffract the incident light. One possible and widely used grating is the saw tooth groove profile illustrated in figure 3.12.

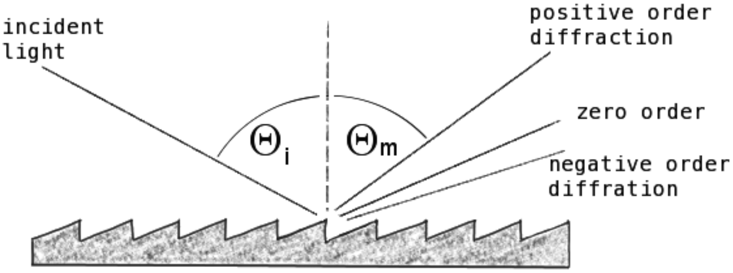


Figure 3.12: Diffraction on a grating.

This structure has the advantage that the angle of the saw tooth, the so called blaze angle, can be chosen in such a way that the reflection is maximized for a certain energy and thereby maximize the efficiency of the monochromator. Especially in the XUV region the efficiency of gratings and mirrors depends very much on both the incident angle and the coating of the surface. To reduce absorption of the incident radiation, the optical elements are usually coated with gold and irradiated in grazing incidence with angles below 5 degrees relative to the surface.

When a nonmonochromatic beam, often referred to as white light, hits a grating different energies are reflected with different angles except for zero order reflection where the grating reflects the radiation like a mirror (Fig. 3.12).

The grating equation for a plane wave can be written as

$$d(sin\Theta_m - sin\Theta_i) = m\lambda \tag{3.3}$$

where Θ_i is the incident angle, m the order of diffraction, λ the wavelength and Θ_m the exit angle of the light with the wavelength λ. It can be seen that with increasing wavelength (decreasing energy) the angle of diffraction decreases in the case of positive orders.

3.3.4 Time delay and compensation

While the above described phenomena of reflecting different energies with different angles is of huge advantage to monochromatize continuous source radiation it leads to problems in terms of time resolution when it comes to pulsed sources in the femtosecond regime.

When a white femtosecond pulse hits a grating the diffraction process leads to a path difference between the energies included in the pulse. This effect can be seen as a tilt of the traveling pulse front where the lower energies travel the shortest way while the higher energies travel a longer way. In laser science this effect is called a spacial chirp since the different energies are separated in space (figure: 3.13). The outcome is an increased pulse length and a drop in peak power.

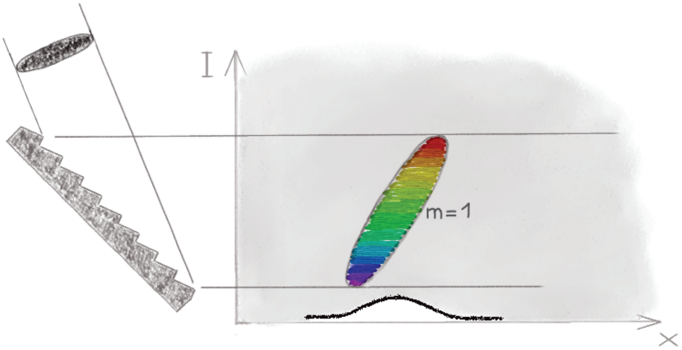


Figure 3.13: The effect of a grating used in positive order diffraction on a short pulse with a broad distribution of energies. The diffracted pulse front is tilted, has become a spacial chirp and the peak power drops drastically.

Different optical layouts are used in todays instruments to compensate for this effect [15]. One solution is to use a second grating in negative order to tilt the pulse back in its original position. However, this solution is mechanically complicated since both gratings have to be moved to change the energy passing the exit slit and the additional grating reduces the efficiency of the monochromator.

The solution we decided for in the HELIOS facility is the so called off-plane mount. In this design the grating is turned by 90 degrees compared to the standard mount and the energies are diffracted in a cone around the groove axis. In this way the effect on the pulse length is very low and thereby acceptable for femtosecond experiments [16, 17].

One possible monochromator layout using this technique is shown in figure 3.14. The radiation diverges from the source on its path to the first collimating mirror and hits the grating as a parallel beam. As the grating is used in off-plane mount the various energies are diffracted in a cone towards the second mirror which focusses the radiation onto the exit slit. This cone structure rotates synchronously with the rotation of the grating which is used to choose the desired energy at the exit slit.

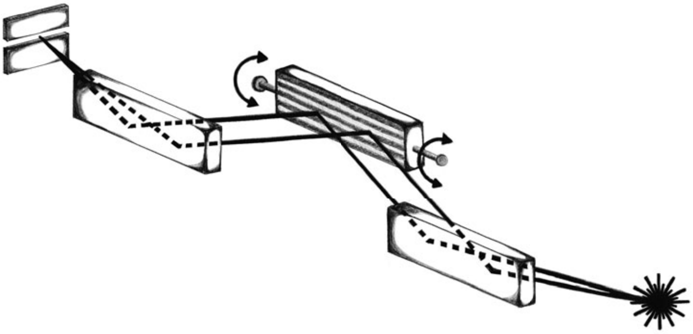


Figure 3.14: Sketch of the off-plane monochromator. From right to left - source, collimating mirror, grating in off-plane mount, refocussing mirror, exit slit.

This system is mechanically simple since only one rotational axis is needed. A further big advantages of this scheme is the rather high efficiency of this design. If the grating is rotated with the value of the blaze angle, the reflection coefficient of the chosen energy is very close to that of a mirror surface. In this way efficiencies above 0.3 have been demonstrated [16].

3.4 X-ray beam chopper

The electron beam circulating in the storage ring of a synchrotron radiation source usually consists of a number of electron bunches with empty spaces in between. Thus the emitted light is modulated at very high repetition rates in the MHz range. Most of the users, however, see the emitted radiation as constant and not pulsed light. To them the time structure of the synchrotron is not important, neither does it affect the outcome of the experiment. Rather more they would like to squeeze as many bunches as possible into the ring to maximize the intensity of the available light. In contrast to that a lot of spectroscopic techniques can only be performed with a pulsed source.

The following chapter describes the use of synchrotrons as pulsed X-ray radiation sources and the application of chopper systems to modulate the time structure of the emitted radiation.

3.4.1 Time structure of synchrotron radiation sources

Filling patterns of electron storage rings differ from facility to facility. They can be loosely divided into multi bunch and single bunch mode. While MAX-II is restricted to multi bunch mode to provide the user with the highest possible photon flux, BESSY-II is frequently switched between multi bunch and single bunch mode. In the latter case only one electron bunch is injected with the rest of the storage ring empty. This gives rise to a repetition rate of the emitted radiation given by the circumference of the storage ring and the speed of light, and the pulse rate which is usually about 500 MHz in multi bunch mode, is reduced to 1.25MHz.

A more useful value for a lot of experiments is the dark time between the emitted X-ray pulses which in this case is 800 ns (exactly 800.5515 ns). Thus, 800 ns is the maximum allowed event time one can study.

The number of electron bunches can not be reduced any more and if one wants to go to longer time scales a chopper system has to be implemented to reduce the number of X-ray pulses further.

3.4.2 X-ray beam chopper

Many different X-ray beam chopper systems have been designed during the last two decades ranging from rotating crystals over triangles to hamster wheels where the radiation has to pass two apertures. The basic principle of all these systems is the same. A fast rotating object with a set of apertures is inserted into the X-ray beam and transmits only a fraction of the incoming radiation.

The design of the applied chopper system depends very much on the nature of the intended experiment. While some demand very low repetition rates in the range of some kHz and long dark times, others prefer to adjust the frequency of the light pulses above a hundred kHz.

The discussion of transmitted intensity has to be divided into the application of the chopper system to modulate continuous sources and the application to reduce the frequency of pulsed sources. In the first case the transmitted intensity only depends on the ratio between apertures (openings) and blocking parts of the rotating object and not on the rotational frequency. If a chopper system is used to reduce the frequency of a synchrotron in single bunch mode, the transmitted intensity depends on the number of apertures and the quality of synchronization. Only if the synchronization works well the maximum possible number of pulses is transmitted and thus the intensity maximized.

