

# **CRG Report MBI-BESSY-Beamline U125/1-SGM**

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Preamble.....	3
1. Technical status .....	4
1.1 Properties of the monochromator .....	4
1.2 Properties of the Laser systems .....	4
1.3 Endstation for photoemission experiments at solid surfaces .....	6
1.4 Endstation for photoemission experiments at liquid jet surfaces.....	6
2. Financial and human resources .....	6
2.1 Beamline maintenance and user support.....	6
3. Usage of beamline .....	8
4. Research activities.....	8
4.1 Overview.....	8
4.2 Technical achievements .....	9
4.3 Electronic excitation at semiconductor surfaces .....	10
4.4 PTCDA (perylene-tetracarboxylic dianhydride) .....	11
4.5 Sexithiophene (6T) .....	11
4.6 Sexiphenyl (6P).....	12
4.7 Porphyrazine .....	12
4.8 Azobenzene alkanethiol self-assembled monolayers.....	13
4.9 $\beta$ -carotene.....	13
4.10 Liquid water .....	13
4.11 Salt aqueous solutions .....	13
4.12 Activities on other beamlines based on the expertise gained at the MBI beamline.	14
4.13 Highlights from non-CRG users at the beamline .....	14
5. Future developments .....	14
5.1 Technical improvements .....	14
5.2 Research plan for the next two years .....	15
5.3 Long-term future .....	16
6. Appendices.....	16
6.1 List of own publications .....	16
6.2 List of 2000-2002 presentations at conferences and seminars from work done at the MBI-BESSY beamline .....	18
6.3 PhD theses and calls for professorship.....	21
6.4 Research activities of non-CRG users.....	22
6.5 References for Laser-Synchrotron radiation experiments from other groups.....	26

## Preamble

The success and the advances in time-resolved Laser spectroscopy using visible and near-IR radiation have inspired further demand for time-resolved X-ray and EUV spectroscopy techniques. Several strategies, as e.g., the use of Laser higher harmonics or Laser plasmas have been applied. Alternatively, Synchrotron radiation (SR) which already has been widely used as primary radiation for high-resolution X-ray and EUV spectroscopy techniques, can be combined with synchronized Laser pulses. 3rd generation Synchrotron radiation sources provide SR pulse widths sufficiently short to investigate dynamic processes in the time domain of ca. 30 ps up to 1  $\mu$ s. Due to the increasing interest in time-resolved techniques, particularly in view of future UV and X-ray Free-Electron-Laser experiments many Synchrotron centers worldwide are now setting up or planning experiments for combined Laser and SR.

Already in 1991, when the German Science Council recommended the foundation of the „Institute for Nonlinear Optics and Short Pulse Spectroscopy“ (the present Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy im Forschungsverbund Berlin e.V., short MBI) it referred explicitly to the potential of combined experiments with Laser and Synchrotron radiation which would become possible by establishing both, the MBI and BESSY II in Berlin Adlershof\*.

The research activities and research program of the MBI-CRG ( presented here, focus on establishing the basis for experiments with combined Laser and Synchrotron radiation (SR). This includes time-resolved photoelectron spectroscopy on the basis of the intrinsic SR pulse structure (pump-probe spectroscopy) as well as the spectroscopy of Laser-excited electronic states and processes. To achieve this, versatile Laser systems which meet the requirements for different applications need to be synchronized to the SR pulses. Finally, the unique research opportunities of combined Laser and SR experiments should be easily accessible to the scientific community. To achieve this an operation as user facility had to be established. This facility is embedded within the European IHP "Access to Large Scale Infrastructures" programme.

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\* Aus "Stellungnahmen zu den außeruniversitären Forschungseinrichtungen der ehemaligen Akademie der Wissenschaften der DDR auf den Gebieten der Physik", 1991:

Bei der Übernahme der im ZOS mit Hilfe laserspektroskopischer Methoden bearbeiteten wissenschaftlichen Themen sollte die thematische Vielfalt merklich eingeschränkt werden. Bevorzugt sind solche Themen aufzugreifen, die die Weiterentwicklung spektroskopischer Methoden befruchten und ihre Möglichkeiten optimal nutzen. In diesem Zusammenhang begrüßt der Wissenschaftsrat die Bestrebungen der Berliner Elektronenspeicherring Gesellschaft für Synchrotronstrahlung (BESSY) und des Landes Berlin, die Synchrotronstrahlungsquelle BESSY II auf dem Forschungsgelände in Adlershof zu realisieren. Auf die führende Stellung der Bundesrepublik auf vielen Gebieten der Atom- und Molekülphysik sowie der Materialforschung durch die Verfügbarkeit hochwertiger Synchrotronstrahlungsquellen hat der Wissenschaftsrat bereits hingewiesen. Da die Spektroskopie im Vakuum-UV und weichen Röntgengebiet bei hoher spektroskopischer, räumlicher und zeitlicher Auflösung der wesentliche Schwerpunkt bei BESSY II sein wird, würden sich die beiden Institutionen sowohl bei den wissenschaftlichen Fragestellungen als auch in methodischer Hinsicht wechselseitig ergänzen. Darüberhinaus könnten neuartige Experimente (Studium angeregter Zustände) in der Atom-, Molekül-, und Festkörperphysik durchgeführt werden, für die die kombinierte Anwendung von Laser- und Synchrotron- bzw. Undulatorstrahlung erforderlich ist.

## 1. Technical status

The MBI-BESSY beamline located at the undulator U125/1 consists of a spherical grating monochromator (SGM) which covers an energy range from 15 to 180 eV (details see Tab. 1).

In contrast to the SX-700 concept, translation and rotation of the plane mirror in front of the grating are independent variables in the MBI beamline design. This makes the MBI design far more demanding regarding the control of the mirror movement and therefore the time to set the photon energy much longer.

Two different experimental endstations (surface science and liquid jet apparatus) can be served by switchable refocusing optics. Due to the spatial requirements of the two experimental endstations the exit slit is imaged approx. 2-times magnified onto the sample. Two Laser systems (a tunable Ti:Sapphire Laser and a Nd:YVO<sub>4</sub> Laser operating at repetition rates of 83, and 1.25 MHz; details see Tab. 2) can be synchronized to either the SR multi bunch or the single bunch pulses.

### 1.1 Properties of the monochromator

Tab.1: Properties of the MBI-BESSY beamline

General Features	two spherical gratings & moving plane mirror <b>two toroidal refocusing mirrors for two endstations</b>
Energy Range	<b>15 eV –180 eV</b> *
Flux	4·10 <sup>12</sup> Photons/s·0.1A @ 64 eV, 200 μm exit slit
Resolution	<b>6000 @ 64 eV</b>
Spot Size	450 μm × 250 μm (exit slit: 100 μm) *
Polarization	<b>linear</b>
Higher Harmonics	<b>&lt;1% (with Al-window &lt;0.1%)</b>

The suppression of higher harmonics to <0.1% is important for spectroscopy of excited states to reduce the background signal.

### 1.2 Properties of the Laser systems

Two Laser systems - a tunable Titanium Sapphire Laser and a Vanadate Laser system (presently optimized for two wavelengths) - are available. They operate at repetition rates of 83, and 1.25 MHz; respectively and can be synchronized to either the SR multi bunch or the single bunch pulses. For details see Tab.2.

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\* See 5. for Future developments.

Tab. 2: Features of the Laser systems

	<b>Ti:Sapphire</b>	<b>Nd:YVO<sub>4</sub></b>
Wavelength	720-950 nm, SHG: 360-475nm	1064 nm, SHG: 532 nm
Pulse width	4 ps or 150 fs	14 ps
Pulse energy	Fundamental: 25 nJ/pulse SHG: 6 nJ/pulse	Fundamental: 200 nJ/pulse SHG: 100 nJ/pulse
Repetition rate	83.3 MHz	25 MHz, pulse picked: 1.25 MHz
Size of focal spot	100 $\mu\text{m}$ $\varnothing$ *	100 $\mu\text{m}$ $\varnothing$ *

The uniqueness of the properties achieved at the MBI-BESSY beamline for combined Laser and SR experiments can be seen by comparison with other SR beamlines world wide (Tab. 3). Note also some earlier pioneering experiments, both synchronized and non-synchronized as listed in 6.5.

Tab. 3: Properties of Combined Laser-Synchrotron Radiation experiments world wide

<b>Facility</b>	<b>SR</b>	<b>Laser</b>	<b>Time resolution</b>	<b>Recent publications****</b>
NSLS, Brookhaven	8-10 eV	6 kHz	5-20 ns	[L1,L2]
ESRF, Grenoble	5-40 keV	900 Hz, 35 $\mu\text{J}$	150 ps	[L3-L9]
APS, Argonne	8-10 keV	1 kHz, 10 $\text{mJ}/\text{cm}^2$	90 ps / 11 ns	[L10-L15]
ALS, Berkeley	1.8-12 keV, bending magnet	1 kHz, 12 $\text{mJ}/\text{cm}^2$	100 ps; 300 fs ***	[L16-L22]
Super-ACO, Lure	~130 eV	FEL, 345-355 nm	500 ps	[L23-L27]
ELETTRA, Trieste		UV-FEL 190 nm	no two-color exp.	[L28-L30]
UVSOR, Japan	2.5-300 eV	10-300 kHz, 10 $\mu\text{J}$ , 300 ps, and 80 MHz	1.5 ns	[L31-L34]
SLS, Switzerland	combined Laser SR experiments planned			--
<b>MBI-BESSY</b>	<b>20-180 eV</b>	<b>83, 25, 1.25 MHz; 10-200 nJ</b>	<b>30-60 ps**</b>	[QBW98,WGQ98 Wid02,WWH03W WW03,PWF03W WS03,WBG03G WB03]

\* Focal spot size of the Lasers has been adjusted to the present Synchrotron spot size; minimum Laser spot size 10 $\mu\text{m}$ .

