

European Science Foundation  
Standing Committee for Life, Earth and Environmental Sciences  
(LESC)  
Standing Committee for Physical and Engineering Sciences (PESC)

**ESF LESC-PESC EXPLORATORY WORKSHOP**

**Recent Progress and Future  
Perspectives in Infrared Microscopy and  
Spectroscopy with Advanced Light  
Sources**



**Trieste, Italy, 28-30 October 2004**

**Convened by:**  
**Maya Kiskinova and Luca Quaroni**

---

ELETTRA, Sincrotrone Trieste

---

## **Workshop Objectives**

Infrared microspectroscopy with synchrotron radiation (SRIR) and free-electron lasers (FEL) has proven to be a powerful technique for imaging and analysis of matter at the molecular level. Current applications cover a range of disciplines, including material science, forensics, analytical chemistry, biochemistry, biomedical science, archaeometry and geochemistry.

The aim of this workshop is to probe the state-of-the-art of the technique, catalyze the development of new applications and disseminate the possibilities of SRIR and FEL IR to a wider public. Presentations by lead scientists in the field will be addressed to an interdisciplinary audience. Scientists from outside the traditional community of synchrotron users and in the early stages of their career are particularly encouraged to participate.

## **Executive Summary**

### ***Dates and Location***

The workshop was convened by Dr. Maya Kiskinova and Dr. Luca Quaroni, from Elettra Synchrotron Light Laboratory. The event was held in Grignano, Trieste, Italy, from October 27<sup>th</sup> to October 30<sup>th</sup> 2004 and was located in the structures of the International Center of Theoretical Physics (ICTP). It involved thirteen invited speakers, plus fifteen additional participants, overall representing eleven European countries plus the US. The event was funded mainly by ESF grant EW03-076, with additional support coming from Elettra, ICTP and Bruker Optics. Local organization was managed by Ilde Weffort (Elettra).

The workshop was structured in 17 presentations, held over the first two days, a standing poster presentation, and a round table discussion. Two of the presentations were delivered by young scientists (A. Perucchi and J. Chwiej), attending with ESF financial support. The activity was concluded by a social dinner on Friday 29<sup>th</sup> and a visit to Elettra on Saturday 30<sup>th</sup> with additional informal discussion.

The meeting was opened on Thursday 28<sup>th</sup> with a welcome address by Dr Giorgio Paolucci, Elettra, followed by an introduction on ESF activity. Because the ESF representative, Prof. Salvatore Cannistraro, was unable to attend, a shortened version of the ESF presentation, focused on the objectives of the workshop, was delivered by Luca Quaroni.

Scientific activity proper was initiated by a keynote presentation by Larry Carr (NSLS, USA) that traced the history of the production and use of IR from synchrotron and FEL sources, up to current developments. Four sessions of lectures, covering specific topics, followed over the course of two days, as detailed in the scientific section.

Posters were put on display at the very beginning of the meeting and made accessible throughout the meeting. Poster discussion took place during lunch and coffee breaks and during a final session before the social dinner. A round table discussion was held on the evening of October 28<sup>th</sup>, chaired by Dr Paul Dumas.

Participants included representatives of groups involved in the production of SR and FEL IR radiation, of groups currently involved in application of IR spectroscopy and imaging, and of

groups tentatively exploring the possibilities of the field. Presentations were organized so as to cover a wide range of disciplines and issues, including both areas of research in which the use of SR/FEL IR is established and areas in which it is a promising technique. Speakers were invited to cover all the most active areas and to achieve a team as widely representative as possible of the European scientific community. An emphasis was placed on the participation of younger scientists. This was implemented in the selection of speakers, and in providing travel grants and two presentation slots for researchers in the early stages of their career.

## Scientific Content and Activity

### Background

Fourier-Transform infrared (FTIR) microspectroscopy has emerged as a powerful tool for chemical analysis because of its ability to provide detailed information on the spatial distribution of chemical composition at the molecular level. In applications requiring qualitative and quantitative analysis, the capability of IR spectroscopy to identify chemical components via fingerprinting analysis of their vibrational spectrum is unsurpassed. When this capability is coupled to an IR microscope, microspectroscopy of  $\mu\text{m}$  size samples and high contrast microscopy of 2-D samples based on chemical composition become possible. Its applications cover a range of disciplines including material science, forensics, biochemistry, biomedical science, geochemistry, comprising both basic and applied research lines.

The introduction of synchrotron radiation (SR) as a source for IR spectromicroscopy has greatly expanded the capabilities of the technique and allowed it to access a wider range of applications. Most notably the gain of up to three orders of magnitude in source brightness provided by SR has made it possible to extend the spatial resolution of IR microscopy to the diffraction limit by reducing source size, thus overcoming the main limitation of microscopy conducted with traditional IR sources. Using thermal sources a space resolution of  $75\ \mu\text{m}$  is typically achieved, whereas SR radiation allows a resolution of down to a few  $\mu\text{m}$ , according to the wavelength used. The same gain in brightness has permitted to increase signal-to-noise and decrease measurement times several folds, providing access to smaller or more delicate samples and to the study of transient phenomena. In addition, SR emission is structured in pulses allowing for time-resolved measurements of processes on the nanosecond time scale. Finally, the spectral range accessible to SR extends from the far IR to higher energies, with complete tunability throughout, and availability of both linearly and circularly polarized radiation. No traditional IR source is capable of providing all these features concomitantly. The development of the free electron laser (FEL), using either a storage ring or a LINAC, has further extended the available brilliance and the flexibility in developing pump-probe experiments.

Oral presentations and posters covered the following subjects.

- FEL sources.
- High-resolution spectroscopy.
- High-pressure studies.
- Medical diagnosis and histology.
- Microscopy and spectromicroscopy with synchrotron IR.
- Near-field techniques.
- Pump-probe measurements.
- Spectromicroscopy in confined spaces.
- Spectroscopy of superconducting materials.
- Surface adsorption and interface structure.
- THz imaging and spectroscopy.
- THz radiation production.

## Presentation and Poster Abstracts

### A New Infrared Microspectroscopy Facility at the Daresbury SRS – Current Performance, Latest Results and Future Developments.

*Mark Tobin  
Synchrotron Radiation Department  
Daresbury Laboratory, Warrington  
m.j.tobin@dl.ac.uk*

A new beamline, dedicated to infrared microspectroscopy, has been commissioned at the Daresbury Laboratory Synchrotron Radiation Source (SRS) in the UK. This facility has been optimised for operation in the mid infrared region of the spectrum, and became a user facility in late 2003. The beamline supersedes the microscopy endstation previously operating on the far infrared surface science beamline, and which had operated successfully for several years. Improvements incorporated in the new facility include a more stable mounting platform for the microscope and its optics, a higher throughput of mid infrared radiation, and a more spacious user accommodation at the beamline.

The optical components of the new beamline can be considered in two sections: the primary extraction optics installed in the synchrotron ring tunnel, and the secondary collimating optics on the synchrotron roof. A high aperture dipole vessel allows extraction of  $30 \times 30$  mrad of synchrotron light which is collected by a spherical mirror  $M_1$  situated 5 m from the source. This mirror reflects and focuses the beam back towards the source, deflecting the beam downward by  $2.7^\circ$ . The beam is then collected by a plane mirror  $M_2$  and reflected upward toward the synchrotron vacuum exit window which is made of KRS5 (thallium bromoiodide) and located above the synchrotron shield roof. This produces a 1:1 image of the source approximately 50 mm above the synchrotron exit window. The secondary optics are situated above the synchrotron exit window and comprise a plane mirror  $M_3$  reflecting the beam onto a spherical mirror  $M_4$  located so as to produce a horizontal collimated beam. This beam is transported to the endstation by two adjustable plane mirrors. The secondary optics are maintained under vacuum at about  $5 \times 10^{-3}$  Torr, with the beam exiting through a caesium iodide window into the final beamline section, which is purged with dry air. Three alternative focal length  $M_4$  mirrors are available at different distances from the beam focus, allowing the resulting collimated beam to be tailored more closely to the experimental equipment in use.

As expected, the performance of this facility is significantly better than the original microscopy endstation, with high signal-to-noise, and an unapertured beam footprint at the sample of  $8 \times 8$  microns.

Future developments include the installation of a Perkin Elmer Spotlight imaging system, and the upgrade of the Thermo Nicolet Continuum microscope to operate with a high speed  $8 \times 8$  element detector. Near field developments based on the photothermal IR technique are also continuing at the SRS.

The new beamline is currently fully subscribed until March 2005, and is being used by a significant number of biomedical researchers. Applications for the study of breast cancer, cervical cancer, bone degeneration, prostate cancer and lung cancer have been received. The research group at Daresbury has been continuing to explore the possible application of infrared spectroscopy in the screening for cancer. Infrared transmission spectra were collected from individual cells within normal and cancerous tissues, at a spatial resolution of 10 microns. The spectra were then analysed using the chemometrics package Pirouette<sup>®</sup> (Infometrix Inc., USA) by both hierarchical cluster (HC) analysis and principal component (PC) analysis. HC analysis was able to discriminate between malignant cell and stroma within tumour sections, as well as keratinised tumour cells. By applying Nearest Neighbour classification following PC analysis,

the data set built up was found to be suitable for the correct classification of cells within similar tissue regions, including those from other patients.

## **Probing Surface-Catalysed, Microbial Reduction of Hexavalent Chromium Using Synchrotron Infrared Spectroscopy**

*Bryne T. Ngwenya<sup>1</sup> and Fariba Bahrami<sup>2</sup>.*

<sup>1</sup>*School of GeoSciences, University of Edinburgh, Grant Institute, West Mains Road, Edinburgh EH9 3JW, UK.*

<sup>2</sup>*CCLRC Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, UK.*

The use of microbes for the electrochemical reduction (metabolic or non-metabolic) of Cr(VI) to Cr(III) is widely believed to provide a viable and sustainable strategy for remediation of Cr(VI) contaminated wastewaters. When reduction occurs through the non-metabolic pathway, the rate of Cr(VI) reduction is favoured at acidic pH and decreases almost linearly with increasing pH. It has been suggested that this behaviour is due to a decrease in adsorption of Cr(VI) to the microbial cells as the pH increases. We have conducted preliminary chromium reduction experiments in the presence of an *Enterobacter* sp. of bacteria to test the hypothesis that the reduction reaction is surface-catalysed and hence that adsorption of Cr(VI) onto the cells is a pre-requisite.

Because bacterial cell walls contain carboxyl functional groups which deprotonate at near-neutral pH values to render the cell negatively-charged, we reasoned that blocking these groups would maximise adsorption of Cr(VI) at near-neutral pH and accelerate the reduction reaction. We blocked carboxyl functional groups by esterification with methoxymethane (63°C, 30 minutes) in the presence of concentrated sulphuric acid. Chromium reduction experiments were conducted with the esterified biomass at pH 2.5 and 5.2.

These experiments showed that the reduction rate was first order with respect to Cr(VI) concentration. Moreover, there was no difference in reduction rate between esterified cells and heat-killed (65°C, 30 minutes) cells at low pH (2.5). However, the reduction rate for esterified biomass showed up to 3-fold increase over the rate for heat-killed controls at pH 5.2. This increase brings the reduction rate at pH 5.2 to within 0.5 times the rate at pH 2.5. However, the increase in reduction rate at pH 5.2 does not appear to be associated with significantly enhanced adsorption relative to heat-killed controls.