3.4.3 Time of flight spectroscopy

In hemispherical electrostatic electron analyzers the presence of the smallest magnetic fields is avoided since it strongly affects the path of the electrons into the analyzer lens system. In contrast to that time of flight spectroscopy (TOF) based on so-called magnetic bottles [18, 19] makes use of strong permanent magnets in so called magnetic bottle analyzers. Figure 3.15 illustrates such a system where a magnet forces the entire 4π solid angle of the ejected electrons to move towards the electron detector which is located at the end of a long flight tube. Since these analyzers measure the flight time of the expelled electrons, from the interaction point to the detector, pulsed radiation sources have to be used. The arrival of an X-ray pulse gives the starting point for the measurement and the detection of an electron at the end of the flight tube the stop signal. This flight time can than be related to the kinetic energy of the electron.

If the flight time exceeds the dark time between the X-ray pulses it becomes difficult to relate this electron to the correct light pulse [20]. This leads to comparatively large backgrounds in multi-dimensional electron coincidence data projected into spectra reminiscent to conventional photoelectron spectra as well as to difficulties in measuring low kinetic energies over all.

Paper II reports on how the chopper system developed within the framework of this thesis is used to adjust the repetition rate of the BESSY-II storage ring in oder to expand the possibilities of this kind of electron correlation spectroscopic technique.

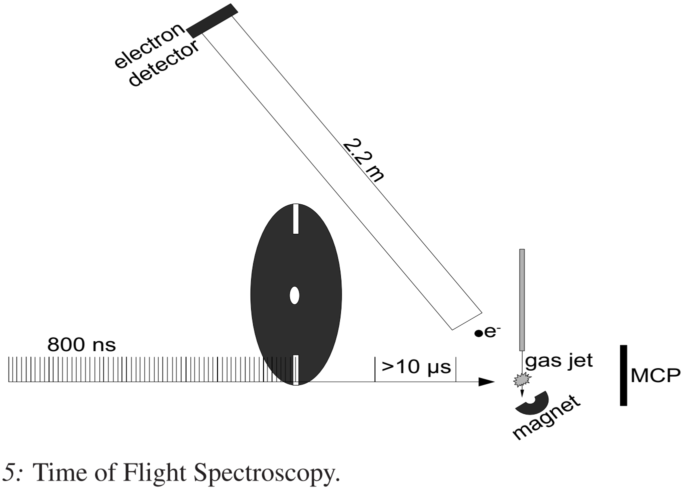


Figure 3.15: Time of Flight Spectroscopy.

3.4.4 Laser pump X-ray probe spectroscopy

Besides the application of X-rays from high-harmonic generation sources to pump-probe experiments, synchrotron radiation is a very interesting complement to these techniques. Either one synchronizes a high repetition rate laser source to the single bunch mode of a synchrotron, or the synchrotron radiation is modulated by means of a chopper system. Applied to the semi continuous radiation of a multi bunch mode, nano and microsecond pulses can be modulated and in combination with a pulsed laser source used for pump-probe experiments within these time scale.

In these experiments there is no need of a time resolved detector and hemispherical electron analyzers can be used. The delay of pump and probe pulses can be adjusted and data accumulated for every point until the statistics are sufficient.

Another advantage of this technique is the possibility of high energy resolution. Modern undulator beam lines are intense enough to record spectra with good statistics and energy resolution in the meV range even if the flux is substantially reduced by the chopper system. Furthermore, high photon energies can be used to reach core level electrons.

3.5 Application to functional materials

To design more powerful, more stable or even new instrumentation which has not been available before is one motivation in instrument development. Another motivation is to develop instruments with the aim of solving a specific scientific problem or question in order to improve a functional material device. For the radiation sources and instruments developed in this thesis both motivations have been important. Aside from my interest in what is possible in terms of instrumentation, a second driving force is the development of devices in the area of renewable energies and in particular dye-sensitized solar cells.

3.5.1 The dye-sensitized solar cell

In contrast to conventional silicon based solar cells where all the necessary processes for light to electrical energy conversion are based on one material, the dye-sensitized solar cell uses different material components for different processes and the charge separation occurs at the interface between those [21, 22, 23]. A semiconductor is responsible for the electron transport to the anode, a so called dye molecule for the absorption of sunlight and a third material, often an electrolyte, is responsible for the hole transport.

One of the most commonly used semiconductor materials in this application is nanoporous TiO_2 which, due to its large band gap, is nearly insulating and transparent to visible light. This material can be produced as particles with about 10 nm diameter and after applying onto the electrode in form of solution, sintered by heat to a compact film with a thickness of about 10 μm. The surface area achieved by this process that is about 1000 times larger compared to a flat TiO_2 surfaces. This semiconductor electrode is dipped into a dye-molecule solution in order for dye-molecules to attach to the TiO_2 surface. On top of this either a solid or liquid hole conductor is applied and in the last step the system is sealed with a second piece of conducting glass as a counter electrode.

When the interface is illuminated, the dye-molecules absorb light by electron excitation. From the excited molecule the electron is injected into the conduction band of the TiO_2 and transferred through the nanoporous network to the conducting substrate (anode). The transported electron leaves a hole in the valence levels of the dye-molecule which is now filled by an electron from the hole conducting material. This hole is transported through the material to the counter electrode (cathode). The end result from this many step process is a charge separation with a hole on the cathode and an electron on the anode. The potential energy difference between these two states is the voltage the cell generates. Figure 3.17 illustrates this charge separation in an energy level scheme. Included are also the corresponding photoelectron spectra.

None of these processes happen instantaneously and various time scales from femtoseconds to milliseconds are involved in this conversion process. The injection is in the femto- to picosecond time range and the recombination processes, preventing successful charge separation, of the photgenerated charges are in the micro to millisecond region. Figure 3.18 shows some of the important processes with their time scales and the electronic structure, which can be investigated by means of pump-probe experiments (visible pump X-ray probe) with pulsed radiation either form e.g. the HHG

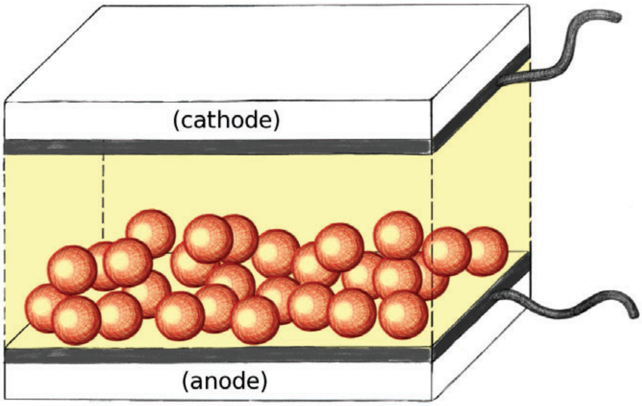


Figure 3.16: The figure shows the with dye-molecules covered TiO_2 nano particles incapsulated between the electrodes. The electrolyte is indicated.

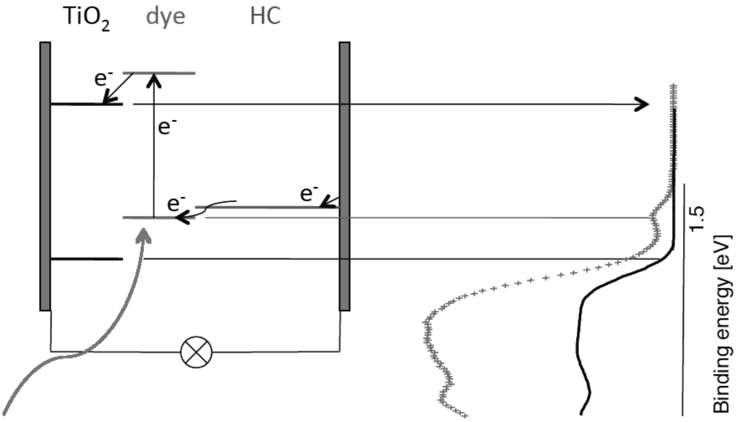


Figure 3.17: Energy levels in a dye-sensitized solar cell interface and the corresponding photoelectron spectrum (without hole conducting material). The TiO_2 valence and conduction band (left), dye molecule ground and excited state (middle), hole conductor valence level(right).

source or modulated radiation from the chopper system. In an ideal case an additional peak originating from an electron from the excited state appears in the photoelectron spectrum and decreases with a certain time scale. In combination with core-level spectroscopy such experiments could therefore give element specific informations about the dynamic processes of such functional interfaces.