\*\* Time resolution 2-5 ps planned.

\*\*\* By time-slicing technique which reduces photon flux typical by a factor of 10<sup>6</sup> to 10<sup>7</sup>.

\*\*\*\* For references see Appendix 6.5.

The properties of the MBI-BESSY beamline offer unique experimental conditions with respect to repetition rate and time-resolution. With respect to time-resolution the bunch-slicing technique (which is presently under development at BESSY in collaboration with the MBI) is superior; however, with the SR photon flux being reduced by orders of magnitude only very selected experiments will be possible.

### **1.3 Endstation for photoemission experiments at solid surfaces**

This setup has been designed for angle-resolved photoelectron spectroscopy and consists of an UHV analysis chamber equipped with a hemispherical electron analyzer (EA125, Omicron, home built detector readout for time-resolved electron detection) which is rotatable around the SR beam axis, a X-ray source (DAR15, Omicron), a VUV source (HIS13, Omicron). Additionally, several diagnostic tools within the analysis chamber (fast x-ray photodiode, pinhole, and fluorescence detector) are available for combined Laser and SR experiments. An UHV preparation chamber equipped with a 4-grid reverse view LEED/AES (ErLEED, VSI), an ion source (IS2000, VSI) and an evaporator (EFM3, Omicron), a Knudsen cell and a loadlock chamber for sample transfer is connected via a long-travel manipulator. The sample (temperature range: 120 K – 1500 K) has the following degrees of freedom: x- and y-translation:  $\pm 12.5$  mm, z-translation:  $\sim 550$  mm, rotation around the surface normal:  $\pm 90^\circ$ , tilt:  $\sim 110^\circ$  and the rotation around the Synchrotron beam axis.

### **1.4 Endstation for photoemission experiments at liquid jet surfaces**

To enable photoelectron spectroscopy at surfaces of highly volatile liquids as, e.g., water or aqueous solutions, a second endstation which can generate a free liquid jet of 6  $\mu\text{m}$  diameter in a high vacuum environment ( $10^{-5}$  mbar) has been setup in collaboration with the Max-Planck-Institut für Strömungsforschung, Göttingen. Using liquid- $\text{N}_2$  cold traps to dump the jet and differential pumping techniques between the jet and the SR beamline as well as between jet and the detector, sufficient vacuum conditions can be maintained to establish an effective photoelectron spectrometer with a dispersive energy analyzer. It is now possible to analyze photoelectrons emitted from laminar flowing liquid surfaces with all the potential of a third generation SR source (presently for photon energies up to 130 eV) in combination with Laser excitation. To our knowledge this is a unique experimental setup at SR-sources worldwide.

## **2. Financial and human resources**

### **2.1 Beamline maintenance and user support**

For the support of beamline users, the development and the maintenance of the beamline (including the Laser systems) the MBI operates presently a research group with 2-3 postdoctoral researchers, two PhD students and two technicians dedicated for Laser and UHV maintenance. For additional support on small repairs and services a mechanical engineer is available. When needed, the MBI workshop as well as the EDV service of the MBI can be used.

For defining, choosing, modifying and setting up the Laser systems extensive use was made of the expertise and manpower available in the MBI Laser groups. These experts will also be available according to future demands at the beamline, e.g. for new developments or for the unlikely event of major malfunctions with the present equipment.

## 2.2 Experimental endstations, expenses

Tab. 4: Expenses

	<b>Acquisition value 1995-2003 (EUR)</b>	<b>Manpower at BESSY 2000-2003 (man month)</b>	<b>Funding</b>
Beamline	1.080.000	60	MBI
Monochromator optics and control	433.000	50	MBI
Laser systems Ti:Sapphire / Verde and Nd:YVO <sub>4</sub>	330.000	60	MBI
Photoemission Endstation	400.000	37.5*	BMBF (05 650BMA 6)
Endstation for levitated nanoparticles	96.000	36	BMBF (05 KS1 BMA)
Monochromator modifications 2003**	239.000	10	MBI

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\* (between 1997-2000)

\*\* See 5. for Future developments.

### 3. Usage of beamline

Tab. 5: Allocated beamtime in weeks

Year	Group	Duration [weeks]
<b>2000</b>	Leising* (TU Graz, Austria), Koch (U Princeton, USA)	3
	Faubel (MPI für Strömungsforschung)	4
	Schütz (U Würzburg)	2
	CRG (MBI)	14
<b>2001</b>	Faubel (MPI für Strömungsforschung)	2
	Schütz (U Würzburg)	4
	Zahn (TU Chemnitz)	2
	CRG (MBI)	16
<b>2002</b>	Schütz (MPI für Metallforschung Stuttgart)	5
	Richter, Esser (TU Berlin)	2
	Pietsch (U Potsdam)	2
	Wurth (U Hamburg)	1
	Johansson* (U Karlstad, Sweden)	2
	CRG (MBI)	20
<b>2003 (-06)</b>	Johansson* (U Karlstad, Sweden)	2
	Wurth (U Hamburg)	2
	Galan* (U Madrid, Spain)	2
	CRG (MBI)	10

### 4. Research activities

#### 4.1 Overview

The scientific results of the CRG users are divided into i) the investigation of electronic excitations at semiconductor surfaces, ii) results on the electronic structure of large organic molecules in thin films, and iii) results on the electronic structure of liquid water surfaces and solvated ions. A large amount of these research activities was focused on combined Laser and SR photoemission experiments or on photoemission studies of potentially interesting systems for such two-photon photoemission experiments. But there are also results of photoemission experiments from liquid water surfaces, which until now have not involved Laser excitation. Since the latter studies explore a completely new field of research it was necessary to first

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\* Supported in the frame of the EU-IHP Access to Large Scale Infrastructures Programme

understand the spectroscopic information from one photon photoelectron spectroscopy before the more complex 2 photon processes are attempted.

It is important to note that the scientific results are strongly related to the necessary technical developments for Laser-SR pump-probe or single-pump multiple-probe experiments. This includes also dedicated non-commercial detector concepts, and experiment software for efficient use of the Synchrotron radiation intensity and for the possible future use of amplified Lasers with low repetition rates. The latter might be required in order to achieve larger pulse energies (see 5. for Future developments).

## 4.2 Technical achievements

For single bunch experiments a specially designed Nd:YVO<sub>4</sub> Laser system has been installed in September 2001. It operates at 25 MHz repetition rate, can be pulse picked to 1.25 MHz (pulse width 14 ps) and is synchronized to the revolution frequency (1.25 MHz) of a single electron bunch in the Synchrotron storage ring. The time delay between Laser and SR can be controlled electronically in the 0 to 800 ns range and additionally in the 0 to 3 ns range by an optical delay line. Both, Laser fundamental as well as the second harmonic generated in a periodically poled crystal, 1064 and 532 nm, respectively, have been used in experiments. The overall time resolution of the experiments is about 60 ps which is the length of the SR pulse (in single bunch). It has been measured by SFG cross correlation in a BBO crystal using collinear Laser and white light SR as shown in Fig. 1.

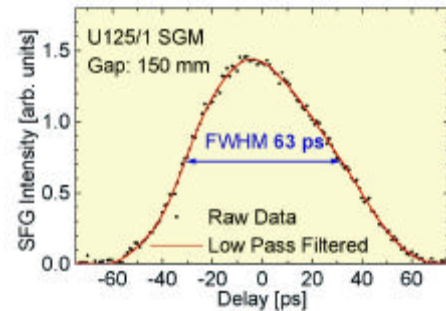


Fig. 1: SFG cross correlation between the 1.25 MHz Nd:YVO<sub>4</sub> Laser pulses and a Synchrotron white light component in a BBO crystal.

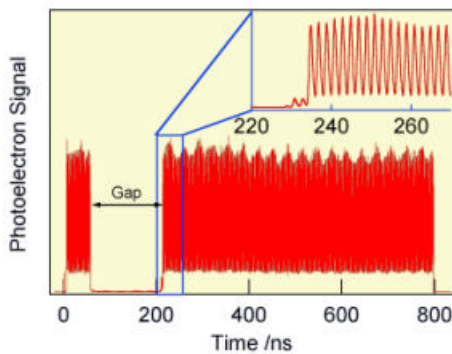


Fig. 2: Time-resolved SR photoemission signal at the exit slit of an energy-dispersive analyzer.

shows the time-resolved photoelectron probe signal at the exit of a 125 mm radius hemispherical energy analyzer triggered at the electronic SR bunch marker. Within the 800 ns bunch revolution time the non-uniform filling structure of the SR storage ring with a dark period of about 150 ns is clearly visible in the photoemission signal. Furthermore the signal from consecutive bunches, with a time interval of 2 ns, can be well separated as shown in the inset. Such a detection of individual bunches increases the overall time-resolution, which is limited by the SR pulse length only, by two orders magnitude. The success of this single-pump multiple-probe technique now enables efficient Laser-SR experiments in the more

To overcome the special need of single bunch operation (available only four weeks per year), a single-pump multiple-probe setup either uses the Nd:YVO<sub>4</sub> Laser operating at 25 or 1.25 MHz repetition rate or a Ti:Sapphire Laser system (modified MIRA system) with a repetition rate of 83 MHz. Successful application of the single-pump multiple-probe scheme requires the separation of photoelectrons originating from two adjacent SR pulses, i.e.  $\Delta t = 2$  ns. Although this is trivial for light detection, it needs special considerations for photoelectron detection due to the much longer time-of-flight of electrons through a energy-dispersive analyzer. Figure 2

common multi bunch injection mode with a higher flexibility as to the choice of Laser repetition rates (see 5. for Future developments).

