

# Tuesday Morning, October 21, 2008

## Synchrotron-based Spectroscopy and Spectro-Microscopy Topical Conference

Room: 310 - Session SY+SS+BI-TuM

## Synchrotron-based Spectroscopy and Spectro-Microscopy

Moderator: M. Grunze, University of Heidelberg, Germany

8:00am **SY+SS+BI-TuM1 X-ray Studies of Hydrogen Bonding in Water; the Liquid Phase and on Surfaces, A.R. Nilsson**, SSRL/Stanford University and Stockholm University, Sweden **INVITED**

Water and its ability to form Hydrogen bonding (H-bonding) is the basis for all life on the planet earth. The understanding of water adsorption, wetting and reactions at solid surfaces is of importance for many different areas of science such as biomaterials, catalysis, electrochemistry, corrosion, environmental science and technologies related to hydrogen as a future energy carrier. There are recent experiments that have raised the question whether we really understand the nature of H-bonding and the structure of liquid water. We have recently devoted a major effort to the development of x-ray spectroscopy measurements of water in the different aggregation forms and adsorbed on surfaces. Using x-ray absorption spectroscopy (XAS), x-ray Raman scattering (XRS), x-ray emission spectroscopy (XES), small angle x-ray scattering (SAXS) and x-ray diffraction together with density functional theory (DFT) calculations we have demonstrated the appearance of specific spectral features that can be related to two different types of water species in the liquid, tetrahedral water and asymmetric H-bond configurations. The latter species dominates the liquid. I will address fundamental questions regarding geometric structure, electronic structure, nature of surface chemical and hydrogen bonding and reactivity of water on surfaces. The connection between studies performed at both UHV and ambient conditions will be emphasized. Several examples of different water adsorption system will be illustrated such as Pt(111), Ru(001), Cu(110), Cu(111), TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and MgO.

8:40am **SY+SS+BI-TuM3 Soft X-ray Spectroscopy of Liquids and Liquid-Solid Interfaces, C. Heske**, University of Nevada Las Vegas **INVITED**

With the advent of high-brightness synchrotron radiation in the soft x-ray regime it has become possible to investigate vacuum-incompatible sample systems such as liquids using suitably designed in-situ cells. In such cells, thin membranes (e.g., made of SiC, SiN<sub>x</sub>, or polyimide) separate non-vacuum sample environments from the ultra-high vacuum necessary for soft x-ray synchrotron beamlines. If the membranes are thin (e.g., on the order of 100 nanometer to 1 micrometer), it is possible to transmit soft x-rays with sufficient intensity for spectroscopic experiments. Two experimental techniques are of particular interest, namely x-ray absorption spectroscopy (XAS) to study unoccupied electronic states and x-ray emission spectroscopy (XES) to investigate the occupied electronic levels. The combination of the two approaches, i.e., the collection of XES spectra at variable resonant excitation (resonant inelastic soft x-ray scattering - RIXS), gives unprecedented insight into the electronic structure of hitherto inaccessible samples, such as liquids and liquid-solid interfaces. In this presentation, the experimental requirements for such studies will be discussed and it will be demonstrated how XAS, XES, and RIXS can give unique insights into the electronic, chemical, and dynamic properties of liquids (in particular water) and liquid-solid interfaces.

9:20am **SY+SS+BI-TuM5 High-Resolution X-Ray Photoelectron Spectroscopy as a Versatile Tool for the Characterization of Monomolecular Self-Assembled Films, M. Zharnikov**, Universität Heidelberg, Germany **INVITED**

Self-assembled monolayers (SAMs) have recently attracted considerable interest in physics, chemistry and biology due to their ability to control wetting, adhesion, lubrication and corrosion on surfaces and interfaces and their capability to become building blocks of future electronic devices. All the above applications rely on deep understanding of properties of these systems and precise knowledge of their structure. We will review recent progress in characterization of SAMs with a chalcogen headgroup on coinage metal and semiconductor substrates by high-resolution X-ray photoelectron spectroscopy (HRXPS). As compared to conventional XPS with a laboratory X-ray source, HRXPS, which usually takes advantage of both ultimate energy resolution and tunable photon energy (synchrotron), is capable to deliver additional information on the objects of interest, including screening phenomena, homogeneity of the bonding configurations, charge transfer upon the headgroup-substrate bond

formation, etc. Also, this technique is very useful when dealing with systems exhibiting a large diversity of chemical species such as, e.g., SAMs on GaAs substrates. A variety of examples will be provided. Further, it will be shown that photoemission in SAMs cannot always be described within the standard theoretical framework, which have important implications for both understanding of the XPS/HRXPS spectra of the relevant SAM-derived systems and practical applications.