A vast variety of different dye molecules are available today. They can have different properties in terms of colors, lifetimes of the excited state, sizes and chemical compositions, still the design of them is generally similar. The molecules have anchor groups to attach to the TiO_2 and a light absorbing part to collect light energy. The anchor group in many of the molecules is a carboxylic acid group which has shown to

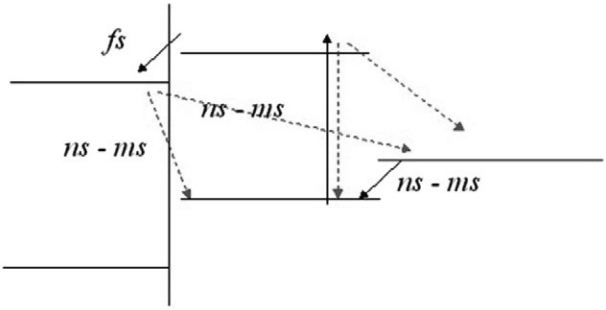


Figure 3.18: Various time scales of the charge transfer processes in a dye-sensitized solar cell interface, involving the valence and conduction bands in the semiconductor (left), the ground and excited state in the dye-molecule (middle) and the hole-conductor (left).

have good adsorption properties. The light absorbing unit often has a charge transfer character with a donor and an acceptor. Different complexes have been tested including pure organic molecules such as triarylamines and perylenes, as well as inorganic complexes such as ruthenium polypyridines. However, recently the most efficient solar cells are made with the metal base porphyrin dye [23, 24]. Figure 3.19 shows two dye families which are connected to the work presented in the current thesis.

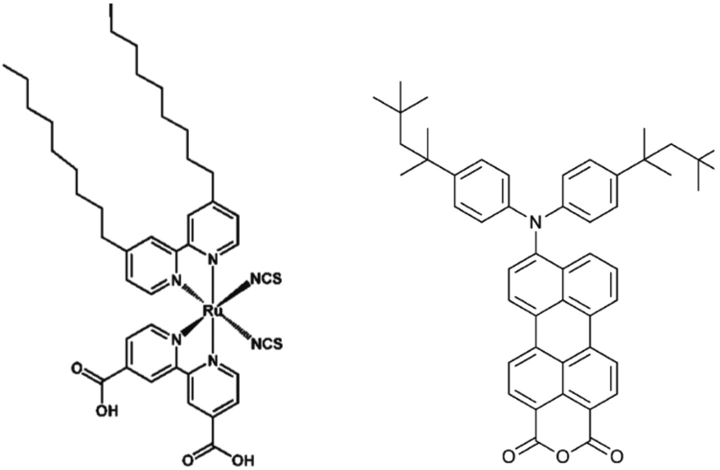


Figure 3.19: The ruthenium based sensitizer Z907 and organic perylene sensitizer ID28.

4. Summary of the results

During many years unique spectrometers and radiation sources have been developed at our department and applied to the investigation of matter. The work in this thesis is dedicated to the further development of electron spectroscopic techniques with a focus on the possibilities for X-ray based time resolved studies with improved element specificity.

Paper I reports on the development of a new XUV source for time resolved measurements. It describes the high harmonic generation laboratory HELIOS, the design and first measurements of its performance.

Paper II shows how to modulate the time structure of existing X-ray sources. It reports on the development and realization of a synchronized chopper system which was use for time of flight spectroscopy (TOF) in combination with a magnetic bottle analyzer. The paper also include laser pump – X-ray photoelectron spectroscopy probe (LPXPS) measurements utilizing a hemispherical electron analyzer.

The work in paper III was performed in order to develop possible preparation techniques for well defined interfaces. In combination with the methodologies in paper I and II, this demonstrates how future time resolved X-ray photoelectron studies can be used to obtain atomic scale dynamic information on functional interfaces.

In paper IV measurements based on hard X-ray excitation is implemented for obtaining atomic scale information in the valence structures. These new opportunities demonstrate that further variation in the energies of the X-rays can be efficiently used for improved element specificity in the valence region as well as for probing bulk structures.

4.1 High harmonic generation

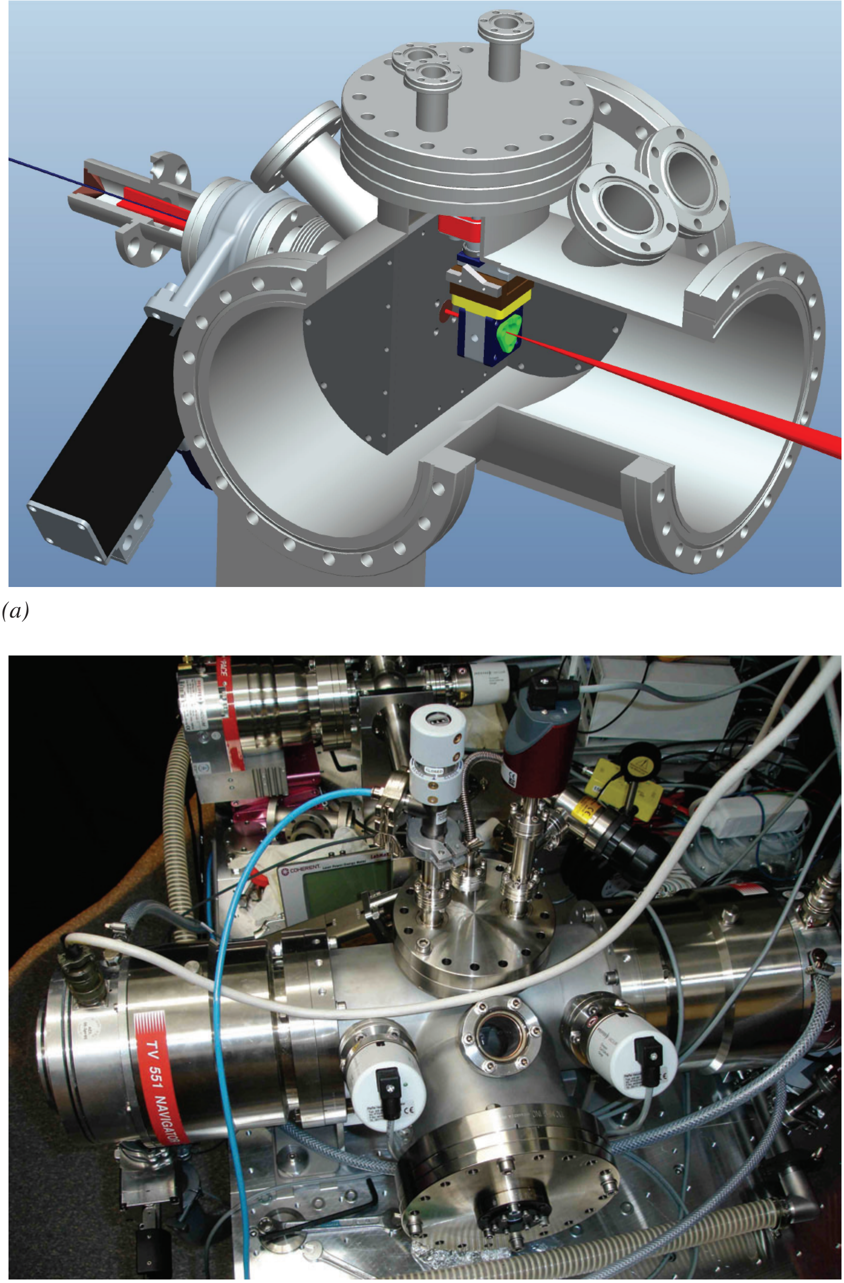
The work on high harmonic generation in this thesis has been aimed at the design of the HELIOS laboratory for time-resolved spectroscopy. It was designed to provide the user with femtosecond XUV radiation in the photon energy range between 15-100 eV at an energy resolution of better than 300 meV. For pump-probe experiments wavelengths between 240 nm and 20 μm can be chosen for the pump pulse.

The system main parts are a gas cell for the generation of the harmonics, an off-plane mount grating monochromator followed by a collimating stage and two beamlines which can be equipped with a number of different end-stations. These subparts are described below.

The HHG generation chamber including the gas cell is shown in figure 4.1. The gas cell consists of two replaceable metal plates functioning as entrance and exit "windows". The assembly is mounted on a translational stage in order to align the cell in the propagation direction of the fundamental beam. The laser drills optimal size holes into this plates which typically are about 100 μm in diameter. The generation chamber itself is split up into two sections which are separated by a solid wall with a third laser drilled metal plate working as a self aligning differential pumping aperture. After realignment of the laser path due to for example damaged optics, these metal plates are easily replaced and the focused beam machines new apertures in the right place. Both parts of the chamber are pumped by 550 L turbo-molecular pumps. Typical pressure readings are listed in Table 4.1.