### 4.3 Electronic excitation at semiconductor surfaces

The time-resolved charge carrier surface recombination at SiO<sub>2</sub>/Si(100) surfaces has been investigated by combined Laser-SR pump-probe photoelectron spectroscopy at the Si 2p core level. Charge carriers are generated by a Laser pulse and the temporally excited sample, characterized by a dynamic surface photo voltage, is probed with core level photoemission. Two different timing techniques have been used: i) Classical Laser-pump SR-probe photoelectron spectroscopy with Laser and SR (in single bunch mode) both operating at repetition rates of 1.25 MHz, and ii) the single-pump multiple-probe scheme suitable for the SR 500 MHz repetition rate in multi bunch mode using time-resolved photoelectron detection.

The recombination dynamics at the SiO<sub>2</sub>/Si(100) interface after Laser excitation at 532 nm can be followed by the core level shift as a function of the Laser-pump SR-probe delay. It shows a non-exponential decay in *time* as is shown in Fig. 3 (a) and (b) on a ps and ns time scale, respectively. Data for thinner oxide layers on Si(100) exhibit smaller shifts and faster decays. However, in all cases the data can be described by a decay rate, which depends exponentially on the absolute *peak shift* (dynamic band bending) with an initial fast and subsequent decelerating decay as indicated by the solid line. Note that the dynamics of the onset (at negative time delays) stems from the long-range interaction of the outgoing photoelectron with the time-dependent electric field in front of the sample.

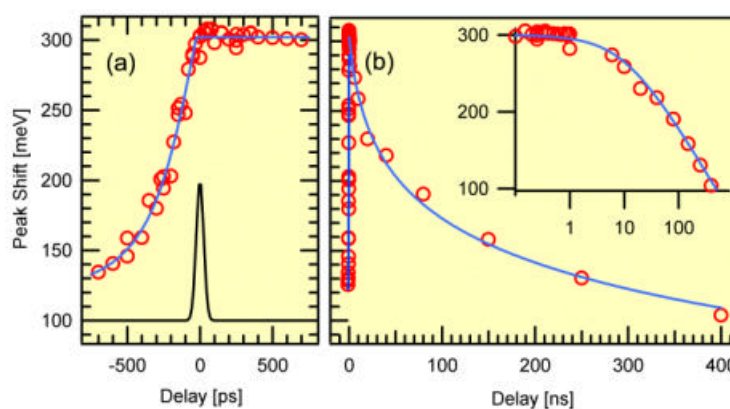


Fig. 3.: Si 2p Core level shift for a 15Å thick SiO<sub>2</sub>/Si(100) surface as function of the Laser-pump Synchrotron-probe delay on a ns and a ps time scale, (a) and (b), respectively. The inset in (a) display the same data on a logarithmic time scale. The Gaussian-like curve in (b) indicates the temporal resolution of the experiment.

Dynamic changes of the surface photovoltage are common at semiconductor surfaces and for organic thin films (see below). Therefore, their understanding is important for any further time-resolved photoelectron spectroscopy.

Concerning the electronic structure of organic thin films, the focus has been on vacuum-sublimated thin films of conjugated organic materials due to their interest with respect to developing optical and electronic devices, but also because of their fundamental physical properties. Specifically, thin films of sexiphenyl (6P), tris-(8-hydroxy quinoline) aluminium (Alq<sub>3</sub>), sexithiophene (6T), perylenetetracarboxylic dianhydride (PTCDA), and different porphyrazine molecules have been investigated. These studies include the preparation of the systems, sometimes also the synthesis, morphology, photostability, film charging during photoemission, coupling between molecule and substrate. The long-term goal is to characterize the electronic structure of optically excited molecules by photoelectron spectroscopy in order to address various aspects of photon-induced processes. So far the combined Laser SR photoemission experiments revealed only in one case (PTCDA) indications of optically excited molecular states, whereas for all other systems the excitation densities were too low to be detectable (see 5. for Future developments).

For porphyrazine thin films the interest has been on the interaction (charge transfer processes)

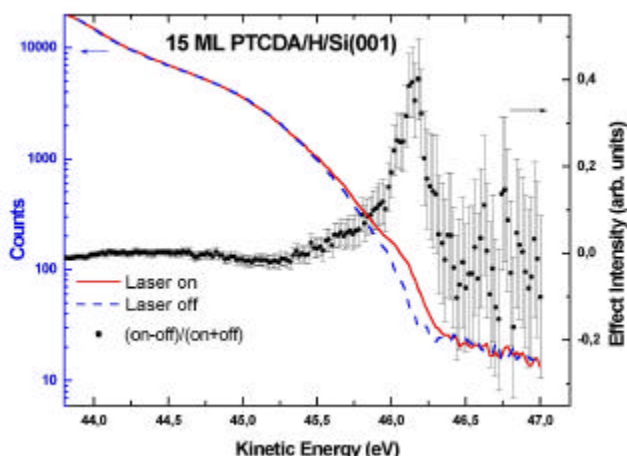


Fig. 5: UPS spectra of a 15 ML thin film of PTCDA on H-passivated Si(001) with (solid) and without (dashed) Laser excitation at 532 nm on a logarithmic scale. The normalized difference  $\epsilon$  is shown with error bars.

of a central metal atom with the surrounding organic ligand system. Azobenzene alkanethiol self-assembled monolayers (SAMs) have been investigated with focus on the evolution of the electronic structure if the terminating azobenzene-group is transformed from *trans*- to *cis*-conformation by Laser irradiation. For thin films of  $\beta$ -carotene which is an example for a biological system (pigment-protein complex), it was demonstrated that thermal deposition on an Au single crystal under UHV conditions combined with photoelectron spectroscopy, may provide valuable information on a system relevant for photosynthesis.

#### 4.4 PTCDA (perylene-tetracarboxylic dianhydride)

A combined Laser Synchrotron radiation pump-probe photoemission study on thin organic films of perylene-tetracarboxylic dianhydride (PTCDA) on hydrogen-passivated Si(001)-(2x1) surfaces has been performed in collaboration with the group of Prof. L. Johansson, Karlstad University, Sweden. Two Laser-induced features could be identified for a 15 monolayer thick film. Upon Laser excitation at 532 nm which corresponds to the  $S_1[0-0]$  transition a new Laser-induced photoemission peak about 2.5 eV above the highest occupied molecular orbital (HOMO) of PTCDA has been observed. For the experimental conditions used the intensity of this feature is about  $10^{-3}$  of that of the HOMO. Additionally, a rigid shift of the photoelectron spectra of 0.12 eV to smaller kinetic energies is interpreted as a Laser-induced surface photovoltage shift. Its dynamic behavior can be seen from the time-dependent intensity at a fixed binding energy (corresponding to edge of the HOMO) as demonstrated in Fig. 6. As mentioned above, understanding the dynamics of the surface photovoltage will be important for the analysis of excited-state photoemission spectra. The measurements presented here have been performed using the single-pump multiple-probe technique in SR multi bunch mode. A decay rate of about 125 ns has been estimated for the shift.

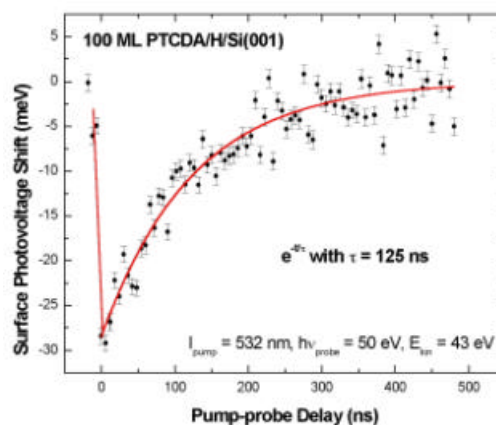


Fig. 6: Surface photovoltage shift for a thick PTCDA film upon Laser excitation at  $t = 20$  ns.

#### 4.5 Sexithiophene (6T)

Thin films of oligothiophenes have high application potential within organic light-emitting devices. Their optical properties can be tuned by the number of thiophene units within the molecule with respect to several properties, e.g. the light absorption maximum. Additionally, they are known to grow highly ordered on hexagonally close-packed metal surfaces. Here the growth of 6T on the missing-row reconstructed Au(110)-(1x2) surface has been studied by LEED and ARUPS to investigate if well-oriented (single-domain) thin films can be grown on

the one-dimensional Au(110) surface which would be particularly attractive for spectroscopic studies on excited molecular states. The existence of well-ordered adsorbate phases in the low coverage range (<3 ML) on Au(110) could be determined by LEED. Even for films of about 100 ML thickness, the molecular orientation with respect to the substrate is partially maintained as indicated from the pronounced azimuthal dependencies seen in ARUPS. However, by atomic force microscopy a rather inhomogeneous long range film structure has been found with a strong tendency for growth of narrow crystallites. Experiments with combined Laser and SR pulse excitation demonstrated that rather low-power Laser irradiation very efficiently compensates for charging of thick 6T films. This increases the energy resolution of all spectral features and improves the signal background near the LUMO pump-probe signal. It is interesting to note that the Laser-induced spectral shift (band bending or decharging) depends on the sample azimuthal orientation.