To further probe this paradoxical result, we characterised the biomass with both lab based and Synchrotron Fourier Transform Infrared Spectroscopy. Synchrotron Infrared Spectroscopy revealed a significant decrease in infrared absorption for the esterified biomass around the 1400-1350 cm<sup>-1</sup> absorption region, where we expect carboxyl stretching. These changes were not resolvable using with thermal FTIR or acid-base titrations, presumably because the surface densities of the functional groups are rather low (~10<sup>-5</sup> mol/g cells). Thus the high photon flux of the synchrotron source appears to be necessary to detect changes in surface speciation. Nonetheless, these observations suggest that the surface-catalysed reduction reaction is rather complex and that its pH dependence cannot be explained fully by changes in adsorption of Cr(VI).

## Structure and dynamics of on-surface and subsurface oxygen adsorbed on Ag(210) and Ag(410)

*N. Bonini,<sup>1</sup> A. Kokalj,<sup>1,2</sup> A. Dal Corso,<sup>1</sup> S. de Gironcoli,<sup>1</sup> and S. Baroni<sup>1</sup>*

<sup>1</sup> *SISSA - Scuola Internazionale Superiore di Studi Avanzati, and  
INFN DEMOCRITOS National Simulation Center, Trieste, Italy*

<sup>2</sup> *Jozef Stefan Institute, 1000 Ljubljana, Slovenia*

The structure and dynamics of on-surface and subsurface oxygen adsorbed on Ag(410) and Ag(210) surfaces have been investigated using density functional theory. Our results show that the adsorption configuration in which O atoms decorate the upper side of the (110) steps forming  $\bar{O}Ag\bar{O}$  rows is particularly stable for both surfaces. While on Ag(210) this arrangement is significantly favoured with respect to other adsorption configurations, on Ag(410) adsorption on the terrace and at the step edge are almost degenerate, the former being slightly preferred at low coverage while the latter is stabilised by increasing the coverage. The inclusion of oxygen into interstitial subsurface sites results in significant lattice distortion which makes these sites energetically unfavoured. However subsurface species can be stabilised when a sufficient amount of O atoms is present on the first metal layer. In particular, at high enough O coverage on Ag(210) the mixed on-surface + subsurface O adsorption configurations are more stable than purely on-surface ones. On Ag(410), instead, at the coverage we have considered, the availability of stable terrace sites makes the subsurface O incorporation less favourable. These results and the study of the vibrational properties of some O/Ag(n10) configurations—calculated within density-functional perturbation theory—are used to interpret the HREEL data which have been recently measured for these systems.

## Synchrotron Infrared Science: Past, Present and Future\*

*G. Lawrence Carr  
National Synchrotron Light Source  
Brookhaven National Laboratory, Upton,  
New York 11973-5000 USA  
carr@bnl.gov*

The development of infrared synchrotron radiation (IRSR) as a source began in the early 1980s, with emphasis on studies of materials under UHV conditions. Applications of IRSR expanded rapidly in the early 1990s with the development of feedback systems to stabilize the beam, and updated RF systems that reduced higher frequency noise. Though IRSR has been used for a variety of experimental techniques and over a broad spectral range, mid-IR microspectroscopy for chemical imaging has evolved to become the dominant experimental technique. Today, nearly all of the IRSR sources around the world include a microspectrometer endstation, and developments continue toward the goal of achieving higher spatial resolution while imaging larger areas. As with other fields of synchrotron science, advances are not limited to beamline designs and endstations. The drive towards producing shorter electron bunches for time-

resolved spectroscopy and for VUV/x-ray FELs has opened the new field of accelerator-produced coherent THz pulses. Though still in its infancy, coherent THz synchrotron radiation (e.g., the Jefferson Lab FEL, BESSY-II, the NSLS SDL and others) has already been shown to possess significant power advantages over alternative sources, and new accelerator-based coherent light sources are being proposed (e.g., CIRCE, 4GLS). Though the expression may be overused, it nonetheless remains true: the future of infrared synchrotron radiation is bright.

\* in collaboration with L.M. Miller, G.D. Smith, R.L. Smith, J.B. Murphy, X.-J. Wang, H. Loos, B. Sheehy, C.C. Homes, R.P.S.M. Lobo, D.B. Tanner, L. Mihaly, G.P. Williams, C.J. Hirschmugl and P. Dumas.

## **Researches on neurodegeneration using techniques based on synchrotron radiation**

*J. Chwiej<sup>1</sup>, M. Lankosz<sup>1</sup>, M. Szczerbowska-Boruchowska<sup>1</sup>, S. Wójcik<sup>1</sup>, D. Adamek<sup>2</sup>, A. Krygowska-Wajs<sup>2</sup>, B. Tomik<sup>2</sup>, S. Bohic<sup>3</sup>, J. Susini<sup>3</sup>, A. Simionovici<sup>3</sup>, P. Dumas<sup>4</sup>, G. Falkenberg<sup>5</sup>, Z. Stegowski<sup>1</sup>*

*<sup>1</sup>Faculty of Physics and Nuclear Techniques, AGH, University of Science and Technology, Krakow, Poland; [chwiej@novell.ftj.agh.edu.pl](mailto:chwiej@novell.ftj.agh.edu.pl)*

*<sup>2</sup>Institute of Neurology, Collegium Medicum, Jagiellonian University, Krakow, Poland*

*<sup>3</sup>European Synchrotron Radiation Facility, Grenoble, France*

*<sup>4</sup>LURE, Centre Universitaire Paris-Sud, Orsay, France*

*<sup>5</sup>Hamburger Synchrotronstrahlungslabor HASYLAB at DESY, Hamburg, Germany*

The most frequently cited theories of degeneration and atrophy of neurons in neurodegenerative disorders are oxidative stress, excitotoxicity, protein aggregation, and mitochondrial dysfunction [1-5]. In all of these processes metal ions play a very important role. As it is also known, in most cases trace metals in tissue are bounded into metallo-organic complexes [4]. The mechanisms mentioned above lead to changes in main bio-organic components such as nucleic acids, lipids, proteins, etc. Moreover, the disruption of intracellular homeostasis is reflected by the products of these abnormal reactions or by intensive production of the defense system factors (such as antioxidants) [5]. Comparison between distribution of elements and organic components including the relative secondary structure composition of the protein compounds in the tissue at the single cell level may shed some light on processes leading to neurodegeneration. Two neurodegenerative disorders i.e. Parkinson's disease (PD) and amyotrophic lateral sclerosis (ALS) were investigated with the use of synchrotron radiation microbeam. The autopsy samples of selected parts of brain and spinal cord were studied. The synchrotron microbeam X-ray fluorescence technique (micro-SRXRF) was used for topographic and quantitative analysis of selected elements. The evaluation of Fe and Cu chemical state in the neuron was performed with the use of microscopic X-ray absorption near edge structure spectroscopy (micro-XANES). The synchrotron Fourier transform IR microspectroscopy (SR-FTIR) was applied for investigation of the biochemical components of the tissues, as well as the relative secondary structure composition of the proteins.

References:

1. Bains JS, Shaw CA. Brain Res. Rev. 1997, 25, 335.
2. Robberecht W. J Neurol. 2000, 247, 1/1 1/6.
3. Mattson MP, LaFerla FM, Chan SL, Leissring MA, Shepel PN, Geiger JD. Trends Neurosci. 2000, 23, 222.
4. Bush AI. Current Opinion in Chemical Biology. 2000, 4, 184.
5. Cassarino DS, Bennett JP. Brain Res. Rev. 1999, 29, 1.

## High pressure study of Pentaerythritol: a synchrotron infrared study

*S.K. Deb*<sup>1</sup>, *Ankita Banerji*<sup>1</sup>, *R.J. Kshirsagar*<sup>1</sup> and *S.M. Sharma*<sup>1</sup>

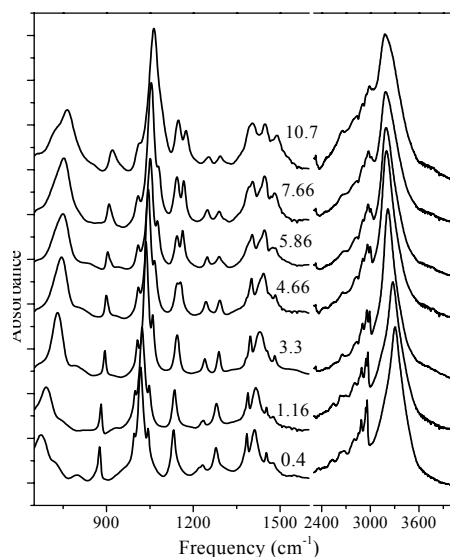
<sup>1</sup>Synchrotron Radiation Section, BARC, Mumbai 400085

*P. Dumas*<sup>2</sup>, *T. Marin*<sup>2</sup>, *J.C. Chervin*<sup>3</sup> and *B. Canny*<sup>3</sup>.

<sup>2</sup>LURE, Centre Universitaire Paris Sud, F91898 Orsay, France

<sup>3</sup>Université Pierre et Marie Curie, Paris 75006 France

*Pentaerythritol (PET) is a simple molecule, which crystallizes as a solid in tetragonal  $I\bar{4}$  space group under ambient condition. The crystal has a layered structure with the PET molecules in the  $a$ - $b$  plane connected by hydrogen bonding whereas the interlayer coupling is through weak Van der Waals force. Here we report a synchrotron radiation infrared high-pressure study upto a pressure of  $\approx 11$  GPa. The high-pressure experiments were carried out on 6% PET mixed with KBr powder in a membrane DAC with  $450 \mu\text{m}$  culet. The IR radiation from the Mirage beamline at LURE synchrotron was focused on a  $100 \mu\text{m} \times 100 \mu\text{m}$  spot in the DAC using a [NicPlan](#) IR microscope coupled to a FTIR spectrometer ([Thermo Nicolet Magma 560](#)). The figure shows the changes in the IR spectra with increasing pressure over the ranges  $650 - 600 \text{ cm}^{-1}$  and  $2300 - 4000 \text{ cm}^{-1}$  covering the internal modes of PET. The qualitative features of the spectra remain unchanged till  $\approx 4.7$  GPa beyond which the C-C skeletal stretch mode at  $1131 \text{ cm}^{-1}$  and the O-H deformation mode at  $1410 \text{ cm}^{-1}$  split into two modes. The changes in the frequencies of the bending, twist, deformation etc modes with increasing pressure shows that the modes at  $662 \text{ cm}^{-1}$ ,  $1375 \text{ cm}^{-1}$ ,  $1384 \text{ cm}^{-1}$  and  $1410 \text{ cm}^{-1}$  modes exhibit sudden*



*decrease in the slope beyond 4.7 GPa. The O-H mode at  $3227 \text{ cm}^{-1}$  shows anomalous shift with the frequency decreasing at the rate of  $27 \text{ cm}^{-1}/\text{GPa}$  till  $4.7$  GPa and then much more slowly with  $3.7 \text{ cm}^{-1}/\text{GPa}$ . All these changes occurring at  $4.7$  GPa indicate that the crystal undergoes a phase transition beyond this pressure. On reducing the pressure, the spectrum changes to the ambient phase below  $\approx 4.6$  GPa showing that the transition is completely reversible. The transition pressure is close to the prediction made based on steric hindrance between the non-bonded hydrogen atoms.*



## **Main advantages of Synchrotron Infrared Microscopy: Present and Future**

*Paul Dumas*  
*Synchrotron SOLEIL*  
*L'Orme des Merisiers*  
*Saint-Aubin - BP 48*  
*91192 GIF-sur-YVETTE CEDEX, France*  
*paul.dumas@synchrotron-soleil.fr*

Facilities for IR synchrotron radiation can be found throughout the world, serving to produce light for the scientific community. Infrared microscopy beamlines are operational or under construction in several facilities<sup>1</sup>. The brightness advantage (about two orders of magnitude) of the synchrotron source compared to a classical thermal source has attracted several microscopists from various communities: Geology, Soft Matter, Forensic, Biology and Biomedical.