Table 4.1: *Pressure readings at different Ar pressures in the gas cell. The HHG chamber (stage 1), differential pumping stage (stage 2), detector chamber*

gas cell pressure	pressure stage 1	pressure stage 2	detector chamber pressure
10 mbar	$3 \cdot 10^{-4}$	$5 \cdot 10^{-7}$	$7 \cdot 10^{-8}$
60 mbar	$1 \cdot 10^{-3}$	$3 \cdot 10^{-6}$	$9 \cdot 10^{-8}$
200 mbar	$>1 \cdot 10^{-3}$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-7}$



(a)

(b)

Figure 4.1: (a) A cut through the generation chamber; (b) A photograph of the generation chamber.

For the monochromatization we decided for an off-plane mount grating monochromator setup shown in figure 4.2. As described in section 3.3.4 the first mirror collimates the light and is thereafter diffracted by the grating. The following mirror focuses the radiation onto the exit slit where the energies are distributed over a cone and can be selected by rotating the grating. Energies between 15-100 eV can be chosen by the insertion of different gratings. First experiments are done with a gold coated 60 grooves/mm grating which is optimized for 27 eV. The recorded spectrum shows H15 to H21 in first, second and third order diffraction (Fig. 4.3).

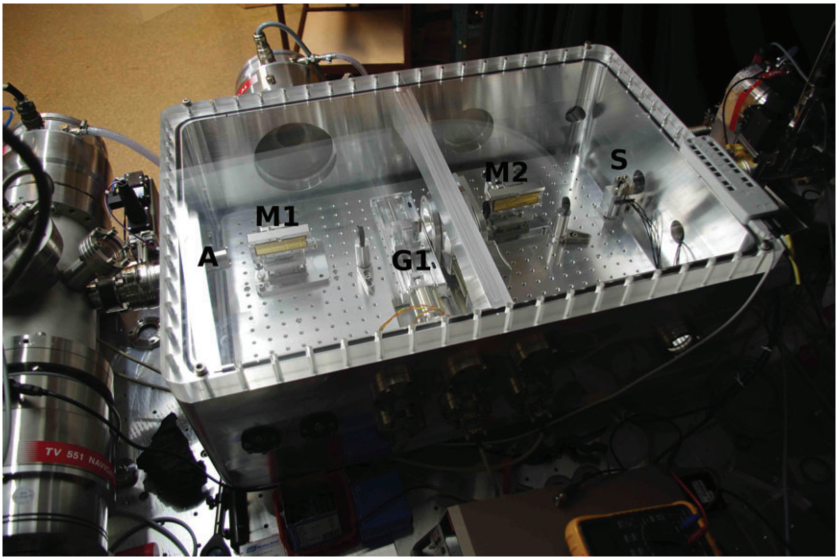


Figure 4.2: The off-plane grating monochromator. (A) entrance aperture, (M1) collimating mirror, (G1) grating, (M2) focussing mirror, (S) exit slit.

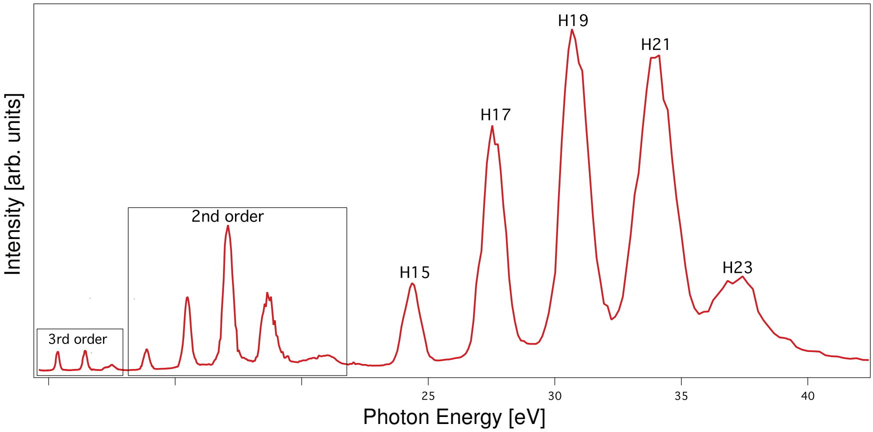


Figure 4.3: The spectrum shows H15 to H23 in first, second and third order diffraction from a grating with 60 grooves/mm.

For the measurement of the spectrum shown in figure 4.3 the exit slit was set to 20 micrometer and two aluminum filters were used in order to block the fundamental beam. The radiation was measured with a XUV photo diode (SXUV100, IRD-inc) and a Keithley picoamperemeter. With the monochromator set to the 19th harmonic a maximal flux of $1.2 \cdot 10^{10}$ photons/second was measured which corresponds to $2.5 \cdot 10^{10}$ photons/second from the source due to the limited transmission of the aluminum filters.

A collimation stage is planned after the monochromator in order to send a parallel beam towards the refocusing mirror. This might seem unnecessary but was chosen in order to get the most versatile beamlines for the users. The refocusing mirrors are designed to have 400 and 600 mm focal length in the gas phase and surface station respectively. According to numerical raytracing a focal size of below 20 micrometer in the gas phase beamline will be possible.

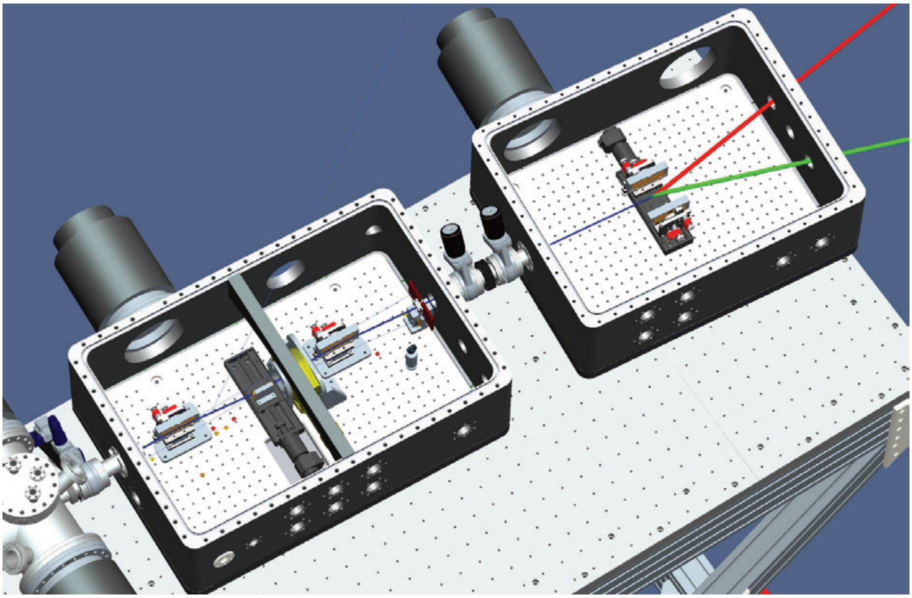


Figure 4.4: The HHG generation chamber (left), the monochromator (middle) and the collimator (right) are shown.

4.2 X-ray beam chopper

The chopper system presented in paper II was implemented to modulate the time-structure of an existing X-ray source. It is designed, manufactured and implemented to TOF spectroscopy and LPXPS. By compromising two sets of apertures on one disc assembly, which is directly mounted on the axis of a servo motor, it is able to provide the user with repetition rates from about 5 kHz to 120 kHz. The system is mounted with its rotational axis parallel to the propagation direction of the X-ray pulses and the repetition rate can be chosen by moving the wanted set of apertures into the beam. Figure 4.5 shows the mounted chopper system at beamline U49PGM2 at BESSY-II in Berlin.