10:40am **SY+SS+BI-TuM9 Chemical Imaging and Spectroscopy at Sufficiently High Spatial Resolution to Uncover Functions of Nanoscale Phenomena, M. Kiskinova**, Sincrotrone Trieste, Italy **INVITED**

The complementary capabilities of different microscopy approaches in terms of imaging, spectroscopy, spatial and time resolution are strongly requested by the multi-disciplinary research programs at the synchrotron facilities and have motivated continuous investments in development of instrumentation for imaging with spectroscopic analysis. The major part of the lecture will be focused on the potential of modern x-ray photoelectron microscopes in chemical imaging and micro-spot photoelectron spectroscopy.<sup>1</sup> Among the selected research topics, as representative examples are (i) addressing the surface properties of the individual C and oxide nanostructures and supported catalyst micro and nano-particles (ii) mass transport driven self-reorganization processes which can introduce lateral heterogeneity in the composition and reactive properties of surfaces (iii) quantum-size effects on the local chemical reactivity measured for ultrathin films with spatially varying thickness. The final part of the lecture will briefly illustrate the most recent achievements in combining the potential of soft x-ray transmission microscopy with multiple contrast approaches and fluorescence analysis.

Günther, S., Kaulich B., Gregoratti L., Kiskinova, M.: Prog. Surf. Sci. 70, 187, 2002.

11:20am **SY+SS+BI-TuM11 Hard X-ray Photoelectron Spectroscopy up to 15 keV: State-of-the-Art and Recent Results, M. Merkel**, FOCUS GmbH, Germany, **J. Rubio-Zuazo, G.R. Castro**, SpLine Spanish CRG Beamline at the European Synchrotron Radiation Facility, France, **M. Escher**, FOCUS GmbH, Germany

Hard X-ray photoelectron spectroscopy (HAXPES) gains momentum as a new non-destructive nanoanalytical method more and more. On one hand the request for non destructive and bulk sensitive analysis methods is highly visible. On the other hand the availability of a number of suitable high energy synchrotron beam lines allows for the realization of such dedicated instrumentations. A new electron analyzer that fulfils the requirements imposed by the XRD and HAXPES techniques is presented. The analyzer of the cylindrical sector type<sup>1</sup> in use (FOCUS HV CSA) is a very compact and at the same time highly efficient approach for this kind of electron spectroscopy. It is capable to handle kinetic energies up to 15 keV down to a few eV with the same analyzer setup and power supply.<sup>2</sup> The recent implementation of a 2D event counting detector for parallel data acquisition will be described also. By means of this detector the measurement speed is increased to overcome the restrictions imposed by the reduced sample cross sections and analyser transmission at high kinetic energies. Buried layers, as they are common for a number of nanotechnological applications, are invisible with most of the known non destructive analytical methods. To demonstrate the potential of electron spectroscopy at really high kinetic energies we used thin Au layers deposited onto a Cu substrate as a model system for bulk sensitive photoemission. The comparison of the Cu3s and Au5s peaks show the energy dependence of the depth information. It is seen that substrate properties can be probed for kinetic energies  $\geq 10$  keV effectively. By means of such measurements we derived the energy dependence of the effective attenuation length (EAL) for electrons in Au also. For this purpose core level spectra of different energies are taken for different film thicknesses. The extracted EAL of Au shows an energy dependence of  $(E_{kin})^{0.622}$  what is in good agreement with literature data. This work was supported through the Spanish Ministry of Education and Science (MEC), grants nos. FAP-2001-2166 and MAT1999-0241-C01 and the German Ministry of Education and Research (BMBF) under grant no. FKZ 13N9033.

<sup>1</sup> Risley J.S., Rev. Sci. Instrum. 43 (1971) 95; Sar-El H.Z., Rev. Sci. Instrum. 38 (1967) 1210; Sar-El H.Z., Rev. Sci. Instrum. 41 (1970) 561.

<sup>2</sup> J.R.Rubio-Zuazo, M.Escher, M.Merkel and G.R.Castro, J. of Phys. Conf. Ser. 100 (2008).

11:40am **SY+SS+BI-TuM12 A Comparative Study of Interface Formation for Ca/PDHFV and Ca/PHF by Synchrotron Radiation Photoemission, Y.X. Guo, W. Zhao, X.F. Feng, L. Zhang, W.H. Zhang, J.F. Zhu**, University of Science and Technology of China

Interfaces of metal/polyfluorene have attracted much research interests in both technological and scientific point of view. Polyfluorene-based light emitting devices have been proved to have a high luminescence efficiency.