The synchrotron source has to be accurately known and characterize in order to collect efficiently, then propagate the beam to the infrared spectrometer. Simulation is becoming a useful means for efficiently coupling the emitted photons with the spectrometer and the microscope, in order to achieve the best performances. This will be illustrated in this presentation.

Besides spectroscopy, chemical imaging is one of the main issues of microscopists. Chemical imaging requires high spatial resolution, high spectral quality, fast recording time, and, importantly, contrast fidelity! This contrast fidelity suggests that no artefact is introduced into the chemical image. I will show that conventional microscopes, equipped with focal plane array detectors, are not keeping the contrast fidelity when the spatial resolution is approaching the diffraction limit!

Several examples of the actual performances of synchrotron infrared spectroscopy will be presented: inclusions in geology, single cells and human tissues analysis.

However, the usefulness of the synchrotron beam, its uniqueness, may appear to be challenged by the recent development in detector technology (one dimensional, and two dimensional array detectors are now available) , which has led to much higher spectral quality and much faster recording time with thermal source. The basic reasons of such improvements will be presented.

In this talk, I will show why the synchrotron source is the unique source for analysis at the diffraction limit. Future directions will be suggested. Expectations of an improvement

---

<sup>1</sup> Active IR microspectroscopy beamlines are found at NSLS, Brookhaven, ALS, Berkeley and SRC, Stoughton (USA); UVSOR, Okasaki and SPring8, Nishi-Harima (Japan); NSRRC, Hsinchu (Taiwan). In Europe, IR activities continue at the SRS, Daresbury (UK); ESRF, Grenoble (France); MAXLAB, Lund (Sweden); and at DaΦne, Frascati (Italy); ANKA, Karlsruhe (Germany); BESSY II, Berlin (Germany). Other facilities that are planning IR microspectroscopy programs include Diamond, Rutherford Lab (UK); SOLEIL, Paris (France); DELTA, Dortmund (Germany); ELETTRA, Trieste (Italy); SLS, Villigen (Switzerland); Duke-FEL, Durham (USA); CLS, Saskatoon (Canada); CAMD, Baton Rouge, (USA); SURF-3, Gaithersburg (USA); Australian Synchrotron, Melbourne (Australia); and NSRL, Hefei (China).

of a factor of 2 to 3 in spatial resolution can be made by considering the Point Spread Function method of a large pixelated detector<sup>2</sup>.

## **Biomolecules thin films prepared by Pulsed Laser Deposition**

***M.A. Hernandez-Perez<sup>1</sup>, C. Champeaux<sup>2</sup>, C. Garapon<sup>1</sup>  
W. Coleman<sup>3</sup>, J. Mugnier<sup>1</sup>***

<sup>1</sup> *Physico-Chimie des Matériaux Luminescents, CNRS-Université Lyon1, France,*

<sup>2</sup> *Science des Procédés Céramiques et Traitement de Surface,  
CNRS-Université Limoges, France*

<sup>3</sup> *Institut de Biologie et Chimie des Protéines, CNRS- Université Lyon-I, France  
hernandez@pcml.univ-lyon1.fr*

Thin films of biological molecules such as amino-acids or proteins are of increasing interest for applications for bio-sensors or biocompatible coatings and their development needs diversification in the methods used to elaborate and structure them. Such films are generally prepared as monomolecular layer from solutions (Langmuir-Blodgett) or by chemical grafting of portion of biopolymer chains on surface. In order to investigate alternative methods, we study the ability of pulsed laser deposition to provide thin films, for which the molecular structure is preserved and which have, in addition, optical waveguiding properties, which may lead to interesting applications for sensors.

Three kinds of molecules have been studied to evaluate this capacity: amino-acids (phenylalanine, tyrosine...), calix-[n]-arene, which are macrocyclic molecules exhibiting specific complexation properties for amino-acids or proteins and a protein, the bovine serum albumin (BSA).

The thin films were deposited on silica substrates, using ablation of pressed powder targets by a KrF excimer laser at room temperature and low pressure (about  $10^{-5}$  mbar). Films with thickness of about 500nm to several  $\mu\text{m}$  could be obtained. The conservation of the chemical structure of the molecules was verified by IR spectroscopy and could be obtained for laser fluences of some hundreds  $\text{mJ}/\text{cm}^2$ . The surface roughness and morphology were examined by AFM. The films of the three kinds of molecules are optical waveguides and their thickness and refractive index were measured by m-line spectroscopy.

Films of phenylalanine have low roughness and high refractive index. They have the orthorhombic structure of the crystalline phenylalanine powder but the arrangement of the molecules, revealed by the hydrogen bonding, is slightly modified.

Films of <sup>t</sup>Bu-calix-[4]-arene are characterised by refractive index clearly higher than those of films obtained by thermal evaporation or from solutions, low surface roughness and specific cristallisation properties after annealing.

Waveguiding thin films of the globular protein BSA could be obtained without degradation of the molecular structure. Observation by AFM of the film surface shows the presence of particles of about 100 nm diameter, a morphology different from that of

---

<sup>2</sup> G.L.Carr, O. Chubar and P. Dumas « Multichannel Detection with a Synchrotron Light Source: Design and Potential » to appear in SPECTROCHEMICAL ANALYSIS USING MULTICHANNEL INFRARED DETECTORS, Analytical Chemistry Series

films cast from solution. These films are characterised by a very low roughness (rms=1.3nm).

## **Synchrotron Infrared ellipsometry for characterisation of organic films**

*Dr. Karsten Hinrichs*  
*ISAS - Institute for Analytical Sciences*  
*Department Berlin*  
*Albert-Einstein-Str. 9*  
*12489 Berlin, Germany*  
[hinrichs@ansci.de](mailto:hinrichs@ansci.de)

FT-IR reflectance methods such as infrared spectroscopic ellipsometry (IRSE) provide valuable information about the sample properties by probing the reflectance for radiation differently polarized with respect to the plane of incidence [1-4]. From IRSE not only the real and imaginary part of the optical constants are derived but also the depolarisation within the sample can be elucidated. The in-house-built photometric mid infrared ellipsometers at ISAS together with the unique microfocus infrared ellipsometer at the synchrotron BESSY II [4] enable the implementation of microscopic effects e.g. roughness or polydomain structures into the optical model. The high analytical potential of IRSE is based on (i) a non-contact and non-invasive measurement (ii) monolayer sensitivity (iii) identification of chemical bonds of the film and interface by vibrational absorption bands and (iv) optical modelling with respect to molecular orientations and structure. Ellipsometric measurements require well defined optical conditions since reflectance depends strongly on the angle of incidence and the polarization azimuth of the incident radiation. As a consequence the focussing optic is restricted to rather moderate f-numbers and the signal to noise ratio limits ellipsometric investigations to rather large samples. Depending on technical limitations typical sample sizes for infrared ellipsometry are around a few 10 mm<sup>2</sup> when using a conventional FT-IR ellipsometer. Due to the high brilliance of synchrotron radiation micro IRSE with defined angles of incidence is possible for lateral resolutions below 250 μm<sup>2</sup>. In this contribution several applications of synchrotron infrared ellipsometry at BESSY II for investigations of small and heterogeneous organic thin film samples (polymers, proteins, functional molecules) are reviewed.

[1] Hinrichs K., Tsankov D., Korte E.H., Röseler A., Sahre K. and Eichhorn K.-J., *Appl. Spectrosc.*, 2002, 56, 737

[2] Hinrichs K., Röseler A., Gensch M. and Korte E.H., *Structure analysis of organic films by mid infrared ellipsometry, Thin Solid Films* 455-456 (2004) 266-271

[3] Hinrichs K., Gensch M., Sahre K., Eichhorn K.-J., Esser N., Schade U., Röseler A., Korte E.H., *FT-IR synchrotron ellipsometry for studying the anisotropy of small organic samples, Appl. Spectrosc.* 57 (2003) 1250-1253

[4] Gensch M., Hinrichs K., Schade U., Röseler A., Korte E.H., *Instrumentation for FT-IR reflectance spectroscopy with synchrotron radiation, Anal. Bioanal. Chem.* 376 (2003) 626 - 630

## Synchrotron IR ellipsometry for characterization of ultra thin and heterogeneous films

M. Gensch<sup>1a,2</sup>, K. Roodenko<sup>1a</sup>, U. Schade<sup>3</sup>, E.H. Korte<sup>1b</sup>, N. Esser<sup>1a</sup>, K. Hinrichs<sup>1a</sup>  
and A. Röseler<sup>2</sup>

<sup>1</sup>ISAS – Institute for Analytical Sciences,

<sup>a</sup>Department Berlin, Albert-Einstein-Str. 9, 12489 Berlin, Germany

<sup>b</sup>Bunsen-Kirchhoff-Str.11, 44139 Dortmund, Germany

<sup>2</sup>Gesellschaft zur Förderung angewandter Optik, Optoelektronik, Quantenelektronik und Spektroskopie  
e.V., Rudower Chaussee 29, 12489 Berlin, Germany

<sup>3</sup>Berliner Elektronenspeicherring-gesellschaft für synchrotronstrahlung m.b.H. (BESSY), Albert-Einstein-  
Str. 15, 12489 Berlin, Germany

[hinrichs@ansci.de](mailto:hinrichs@ansci.de)

It was shown recently that the detection limits of infrared ellipsometry can be improved by use of appropriate measurement strategies [1] and dedicated sources such as synchrotron infrared beamlines [2]. The method now facilitates the investigations of ultra thin films or even submonolayers of adsorbates on semiconducting surfaces. This has great technological relevance since such films, e.g. molecular films on silicon, are believed to have a potential application in the IC industry. Another question is if also biological or other samples with considerable spatial variations of the optical and chemical properties can be investigated with this method. The evaluation of the anisotropic optical constants and of the structural parameters (e.g. molecular orientation) of such samples requires an understanding of the contributions due to deviations from the commonly in ellipsometry applied layer models. This presentation shows that small and heterogeneous samples can be investigated with respect to thickness, structure and composition [3,4]. With the degree of phase polarisation  $P_{ph}$ , ellipsometry determines a value that directly reflects the heterogeneity of real world samples. It is outlined how different contributions such as roughness, varying thickness and chemical properties can be separated by applying the optical models, in particular if a highly brilliant source is used.

[1] Hinrichs K., Gensch M., Röseler A., Esser N., J. Phys.: Cond. Matt. 16 (2004) S4335.

[2] Gensch M., Hinrichs K., Schade U., Röseler A., Korte E.H., Anal. Bioanal. Chem. 376 (2003) 626 – 630.

[3] Hinrichs K., Röseler A., Gensch M. and Korte E.H., Thin Solid Films 455-456 (2004) 266-271.

[4] Hinrichs K., Gensch M., Sahre K., Eichhorn K.-J., Esser N., Schade U., Röseler A., Korte E.H., Appl. Spectrosc. 57 (2003) 1250-1253.