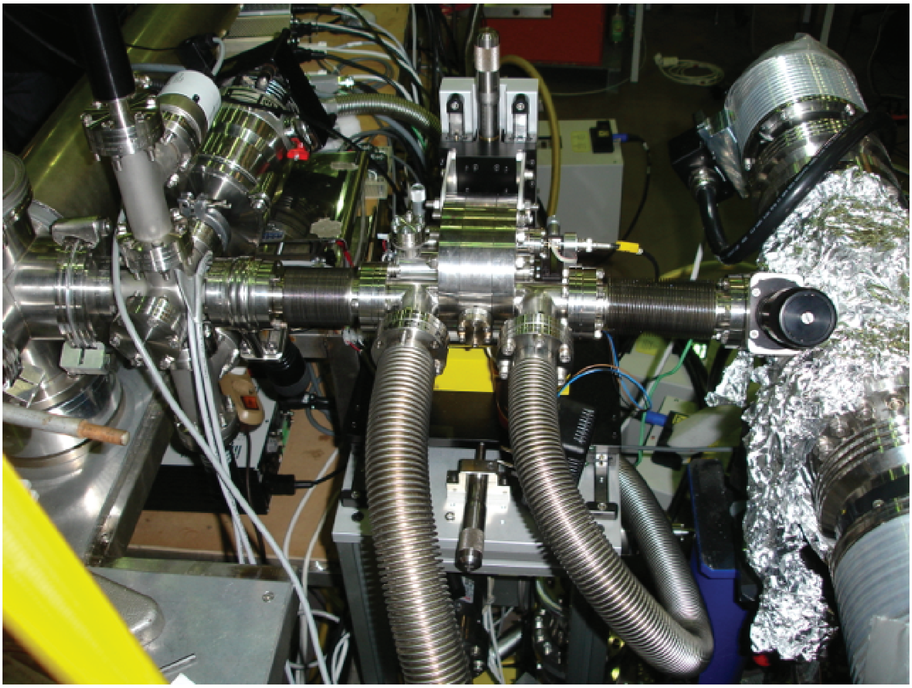


Figure 4.5: The chopper system mounted between the exit slit (right) and experimental setup (left).

The system was shown to work synchronized to the RF frequency of the synchrotron radiation source BESSY-II and transmitted frequencies of 9.747 kHz ($\frac{RF}{128}$) and 78.06 kHz ($\frac{RF}{16}$). The transmitted frequency shows that the system is phase locked with an accuracy of more than 99% (table 4.2).

Figure 4.6 shows the comparison of the TOF spectra of Kr triple ionization measured with and without the beam chopper system. A major reduction of the background is achieved and a new structure, which is assigned to be of ^{2}p character, is revealed.

Table 4.2: *X-ray intensities and transmitted frequencies recorded for different operation conditions of the chopper system.*

	fixed slit	15 slit circle	120 slit circle
applied integer divider	–	128	16
theoretical transmitted f [kHz]	1249.138	97.59	78.07
transmitted f_{trans} [kHz]	1249.138	9.747	78.06
phase lock stability [f/f_{trans}]	–	0.9988	0.9999
transmitted intensity	15 nA	0.12 nA	0.95 nA
15 nA / transmitted intensity	1	125	15.8

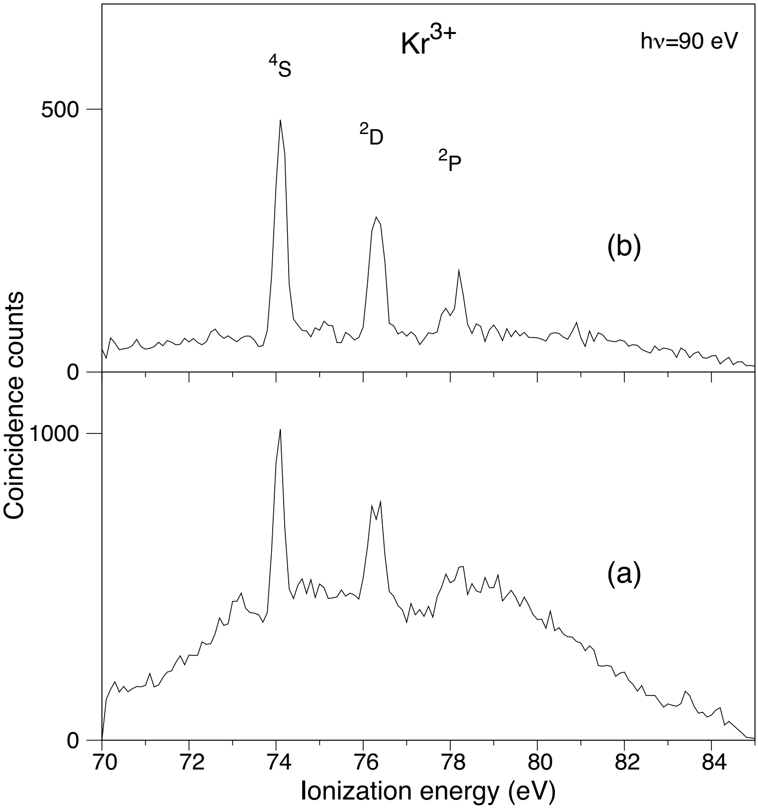


Figure 4.6: The Kr triple ionization spectra recorded with (b) and without (a) the chopper system.

A second achievement of this system was the utilization of laser pump – X-ray photoelectron spectroscopy. In these experiments the system was used to modulate either the semi continuous radiation of MAX-II or the continuous light of a high intensity helium discharge lamp in our home lab.

In both cases a 532 nm pulsed laser system was triggered by a signal generated in the chopper system in order to perform pump-probe experiments with variable time delays. Figure 4.7 shows the spectra recorded at 5 kHz repetition rate and a visible light pump energy of 8 μJ. The spectra where recorded at beamline I411 of the MAX-II storage ring with a photon energy of 60 eV [25, 26]. Similar results were obtained in experiments with a helium discharge lamp as a radiation source.

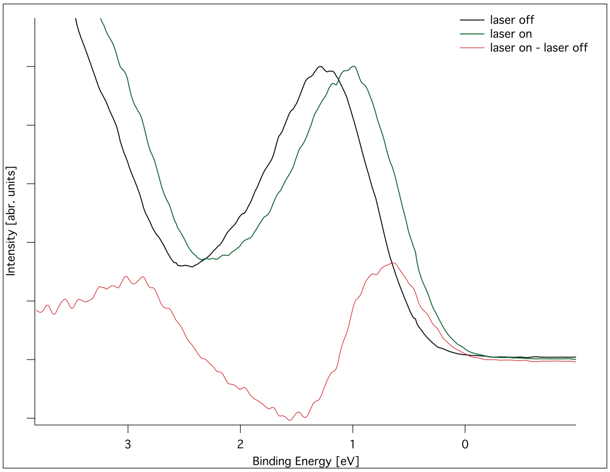


Figure 4.7: The valence spectra of a nanoporous TiO_2 electrode sensitized with the ruthenium based dye-molecule 520DN.

4.3 Preparation and investigation of solar cell related materials under UHV conditions

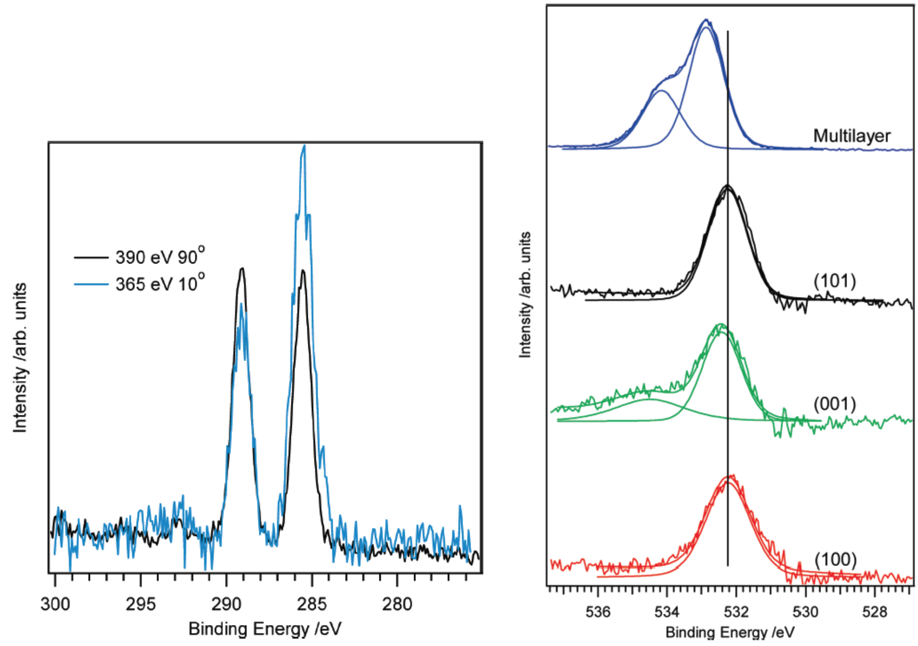
Fundamental understanding of processes in applied systems often relies on studies of well defined systems. One important part of the implementation of new spectroscopic instrumentation is therefore the development of sample preparation techniques, especially of well defined systems. Ultra pure sample preparation under ultra high vacuum conditions is one possibility to achieve this. In paper III such an approach is developed and demonstrated.