#### 4.6 Sexiphenyl (6P)

Intense Synchrotron irradiation causes a loss of conjugation in thin films of 6P as evidenced by an intensity decrease of delocalized  $\pi$ -orbitals (HOMO, HOMO-1) in the valence photoemission spectra. The observed spectral changes are ascribed to the occurrence of bond breaking and/or cross-linking within the organic material. Photo-damaged films also exhibit considerable steady-state surface charging, which may be compensated by Laser pulse irradiation as in the case of 6T. This is due to electron-hole creation which increases the film's conductivity. This method of increasing the conductivity appears to provide an appreciable means to get around problems associated with surface charging. Notice that the Laser tool may be much better suited than electron flooding (flood gun often used in photoemission from non-conductive samples), the latter being more destructive. For 6T thick films (see above) Laser irradiation is in fact necessary for obtaining well-resolved photoemission spectra.

#### 4.7 Porphyrazine

The electronic structure of tert-butyl- or phenyl-substituted metal-free, Cu-, and Zn-porphyrazines (-tetraazaporphyrin TAP, -phthalocyanine Pc, -naphthalocyanine Nc, -anthracyanine Ac) thin films deposited on gold substrates has been studied by valence band photoemission and resonant photoemission. Information on the initial electron charge transfer in the organometallic system and also on the re-distribution of charge during the photoemission process could be extracted. By comparing the Cu- and Zn-porphyrazines photoemission spectra with those of the corresponding metal-free compounds, metal contributions have been identified. A resonant enhancement of the copper and zinc satellite peaks near 75.3 and 91.7 eV binding energy, respectively, could be investigated in detail. Differences of the photoemission satellite to main line intensity ratio as a function of ligand size could be interpreted in terms of the ionicity of the metal-nitrogen bond in these molecules. The underlying charge transfer is proposed to correlate with the size of the inner  $C_8N_8$  ring of the molecule, which depends on both the central metal and the extension of the ligand. As a function of the ligand size, the energetic position of the HOMO shifts to lower binding energies for the metal-free porphyrazines which agrees with theoretical predictions.

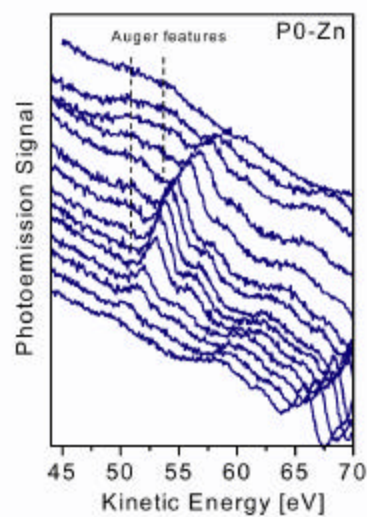


Fig. 7: Resonant photoemission spectra for the organic compound zinc tetra(tert-butyl) porphyrazine for photon energies in the range of 87 (bottom) to 99 eV (top).

#### 4.8 Azobenzene alkanethiol self-assembled monolayers

Photoelectron spectra from CF<sub>3</sub>-azobenzene-terminated alkanethiol SAMs have been studied (in collaboration with the group of L. Brehmer, U Potsdam) with emphasis on a photoinduced *trans-to-cis* isomerization of the azobenzene unit. Due to the orientational order of the molecules within the films, as indicated by the pronounced angle dependence of the photoemission spectra, it is possible to identify Laser-induced optical switching of the molecules using combined Laser and SR pulses. Molecular switching upon Laser irradiation at 360 nm, i.e. photoisomerization, has been recognized by relative intensity changes of the photoemission peaks and also by spectral shifts to higher binding energies. These shifts result from a change of the molecular dipole moment (size and orientation) associated with the *trans-cis* Laser-induced photoisomerization of the azobenzene-CF<sub>3</sub> group. An increase of the SAM free volume is found to facilitate isomerization. This is inferred from the nonlinear behavior of the energy shifts as a function of the azobenzene thiol density.

#### 4.9 $\beta$ -carotene

Photoelectron spectra of carotenoids are known for gas-phase molecules or for rather poorly defined samples containing solvent residuals only. Since in carotenoids the lowest energy optical transition is symmetry forbidden, a combination of valence band photoemission and NEXAFS have been necessary to determine the binding energies of the HOMO and the LUMO for vacuum-sublimed  $\beta$ -carotene thin films. From the resulting ionization energy and the core transition to the lowest  $\pi^*$  orbital, the energy of the first excited singlet state S<sub>1</sub> of  $\beta$ -carotene has been estimated. The optically dark S<sub>0</sub>-S<sub>1</sub> transition has been determined at 650 nm.

#### 4.10 Liquid water

Using a micron-sized liquid jet valence band photoemission spectra from liquid water have been measured in the 30-120 eV photon energy range (in collaboration with M. Faubel, MPI Göttingen). The spectra exhibit differential energy shifts as well as peak broadening relative to the corresponding gas-phase features. These differences are of multiple origin, including bond contraction induced by hydrogen bonding, electronic polarization, and surface dipoles. The 1b<sub>1</sub> derived valence band center is located 11.20 eV below the vacuum level and has a width of 1.49 eV. The binding energies of the subsequent valence orbitals, 3a<sub>1</sub>, 1b<sub>2</sub> and 2a<sub>1</sub>, are 13.61, 17.38 and 30.94 eV, respectively. Largest peak width, ca. 2.7 and 3.2 eV, are observed for the a<sub>1</sub> symmetry orbitals 3a<sub>1</sub> and 2a<sub>1</sub>, respectively. Weak but distinctly structured emission features at constant binding energies, superimposed on a broad background, arise from photoelectron energy losses in the liquid with the loss channels corresponding to the optical absorption of liquid water. The effect is most clearly observable for 18 eV energy losses of 2a<sub>1</sub> photoelectrons. Relative photoionization *partial* cross sections of the molecular orbitals of liquid water have been determined in the 60 to 100 eV photon energy range. As compared to gas-phase water molecules, the relative intensity of the 3a<sub>1</sub> orbital is substantially decreased. This is attributed to molecular orbital changes due to H-bonding and can be interpreted in terms of variations of the respective anisotropy parameters  $\beta_i$ .

#### 4.11 Salt aqueous solutions

Electron binding energies well above threshold ionization have been determined for the anions and the cations of aqueous alkali-metal halide solutions for the first time. Systematic studies of different counter ions in moderately concentrated aqueous salt solutions, XI or XCl (X = Li, Na, K, Cs, Ca), show no effect on the anion binding energy. Similarly, the sodium cation binding energy is identical for the small iodide counter ion and the spatially more extending Na<sub>4</sub>[Fe(CN)<sub>6</sub>] counter ion. The results imply that the solvation shell structures must be almost identical for the ions studied, and there is negligible interaction between solvated

anions and cations. Experimental binding energies of aqueous ions fairly well agree with the Gibbs free energies of solvation (as calculated within the Born continuum model). For NaI solutions a nonlinear (sublinear) increase of the photoemission intensity with concentration has been found near the saturation concentration. This is interpreted as relative ion depletion near the surface due to destabilization of the solvation complexes. Tetrabutylammonium iodine, But<sub>4</sub>NI, easily segregates at the water surface due to the hydrophobic butyl chains. It is thus particularly interesting to study the surface segregation layer by the inherently surface-sensitive photoelectron spectroscopy. Enrichment of the But<sub>4</sub>NI salt at the water surface was confirmed by a ca. 30-time increase of the I(4d) signal as compared to a NaI aqueous solution where ions are rather uniformly dispersed in the bulk. The completed segregation layer (electric double layer), which corresponds to a *single* surface monolayer of salt anion and cation pairs, can be identified by a constant iodide signal and a constant water signal depletion with salt concentration. The effects are not as pronounced for the shorter, less hydrophobic tetrapropylammonium iodide, Prop<sub>4</sub>NI. For both salt solutions the uniform spectral shifts of the photoemission spectra as a function of the concentration is largely attributed to work function changes associated with the molecular dipole within the segregation layer. Dehydration effects of near-surface ions have not been observed.

#### **4.12 Activities on other beamlines based on the expertise gained at the MBI beamline**

The results of a research project in collaboration with the group of H. Dürr, BESSY, on time-resolved (upon Laser excitation of polarized conduction electrons) magnetic x-ray dichroism of a diluted magnetic semiconductor, MnGaAs, which is closely related to the research of the CRG group are not described here in detail since the experiment has been performed at a different (circularly polarized) beamline. However, it facilitates the MBI Laser setup and synchronization electronics for combined Laser-SR experiments developed for the MBI-BESSY beamline.

#### **4.13 Highlights from non-CRG users at the beamline**

Details of the research activities by non-CRG users are given in the appendix 6.4.