## **Lab-on-a-chip devices as enabling technology for novel (bio)chemical studies using mid-IR synchrotron radiation**

*Nina Kaun<sup>1</sup>, Stephan Kulka<sup>1</sup>, Josefa R. Baena<sup>2</sup>, Ulrich Schade<sup>3</sup>, Michiel Vellekoop<sup>4</sup>,  
Ersilia De Lorenzi<sup>5</sup> and Bernhard Lendl<sup>1</sup>*

*<sup>1</sup>Inst. of Chemical Technologies and Analytics, Vienna University of Technology,  
Getreidemarkt 9/164, A-1060 Vienna, Austria*

*<sup>2</sup>Dep. of Anal. Chem., University of Córdoba, E-14071 Córdoba, Spain*

*<sup>3</sup>Bessy II, Albert-Einstein-Str. 15, D-12489 Berlin, Germany*

*<sup>4</sup>Inst. of Sensor and Actuator Systems, Vienna University of Technology,  
Gusshausstrasse 27-29, A-1040 Vienna, Austria*

*<sup>5</sup>Laboratory of Pharmaceutical Analysis, University of Pavia,  
Via Taramelli 12, I-27100 Pavia, Italy*

*[ninakaun@pop.tuwien.ac.at](mailto:ninakaun@pop.tuwien.ac.at)*

Microchips for rapid mixing of two aqueous streams have been produced using CaF<sub>2</sub> wafers and SU-8 microstructuring technology. A special design allows fast mixing of minimal amounts of solutions. These lab-on-a-chip devices were tested at the IR beamline of Bessy II in Berlin, Germany. Advantage of the synchrotron radiation over thermal global sources for measuring at sample spots close to the diffraction limit of the employed mid-IR radiation have been documented. The capability of the experimental set-up to initiate and monitor chemical reactions label-free in pL volumina was verified. Simple chemical reactions such as titration of acetic acid and conformational change of the protein  $\beta$ 2-microglobulin have been recorded.

Similarly fabricated lab-on-a-chip devices for fast separation based on capillary electrophoresis (CE) have been employed in preliminary experiments at ANKA, Germany.

In order to employ the advantage of the imaging capabilities of the IR microscopes at Synchrotron beamlines cells could be immobilized by patch clamping at the sample spots of IR radiation. This would allow to monitor in-situ responses to chemical pulses generated by liquid handling in a lab-on-a-chip.

## **The influence of gamma rays on the molecular bone structure. A Synchrotron FT-IR study**

*P. Kolovou and J. Anastassopoulou*

National Technical University of Athens, Chemical Engineering School, Radiation Chemistry and Biospectroscopy, Zografou Campus, 5780 Zografou, Athens, Greece  
*pkolovou@central.ntua.gr*

Infrared Fourier Transform (FT-IR) spectroscopy is widely used in the last two decades to characterize the molecular structure of bones. On the other hand, in bone cancers the irradiation with ionised radiation is the most common method of cancer treatment or the reduction of the bone pain. In this work FT-IR spectroscopy was used to investigate the influence of gamma rays ( $\gamma$ - $^{60}\text{Co}$ ) on human bones. The samples were taken from 30 patients who went under a surgery for various reasons. From the study were excluded patients who had bone cancer. The bone samples, after treatment with hydrogen peroxide and acetone to remove the blood and fat of the bones, were irradiated with 59.22, 98.7, 197.4 and 592.2 Gy. Comparison of the FT-IR spectra before and after irradiation showed changes depending on the dose of irradiation. From the new band at  $1672\text{ cm}^{-1}$ , which is attributed to primary amines with aliphatic chain with less than ten carbon atoms, it was concluded that the chain of proteins are broken from the free radicals that are produced upon irradiation. It was also observed that the irradiation of collagen changed from alpha helix to random coil. In addition, the calcium carbonate ( $\text{CaCO}_3$ ) changed from calcite to another crystal system. Changes were also observed in the region  $900\text{-}1020\text{ cm}^{-1}$ , where the phosphate ( $\text{PO}_4^{3-}$ ) absorbs. These changes seem to be due to crystal effects in the bones and degree of crystallinity. It is also important to note that there were no changes in the spectra after irradiation, if the bones were irradiated after treatment with DMSO. In this case the spectra remained unchanged until a dose of up to 592.2 Gy.

## **Spatially Resolved IR Microspectroscopy of Single Cells and Tissues**

*Peter Lasch*

*P25 "Biomedical Spectroscopy",  
Robert-Koch-Institut, Nordufer 20,  
13353 Berlin, Germany  
LaschP@rki.de*

Characterisation of biomedical samples, specifically of eucaryotic cells and tissue sections by spatially resolved Fourier Transform Infrared (FT-IR) microspectrometry is an emerging new technology. This technique provides spectral information with unique biomarker profiles with minimal sample preparation. Due to its rapidity and high analytical and diagnostic sensitivity this method shows in combination with digital imaging techniques a great promise for in-vivo and ex-vivo medical diagnosis.

In the presentation we will discuss strategies of FT-IR microspectroscopy on the basis of experimental data obtained on individual cells, colorectal adenocarcinoma sections, and an USAF resolution target. Based on spectral data acquired by the use of IR imaging systems employing either conventional (thermal) or synchrotron light sources, we will emphasize technical aspects of data acquisition. Particularly we will focus on the importance of spatial resolution for biomedical applications of infrared microspectrometry.

## **Beating the Diffraction Limit: Near-field Microscopy with Advanced Photon Sources**

*Giorgio Margaritondo*

*Vice President Academic Affairs, EPFL*

*[Giorgio.Margaritondo@epfl.ch](mailto:Giorgio.Margaritondo@epfl.ch)*

*A. Cricenti and P. Perfetti*

*ISM-CNR, Frascati, Rome Italy*

*N.H. Tolk*

*Department of Physics and Astronomy, Vanderbilt University,  
Nashville, Tennessee, USA*

Scanning near-field optical microscopy (SNOM) makes it routinely possible to overcome the fundamental diffraction limit of standard (far-field) microscopy. The potential performances of SNOM are enhanced by the use of advanced photon sources and in particular by infrared free electron lasers. Recently, infrared SNOM performed in the spectroscopic mode started delivering spatially-resolved information on the distribution of chemical species and on other laterally-fluctuating properties. The practical examples that will be presented show the great potential of this new technique both in materials science and in the life sciences.

## **Synchrotron Infrared Science: Physics, Biology, Environmental Science and Coherence**

*Michael C. Martin*

*Lawrence Berkeley National Laboratory*

*1 Cyclotron Road, Bldg 6R2100*

*Berkeley, CA 94720-8226*

*[CMartin@lbl.gov](mailto:CMartin@lbl.gov)*

## High Resolution FTIR for Surface Chemistry: Bridging the Pressure Gap

*Attila Farkas<sup>(1)</sup>, Georg Ch. Mellau<sup>(1)</sup>, Hansjörg Ruppender<sup>(2)</sup> and Herbert Over<sup>(1)</sup>*  
*(1) Physikalisch-Chemisches-Institut, Justus-Liebig-Universität Giessen,  
Heinrich-Buff-Ring 58, D-35392 Giessen, Germany*  
*(2) OMNI VAC. Vakuumanlagenbau, Konrad-Adenauer Str.90,  
D-67663 Kaiserslautern, Germany*  
*georg@mellau.org*

The recent use of surface sensitive methods has contributed significantly to elucidate the molecular mechanisms of heterogenous catalysis. Necessarily, there are two objections to this approach. First, the surface has to possess a well defined crystalline structure. Second, it is only in the ultra-high vacuum (UHV) domain of reactant gases pressure, that the proposed molecular mechanisms can be ascertained to work.

The materials and pressure ranges involved in real-world catalytic processes do not share any of these features. In popular language, the price paid for using surface sensitive methods is a materials- and pressure gap, respectively. To clarify the relevance of the surface sensitive approach to real catalytic processes, it is necessary to follow these processes by direct observation, on the same substrate in a wide pressure range, extending from UHV conditions up to atmospheric pressure.

In the higher pressure domain optical spectroscopy has to replace the electron spectroscopies (HREELS) customary to the UHV studies. During the last three decades, reflection-absorption infrared spectroscopy (RAIRS) was perfected for the study of layers of molecules adsorbed onto metallic surfaces. The beam is sent at grazing incidence onto the metal substrate, producing an excitation of the molecular electric dipole oscillations normal to the substrate only. The absorption signal carries a wealth of information such as the position of the molecule relative to the substrate and the structure of the adsorbed molecule itself.

For the direct observation of catalytic reactions on surfaces, further specializations of the RAIRS technique are needed. Customarily, RAIRS is used for the study of relatively thick adsorbate films, which could produce alone a sufficient absorption signal. This is not the case with adsorbate layers on catalyzer surfaces, which are at most one molecule thick.

We report here the new RAIRS experimental set up designed for the Bruker IFS 120 HR spectrometer in Giessen.



**SyMath : Data analysis platform on Mathematica**  
**SpectrumFit : Analytical spectrum analysis software**  
**SyMath-Molecule : Analysis and prediction of quantum states and**  
**transitions with matrix mechanics**

*Georg Ch. Mellau<sup>(1)(2)</sup>*

*(1) Physikalisch-Chemisches-Institut, Justus-Liebig-Universität Giessen,  
Heinrich-Buff-Ring 58, D-35392 Giessen, Germany*

*(2) Mellau Consulting, Anneröder Str. 3 35463 Fernwald, Germany*

After many years of development and testing we present a new type of scientific software. The basic idea is to shift the scientific software development from algorithm development to setting up and solving a set of equations. Two general software systems are used to achieve this task: Mathematica [1] and SyMath [2].

**SyMath** is a data analysis software platform running under Mathematica ver. 4.1.2. **SyMath** implements a powerful user interface allowing the input of physical symbols, parameters and calculation formulae. These symbols and formulae are converted to executable functions and used for the calculations; also they can be saved in a database file and reloaded at any time in the program. The database set up for an analysis contains not only the numerical values of the parameters, BUT all symbol definitions and formulae.

**SpectrumFit** is a data analysis program running on the **SyMath** platform for “spectrum” type data as low or high resolution molecular spectra. The program implements spectrum analysis tasks as peak search, background correction or lineshape fit. New in this program is the feature that any function can be used as “lineshape function”, the user has only to type the formula of your lineshape function using the LineshapeEditor and start fitting the lineshape parameters to the measured spectrum. EACH parameter for EACH peak can be set to FIT or FIX for the fit, any number of peaks can be fitted together.

**SyMath-Molecule** program adds analytical matrix mechanics modules to the general SyMath system allowing the prediction and analysis of transitions and states of any quantum system described through the analytical formulas of the matrix elements. Using this program the user can simulate or analyze high resolution rotation-vibration spectra of molecules in gas phase.

(1) <http://www.wolfram.com>

(2) <http://www.symath.com>

# Synchrotron IR microspectroscopy of biomolecules in microfluidic systems

David Moss

Synchrotron Light Source ANKA, Forschungszentrum Karlsruhe,  
P.O. Box 3640, 76021 Karlsruhe, Germany  
david.moss@anka.fzk.de

FTIR spectroscopy of proteins has the unusual disadvantage of providing too much information. Thousands of individual bands contribute to the spectrum, leading to an overlap so extensive that essentially all detail is obscured. FTIR difference spectroscopy is a perturbation approach designed to overcome this problem: instead of the complete FTIR spectrum, only the changes in the spectrum in response to a biologically interesting perturbation of the sample are recorded [1]. The resulting difference spectra are far simpler than complete infrared spectra, and thus can be interpreted at the level of individual molecular bonds. But at the same time, they retain all the information pertaining to the structural dynamics related to the protein's catalytic cycle, and are thus of direct relevance to the study of molecular mechanisms in protein reactions.