The linker group in the organic molecule maleic anhydride (MA) is used as binding group in a number of organic dye molecules [27, 28, 29] and was therefor used here to better understand the binding configuration to TiO_2 as well as possible preparation techniques. The three anantase TiO_2 (101), (100), (001) single crystal surfaces were prepared under UHV conditions and investigated by XPS and NEXAFS. Preparation in UHV condition has the advantage of high control over the material composition with very limited effects from contamination. However, this environment puts constraints on means for preparation and it is important to develop sample specific procedures including sputtering, annealing and evaporation.

In paper III the single crystal surfaces were treated by 20 min Ar sputtering at 1 keV and afterwards annealed at 770 K under the presence of 10^{-6} O_2. The structure of the surfaces were investigated by LEED and subsequently investigated with respect to contamination by electron spectroscopy. After the surfaces were found to be clean a submonolayer of MA was deposited at room temperature by means of an adjustable leak valve. In a later stage a multilayer was deposited and used as a reference and to prove that the molecule was evaporated without decomposing.

Figure 4.8 shows the C1s and O1s spectra of the adsorbed molecules and a multilayer. The intensity and chemical shifts demonstrate that the molecule was successfully evaporated and adsorbed to the surface. The angle dependence in the C1s spectrum together with the comparison of the multilayer and the submonolayer in case of the 101 surface allows for two conclusions. The molecule adsorbs to the surface by a ring opening at the middle oxygen atom and stands right up with the two carbon atoms sticking away from the surface as illustrated in figure 4.9.

These experimental data and the proposed binding geometry is in good agreement with theoretical data and the overall understanding of the surface attachment of the light absorbing molecules containing similar binding groups. This work demonstrates one usable scheme of cleaning and restructuring anatase TiO_2 surfaces and the deposition of small molecules which can be used for future experiments with the developed HHG source or LPXPS at synchrotron facilities.



(a) *(b)*

Figure 4.8: (a) C1s spectra of a submonolayer of MA adsorbed onto anatase TiO_2 (101); (b) C1s spectra of a submonolayer of MA adsorbed onto anatase TiO_2 (101).

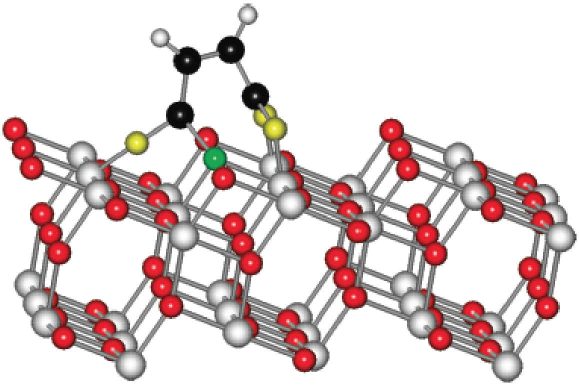


Figure 4.9: Illustration of the suggested molecular structure of maleic anhydride adsorbed onto anatase TiO_2 (101). The green oxygen atom shows the one shared with the surface.

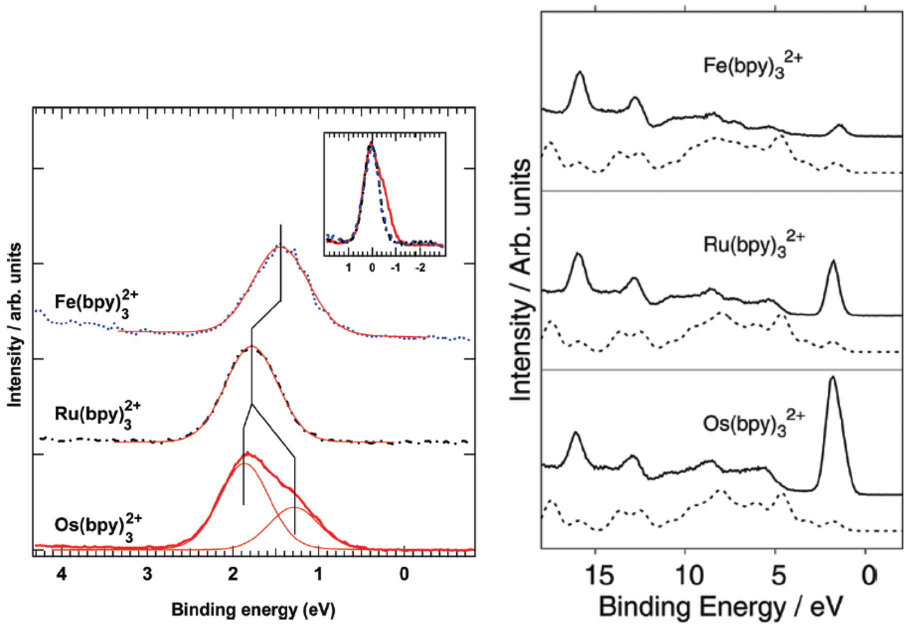
4.4 Hard X-ray photoelectron spectroscopy

The main theme in this thesis is techniques and application of electron spectroscopy based on novel X-ray sources. This is demonstrated in paper IV were the implementation of hard X-ray allows for studies of a broader range of resonance processes and also to obtain improved element specificity in the valence level structure.

Specifically, hard X-rays were used for the investigation of three ex-situ prepared multilayers consisting of $Fe(bpy)_3^{2+}$, $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$. Measured at electron kinetic energies of about 2800 eV the mean free path of the escaping electrons is in the range of 5 nm, which implies that the contribution from layers lying deeper than 5 nm from the surface is in the range of 40%. Thus the surface signal is strongly suppressed and the data can be interpreted as information on the bulk structure.

Another advantage of such high photon energies is the difference in photoemission cross section between metal atom and lighter atom orbitals. Thereby spectral contributions from the metal centers of the molecules are enhanced while carbon and nitrogen contributions are suppressed. Figure 4.10 shows the valence spectra of the investigated compounds measured at 2800 eV. The peak below 4 eV binding energy can be assigned to the metal center and the experiments demonstrate how hard X-ray can be used to follow the metal partial density of states in the valence region. The different intensities of the lowest binding energy peak depends on the difference in photoemission cross section for Fe, Ru and Os. The structures above 4 eV are mainly from the carbon atoms in the molecule and as observed in Figure 4.10b these contributions are very similar for the different samples.

Figure 4.11 illustrates the effect of resonant excitation using hard X-rays. By tuning the radiation to 2841 eV, electrons from the $Ru2p_{3/2}$ are excited to the unoccupied valence states with Ru character. As can be seen in figure 4.11 the feature at 2 eV binding energy is strongly enhanced by measuring with 2841 eV photon energy with respect to off-resonance excitation at 2800 eV and 2850 eV which verifies the Ru4d character of this peak.



(a) *(b)*

Figure 4.10: (a) a comparison between the experimental (full) and calculated density of states (dashed); (b) the highest occupied valence electronic structure of the three compounds.

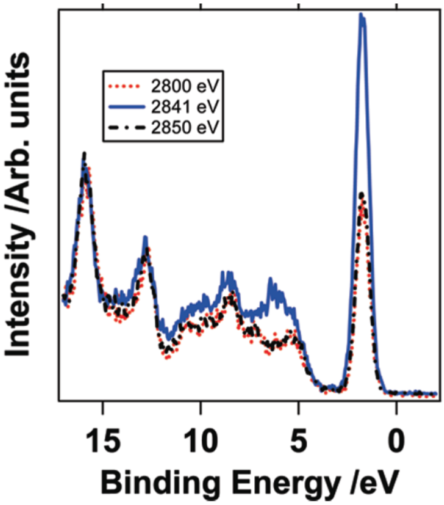


Figure 4.11: Valence band structures of Ru(bpy)$_3^{2+}$ measured at 2800 eV, 2841 eV and 2850 eV.