### **5. Future developments**

#### **5.1 Technical improvements**

The unique possibilities of combined Laser-SR photoemission experiments at the CRG beamline still suffer from low Laser excitation densities as some of the presented scientific results indicate. Higher Laser excitation densities can be achieved by either a decrease of both the Laser and SR spot sizes or by an increase of the Laser pulse energy. Both routes (30x40  $\mu\text{m}^2$  spot size and amplification of the Laser systems) are planned at the MBI-BESSY beamline, which will increase the excitation density by three orders of magnitude.

##### **5.1.1 Modifications of the monochromator and focusing**

As result of a detailed discussions with BESSY scientists on the necessary improvements of the beamline, which will also extend the energy range from 20 to 600 eV and increase the resolving power up to 100.000 (or lower resolution at increased flux), a modified PGM concept (as developed by R. Follath; design report 19. Sep. 2002) has been favored. It consists of the existing U125/1-PGM beamline with exchanged refocusing optics. All required optical elements are being ordered and will be installed in the next shut-down period at the end of 2003. This new concept will overcome all SGM-based limitations (see section 1). In particular it will give a significantly improved focus, hence allowing for about a factor of 100 enhancement of the target excitation density. Expansion of the wavelength range will allow

e.g. to use inner shell excitation e.g. at the carbon K-edge for efficient structural studies after Laser excitation (see 5.2).

### **5.1.2 Further Laser development**

The amplification of the Nd:YVO<sub>4</sub> Laser with a cw diode-pumped amplifying chain is planned for 2004 (based on a design by F. Noack and V. Petrov, MBI). It will result in a 10-20 times higher pulse energy (2-4  $\mu$ J).

A further development which will be possible with the higher Laser intensity then available is to establish tuneability of the Laser radiation within the visible spectral range by optical parametric methods – thus extending the flexibility of the beamline setup substantially.

With setting up the single-pump multiple-probe photoemission technique, further increase of the pulse energies has become possible by using synchronized Laser systems with significantly reduced repetition rates (but comparable average power).

### **5.1.3 Making the Laser systems generally available**

As first successful experiments have shown (see 4.12) activities on other beamlines will profit from the know-how with combined Laser Synchrotron experiments gained at this beamline as well as from sharing the Laser systems available. One important aspect of the future work on the Laser systems will therefore focus on making the Laser systems easily portable and available for other beamlines. This will – at least partially – already be established with the major beamline changes planned for the shut down period end of 2003/beginning 2004 (see 5.1.1).

### **5.1.4 Making use of advanced temporal structures at BESSY**

In close contact with the management of BESSY, it is planned to combine the Laser-SR photoemission experiments with the unique and just recently at BESSY characterized feature to operate the Synchrotron storage ring in a special 'low- $\alpha$ ' mode. This mode allows for SR pulse widths down to 2 ps as compared to typical 30 or 60 ps in multi- or single-bunch operational modes, respectively. However, up to now the Laser pulse duration was matched in an optimal manner to the 30 ps SR pulse duration. The shorter pulse duration will require corresponding reduction of the Laser pulse length, which can be achieved without problems with the Ti:Sapphire Laser (not with Vanadate Laser system) but will require some further equipment.

## **5.2 Research plan for the next two years**

The experiments of the MBI group will concentrate on combined Laser-SR photoemission studies of the electronic structure of long-lived excitations at solid and liquid surfaces, adsorbates and thin films. One focus will be on thin films of organic molecules with extended  $\pi$ -electron systems which are of importance regarding fundamental aspects as well as for opto-electronic applications. This continues some of the ongoing work. With the improved experimental setup (extended energy range, higher excitation densities), the methods which will be used to study the Laser-excited systems are ARUPS, high-resolution XPS, and NEXAFS. ARUPS will be used to investigate the symmetry and orientation of electronically excited states for oriented species. XPS can be used to probe the local element-specific changes of the electronic structure. It is planned to use NEXAFS to address the changes of the unoccupied states, to study directly the Laser-depleted states, and the orientation of organic molecules upon Laser-excitation (e.g. as important in molecular switches). Additionally, where details of the structure of the Laser-excited species around a specific chemical element is important photoelectron diffraction (PED) might be applied. The organic molecules will be

preferentially studied in orientated thin films (as e.g. growth structure induced by the substrate) on metal, semiconductor, and oxide single crystal surfaces.

A second focus will be on long-lived surface states at semiconductor and oxide surfaces. The lifetime and dispersion of excited surface states can be studied momentum-resolved (e.g. in the case of Si(001)-(2x1) lifetimes in the order of 100 ps are expected) by applying ARUPS upon Laser excitation from bulk states or occupied surface states into unoccupied states. These experiments had been proposed earlier but failed due to the limited Laser excitation. However, with the higher excitation densities these experiments seem possible.

A third focus will be devoted to combined Laser-SR photoemission experiments on the free liquid water (or aqueous solution) jet. One possible target involves aqueous triiodide. In recent photoemission experiments the aqueous triiodide complex has been studied, which is formed in solution through the equilibrium reaction  $I^- + I_2 \rightleftharpoons I_3^-$ . Each species could be identified by its I 4d binding energy. Following femtosecond Laser excitation (approx. 300 to 400 nm), triiodide dissociates and about 50% of the fragments recombine (due to solvent caging) via different processes. These temporal phases are characterized by time scales of about 2, 45, and 350 ps. The temporal appearance and characterization of the fragment species upon Laser excitation will be studied by time-correlated core-level photoemission.

### 5.3 Long-term future

The goal of the present CRG activity is to enable combined Laser-SR photoemission experiments for a wider user community. This should be achieved by the combination of the local expertise of both institutes, MBI and BESSY within the next two years. When the planned modifications (see 5. for Future developments) at the beamline have been carried out, a breakthrough in the Laser-Synchrotron two-photon photoelectron spectroscopy on solid and liquid surfaces is expected. The experiment will then be optimized in terms of performance reliability and convenient user handling.

At this point the MBI intends to fully open this beamline to the BESSY user community, which implies that the present MBI CRG status changes to a regular user status. However, the teams knowledge will even in future be available for the users of the MBI beamline. Future MBI-BESSY activities will focus on experiments involving significantly shorter time scales (fs), for instance the time-slicing and FEL projects performed in cooperation with BESSY.

## 6. Appendices

### 6.1 List of own publications

**QBW98 Excited-state photoemission with combined Laser/Synchrotron pulse excitation from C-60 chemisorbed on Ni(110)**

T. Quast, R. Bellmann, B. Winter, J. Gatzke, and I. V. Hertel; *J. Appl. Phys.* 83, 1642-48 (1998).

**GWQ98 MBI facility at BESSY II for time-resolved pump probe techniques with Laser and undulator radiation**

J. Gatzke, B. Winter, T. Quast and I. V. Hertel; in *Proceedings of the conference on time structure of x-ray sources and its applications*, (SPIE - The International Society for Optical Engineering, 1998) Vol. 3464

**WGQ98 Dynamics of photon-induced processes in adsorbate-surface systems studied by Laser-Synchrotron pump-probe techniques**

B. Winter, J. Gatzke, T. Quast, I. Will, A. Liero, D. Pop, and I. V. Hertel; in *Proceedings of the conference on time structure of x-ray sources and its*

*applications*, (SPIE, The International Society for Optical Engineering, 1998)  
Vol. 3451 pp.62-69

- HNA99** **Electron transmission through organized organic thin films studied by discrete initial electron kinetic energies**  
A. Haran, R. Naaman, G. Ashkenasy, A. Shanzer, T. Quast, B. Winter, and I. V. Hertel; *Eur. Phys. J. B* **8**, 445-51 (1999).
- BSL01** **Evaluation of the energetic position of the lowest excited singlet state of beta-carotene by NEXAFS and photoemission spectroscopy**  
M. Beck, H. Stiel, D. Leupold, B. Winter, D. Pop, U. Vogt, and C. Spitz; *Biochim. Biophys. Acta-Bioenerg.* **1506**, 260-67 (2001)
- KPW01\*** **Radiation induced degradation and surface charging of organic thin films in ultraviolet photoemission spectroscopy**  
N. Koch, D. Pop, R. L. Weber, N. Böwering, B. Winter, M. Wick, G. Leising, I. V. Hertel, and W. Braun; *Thin Solid Films* **391**, 81 (2001)
- Wid02** **Time-resolved core level photoemission: Surface photovoltage dynamics at the SiO<sub>2</sub>/Si(100) interface**  
W. Widdra *et al.*; *Proceedings Symposium on Surface Science*, St. Jakob(2002)
- ZPK02** **Tuning Schottky Barrier Heights by Organic Modification of Metal-Semiconductor Contacts**  
D.R.T. Zahn, S. Park, T.U. Kampen; *Vacuum*, **67** (2002) 101
- WWH03\*** **Photoemission from azobenzene alkanethiol self-assembled monolayers**  
R. L. Weber, B. Winter, I. V. Hertel, B. Stiller, S. Schrader, L. Brehmer, and N. Koch; *J. Chem. Phys.* in press (2003).
- WWW03\*** **Full valence band photoemission from liquid water using VUV/XUV Synchrotron radiation**  
B. Winter, R. L. Weber, W. Widdra, M. Dittmar, and M. Faubel; *J. Phys. Chem.* submitted (2003)
- PWF03** **Electronic structure of metal-free porphyrazines in thin films**  
D. Pop, B. Winter, W. Freyer, I. V. Hertel, and W. Widdra; *J. Phys. Chem.* submitted (2003)
- WWS03** **Photoemission from aqueous salt solutions using VUV/XUV Synchrotron radiation**  
R. L. Weber, B. Winter, P. M. Schmidt, W. Widdra, M. Dittmar, and M. Faubel; *J. Chem. Phys.* submitted (2003).
- WBG03\*** **Time-resolved core level photoemission: Surface photovoltage dynamics at the SiO<sub>2</sub>/Si(100) interface**  
W. Widdra, D. Bröcker, T. Gießel, I. V. Hertel, W. Krüger, A. Liero, F. Noack, V. Petrov, D. Pop, R. L. Weber, I. Will, and B. Winter; *Surface Science* submitted (2003).
- GWB03\*** **Time-resolved photoelectron detection applied for pump-multiple probe experiments with combined Laser and Synchrotron radiation**  
T. Gießel, W. Widdra, D. Bröcker, I. V. Hertel and B. Winter, *Rev. Sci. Instr.* submitted (2003)

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\* Reprints of these publications are enclosed.