An essential ingredient of an FTIR difference spectroscopy experiment is a method for triggering the desired reaction while avoiding any unwanted perturbation of the sample. Here, rapid mixing techniques have the advantage over standard approaches such as photochemistry [2-4] or electrochemistry [5], because the former are universally applicable: perturbations such as ligand, substrate or inhibitor binding, changes in pH or ionic strength, enzymatic degradation, etc. can be applied to essentially any protein. Achieving rapid fluid mixing in a 10  $\mu\text{m}$  cell pathlength suitable for FTIR spectroscopy of aqueous solutions is quite a challenge, but several elegant solutions based on microsystems technology have been described [6-11].

The brilliance advantage of synchrotron light sources can be exploited to implement rapid mixing FTIR spectroscopy in microstructured fluidic systems much smaller than those presented to date [12]. In addition to the obvious advantages of drastically decreased sample material requirements, this can be expected to improve the performance of such experiments by decreasing the distances to be covered in diffusional mixing.

## References

1. H. Fabian and W. Mänteles, (2002) in *Handbook of Vibrational Spectroscopy* (J. M. Chalmers and P. R. Griffiths, Eds.), pp. 3399-3425, John Wiley & Sons, Chichester
2. K. J. Rothschild, W. A. Cantore and H. Marrero (1983) *Science* **219**, 1333-1335
3. F. Siebert and W. Mänteles, *Eur. J. Biochem.* **130**, 565-573 (1983)
4. W. Mänteles, E. Navedryk, B. A. Tavitian, W. Kreutz and J. Breton (1985) *FEBS Lett.* **187**, 227-232
5. D. A. Moss, E. Navedryk, J. Breton and W. Mänteles (1990) *Eur. J. Biochem.* **187**, 565-572
6. D. A. Moss, K. Fuchsle, R. Masuch and A. Wolf (2000) *SPIE Proc.* **3918** (2000), 97-105
7. N. S. Marinkovic, A. R. Adzic, M. Sullivan, K. Kovacs, L. M. Miller, D. L. Rousseau, S.-R. Yeh and M. R. Chance (2000) *Rev. Sci. Instrum.* **71**, 4057-4060
8. P. Hinsmann, J. Frank, P. Svasek, M. Harasek and B. Lendl (2001) *Lab on a Chip* **1**, 16-21
9. P. Hinsmann, M. Haberkorn, J. Frank, P. Svasek, M. Harasek and B. Lendl (2001) *Appl. Spectrosc.* **55**, 241-251
10. E. Kauffmann, N. C. Darnton, R. H. Austin, C. Batt and K. Gerwert (2001) *Proc. Natl. Acad. Sci. USA* **98**, 6646-6649
11. R. Masuch and D. A. Moss (2003) *Appl. Spectrosc.* **57**, 1407-1418
12. S. Kulka, N. Kaun, J. R. Baena, J. Frank, P. Svasek, D. Moss, M. J. Vellekoop and B. Lendl (2004) *Anal. Bioanal. Chem.* **378**, 1735-1740

# High resolution gas phase spectroscopy in the far infrared with a synchrotron radiation source

*Bengt Nelander*  
*University of Lund*  
*Department Physical Chemistry, Hs 1*  
*S-22100 Lund, Sweden*  
[bengt.nelander@chemphys.lu.se](mailto:bengt.nelander@chemphys.lu.se)

The far infrared spectrum contains information on the energetics of molecular deformations such as torsions around single bonds and large scale vibrations of ring compounds. The intermolecular motions of molecular clusters fall in the far infrared spectrum. Far infrared data is therefore important as input to molecular mechanics programs for simulations of macromolecular conformations and of macromolecular solvation dynamics.

High resolution gas phase measurements can give data which are unpolluted by solvation effects. Compared to the mid infrared very few high resolution gas phase studies have been published. The reason seems to be that the achievable signal to noise ratio in the far infrared region is determined by the intensity and stability of the source. The generally available source is a black body radiator, where the intensity is determined by the source temperature. It has been known for a long time that the synchrotron radiation from a storage ring can be a high resolution source with an order of magnitude higher intensity. However Fourier spectroscopy requires a very stable source. This puts very stringent requirements on the position stability of the electron beam of the storage ring. Max-I in Lund has proven to be a good source for high resolution spectroscopy. Examples of successful measurements will be given, and the limitations of Max-I will be discussed.

## **SISSI** **A new IR beamline at ELETTRA**

*A. Nucara*  
*Coherentia- INFN and Università di Roma La Sapienza*  
*Piazzale A. Moro, 5*  
*I-00185 Roma - Italy*  
[nucara@roma1.infn.it](mailto:nucara@roma1.infn.it)

Nowadays, several infrared synchrotron radiation (IRSR) beamlines have been built on third-generation synchrotron, and many others are under test or commissioning. The beamline SISSI (Source for Imaging and Spectroscopical Studies in the Infrared), has been projected and realized to work on an exit port ELETTRA. We present a detailed study on the infrared source in term of conventional dipole emission (DE) as well as dipole edge emission (DEE), being both properties significant for this beamline. The optical design of the infrared beamline, including evaluation of the tolerance on mirrors parameter and thermal effects, is also presented. On the basis of the IRSR features and taking into account the optics of the beamline the principal figures of merit, i.e. the Brilliance Ratio and the Polarization Degree, have been evaluated by numerical

simulation. We demonstrate that, even if third-generation synchrotron are not optimized for the collection of radiation in the infrared region, the beamline SISSI is suitable for experiments requiring high flux, brilliance and polarized light.

A few scientific cases will be also discussed for a future scientific program. Typical applications of infrared synchrotron radiation in the field of solid state physics will be shown, with particular emphasis to high-temperature-superconductor experiments and high-pressure measurements with diamond anvil cell. Biological and environmental use of IRSR at SISSI will be also discussed.

A.Nucara, S. Lupi and P. Calvani, Review of Scientific Instruments, 74, 3934, (2003).  
S. Lupi, A. Nucara, P. Calvani and M. Ferianis, Synch. Rad. News, 14,319, (2001).

## **Experiments with the CLIO infrared FEL**

**J.M. Ortega**

*LURE, 209d, Université de Paris Sud  
BP 34, 91898 ORSAY cedex, FRANCE.  
jean.michel.ortega@lure.u-psud.fr*

The infrared free-electron laser offers the advantage of a potential large tunability since the FEL gain itself remains substantially high throughout the infrared spectral range, and the reflectivity of metal mirrors used in the optical cavity remains also close to unity. The main limitation comes from the diffraction of the optical beam due to the finite size of the vacuum chamber of the undulator and other optical cavity elements. At CLIO, we have obtained an FEL tunable from 3 to 120  $\mu\text{m}$  by operating the accelerator between 50 and 14 MeV and we plan to extend further this spectral range. Various type of experiments are taking place at the CLIO FEL facility. We discuss, in particular, the infrared near-field experiments that have been undertaken. We emphasize the spectroscopic near-field measurements and discuss some limitations that may appear in practice and theoretically. We present also preliminary measurements obtained with photoacoustic methods aimed at increasing the signal over noise ratio obtained with small objects.

# The superconductor MgB<sub>2</sub> and the charge density wave NbSe<sub>3</sub> system: an optical perspective of their broken symmetry ground states

*A. Perucchi<sup>1</sup>, J. Karpinski<sup>1</sup>, L. Degiorgi<sup>1</sup>, and R.E. Thorne<sup>2</sup>*

*<sup>1</sup>Laboratorium für Festkörperphysik, ETH Zürich, CH-8093 Zürich, Switzerland*

*<sup>2</sup>Department of Physics, Cornell University, Ithaca NY 14853, U.S.A.*

*perucchi@phys.ethz.ch*

Broken symmetry ground states, like superconductivity or charge density wave (CDW), are collective states in condensed matter and attracted a lot of interest over several years.

First of all, we address superconductivity in MgB<sub>2</sub>. We present magneto-optical reflectivity results in the basal-plane from the ultraviolet down to the far infrared (IR) as a function of temperature and magnetic field oriented along the c-axis. In the far IR there is a clear signature of the superconducting gap with a gap-ratio  $2\Delta/k_B T_c \sim 1.2$ . The gap is suppressed in an external magnetic field, which is a function of temperature. We extract the temperature dependent upper critical field  $H_{c2}$  along the c-axis, compatible with the Helfand-Werthamer behavior.

Secondly, we present data on the CDW material NbSe<sub>3</sub>. This system exhibits two CDW phase transitions at 145 and 59 K, where the resistivity shows sharp anomalies upon decreasing temperature. In the mid to the far IR region we find a depletion of the optical conductivity with decreasing temperature. This leads to a redistribution of spectral weight from low to high energies due to partial gapping of the Fermi surface as consequence of the CDW transitions. We establish also how much of the Fermi surface is gapped by the transitions. Finally, we deduce the bulk magnitudes of the CDW gaps and discuss the scattering of the ungapped free charge carriers and the role of fluctuation effects.

A better understanding of both MgB<sub>2</sub> and NbSe<sub>3</sub> may take great advantage from future investigations with infrared synchrotron radiation (IRSR). The high brightness of IRSR can help to overcome difficulties in measuring the electrodynamic response of such materials under extreme experimental conditions (low temperature, high magnetic field, and high pressure). The possibility to extend measurements at frequencies normally not accessible to conventional IR thermal sources may shed more light on the behavior of the collective phenomena characterizing broken symmetry ground state systems.

## ***Electrical Properties in Yttria Stabilized Zirconia Investigated by Impedance Spectroscopy***

*D. Vladikova<sup>a</sup>, G. Raikova<sup>a,\*</sup>, Z. Stoynov<sup>a</sup>, J. A. Kilner<sup>b</sup> and S. J. Skinner<sup>b</sup>*

*<sup>a</sup>Institute of Electrochemistry and Energy Systems– Bulgarian Academy of Sciences,  
Acad. G. Bonchev Str., bl. 10, 1113 Sofia, BULGARIA*

*<sup>b</sup>Centre for Ion Conducting Membranes, Department of Materials,  
Imperial College of Science, Technology and Medicine, London SW7 2BP, UK*

*\*Corresponding author: [graikova@bas.bg](mailto:graikova@bas.bg)*

Yttria Stabilized Zirconia (YSZ) is an important solid electrolyte with applications in solid oxide fuel cells (SOFC) and oxygen separators, due to its good electrical and mechanical properties. This work aims at a deeper insight into the complicated factors influencing the conductivity of YSZ with the help of the Impedance Spectroscopy. The impedance data analysis is performed by the recently developed new structural approach called Differential Impedance Analysis (DIA) [1-8]. It eliminates the need of an initial hypothesis about the system, extracting the impedance model directly from the experimental data.