5. Outlook

As described above the main focus of my thesis work has been on the development off novel instrumentation for X-ray based spectroscopy. In the future I would like to continue with this work and below I describe some thoughts and plans for future development of HELIOS and the X-ray beam chopper system as well as possible experiments.

5.1 The HELIOS laboratory

After the first performance test of the source and monochromator the latter will be equipped with additional gratings in order to allow the user to choose different energy intervals with high efficiencies. The design goal is still to get an energy resolution of about 300 meV while keeping a pulse length comparable with that of the fundamental pulse. However, low energy resolution gratings such as the one of the first measurements will also be used in order to get the maximum intensity from one harmonic.

The next step in the construction of the HELIOS laboratory is the commissioning of the collimator and the beamlines. This will take place in the first half of 2012.

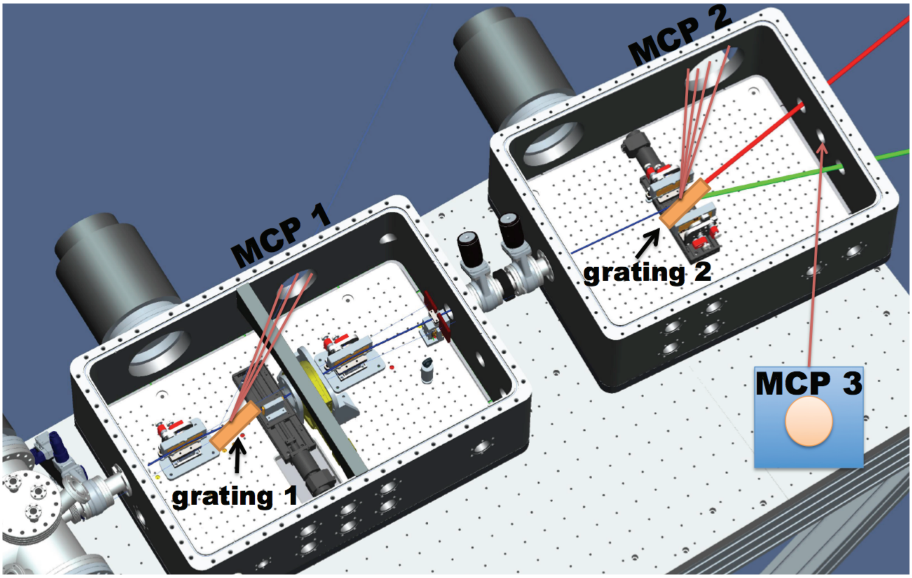


Figure 5.1: The figure illustrates the planned grating and detectors.

Both the monochromator and the collimator chamber will be equipped with gratings mounted in standard orientation dispersing the energies on a MCP detector. One detector will be located between the entrance mirror and the off-plane grating to allow for a direct analysis of the radiation from the gas cell (Fig. 5.1 grating 1, MCP 1). This real time monitoring will be of huge advantage when adjusting the critical parts of the source like gas pressure, lens position and iris opening which controls the laser intensity. The second detector, located in the collimator chamber, will use the exit slit as a source and be very helpful while aligning the monochromator or measuring the actual energy resolution prior to an experiment (Fig. 5.1 grating 2, MCP 2). A third MCP detector will be located in the beam path of the radiation transmitted by the exit slit (Fig. 5.1 MCP 3). This will be used to directly analyze the beam divergence and circularity in order to optimize the monochromator optics.

A more general approach for the future of HELIOS will be to aim for higher photon energies in order to reach deeper core levels and to vary the probe depth in photoelectron spectroscopy. Higher repetitions rates are desirable for experiments where too high intensities lead to problems with space charge, or spectroscopic techniques where only one electron per X-ray pulse can be handled by the detector system (e.g. Scienta ARTOF). Experiments demanding a high photon flux will benefit from higher repetition rates as well.

The list of possible experiments is long and the following examples are meant to indicate what could be done.

In the surface since end-station one very well suited sample for pump-probe experiments are dye-sensitized solar cell interfaces. The widely used unsensitized TiO_2 electrode can directly be excited by wavelengths below 350 nm to investigate the electron excitation dynamics from the valence to the conduction band.

For the solar cell application, the adsorbed dye-molecule can be excited over the full range of visible light into the infrared. This can give important insight into the absorption, excitation and injection processes as well as into the unwanted recombination between electrons in the conduction band of TiO_2 and the dye-molecule.

Another interesting possibility for new experiments is related to studies of liquid jets. A liquid jet which is directly shot into the vacuum chamber has a diameter of about 20 micrometer, nicely matching that of the HHG photon beam. This is surrounded by the vapor originating from the liquid jet. In order to probe the liquid and not the vapor the focal size has to be of the same size or smaller than the liquid beam. Interesting samples here are e.g. dye-molecules in solution in order to reveal the molecular dynamics of the dissolved single molecules.

Moreover, magnetic materials is a further area of great interest where the dynamics may be analyzed with pump-probe techniques using the present HHG source.

5.2 X-ray beam chopper

The versatility of the chopper allows it to be combined with many X-ray sources including a He lamp (Fig. 5.3) or synchrotron radiation source in the hard X-ray regime. The system as presented in paper II is on a regular basis used for time of flight spectroscopy with a magnetic bottle analyzer at BESSY-II in Berlin. In a current development this research group combines the measurement of electrons and ions. The latter are forced by a pulsed high voltage source to travel towards the detector. Due to limitations of this high voltage supply to frequencies of about 10 kHz the application of a synchronized low repetition rate chopper system is crucial.

A second part of the development is the combination of surface sensitive pump-probe experiments as described in paper II with a bulk sensitive pump-probe technique (Fig. 5.2). One sample group which would benefit from this would be dye-sensitized solar cells. These dye-molecule TiO_2 interfaces are usually made with a transparent electrode on a supporting glass (Fig. 3.16) which opens up the possibility for these experiments. An initial experiment on these interfaces is described in paper II where the sample was excited by a visible pulsed laser (laser one) and probed by means of photoelectron spectroscopy. To this spot on the sample a second continuous wave laser (laser two) could be aligned. Due to the transparency of the interface this light can penetrate through the sample and be picked up by a photodiode detector on the back side. When a pulse from laser one excites the sample the dye-molecules change their absorption curve which either leads to an enhanced absorption or an enhanced transmission of laser two, which can be monitored by the photodiode detector. In an advanced version, laser two could be exchanged to a white light source and the photodiode detector with a visible light spectrometer in order to measure the difference of the absorption curve simultaneously and combine this data with the surface sensitive photoelectron information.

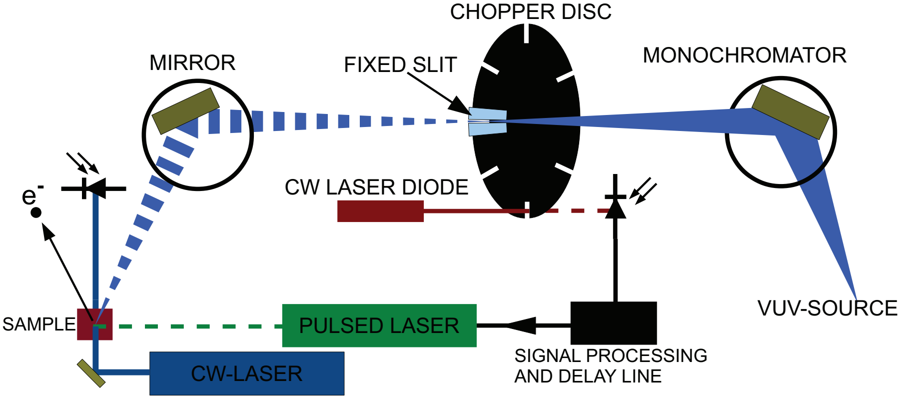


Figure 5.2: The figure illustrates the combination of surface sensitive laser pump - VUV probe experiments with the bulk sensitive transient absorption measurements.