- ZKM03 Transport gap of organic semiconductors in organic modified Schottky contacts**  
D.R.T. Zahn, T. U. Kampen, H. Méndez; Appl. Surf. Sci., in press
- KZB03 Surface properties of chalcogen passivated GaAs(100)**  
T.U. Kampen, D. R. T. Zahn, W. Braun, C. González, I. Benito, J. Ortega, L. Jurczyszyn, J. M. Blanco, R. Pérez, F. Flores; Appl. Surf. Sci., in press
- KSP03 Orientation of Perylene Derivatives on Semiconductor Surfaces**  
T.U. Kampen, G. Salvan, A. Paraian, C. Himcinschi, A.Yu. Kobitski, M. Friedrich, D.R.T. Zahn; Appl. Surf. Sci., in press.
- KGM02 Electronic properties of interfaces between perylene derivatives and inorganic/organic semiconductor interfaces**  
T.U. Kampen, G. Gavrilă, H. Méndez, D.R.T. Zahn, A. R. Vearey-Roberts, D. A. Evans, J. Wells, I. McGovern, W. Braun; Journal of Physics C: Solid State Physics (special issue), submitted

## 6.2 List of 2000-2002 presentations at conferences and seminars from work done at the MBI-BESSY beamline

1. M. Dittmar *together with* B. Winter, M. Faubel, N. Böwering, R. Weber, and W. Braun, DPG Frühjahrstagung (Regensburg, 2000) *Photoelektronenspektroskopie an einer Wasseroberfläche an der Synchrotronstrahlungsquelle BESSY*
2. M. Dittmar *together with* M. Faubel, R. Weber, and B. Winter, BESSY User Meeting (Berlin, 2000) *Photoelectron spectroscopy on a liquid beam of pure water and alkali halide solutions using BESSY II radiation*
3. M. Faubel and B. Winter, BESSY User Meeting (Berlin, 2000) *Photoelectron spectroscopy of liquid water solutions (invited)*
4. N. Koch, D. Pop, R. L. Weber, N. Böwering, B. Winter, G. Leising and W. Braun, BESSY User Meeting (Berlin, 2000) *Radiation induced degradation and surface charging of p-sexiphenyl in ultraviolet photoemission spectroscopy*
5. N. Koch and B. Winter, Seminar (Princeton University, Dep. of Electrical Engineering, 2000) *Organic/metal interfaces studied by photoemission spectroscopy: Surface charging and its removal by high intensity Laser irradiation*
6. D. Pop *together with* R. Weber, N. Koch, B. Winter, W. Freyer, N. Böwering, W. Braun, and I. V. Hertel, International Conference on Electronic Spectroscopy & Structure (Berkeley, USA, 2000) *Surface dynamics in organic films studied by time-correlated Laser and Synchrotron pulses*
7. D. Pop *together with* R. Weber, B. Winter, N. Koch, T. Gießel, W. Freyer, and I. V. Hertel, BESSY User Meeting (Berlin, 2000) *Surface dynamics in organic films studied by time-correlated Laser and Synchrotron pulses*
8. D. Pop and C. Spitz *together with* N. Böwering, B. Winter, and C. Stiel, DPG Frühjahrstagung (Regensburg, 2000) *Excited-state photoemission spectroscopy of carotenoids*
9. R. Weber *together with* D. Pop, N. Böwering, B. Winter, N. Koch, I. V. Hertel, and G. Leising, DPG Frühjahrstagung (Regensburg, 2000) *Photoelectron spectroscopy of conjugated organic materials: Surface charging and its removal*

10. R. Weber *together with* D. Pop, B. Winter, N. Böwering, B. Langer, M. Wick, J. Gatzke, and I. V. Hertel, DPG Frühjahrstagung (Regensburg, 2000) *User facility for time-correlated Laser and Synchrotron pulse*
11. R. Weber *together with* D. Pop, B. Winter, T. Gießel, N. Böwering, M. Wick, B. Langer, J. Gatzke, I. V. Hertel, and W. Braun, International Conference on Electronic Spectroscopy & Structure (Berkeley, USA, 2000) *Two-color photoemission by time-correlated Laser and Synchrotron pulses*
12. R. Weber *together with* D. Pop, N. Böwering, B. Winter, B. Langer, T. Gießel, M. T. Wick, J. Gatzke, and I. V. Hertel, 7th International Conference on Synchrotron Radiation, Instrumentation (SRI 2000) (Technische Universität Berlin, 2000) *Photoemission with time-correlated Laser and Synchrotron pulses*
13. B. Winter, Workshop LSWAVE 2000, Satellite Conference of the 7th Intern. Conf. on Synchrotron Radiation Instrumentation (SRI) (Technische Universität Berlin, 2000) *The MBI BESSY II Beamline: application laboratory for combined Laser/Synchrotron radiation (invited)*
14. M. Faubel *together with* M. Dittmar, R. Weber, and B. Winter, BESSY User Meeting (Berlin, 2001) *Liquid microjet photoelectron spectroscopy*
15. M. Faubel and B. Winter, *together with* M. Dittmar, and R. Weber, Bunsentagung (Stuttgart, 2001) *Photoelectron spectroscopy of salt ions in liquid water using BESSY Synchrotron radiation (invited)*
16. M. Faubel and B. Winter *together with* M. Dittmar, and R. Weber, Symposium on Low Energy Electron-Molecule Interactions, LEEMI (Going/Kitzbühel, Austria, 2001) *Liquid microjet photoelectron spectroscopy (invited)*
17. N. Koch *together with* D. Pop, R. L. Weber, B. Winter, M. Wick, G. Leising, I. V. Hertel, and W. Braun, BESSY User Meeting (Berlin, 2001) *Radiation induced degradation and surface charging of organic thin films in ultraviolet photoemission spectroscopy*
18. D. Pop *together with* W. Freyer, R. Weber, B. Winter, and I. V. Hertel, BESSY User Meeting (Berlin, 2001) *Metal-to-ligand charge transfer in organometallic compounds studied by resonant photoemission*
19. D. Pop *together with* W. Freyer, R. Weber, B. Winter, and I. V. Hertel, DPG Frühjahrstagung (Hamburg, 2001) *Metal-to-ligand charge transfer in organometallic compounds*
20. D. Pop *together with* B. Winter, W. Freyer, R. Weber, I. V. Hertel, and W. Widdra, European Conference on Organic Electronics and Related Phenomena (University of Potsdam, 2001) *Organometallic compounds studied by resonant photoemission*
21. B. Stiller and B. Winter *together with* R. Weber, S. Schrader, P. Karageorgiev, D. Prescher, and I. V. Hertel, 8. European Conference Organized Film (Otranto, Lecce, Italy, 2001) *Optical switching and valence electronic structure of self-assembled monolayers (SAMs) of substituted azobenzene alkyl thiols on gold*
22. T. Timpanaro and B. Winter *together with* S. Schrader, B. Stiller, L. Brehmer, and R. Weber, TMR Meeting/EUROLED (IBM Zürich, 2001) *STM induced switching of azobenzene self-assembled layers*
23. R. Weber *together with* B. Winter, I. V. Hertel, B. Stiller, S. Timpanaro, S. Schrader, and L. Brehmer, BESSY User Meeting (Berlin, 2001) *Photoemission from azobenzene alkyl thiol self-assembled monolayers*