The high ionic conductivity of cubic stabilized zirconia is realized via the addition of a large concentration of the acceptor dopant  $Y_2O_3$ . For charge compensation oxygen vacancies are formed. It is known that the ionic conductivity of YSZ takes place by a vacancy mechanism. There is an experimental evidence for the elimination of the contribution of cations, as well as of protonic and electronic transport. The high concentration of the dopant  $Y_2O_3$  aids the formation of associates ( $\square$ ) and  $(2\square)^x$  [9], which serve as vacancy trapping centres and thus a very small part of the oxygen vacancies take active part in the conductivity process. What is not well known is the mobility and concentration of the free vacancies able to take part in the mass transport and their temperature dependence. It is supposed that the defect complexes bring to the formation of vacancy ordered phases (microdomains) with different temperature stability.

The conductivity of YSZ can be affected by its complicated microstructure. Some problems may arise from secondary microstructural changes in the bulk such as formation of cubic tetragonal interfaces, internal microcracking and disintegration, which may increase the resistance of the bulk material. The grain boundaries are a serious source for conductivity changes. In principle pure boundaries in fast ion conducting solids show a low boundary resistance. The presence of depletion space charge layers at the boundaries, i.e. depletion of oxygen vacancies is a reason for the grain boundary blocking effect. In some cases the “spillover” effect might be also taken into account for the explanation of YSZ conductivity behaviour [10].

The modeling of the electrode reaction follows the classical electrochemical concept for the charge-transfer process occurring at the three-phase boundary interface (TPB) [11]. Although the publications regarding this process are numerous, a simultaneous observation of the electrolyte conductivity and electrode reaction is not done before.

YSZ samples produced by ESCETF Single Crystal Technology B.V. were investigated. The single crystal with  $\langle 100 \rangle$  orientation comprised 9,5 mol% yttrium oxide, while the

polycrystalline material contained 8.5 mol %. The impedance measurements were done on Solartron 1260 FRA over the frequency ranges 13 MHz - 0,1Hz with density 9 points per decade. The experiments included in this study were carried at amplitude 300 mV and variation of the temperature in the interval from 200 to 950 °C. The samples were covered with porous platinum electrodes. A procedure for corrections of the parasitic inductance of the cell and of the cabling was done before the DIA analysis.

Our first experiments show that Arrhenius plots built for the two materials have a kink at 650 °C for the single crystal and at 600 °C for the polycrystalline sample [12]. The calculated activation energies ( $E_a$ ) coincide - of about 0.3-0.4 eV for temperatures below the kink and of about 1.14 eV above the kink. These results show that the grain boundaries of the polycrystalline sample are clean and do not have a blocking effect.

The following activation energies for electrode reaction were obtained from the Arrhenius plots (Fig. 1a):  $E_a = 0.52$  eV for the temperature interval 500-600°C and  $E_a = 1.62$  eV for temperatures above 600°C. They follow the same tendency as the single crystal sample (Fig. 1b), where  $E_a = 0.66$  eV for temperatures 550-650°C and  $E_a = 1.62$  eV for temperatures above 650°C. The higher activation energy at higher temperatures could be explained with a change in the rate limiting stage of the electrode reaction. We can suppose transport (diffusion) limitation for the low temperature interval up to 650 °C. At higher temperatures an increased surface accumulation of oxygen species is observed. It indicates a slower dissociation in relation to the bulk incorporation, which is in agreement with the conclusions in [13].

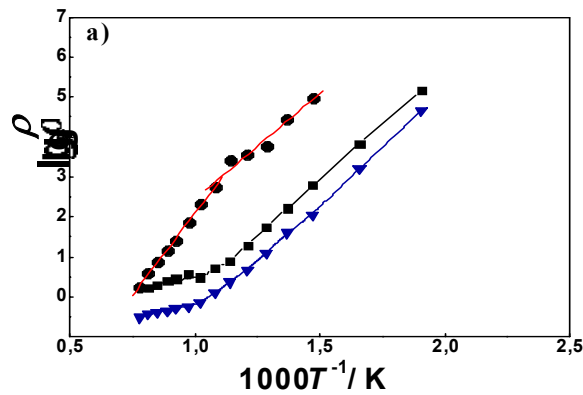


Fig. 1. Arrhenius plots of polycrystalline YSZ (a) and YSZ single crystal (b) for bulk ( $\nabla$ ), grain boundaries ( $\blacksquare$ ) and electrode reaction ( $\bullet$ )

It is interesting to note that the activation energy of the electrode reaction for polycrystalline and single crystal YSZ at lower temperatures is the same, while above the kink that of the polycrystalline material is higher. This result shows that the grain boundaries do not influence the transport mechanism, which is the rate limiting stage at lower temperatures, while at higher temperatures they hamper the bulk incorporation.

It should be mentioned that the kink in the Arrhenius plots for the bulk and for the grain boundaries appears at the same temperature at which it is observed for the

electrode reaction. It confirms the hypothesis for internal relation between the conductivity of the sample and the electrode reaction behaviour.

Obviously the quantitative evaluation of YSZ conductivity and oxygen transfer are of great importance for elucidating the knowledge about this material and thus about the methods for its predictable optimization. A prolongation of this impedance study by the new and powerful techniques as IRSR and ESCA will give a possibility for correlating structure characteristics with chemical and physical properties of the material.

#### References

- [1] Z. Stoynov, Polish J. Chem., 71 (1997) 1204.
- [2] Z. Stoynov, in: "Materials for Lithium-Ion Batteries", C. Julien, Z. Stoynov (eds.), Kluwer Academic Publishers, 3/85 (2000) 371.
- [3] D. Vladikova, P. Zoltowski, E. Makowska, Z. Stoynov, Electrochim. Acta 47 (2002) 2943.
- [4] D. Vladikova, Z. Stoynov, M. Viviani, J. Europ. Ceram. Soc. 24 (2004) 1121.
- [5] Z. Stoynov, Commun. 15<sup>th</sup> Forum on Electrochemical Impedance, Paris, France, December, 2002, p3.
- [6] D. Vladikova, G. Raikova, Z. Stoynov, in: "Nanoscience and Nanotechnology '02", E. Balabanova, I. Dragieva (eds.), Heron Press Science Series, Sofia, 2002, p.66.
- [7] G. Raikova, D. Vladikova, Z. Stoynov, <http://accessimpedance.iusi.bas.bg>, Imp. Contribut. Online, 1 (2003) P8-1; Bulg. Chem. Commun. 36 (2004) 66.
- [8] D. Vladikova, G. Raikova, Z. Stoynov, H. Takenouti, J. Kilner, S. Skinner, "Differential Impedance Analysis of Solid Oxide Materials", to be published.
- [9] V.S. Stubican, R.C. Hink, S.P. Ray, J. Am. Ceram. Soc. 61 (1978) 17.
- [10] D. Tsiplakides, C.G. Vayenas, Solid State Ionics 152-153 (2002) 635.
- [11] A. Schmid, Helv. Chim. Acta 1 (1933) 69.
- [12] D. Vladikova, J. A. Kilner, S.J. Skinner, G. Raikova, Z. Stoynov, "Differential Impedance Analysis of Single Crystal and Polycrystalline Yttria Stabilized Zirconia", to be published.
- [13] P. S. Manning, J. D. Sirman, R. A. De Souza, J. A. Kilner, Solid State Ionics, 100 (1997) 1.



## Complex Adsorbates and Surface Phenomena: how far can IR Spectroscopy take us?

Rasmita Raval  
Director, Surface Science Centre  
Department of Chemistry  
University of Liverpool  
Liverpool L69 7ZD, UK  
raval@liv.ac.uk

Reflection Absorption Infrared Spectroscopy has now established itself as a powerful and versatile technique for monitoring molecular adsorption at defined single crystal metal surfaces. This talk will discuss the nature of the information that can be obtained with this spectroscopy. In particular, the strengths and limitations of Surface Mid-IR and Far-IR spectroscopy in providing information on complex adsorbates, on molecule-molecule interactions, on molecule-metal bonding and in monitoring molecular adsorbate-induced surface reconstructions will be discussed. Systems discussed will include the adsorption of amino-acids, nucleic acids, chiral and prochiral molecules, and simple diatomics at metal surfaces.

- [1] 'Extended Surface Chirality from Supramolecular Assemblies of Adsorbed Chiral Molecules', M.Ortega-Lorenzo, C.J.Baddeley, C.Muryn and R.Raval, *Nature*, 404 (2000) 376.
- [2] 'Complex Organic Molecules at Metal Surfaces: Bonding, Organisation and Chirality' S. Barlow and R.Raval, *Surface Science Reports*, 50 (2003) 201.
- [3] 'From Local Adsorption Stresses to Chiral Surfaces: (R,R)-Tartaric Acid on Ni(110)', V.Humblot, S. Haq, C. Muryn, W.A.Hofer and R.Raval, *J. Am. Chem. Soc.*, 124 (2002) 503.
- [4] *RAIRS Investigation on the Orientation and Intermolecular Interactions of Adenine on Cu(110)*. A.McNutt, S.Haq and R.Raval, *Surface Science*, 531 (2003) 131-144.
- [5] *Synchrotron Far-Infrared RAIRS studies of Complex Oxygen-containing Molecules on Cu(110)*. V.Humblot, C.Bingham, D. Le Roux, E. Mateo Marti, A.McNutt, T.S. Nunney, M. Ortega Lorenzo, A.J. Roberts, J.Williams, M.Surman and R.Raval, *Surface Science*, 537 (2003) 253-264.
- [6] *Local and Global Chirality at Surfaces: Succinic Acid versus Tartaric Acid on Cu(110)*, V. Humblot, M. Ortega Lorenzo, C.J. Baddeley, S. Haq and R. Raval, *J. Am. Chem. Soc.* 126 (2004) 6460-6469.
- [7] *Supramolecular Assembly of Size and Shape-selected Chiral Clusters: Alanine on Cu(110)* *Langmuir*, S.M. Barlow, D. Le Roux, S. Luoafi, J. Williams, S. Haq and R.Raval, 20 (2004) 7171-7176.

## **The FEL-based IR User Facility FELIX: A versatile source for infrared spectroscopy and studies on vibrational dynamics**

*Britta Redlich*

*FOM Institute 'Rijnhuizen', Edisonbaan 14, 3439 MN Nieuwegein, The Netherlands*

*brittar@rijnh.nl*

After a short introduction to the free electron laser, the characteristic features of the free electron laser and the facility will be discussed along with the implications for the kind of experiments that can be done at FELIX. In general, the experiments performed at FELIX cover a wide range of disciplines ranging from physics, chemistry, and material science to biology. Presently, the experiments fall predominantly in one of the following two classes: (i) relaxation phenomena in condensed matter and (ii) spectroscopy of gas-phase species, (bio)molecules and clusters either neutral or ionized.

Experiments of the first group will mostly use the low repetition rate or single pulse mode in view of the relaxation times involved. For those kinds of experiments two setups are available at the facility dedicated to measurements using four-wave mixing techniques as transient bleaching, transient grating and photon-echo. As examples of the first class of experiments studies will be presented on the relaxation of the stretch vibrations of hydrogen and deuterium in amorphous silicon and investigations on the vibrational lifetime of protein modes in the mid- and far-IR.

The second class of experiments is characterized by (very) low absorption of the sample and, because the detection scheme is based on dissociation or ionization of the species, typically a strongly nonlinear dependence on the laser fluence, implying the use of the high repetition mode of FELIX. For these experiments on gas-phase molecular systems, the two key requirements for the FEL are tunability and high fluence on the microsecond time scale. As examples of this class experiments investigations will be discussed on (a) the vibrational properties complexes of CO adsorbed on metal clusters and pure metal clusters, (b) vibrational spectroscopy of biomolecules and (c) studies using sophisticated ion trap machines i.e. a tandem mass-spectrometer and a Fourier Ion Cyclotron Resonance Mass Spectrometer.