However, the occurrence of gap states in most cases will affect the luminescence properties of organic materials. In this paper, the interface formation and energy level alignment for Ca/PDHFV and Ca/PHF have been studied by synchrotron radiation photoemission spectroscopy (SRPES) and X-ray photoelectron spectroscopy (XPS). The results imply that the chemical reaction at the interface of Ca/PDHFV is stronger than that of Ca/PHF. However, no gap states at the Ca/PDHFV interface can be observed, which is different from the observations on Ca/PHF. Both of these two interfaces display low electron injection barrier. Our findings suggest that the gap states can be removed at metal/polyfluorene interface by introducing vinylene units into polyfluorene, which may provide a new way to eliminate the gap states.

# Tuesday Afternoon, October 21, 2008

## Synchrotron-based Spectroscopy and Spectro-Microscopy Topical Conference

Room: 310 - Session SY+SS+BI-TuA

## Synchrotron-based Spectroscopy and Spectro-Microscopy

Moderator: Ch. Wöll, Ruhr-University, Germany

### 1:40pm SY+SS+BI-TuA1 Ultrafast Surface Dynamics in the Light of Soft X-rays from Free-Electron Lasers: First Results and Perspectives, W. Wurth, University of Hamburg, Germany **INVITED**

To investigate ultrafast electron dynamics and atomic motion in real-time is essential for a fundamental understanding of complex wave packet evolution in materials. As ideal tools for this type of investigation one can envision time-resolved spectroscopic techniques in the XUV or soft x-ray regime using femtosecond pulses. Tools such as angle-resolved photoemission (ARPES), electron spectroscopy for chemical analysis (ESCA), x-ray absorption or emission spectroscopy have proven to be extremely useful to study the electronic structure of complex materials in a static mode. Powerful XUV or soft x-ray sources delivering ultrashort pulses will enable us to obtain element-specific information on dynamic changes in the local electronic structure. With the Free-Electron Laser in Hamburg (FLASH) a unique source for femtosecond XUV-pulses with unprecedented brightness is operational since 2005 and a number of pioneering experiments have been performed with this source during the first user runs. In the talk I will review some of these experiments and present some ideas how femtosecond x-ray pulses from free-electron lasers can be used to study dynamic processes at surfaces and interfaces. I will show first examples for time-resolved experiments performed at FLASH including the investigation of XUV induced changes in optical reflectivity<sup>1</sup> as well as time-resolved photoelectron spectroscopy<sup>2</sup> and discuss implications for future experiments.

<sup>1</sup>C. Gahl et al., Nature Photonics 2, 165 (2008)

<sup>2</sup>A. Pietzsch et al., New Journal of Physics 10, 033004 (2008).

### 2:20pm SY+SS+BI-TuA3 Soft X-ray Spectromicroscopy of Protein and Peptide Interactions with Polymer Surfaces, A.P. Hitchcock, B.O. Leung, J.L. Brash, R. Cornelius, McMaster University, Canada, A. Scholl, A. Doran, Lawrence Berkeley National Laboratory **INVITED**

The biocompatibility of a material is dependent on its surface characteristics and how they affect the protein layer which forms upon initial contact with blood or tissue since those proteins mediate subsequent cellular responses. Chemical, mechanical and spatial characteristics are known to play a role in controlling initial protein adsorption. Thus direct measurements of adsorption preferences on structured biomaterials are highly relevant to optimization of biocompatibility. We are using synchrotron based X-ray PhotoEmission Electron Microscopy (X-PEEM) and Scanning Transmission X-ray Microscopy (STXM) to study preferential adsorption of proteins (human serum albumin (HSA), fibrinogen (Fg)) and peptides (sub-6, a cationic antimicrobial) to several phase segregated polymer blend surfaces – PS/PMMA<sup>1,2</sup> and PS/PLA. The X-ray absorption contrast is sufficient to identify and quantify the polymer and protein/peptide components, and peptides can be differentiated from proteins.<sup>3</sup> Single or competitive adsorption is carried out under controlled concentrations, pH, buffer, temperature and exposure times. All of these factors affect adsorption. Image sequences measured in the C 1s, N 1s and O 1s regions are analyzed by pixel-by-pixel spectral fitting to reference spectra. The resulting component maps are placed on quantitative thickness scales, either intrinsically in STXM (when reference spectra are provided on quantitative linear absorbance scales), or by normalizing total signal to a 10 nm measured sampling depth in PEEM. For adsorption on PS/PMMA, under all conditions there is a strong preference to adsorb at the domain interphases, which are thermodynamically favored since both hydrophobic and hydrophilic interactions can be satisfied. Otherwise, HSA and Fg have a preference for PS over PMMA. When sub-6 and HSA are co-adsorbed at neutral pH, there is evidence that the site distribution is controlled by preferential adsorption of a solution complex.<sup>4</sup> Under basic conditions (pH=11) this complex is unstable and the preferential adsorption becomes similar to that seen when each component is adsorbed independently.