24. R. Weber *together with* B. Winter, I. V. Hertel, B. Stiller, S. Schrader, and L. Brehmer, European Conference on Organic Electronics and Related Phenomena (University of Potsdam, 2001) *Photoemission from azobenzene alkyl self-assembled monolayers*
25. W. Widdra, Kolloquium des SFB-546 (Humboldt-Universität Berlin, 2001) *1D-Nanostrukturen: Elektronische und phononische Eigenschaften von Adsorbatketten*
26. W. Widdra, Thirteenth International Conference on Vacuum Ultraviolet Radiation Physics (Triest, Italien, 2001) *Core level shifts of organic molecules on Si(100)-(2x1): A systematic comparison*
27. W. Widdra, Festkörperphysik-Kolloquium (Freie Universität Berlin, 2001) *Elektronische und phononische Zustände in eindimensionalen Adsorbatketten*
28. W. Widdra, Sonderkolloquium (Physik-Department, Technische Universität München, 2001) *Eindimensionale Nanostrukturen auf Oberflächen*
29. W. Widdra, (Fritz-Haber-Institut, 2001) *Elektronische und phononische Eigenschaften niederdimensionaler Adsorbatsysteme*
30. B. Winter *together with* T. Gießel, I. V. Hertel, D. Pop, R. Weber, and W. Widdra, ESF Exploratory Workshop on "Time-resolved Investigations by Neutron and X-rays of Structural Changes in Soft and Solid Matter" (Sommerfeld, 2001) *Two-color photoemission by time-correlated Laser and Synchrotron pulses*
31. D. Bröcker, DPG-Tagung (Regensburg, 2002) *Zeitaufgelöste Messung der OF-Photospannung von SiO<sub>2</sub>/Si(100) durch 2-Photonen Photoemission mit Laser - und Synchrotronstrahlung,*
32. K. Fauth, Seminar für Physik der kondensierten Materie (Univ. Konstanz, 2002) *Magnetic and electronic properties of deposited Fe and Ni clusters*
33. T. Gießel, BESSY User Meeting (Berlin, 2002) *Time- and angle-resolved electron detectors for experiments with combined Laser and Synchrotron radiation (invited)*
34. T.U. Kampen, Seminar (Philips, Aachen, 2002) *Organic modified Schottky contacts: Barrier height engineering and chemical stability*
35. D. Pop *together with* B. Winter, W. Freyer, R. Weber, D. Bröcker, T. Gießel, I. V. Hertel, and W. Widdra, DPG Frühjahrstagung (Regensburg, 2002) *Porphyrazine compounds studied by resonant photoemission*
36. R. Weber *together with* B. Winter, M. Dittmar, W. Widdra, and M. Faubel, DPG Frühjahrstagung (Regensburg, 2002) *Photoemission from a liquid microjet: Electronic structure of water and aqueous salt solutions*
37. W. Widdra, 14. Symposium on Surface Science (St. Christoph, Österreich, 2002) *Time-resolved core level photoemission: Surface photovoltage dynamics at the SiO<sub>2</sub>/Si(100) interface*
38. W. Widdra, Workshop on New Opportunities in Ultrafast Science using X-rays (Napa, California, USA, 2002) *Time-resolved core level photoemission: Surface photovoltage dynamics at the SiO<sub>2</sub>/Si(100) interface*
39. B. Wiesner, DPG spring meeting 2002, *Photoemission an Metallclustern auf Graphit: Einfluß der elektronischen Ankopplung*
40. B. Winter, Seminar (Princeton University, USA, AG Prof. A. Kahn, 2002) *Full valence band photoemission from liquid water and aqueous salt solutions*

41. B. Winter, SLS-Seminar (Swiss Light Source and Paul-Scherrer Institut, 2002) *Time-resolved Laser/Synchrotron photoemission: Perspectives for organic films and liquid surfaces*
42. K. Fauth, Seminar zur Oberflächenforschung (Univ. Bonn, 2003) *Magnetic and electronic properties of deposited transition metal clusters*
43. B. Winter, EUROFET - TMR Meeting (Thurnau, 2003) *Time-resolved Laser/Synchrotron photoemission: Perspectives (invited)*
44. T.U. Kampen, Seminar (University of Cincinnati, Ohio, USA, 2003) *Inorganic/Organic Semiconductor Heterostructures*
45. R. Weber, DPG Frühjahrstagung (Dresden, 2003) *Surface segregation in liquid water probed by photoemission*
46. T. Giessel, DPG Frühjahrstagung (Dresden, 2003) *Time- and Angle-Resolved Electron Detectors for Experiments with combined Laser- and Synchrotron Radiation*
47. D. Bröcker, DPG Frühjahrstagung (Dresden, 2003) *Surface Recombination Dynamics of SiO<sub>2</sub>/Si(100) – A Combined Laser and Synchrotron Radiation Study*

### **6.3 PhD theses and calls for professorship**

#### **Diploma Thesis**

N. Schneider, Univ. Würzburg, 2002, "Rumpfniveau-Photoemissions-Spektroskopie an Platinclustern auf HOPG"

B. Wiesner, Univ. Würzburg, 2002, "Photoelektronenspektroskopie an deponierten Nickelclustern"

#### **PhD Thesis**

Diana Pop, FU Berlin, 2003: "Photoelectron spectroscopy on thin films of Cu-, Zn-, and metal-free extended porphyrines"

Ramona L. Weber, FU Berlin, 2003: "Photoemission study of liquid water and aqueous solutions in free microjets using Synchrotron radiation"

Henry Mendez, TU Chemnitz: "Organic modified metal/semiconductor contacts"

Gianina-Nicoleta Gavrila, TU Chemnitz: "Chemical stability of organic thin films"

Michaela Gorgoi, TU Chemnitz: "Investigation of unoccupied states in organic thin films using inverse photoemission spectroscopy"

#### **Habilitation**

Dr. Thorsten U. Kampen, TU Chemnitz: "Inorganic/organic semiconductor heterostructures"

#### **Calls for Professorship**

Prof. Dr. W. Widdra, Martin-Luther-Universität Halle-Wittenberg

## 6.4 Research activities of non-CRG users

### 6.4.1 Reduction of inhomogeneous Fermi level pinning using organic molecules (group of D.R.T. Zahn, TU Chemnitz)

One possible application of the organic molecules is their use in organic/inorganic heterojunctions for determining the electronic surface state density of the inorganic substrate [Z1].

A perylene derivative, DiMe-PTCDI, was deposited on a substrate of Sulphur passivated gallium arsenide (S-GaAs). The surface properties after deposition of the organic molecule were investigated by SXPS on As3d and Ga3d core levels (Fig.1).

The measurements were performed at U-125/1 (MBI) beamline at BESSY II. The curve fitting is done using a Voigt profile, and the assignment of the components is reported elsewhere [Z2]. A Voigt profile consists of the convolution of Lorentzian and gaussian line shape. Lorentzian broadening results from the core-hole lifetime, and gaussian broadening accounts for the experimental resolution and also for any broadening due to the sample conditions.

After deposition of DiMe-PTCDI organic film a sharpening in As3d and Ga3d core level features is observed. This sharpening can be described by a reduction of the Gaussian contribution in a Voigt profile of the curve fitting (Tab. I).

Tab. I: Gaussian broadening according to the thickness of DiMe-PTCDI organic layer.

	S-GaAs	DiMe-PTCDI +0.3nm	DiMe-PTCDI +0.7nm	DiMe-PTCDI +2.0nm
<b>Ga3d</b>	0.56 eV	0.55 eV	0.52 eV	0.51 eV
<b>As3d</b>	0.6 eV	0.54 eV	0.54 eV	0.54 eV

Other fixed fitting parameters employed are shown in Tab. II.

Tab. II: Fixed parameters employed by curve fitting of Ga3d and As3d core levels.

	Lorentzian contribution	Intensity ratio	Spin-orbit splitting	Binding energy 1	Binding energy 2	Binding energy 3
<b>Ga3d</b>	0.1 eV	1.58	0.48 eV	19.44 eV	19.87 eV	20.42 eV
<b>As3d</b>	0.1 eV	1.45 ± 0.1	0.69 ± 0.01	40.67 eV	41.35 eV	-----

Since the core-hole lifetime and the experimental setup remain unchanged during the experiment, the reduction of the Gaussian broadening is explained in terms of an improvement of the surface properties after deposition of the organic layer. As it was already

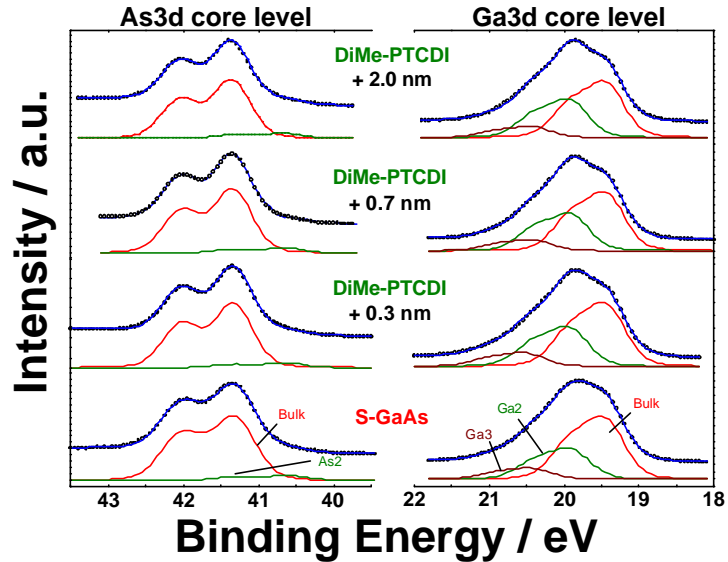


Fig.1. Evolution of As3d and Ga3d core levels of sulphur passivated GaAs after deposition of the organic molecule DiMe-PTCDI.

observed for PTCDA [Z3], other perylene derivative, the DiMe-PTCDI molecule preferentially stacks on defect sites reducing disorder as well as potential variations across the surface which results in inhomogeneous band bending at the surface. Hence, the sharpening of the core levels is an indication of the disappearance of inhomogeneous Fermi level pinning due to preferential absorption of these perylene derivatives on defect sites. This enables the use of organic molecules as a probe for testing defects on surfaces by examination of core levels using X-ray photoemission spectroscopy.