As an outlook, a new project invoking the construction of building a new beam line at Rijnhuizen called 'FELICE' dedicated to intracavity experiments will be introduced.

# Using infrared spectroscopy for understanding the dynamics in confining systems

*Pascale Roy  
LURE Bat.209D  
Centre Universitaire Paris Sud  
BP 34 - 91898 Orsay Cedex  
France  
pascale.roy@lure.u-psud.fr*

## THz microspectroscopy using coherent synchrotron radiation

*K. Holldack<sup>1</sup>, H.-W. Hübers<sup>2</sup>, P. Kuske<sup>1</sup>, U. Schade<sup>1</sup>, G. Wüstefeld<sup>1</sup>  
<sup>1</sup> Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H.,  
Albert-Einstein-Strasse 15, 12489 Berlin, Germany  
<sup>2</sup> Deutsches Zentrum für Luft- und Raumfahrt,  
Rutherford-Strasse 2, 12489 Berlin, Germany  
schade@bessy.de*

Coherent synchrotron radiation (CSR) from LINACs and storage rings is a tool which closes the ‘gap’ between microwaves and thermal black body radiation by offering powerful and broadband radiation in the THz-range. During the past few years, at BESSY a new technique to generate powerful, stable, coherent sub-THz and THz-radiation from the electron storage ring has been developed [1]. The recent reports on this new brilliant coherent far infrared broadband source have found considerable international interest. The spectral range at around 1 mm wavelength (0.3 THz) which can be only poorly accessed by conventional sources is now covered by operating BESSY in special machine modes. Here, up to  $10^8$  more brilliance than from a black body source has been achieved. The feasibility of using the coherent synchrotron radiation in scientific applications has been proven at the infrared beamline IRIS [2]: the Josephson plasma resonance in the sub-THz region of optimally doped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  could be measured for the first time [3]. In addition, the high power of the CSR from the storage ring enables near-field microspectroscopy experiments in the sub-cm and mm wavelength range. Spectral images from biological samples can be obtained with a lateral resolution much lower than the wavelength involved as demonstrated on living leaves [4] and on human tooth samples. The production of stable, high power, coherent synchrotron radiation at THz and sub-THz frequencies at BESSY opens a new region in the electromagnetic spectrum offered at synchrotron radiation sources which can now be applied for imaging, spectroscopic and microscopic methods in solid state physics, biology, and medicine.

- [1] M. Abo-Bakr, et al., Phys. Rev. Lett. **88**, 254801 (2002),  
Phys. Rev. Lett. **90**, 094801 (2003).
- [2] U. Schade et al., Rev. Sci. Instrum. **73**, 1568 (2002).
- [3] J. Singley et al., Phys. Rev. B **69**, 092512 (2004).
- [4] U. Schade et al., Appl. Phys. Lett. **84**, 1422 (2004).

## General conclusions

The overview of applications provided by several speakers has confirmed the validity of using SR in IR spectromicroscopy applications, exploiting the gain in spatial resolution provided by the brilliance of the source. Remarkable examples were provided for archaeometry, polymer chemistry, cosmetic chemistry, histology, geochemistry, analytical chemistry, to name a few. Overall spectromicroscopy has confirmed to be the use of SR IR with the widest appeal for applied and industrial research.

A highly debated topic was the comparison between the performance of IR imaging using synchrotron radiation and of imaging with conventional sources. Confocal IR imaging can achieve the diffraction limit only by exploiting the brilliance of a synchrotron source. Nonetheless the introduction of focal plane array (FPA) IR detectors has considerably increased the performance of bench top IR microscopes, allowing full field imaging. It was shown that comparable image quality can be obtained using a conventional IR source with a PDA array detector and using a SR source for confocal imaging. In addition full field imaging appears to be generally faster than confocal imaging. On the other hand using a SR source couple to a PDA array provides the best combination, allowing for faster image collection than with a conventional source. Because of these observations it was noted that, although the use of SR for IR imaging still retains some advantages, the limited accessibility of synchrotron sources often offsets them in a negative way. As a consequence, given the current state of the art, to several participants the use of a synchrotron source for IR imaging appears to be unnecessary or inconvenient except in the most demanding situations.

The development of strategies to implement near-field IR imaging with SR and FEL radiation has been discussed by several groups. These techniques prove to be particularly advantageous when coupled to the use of THz radiation since they allow overcoming diffraction limited spatial resolution in far-field imaging.

Spectroscopic applications appear to remain a mainstay of SR and FEL IR. Advantages arising from the use of SR and FEL radiation have been shown to include the pulsed structure and broad spectral band emission, ranging down to the Far IR. Applications to time resolved and pump-probe type of experiments have been shown. High resolution spectroscopic studies in the gas phase also take advantage of the Far IR emission of synchrotron radiation.

A rapidly expanding topic is the use of synchrotron and FEL sources for the production of coherent THz radiation. These facilities constitute unique sources of high photon fluxes in this spectral region. The discussion focused both on the need to develop the technology for THz production and on possible applications. Production of THz radiation with storage rings is currently constrained by the need to alter the bunch structure to a state that is not compatible with other synchrotron activity. This is a severe restriction since it requires that the synchrotron be dedicated completely to this activity. To overcome this limitation, the construction of a ring fully dedicated to THz generation has been planned at LBNL. No similar initiative is currently under way in Europe.

A general effort appears to be under way in several synchrotrons to coordinate in-house IR and X-ray activity by creating the conditions to perform multiple technique experiments on the same sample, in particular for imaging and spectromicroscopy applications. This objective is being pursued mostly by the development of interchangeable sample holders that allow sample transfer between different beamlines without losing spatial reference to sample coordinates.

## Future Directions and Activities

In general, the limited accessibility of synchrotron sources appears to be a problem in their effective exploitation. It was noted that for applications that require fast response, this limitation is critical. The point case is that of medical diagnosis. It was shown that SR IR spectromicroscopy possess several characteristics that make it a useful tool in histological studies. Nonetheless, the lengthy process required to access synchrotron beam time and the associated organizational

issues relegate the technique to niche applications in this context. Mostly this is due to the fact that the organization of synchrotron beam time dates from times when synchrotrons were mostly employed to perform lengthy single-session experiments. Streamlining access procedures, to allow for faster access and flexible beamtime schedules, is a requirement to reduce the problem.

Several future collaborations have been born out of the meeting. Given the diversity of the disciplines involved, most of these interactions involve a limited number of groups. Collaborations between users and synchrotron providers will be taking advantage of Marie Curie instruments to favor the exchange of researchers. Several applications are arising to exploit the existing I3 program (IA-SFS) involving European light sources. In particular the instrument will be used to support the collaborative development of instrumentation for improving the imaging capabilities of SR and FEL beamlines.

# PROGRAMME

## Wednesday 27 October 2004

Evening *Arrival*

## Thursday 28 October 2004

8:30 *Registration*

9:00 *Opening Address*

9:15 **Presentation of the European Science Foundation (ESF)**

9:30 **G. L. Carr**  
**Synchrotron Infrared Science: Past, Present and Future**

10:30 *Coffee Break*

11:00 **P. Dumas**  
**Multidisciplinary Applications in Synchrotron Infrared Microscopy: present to future**

11:45 **P. Lasch**  
**Spatially resolved IR microspectroscopy of single cells and tissues**

12:30 *Lunch and Poster Presentation*

14:30 **J.M. Ortega**  
**Experiments with the CLIO infrared FEL**

15:15 **B. Redlich**  
**The Free Electron Laser based IR User Facility FELIX**

16:00 *Coffee Break*

16:30 **A. Nucara**  
**SISSI: A new IR beamline at ELETTRA**

17:15 **M. Tobin**  
**A New Infrared Microspectroscopy Facility at the Daresbury SRS – Current Performance, Latest Results and Future Developments.**

18:00 **K. Hinrichs**  
**Infrared ellipsometry for characterisation of organic films and interfaces**

18:45 *Round Table and Buffet*

## Friday 29 October 2004

- 9:00 R. Raval  
**Complex Adsorbates and Surface Phenomena- how far can IR Spectroscopy take us?**
- 9:45 B. Nelander  
**High resolution gas phase spectroscopy in the far infrared with a synchrotron radiation source**
- 10:30 *Coffee Break*
- 11:00 P. Roy  
**Using infrared spectroscopy for understanding the dynamics in confining systems**
- 11:45 D. Moss  
**Synchrotron IR microspectroscopy of biomolecules in microfluidic systems**
- 12:30 *Lunch and Poster Presentation*
- 14:00 M. Martin  
**Synchrotron Infrared Science: Physics, Biology, Environmental Science and Coherence**
- 14:45 U. Schade  
**THz microspectroscopy using coherent synchrotron radiation**
- 15:30 J. Chwiej  
**Researches on neurodegeneration using techniques based on synchrotron radiation**
- 16:00 *Coffee Break*
- 16:30 A. Perucchi  
**The superconductor  $MgB_2$  and the charge density wave  $NbSe_3$  system: an optical perspective of their broken symmetry ground states**
- 17:00 G. Margaritondo  
**Beating the Diffraction Limit: Near-field Microscopy with Advanced Photon Sources**
- 17:45 *Poster Presentation*
- 20:00 *Conference Dinner*

## Saturday 30 October 2004

- 9:30 Visit to Elettra
- 12:30 *Lunch*
- Departure

## List of Participants

### Convenors:

1. **Maya KISKINOVA**  
ELETTRA Sincrotrone Trieste  
Microscopy Section  
AREA Science Park  
Strada Statale 14 - km 163,5  
34012 Basovizza (Trieste)  
Italy  
Tel: +39 040 375 8549  
Fax: +39 040 375 8565  
Email: kiskinova@elettra.trieste.it
2. **Luca QUARONI**  
ELETTRA Sincrotrone Trieste  
AREA Science Park  
Strada Statale 14 - km 163,5  
34012 Basovizza (Trieste)  
Italy  
Tel: +39 040 375 8729  
Fax: +39 040 375 8776  
Email: luca.quaroni@elettra.trieste.it

### Programme Committee:

3. **Stefano LUPI**  
Department of Physics  
Universita' di Roma 'La Sapienza'  
Fermi Building, 4th floor  
Piazzale A. Moro, 5  
00185 Roma  
Italy  
Email: lupi@roma1.infn.it
4. **Alessandro NUCARA**  
Department of Physics  
Universita' di Roma 'La Sapienza'  
Fermi Building, 4th floor  
Piazzale A. Moro, 5  
00185 Roma  
Italy  
Tel: +39 06 499 13496  
Email: alessandro.nucara@roma1.infn.it

### Local Organiser:

5. **Ildo WEFFORT**  
ELETTRA Sincrotrone Trieste  
Divisione Esperimenti  
AREA Science Park  
Strada Statale 14 - km 163,5  
34012 Trieste  
Italy  
Tel: +39 040 3758522  
Fax: +39 040 3758366  
Email: ilde.weffort@elettra.trieste.it

### Participants:

6. **Ivano ALESSANDRI**  
University of Brescia  
via Branze 38

25123 Brescia  
Italy  
Email: ivano.alessandri@ing.unibs.it

7. **Ioanna ANASTASSOPOULOU**  
Materials Science and Engineering Division  
School of Chemical Engineering  
National Technical University of Athens  
Zografou Campus  
15780 Zografou - Athens  
Greece  
Tel: +30 210 772 3133  
Email: ianastas@central.ntua.gr