<sup>1</sup> C. Morin et al., J Electron Spec, 137 (2004) 785.

<sup>2</sup> L. Li et al., J Phys Chem B 110 (2006) 16763, *ibid.*, 112 (2008) 2150

<sup>3</sup> J. Stewart-Ornstein et al., J. Phys. Chem. B 111 (2007) 7691

<sup>4</sup> B.O. Leung et al., Biointerphases 2008, submitted.

### 3:00pm SY+SS+BI-TuA5 Advances in Scanning Transmission X-Ray Microscopy: Surface Sensitive Electron Spectromicroscopy, B.M. Haines, University of Saskatchewan, Canada, T. Tyliczszak, Lawrence Berkeley National Laboratory, S. Beyhan, S.G. Urquhart, University of Saskatchewan, Canada

Scanning transmission x-ray microscopy (STXM) is a powerful technique that allows for near edge x-ray absorption spectroscopy (NEXAFS) and imaging with chemical speciation at spatial resolutions better than 50 nm. STXM has seen widespread use to study polymers, biological systems, and geochemistry. Many synchrotrons now have at least one beamline dedicated to STXM. It is however a bulk technique with limited surface sensitivity, as such it is not ideal for studying surface phenomenon or monolayers such as Langmuir-Blodgett films where the signal is very weak. Recently we have modified STXM microscopes at the Canadian Light Source and the Advanced Light Source to perform total electron yield (TEY) NEXAFS, which is well suited for studying surface phenomena. We have used TEY-STXM for compositional mapping of phase separated Langmuir-Blodgett films of arachidic acid and perfluorotetradecanoic acid. The films are imaged with the same resolution as STXM with increased contrast and surface sensitivity. TEY-STXM has been used to obtain simultaneous transmission and TEY spectra in addition to compositional maps of Fe<sub>3</sub>O<sub>4</sub> carbon supported nanoparticles less than 75 nm in size. The modification of STXM for TEY detection represents a significant new tool for studies conducted with STXM and opens the window for surface sensitive measurements with STXM.

### 4:00pm SY+SS+BI-TuA8 Recent Advances in Material Research with Synchrotron Infrared Spectromicroscopy at Elettra, A. Perucchi, Sincrotrone Trieste, Italy, S. Lupi, CNR-INFM Coherentia and Universita' di Roma "La Sapienza", Italy, D. Eichert, L. Vaccari, M. Kiskinova, Sincrotrone Trieste, Italy **INVITED**

The infrared beamline SISSI (Source for Imaging and Spectroscopic Studies in the Infrared) at Elettra extracts the infrared and visible components of synchrotron emission for applications of spectroscopy, microspectroscopy and imaging. The applications cover a wide range of research fields, including surface and material science, biochemistry, forensics, geology, biomedicine, microfluidics. We will overview the characteristics of the beamline and discuss recent results. A particular focus will be devoted to the new research opportunities in infrared spectroscopy at high pressures and in the THz range.

### 4:40pm SY+SS+BI-TuA10 The Brightest Light Downunder, R. Lamb, University of Melbourne and Australian Synchrotron **INVITED**

The Australian Synchrotron, a 3 GeV Instrument located in Melbourne, is the newest facility of its type in the world and is poised to become the single largest scientific and technological user facility in the Southern hemisphere. This talk will outline some of the key aspects of the local Science driving the future developments of the facility. An example of work in the area of nanoscale wetting of surfaces will also be described. Synchrotron small angle x-ray scattering (SAXS) has been used to investigate the in situ immersive wetting of ultrarough surfaces which exhibit superhydrophobicity with extreme water contact angle ( $\theta=169$ ). Reduced scattering contrast observed from rough surfaces when partially or totally wetted reveals significant physical differences between superhydrophobic surfaces not otherwise apparent from conventional contact angle measurements. As a complementary technique to static and dynamic contact angle measurements, transmission SAXS-based immersive wetting measurements promise more predictive models for how complex heterogeneous morphologies affect the phenomenon of wetting.