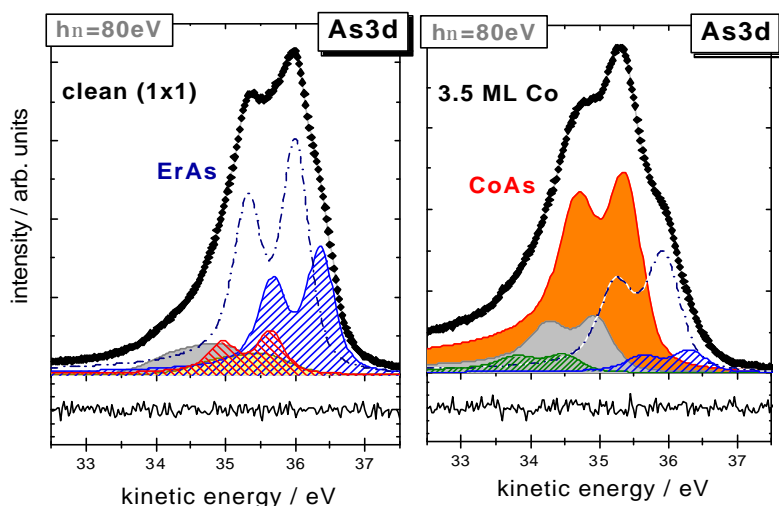
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#### 6.4.2 Photoelectron spectroscopy of semiconductor interfaces (group of N. Esser, W. Richter, TU Berlin)

Experiments at the U125/1-SGM were devoted to investigate the effect of a diffusion barrier, consisting of a ErAs intermediate layer, on the reactions of Co with the GaAs(001) interface.



These systems are interesting for their potential as spintronic devices, which are based on ferromagnetic metal layers on semiconductors, e.g. Co on GaAs(001). Since Co strongly reacts with GaAs, a diffusion barrier is necessary in order to generate a sharp interface. Core level photoelectron spectroscopy has been used to identify the different gallium, cobalt and erbium species,

and to determine their relative amount at the interface by analysis of the Ga3d, As3d and Er4f spectra. The As3d spectra still indicate the presence of the reacted component, despite the ErAs layer. We could show, however, that this is only a thin (0.75 ML) CoAs layer, which is always present at the surface of the growing Co film. Hence, the reaction of Ga, and consequently the formation of compounds containing gallium and cobalt is largely suppressed by the diffusion barrier. A small fraction (<0.5 ML) of escaped Ga exists on the pure ErAs(001) surface, and will be implemented in the interface. As a result the growth of pure ferromagnetic bcc-Co occurs much earlier.

#### 6.4.3 Photoelectron spectroscopy experiments on deposited transition metal clusters (group of K. Fauth, G. Schütz, MPI für Metallforschung Stuttgart)

We have devoted a number of beam times at the CRG beamline U125/1-SGM to the investigation of the electronic properties of transition metal (TM) clusters. The experiments were motivated by our experimental finding of vanishing magnetic moments in Fe clusters consisting of less than 100 atoms when exposed to graphite surfaces, while being strongly magnetized when isolated in an Ar matrix [F1]. Calculations for adatoms [F2,F3] suggest that a combination of (a) repulsive interaction of carbon- $\pi$  with TM-4s electrons and (b) strong carbon- $\pi$ /TM-3d hybridization could indeed be the origin of these observations.

Most of our experiments at U125/1-SGM were carried out on deposited Ni clusters, where the substrate interaction with graphite should have the strongest effect. The experiments were designed such as to allow the direct comparison of rare gas (Ar) matrix isolated clusters to the very same particle ensemble exposed to the substrate surface. Unlike in gas phase spectroscopy [F4], the photoelectron spectra of deposited Ni clusters do not reveal significant fine structure from which direct information about the valence electron structure could be derived (Fig. 1).

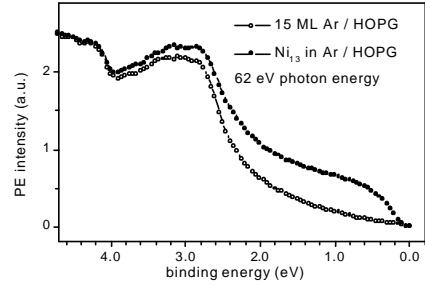


Fig. 1: Low binding energy regime of a photoelectron spectra of Ar covered HOPG, and the same sample with Ni<sub>13</sub> clusters deposited into the Ar film. The Ni coverage amounts to approx. 4% of a monolayer.

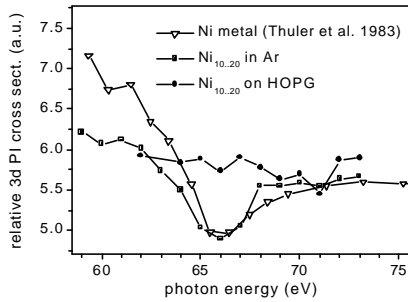


Fig. 2: 3d PI cross section as a function of photon energy for Ni metal, small clusters isolated in Ar, and the same clusters exposed to the HOPG surface.

configuration in the size range (10-60 atoms/cluster) covered by our investigations.

When the clusters are exposed to the graphite substrate by thermal release of the rare gas matrix, the Fano profile is entirely lost (Fig. 2). While this result would be fully in line with the adatom predictions of a  $d^{10}$  configuration [F2,F3], we know from complimentary absorption experiments at the Ni 2p edge that there still is a substantial unoccupied 3d density of states above  $E_F$ . Our results therefore indicate the formation of strongly hybridized 3d- $\pi^*$  resonance states at the interface [F6]. Resonantly excited 3p electrons are then able to diffuse rapidly into the substrate leading to the loss of phase information on the time scale of the core hole decay.

Nevertheless, useful insight into their electronic configuration can be obtained by evaluating the Ni-3d photoionization (PI) cross section for the 3d emission near  $E_F$  as a function of the photon energy, which is swept across the 3p absorption edge (typically 58-75 eV). Fig. 2 displays the result of such an analysis, exemplified for Ni clusters in the size range of 10-20 atoms, along with the analogous result from bulk Ni [F5]. In both cases, the 3d PI cross section displays a Fano profile characteristic of a weak negative coupling parameter (antiresonance). From this behavior it is concluded that like bulk Ni the rare gas isolated clusters possess a predominantly  $d^9$  electronic

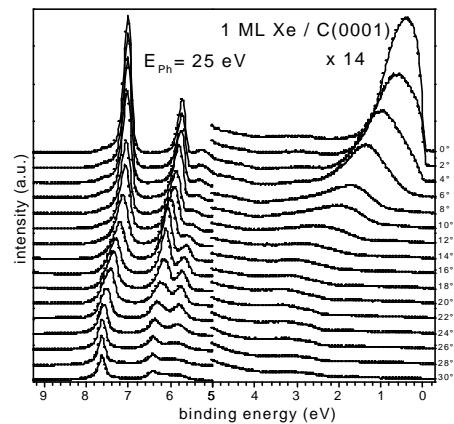


Fig. 3: Angle dependence of the photoemission signal from HOPG covered with a monolayer of Xe. The feature near  $E_F$  is due to an Umklapp process at the overlayer Brillouin zone and disperses accordingly.

As a preliminary investigation for forthcoming experiments we have furthermore characterized the rare gas overlayer induced emission from HOPG. In particular the angle dependence of the observed band corroborates the earlier assignment [F7] of this structure as being due to a surface Umklapp process. We hope to make use of this feature in the future in order to perform “Fano spectroscopy” [F7] of adsorbed metal cluster species.

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#### **6.4.4 Relaxation dynamics of photoexcited states (group of W. Wurth, Uni Hamburg)**

During the last year we have performed experiments at U125/1-SGM MBI using the Laser-pump/Synchrotron-probe experimental set-up of the Max Born institute to study the relaxation dynamics of photoexcited states of C<sub>60</sub>. We investigated fullerene C<sub>60</sub> evaporated onto Cu(111) and single domain (2x1) Si(100) surfaces. On both substrates crystalline films were grown. For pristine and photopolymerized thick C<sub>60</sub> films a short-lived (~1.3ns) singlet exciton and a long-lived (~10-15μs) triplet exciton are reported in the literature. We used the frequency doubled MBI BESSY II Ti:Sapphire Laser system at 3 eV photon energy to optically pump the HOMO - LUMO+1 transition of the fullerenes. The optically excited C<sub>60</sub> was then probed by valence band photoemission, using the time-synchronized Synchrotron radiation at U125/1-SGM. The experiment was performed in two different ways:

1) Taking photoemission spectra at a fixed delay between the optical pump pulse and the Synchrotron pulse.

2) Recording the time dependence of the photoelectron signal at constant kinetic energy relative to the optical pump pulse.

Both measurements are very difficult due to the low count rate which is partly due to the low pulse energy of the pump Laser. However, in the time dependence of the photoelectron signal we see an influence of the periodic recurrence of the Laser pump pulse every 12 ns which indicates that the experimental setup may be used to study the relaxation dynamics of photoexcited fullerenes. For future time-resolved experiments some improvements of the experimental setup would be very helpful, in particular higher peak power of the Laser system, implementation of an on-line synchronization monitor during the measurements, and enhanced capabilities of the XUV beamline.

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