8. **Fariba BHRAMI**  
CCLRC  
Synchrotron Radiation Source Laboratory  
Daresbury WA4 4AD  
United Kingdom  
Email: f.bahrmi@dl.ac.uk

9. **Giuseppe BELLISOLA**  
Section of Immunology  
Dept of Pathology  
University of Verona  
Policlinico G.B. Rossi  
P.le L.A. Scuro, 10,  
37134 Verona  
Italy  
Email: giuseppe.bellisola@univr.it

10. **Nicola BONINI**  
SISSA, Scuola Superiore di Studi Avanzati  
Via Beirut 2-4,  
34014 Trieste  
Italy  
Email: bonini@sissa.it

11. **Paolo CALVANI**  
Università di Roma La Sapienza  
Piazzale A. Moro, 2  
00185 Roma  
Italy  
Email: calvani@roma1.infn.it

12. **G. Lawrence CARR \***  
NSLS  
Brookhaven National Laboratory  
Upton NY 11973-5000  
United States  
Tel: +1 631 344 2237  
Fax: +1 631 344 3238  
Email: [carr@bnl.gov](mailto:carr@bnl.gov)

13. **Joanna CHWIEJ**  
Faculty of Physics  
AGH-University of Science and Technology  
Al. Mickiewicza 30  
30-059 Krakow  
Poland  
Email: [jchwiej@novell.ftj.agh.edu.pl](mailto:jchwiej@novell.ftj.agh.edu.pl)

14. **Marco COLOMBATTI**  
Policlinico G.B.Rossi



- Section of Immunology  
Department of Pathology  
Universita degli Studi di Verona  
piazzale L A Scuro 10  
37134 Verona  
Italy  
Tel: +39 045 807 4007  
Fax: +39 045 820 2459  
Email: [marco.colombatti@univr.it](mailto:marco.colombatti@univr.it)
15. **Paul DUMAS**  
**SOLEIL Synchrotron**  
**l'Orme des Merisiers**  
**BP 48, Saint Aubin**  
**F-91192 Gif sur Yvette Cédex**  
**France**  
Tel: +33-1-69-35-9621  
Email [paul.dumas@synchrotron-soleil.fr](mailto:paul.dumas@synchrotron-soleil.fr)
16. **Mattia FRISANCO**  
Section of Immunology  
Dept of Pathology  
P.le L.A. Scuro, 10  
37134 Verona  
Italy  
Email: [mfrisanco@yahoo.it](mailto:mfrisanco@yahoo.it)
17. **Maria HERNANDEZ PEREZ**  
PCML  
Université Lyon 1  
10 rue Ampère  
69622 Villeurbanne Cedex  
France  
Email: [hernandez@pcml.univ-lyon1.fr](mailto:hernandez@pcml.univ-lyon1.fr)
18. **Stefan HEUN**  
TASC-INFM Laboratory  
Area di Ricerca  
34012 Basovizza (Trieste)  
Italy  
Tel: +39 040 375 6423  
Fax: +39 040 226 767  
Email: [heun@tasc.infm.it](mailto:heun@tasc.infm.it)
19. **Karsten HINRICHS \***  
Department Berlin  
Institute of Spectrochemistry and Applied  
Spectroscopy (ISAS)  
Albert-Einstein-Str. 9  
12489 Berlin-Adlershof, Germany  
Tel: +49 30 63923541  
Fax: +49 30 63923544  
Email: [hinrichs@isas-berlin.de](mailto:hinrichs@isas-berlin.de)
20. **Philippe IWANSKI**  
Enitecnologie Spa  
Via Maritano, 26  
20097 S. Donato Milanese (Milano)  
Italy  
Tel: +39 02 5205 6559  
Fax: +39 02 5203 6347  
Email: [piwanski@enitecnologie.eni.it](mailto:piwanski@enitecnologie.eni.it)
21. **Nina KAUN**  
Institute of Chemical Technologies and  
Analytics  
TU Vienna
- Getreidemarkt 9/164-AC  
Vienna, Austria  
Email: [ninakaun@pop.tuwien.ac.at](mailto:ninakaun@pop.tuwien.ac.at)
22. **Panagiota KOLOVOU**  
School of Chemical Engineering  
National Technical University of Athens  
Zografou Campus  
5780 Zografou - Athens  
Greece  
Email: [kolovoup@central.ntua.gr](mailto:kolovoup@central.ntua.gr)
23. **Peter LASCH \***  
Biophysical Structure Analysis, P34  
Robert Koch-Institut  
Nordufer 20  
13353 Berlin  
Germany  
Tel: +49-30-45472405  
Fax: +49-30-45472606  
Email: [LaschP@rki.de](mailto:LaschP@rki.de)
24. **Bernhard LENDL**  
Institute of Chemical Technologies and  
Analytics  
TU Vienna  
Getreidemarkt 9/164-AC  
Vienna  
Austria  
Email: [blendl@mail.zserv.tuwien.ac.at](mailto:blendl@mail.zserv.tuwien.ac.at)
25. **Giorgio MARGARITONDO \***  
Faculté des sciences de base  
Ecole Polytechnique Federale de Lausanne  
EPFL-SB  
1015 Lausanne  
Switzerland  
Tel: +41 21 693 3302  
Fax: +41 21 693 4666  
Email: [giorgio.margaritondo@epfl.ch](mailto:giorgio.margaritondo@epfl.ch)
26. **Michael MARTIN \***  
Lawrence Berkeley National Laboratory  
Advanced Light Source Division  
1 Cyclotron Road  
Bldg 6R2100  
Berkeley CA 94720-8226  
United States  
Tel: +1 510-495-2231  
Fax: +1 510-495-2067  
Email: [MCMartin@lbl.gov](mailto:MCMartin@lbl.gov)
27. **Georg MELLAU**  
Physikalisch Chemisches Institut  
Justus Liebig Universität  
Heinrich-Buff-Ring 58  
35392 Giessen  
Germany  
Email: [georg@mellau.de](mailto:georg@mellau.de)
28. **David MOSS \***  
Forschungszentrum Karlsruhe  
Institute for Synchrotron Radiation  
Hermann-von-Helmholtz-Platz 1  
76344 Eggenstein-Leopoldshafen  
Germany

Tel: +49-7247-82-2689  
Fax: +49-7247-82-6172  
Email: david.moss@anka.fzk.de

United Kingdom  
Tel: +44 151 794 35 84  
Fax: +44 151 794 32 65  
Email: [r.raval@liv.ac.uk](mailto:r.raval@liv.ac.uk)

29. **Bengt NELANDER \***  
Dept Physical Chemistry  
Chemical Center  
Lund University  
Hs 1  
22100 Lund  
Sweden  
Tel: +46 46 1081 83  
Fax: +46 46 104 533  
Email: [Bengt.Nelander@chemphys.lu.se](mailto:Bengt.Nelander@chemphys.lu.se)
30. **Giuseppe ONORI**  
Dip. Di Fisica  
Università di Perugia  
Via Pascoli  
06100 Perugia  
Italy  
Email: [onori@fisica.unipg.it](mailto:onori@fisica.unipg.it)
31. **Jean Michel ORTEGA \***  
LURE  
Centre Universitaire Paris-Sud  
Bat. 209 D  
BP 34  
91898 Orsay Cedex  
France  
Tel: +33 1 6446 8017  
Fax: +33 1 6446 4148  
Email: [ortega@lure.u-psud.fr](mailto:ortega@lure.u-psud.fr)
32. **Alessandro PACIARONI**  
Dipartimento di Fisica  
Università degli Studi di Perugia  
Via A. Pascoli  
06100 Perugia  
Italy  
Tel: +39 075 585 2785  
Fax: +39 075 44666  
Email: [paciaroni@fisica.unipg.it](mailto:paciaroni@fisica.unipg.it)
33. **Andrea PERUCCHI**  
Laboratorium für Festkörperphysik,  
ETH Zürich - Switzerland  
ETH Hönggerberg HPF F3  
8093 Zürich  
Switzerland  
Email: [perucchi@phys.ethz.ch](mailto:perucchi@phys.ethz.ch)
34. **Gergana RAIKOVA**  
Institute of Electrochemistry and Energy  
Systems  
Bulgarian Academy of Sciences  
Acad. G. Bonchev Str. bl.10  
1113 Sofia  
Bulgaria  
Email: [graikova@bas.bg](mailto:graikova@bas.bg)
35. **Rasmita RAVAL \***  
Surface Science Research Centre  
Department of Chemistry  
University of Liverpool  
P.O. Box 147  
Liverpool L69 7ZD
36. **Britta REDLICH \***  
FOM  
Molecular Dynamics Group  
Institute for Plasma Physics Rijnhuizen  
P.O. Box 1207  
3430 BE Nieuwegein  
Netherlands  
Tel: +31 30 609 6999 (op.), -893 (dir.)  
Fax: +31 30 603 1204  
Email: [brittar@rijnh.nl](mailto:brittar@rijnh.nl)
37. **Pascale ROY \***  
LURE  
Centre Universitaire Paris Sud  
Bat. 209D  
BP 34  
91898 Orsay Cedex  
France  
Tel: +33 1 6446 82 89  
Fax: +33 1 64 46 41 48  
Email: [pascale.roy@lure.u-psud.fr](mailto:pascale.roy@lure.u-psud.fr)
38. **Diego SALI**  
*(Bruker Representative)*  
Bruker Optics  
Via G. Pascoli 70/3  
20133 Milano  
Italy  
Tel: +39 02 70 63 63 70  
Email: [optics@bruker.it](mailto:optics@bruker.it)
39. **Ulrich SCHADE \***  
BESSY  
Albert Einstein Str 15  
12489 Berlin-Adlershof  
Germany  
Tel: +49 30 63923449  
Fax: +49 30 63922989  
Email: [schade@bessy.de](mailto:schade@bessy.de)
40. **Giacinto SCOLES**  
Chemistry Department and  
Princeton Materials Institute  
Princeton University  
70 Prospect Avenue  
Princeton NJ 08540  
United States  
Tel: +1 609 258 5570  
Fax: +1 609 258 6665  
Email: [gscoles@princeton.edu](mailto:gscoles@princeton.edu)
41. **Mark TOBIN \***  
Daresbury Laboratory  
Synchrotron Radiation Department  
Warrington Cheshire WA4 4AD  
United Kingdom  
Tel: +44 1925 603584  
Fax: +44 1925 603124  
Email: [m.j.tobin@dl.ac.uk](mailto:m.j.tobin@dl.ac.uk)

\* denotes speakers

## Statistical Data

Age Range	Speakers (including two young scientists)	Other Participants
20 – 29	2	9
30 – 39	4	5
40 – 49	5	3
50 +	6	6
<b>Gender</b>		
M	13	16
F	4	7
<b>Institution of Origin</b>		
Italy	1	15
France	3	1
Germany	4	1
USA	2	0
UK	2	1
Switzerland	2	0
Sweden	1	0
Netherlands	1	0
Poland	1	0
Bulgaria	0	1
Greece	0	2
Austria	0	2
<b>Nationality</b>		
Italy	2	11
France	3	1
Germany	3	1
USA	3	0
UK	3	1
Switzerland	0	0
Sweden	1	0
Netherlands	1	0
Poland	1	0
Bulgaria	0	2
Greece	0	2
Mexico	0	1
Rumania	0	1
Austria	0	2
Canada	0	1