### 5:20pm SY+SS+BI-TuA12 Digital In-Line Soft X-ray Holography as Microscopy Technique for Biological Samples, A. Rosenhahn, R. Barth, F. Staier, C. Christoffis, University of Heidelberg, Germany, T. Simpson, S. Mittler, The University of Western Ontario, Canada, S. Eisebitt, BESSY, Berlin, Germany, M. Grunze, University of Heidelberg, Germany

Digital in-line soft X-ray holography (DIXH) is used as lensless microscopy technique to investigate biological samples. The experimental setup follows directly the initial idea of Gabor,<sup>1</sup> a holographic projection microscope based on a diverging photon beam. By creating a large divergence and the use of short wavelength, a lateral resolution better than 400 nm can be achieved without using any optical elements such as zone plates. Objects composed of different materials and thickness are used to determine the imaging properties of holographic microscopy in the VUV and soft X-ray wavelength range.<sup>2</sup> By tuning the x-ray energy to core resonances, element specific contrast can be obtained.<sup>3</sup> These results are promising with respect to the possibility to exploit intrinsic contrast

mechanisms for biological samples. Using fibroblasts and other cells, the sensitivity of the technique to resolve small structures inside these extended objects will be discussed. Although the spatial resolution still needs to be improved, we consider these experiments as starting point for future lensless holospectroscopy and as microscopy approach for highly coherent x-ray sources such as free electron lasers.

<sup>1</sup> D. Gabor, Nature 1948, 161, 777

<sup>2</sup> A. Rosenhahn, R. Barth, X. Cao, M. Schürmann, M. Grunze, S. Eisebitt, Ultramicroscopy 2007, 107, 1171

<sup>3</sup> A. Rosenhahn, R. Barth, F. Staier, T. Simpson, S. Mittler, S. Eisebitt, M. Grunze, Journal of the Optical Society of America A 2008, 25(2), 416.

# Authors Index

**Bold page numbers indicate the presenter**

## — B —

Barth, R.: SY+SS+BI-TuA12, 3  
Beyhan, S.: SY+SS+BI-TuA5, 3  
Brash, J.L.: SY+SS+BI-TuA3, 3

## — C —

Castro, G.R.: SY+SS+BI-TuM11, 1  
Christoffis, C.: SY+SS+BI-TuA12, 3  
Cornelius, R.: SY+SS+BI-TuA3, 3

## — D —

Doran, A.: SY+SS+BI-TuA3, 3

## — E —

Eichert, D.: SY+SS+BI-TuA8, 3  
Eisebitt, S.: SY+SS+BI-TuA12, 3  
Escher, M.: SY+SS+BI-TuM11, 1

## — F —

Feng, X.F.: SY+SS+BI-TuM12, 1

## — G —

Grunze, M.: SY+SS+BI-TuA12, 3  
Guo, Y.X.: SY+SS+BI-TuM12, 1

## — H —

Haines, B.M.: SY+SS+BI-TuA5, 3  
Heske, C.: SY+SS+BI-TuM3, 1  
Hitchcock, A.P.: SY+SS+BI-TuA3, 3

## — K —

Kiskinova, M.: SY+SS+BI-TuA8, 3; SY+SS+BI-TuM9, 1

## — L —

Lamb, R.: SY+SS+BI-TuA10, 3  
Leung, B.O.: SY+SS+BI-TuA3, 3  
Lupi, S.: SY+SS+BI-TuA8, 3

## — M —

Merkel, M.: SY+SS+BI-TuM11, 1  
Mittler, S.: SY+SS+BI-TuA12, 3

## — N —

Nilsson, A.R.: SY+SS+BI-TuM1, 1

## — P —

Perucchi, A.: SY+SS+BI-TuA8, 3

## — R —

Rosenhahn, A.: SY+SS+BI-TuA12, 3

Rubio-Zuazo, J.: SY+SS+BI-TuM11, 1

## — S —

Scholl, A.: SY+SS+BI-TuA3, 3  
Simpson, T.: SY+SS+BI-TuA12, 3  
Staier, F.: SY+SS+BI-TuA12, 3

## — T —

Tyliszczak, T.: SY+SS+BI-TuA5, 3

## — U —

Urquhart, S.G.: SY+SS+BI-TuA5, 3

## — V —

Vaccari, L.: SY+SS+BI-TuA8, 3

## — W —

Wurth, W.: SY+SS+BI-TuA1, 3

## — Z —

Zhang, L.: SY+SS+BI-TuM12, 1  
Zhang, W.H.: SY+SS+BI-TuM12, 1  
Zhao, W.: SY+SS+BI-TuM12, 1  
Zharnikov, M.: SY+SS+BI-TuM5, 1  
Zhu, J.F.: SY+SS+BI-TuM12, 1