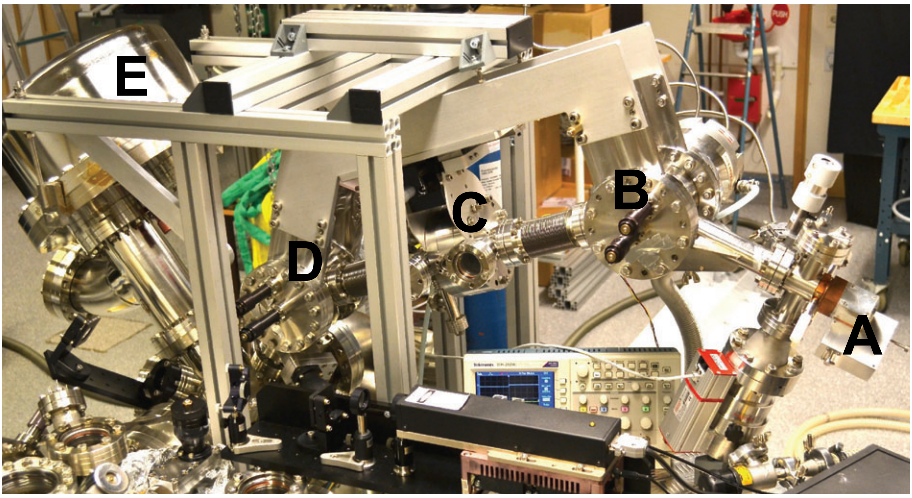


Figure 5.3: The photograph shows the chopper system implemented in combination with a He gas discharge lamp and a SES100 photoelectron spectrometer. (A) UV-lamp, (B) monochromator, (C) chopper system, (D) refocussing mirror, (E) photoelectron analyzer

Sammanfattning

I fysiken finns det två komplementära vägar att gå. Den ena är att med hjälp av olika teorier simulera hur ett system beter sig när man t.ex. belyser detta med röntgenstrålning. Ett annat sätt är att bygga ett modellsystem (ett prov) i labbet och observera hur systemet beter sig när man belyser detta med t.ex. röntgenstrålning. Det senast nämnda kräver instrumentering som är anpassat till den speciella problemställningen man vill undersöka. Det här arbetet är till stor del ägnat åt utveckling av instrumentering för röntgenljus baserad på spektroskopi med inriktning mot så kallade tidsupplösta studier.

Den största andelen av arbetet har varit utvecklingsarbetet i samband med HELIOS laboratoriet. HELIOS, som står för "High Energy Light Induced Overtone Source", är en källa som utnyttjar omvandlingen av mycket starkt laserljus i en gas till röntgenljus. I vårt fall använder vi argon och en pulsad infraröd laser med en våglängd på 800 nanometer (nm). Laserljusets våglängd (färg) ligger nära det synliga området som sträcker sig från 400 nm till 770 nm. Röntgenljuset som skapas har våglängder mellan ungefär 10 nm och 80 nm vilket brukar betecknas som vakuumultraviolett. Eftersom röntgenljusets våglängder har en bred fördelning krävs det en monokromator som väljer ut ett väl bestämt våglängds område som sedan leds vidare till en experimentuppställning för användning vid mätningar. Figure 5.4 visar monokromatorn som utvecklats för att göra detta i HELIOS laboratoriet.

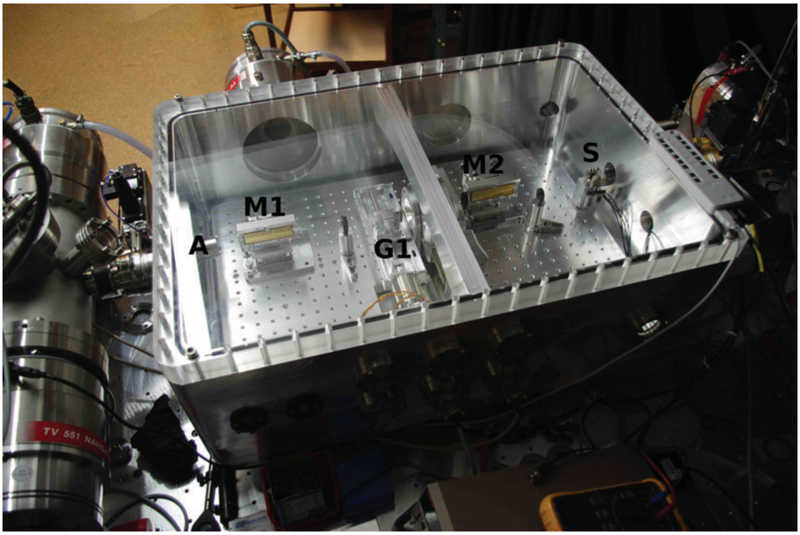


Figure 5.4: Biden visar monokromatorn som utvecklades i samband med HELIOS. M1 och M2 är guldbelagda speglar, G1 ett optiskt gitter och S exit slitten.

Den väl bestämda röntgenstrålningen kan t.ex. användas för att undersöka elektronstrukturen i olika material som gaser, vätskor och fasta ämnen. Eftersom strålningen är pulsad kan man följa vad som händer i provet på en tidsskala. Ett exempel kan vara en solcell som precis har absorberat solljus. Efter en sådan händelse kan man, som med en filmkamera, ta flera bilder för att på molekylär nivå följa vad som händer med den absorberade energin. Det bör nämnas att röntgenstrålning absorberas mycket starkt i luft och att källan, monokromatorn såväl som experimentet är inbyggda i vakuumkammaren.

Det andra utvecklingsprojektet som jag varit delaktig i är utvecklingen av en så kallad "X-ray beam chopper". Den består av en mycket snabb roterande titanskiva med en jämn fördelning av öppningar i form av små utfräsningar. Sätter man in skivan i strålgången av en röntgenkälla så kan ljuset bara passera när en öppning kommer förbi. Skivan är 104 mm i diameter och roterar med upp till 1000 varv per sekund. Med sina 120 respektive 15 öppningar kan den släppa igenom 15000 och 120000 ljuspulser per sekund.

Chopper systemet används idag regelbundet på synkrotronljusanläggningen BESSY-II för att kontrollera repetitionsfrekvensen av ljuspulserna som annars kommer med 1.25 millioner pulser per sekund. Genom att bara släppa igenom ungefär var tionde ljuspuls blir röntgenstrålningen betydligt lämpligare för våra experiment och gör det möjligt att mäta förlopp som inte går att mäta med en högre frekvens på ljuspulserna. Illustration 5.5 visar hur chopperstystemet reducerar frekvensen på ljuspulserna och därigenom anpassar upprepningshastigheten till experimentets krav.

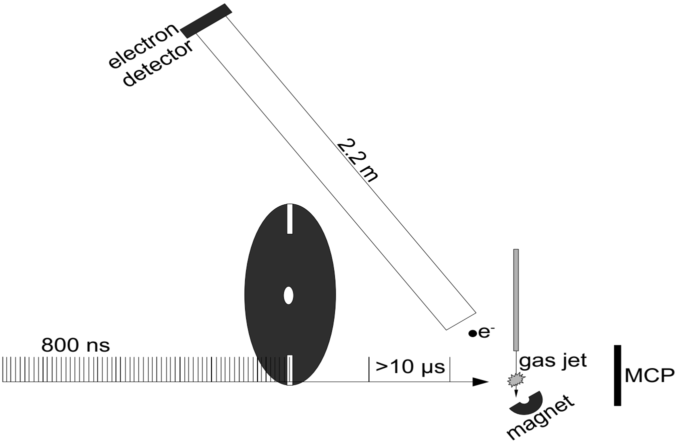


Figure 5.5: Figuren visar schematisk hur upprepningshastigheten av ljuspulserna anpassas till experimentets krav.

Parallellt med utvecklingen av röntgenkällor för tidsupplösta studier innehåller avhandlingen utveckling av experiment där man använder röntgenljus med mycket hög energi. I sådana experiment kan man få en förbättrad atomär förståelse av processer i funktionella material. För att kunna göra väldefinierade experiment behövs inte bara en förstklassig experimentuppställning utan även processmetoder för att syntetisera väldefinierade prover. Avhandlingen innehåller även experiment där provpreparering utvecklas.

Målsättningen med de experimentella utvecklingsarbetena är dels att undersöka nya fysikaliska fenomen. En annan målsättning är att förbättra applikationer som redan finns utvecklade till att fungera effektivare och stabilare. Arbetet som beskrivs i denna avhandling demonstrerar detta genom experiment på molekyler som kan få oss att bättre förstå omvandlingen av ljus till elektrisk energi i molekylära solceller. Specifikt möjliggör utvecklingen som beskrivs i avhandlingen en utökad förståelse för vad som sker när elektroner transporteras mellan material för att bygga upp en elektrisk potential. Vidare kan man med den nya tekniken följa de förlustprocesser som sker i sådana molekylära solceller på atomär nivå och därmed finna metoder för att förbättra dessa solcellers stabilitet och effektivitet.

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