WIRMS 2015

INTERNATIONAL WORKSHOP ON INFRARED MICROSCOPY AND SPECTROSCOPY WITH ACCELERATOR BASED SOURCES

Hyatt Place – Riverhead, Long Island, New York

October 11th to 15th

Oral Presentation Abstracts

U4IR AND NSLS: END OF AN ERA – SEEDS FOR THE FUTURE

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Infrared microscopy and spectroscopy using synchrotron radiation from storage rings or linacs is a blossoming field as evidenced by many facilities all around the world, most of which are represented at this 8th international meeting. This is the first WIRMS workshop to be hosted by the NSLS, a facility where important developments have been developed that have driven the field. In this talk I will talk about this, but will also briefly get down to the roots, introducing the pioneers of this business, who performed experiments under difficult conditions and convinced the funding agencies to support a generation that had to invest heavily in instrumentation design and development. A good portion of that occurred at NSLS and involved many collaborations. In turn, these collaborators have paved the way for most of the developments and the exciting science that we see today and will be hearing throughout this workshop. NSLS has closed now but will re-open soon, and the new facilities at NSLS-2 will now take their turn in benefiting from what has been learned by all of you – our IR family.

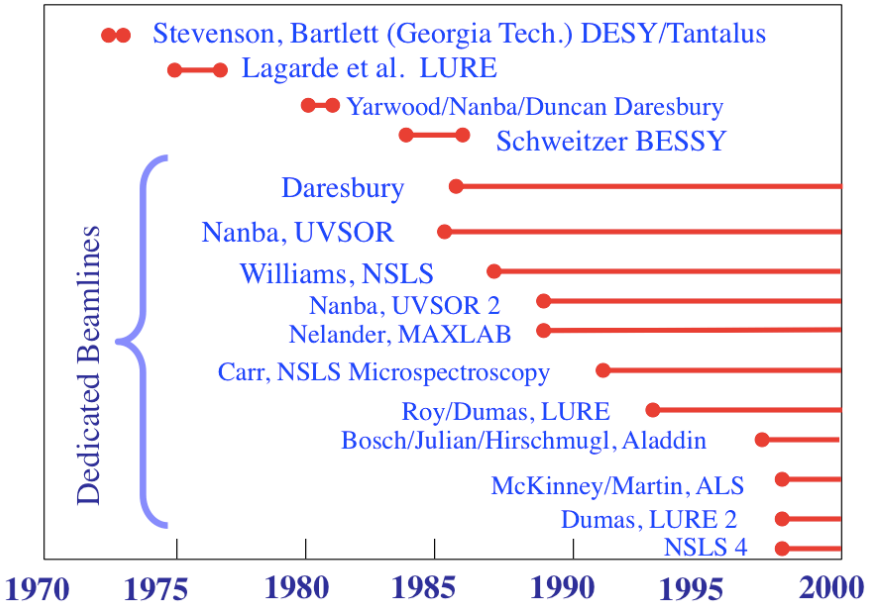

Fig. 1. Schematic showing the time evolution of the field[1].

ACKNOWLEDGMENTS

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SYNCHROTRON INFRARED BEAMLINE DESIGN

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Synchrotron infrared beamlines are powerful tools to perform spectroscopy on microscopic length scales but require working with high intensities which are obtained using large horizontal beamline apertures. Most of the infrared beamlines use a single toroid shaped mirror to conjointly focus both the vertical and the horizontal source emission but generate for large apertures distorted images due to the optical aberrations produced by the depth and the circular shape of the source. In this presentation, we will describe a new optical layout consisting in two optimized shape mirrors, focusing respectively the vertical and the horizontal source emission, and providing low aberration beams for large horizontal apertures. This layout is already operational on the IR beamline of the LNLS /1/.

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MIRAS: THE INFRARED SYNCHROTRON RADIATION BEAMLINE AT THE THIRD GENERATION LIGHT SOURCE ALBA

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MIRAS is one of the phase II beamlines currently under construction at the third generation synchrotron light facility ALBA, located near Barcelona, Spain. Construction of MIRAS was initiated in 2014, is advancing rapidly, and will enter the commissioning phase in 2016. MIRAS will be dedicated to infrared microspectroscopy, with the aim to deliver world class performance in terms of a bright and highly stable photon beam. The beamline will provide ALBA users with a modern infrared microspectroscopy facility covering a wavelength range from 0.4 to 100 µm. The design of the beamline optimizes performance in the mid-IR range and will give significantly enhanced efficiency, compared to a conventional source, in both far-IR and mid-IR regions.

The synchrotron radiation emitted in the infrared range from a bending magnet of the storage ring of ALBA was studied in detail by simulation techniques. A modified dipole chamber allowed the design of the beamline with an acceptance-opening angle of 43(H) x 25.17(V) $mrad^2$. The dipole chamber design implements a horizontal infrared beam extraction geometry using a laterally inserted flat mirror [1]. MIRAS will exploit the infrared synchrotron emission from the two main sources of radiation, edge and constant field of the bending magnet. The optical layout of MIRAS includes the option for splitting the extracted infrared beam in two parts, with one containing the edge radiation of the beam [2]. This configuration will enable the use of the two beams separately at different endstations [3]. The experimental cabin and transport optics are designed to accommodate two additional endstations as a future upgrade of the MIRAS beamline, one based on “bring your equipment” concept. The expected performances of the beamline in terms of flux, spatial distribution of the photons, optimized mechanical design and corresponding heat load profiles have been calculated using both SRW and Ray tracing.

This contribution will present the new infrared beamline MIRAS at the ALBA Synchrotron light facility. Details of the beamline optics, technical considerations of the design and the expected performances of the beamline will be reported.

ACKNOWLEDGMENTS

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SMIS 2.0 – FUTURE PERSPECTIVES

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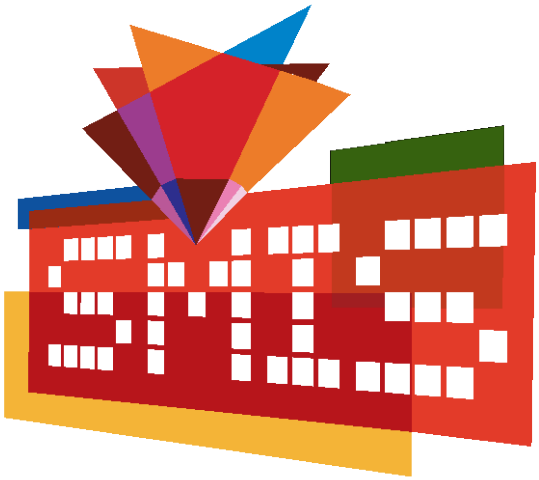
Recent developments and future perspectives of the SMIS beamline in Soleil will be discussed. The developments focus on four specific areas: a) next generation beamline optics, b) IR spectromicropscopy below the diffraction limit, c) large area imaging and tomography and d) development of new data processing tools for spectromicroscopy.



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INFRARED SPECTROSCOPIC IMAGING FOR BIOMEDICAL APPLICATIONS – EMERGING OPPORTUNITIES AND CHALLENGES

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Infrared (IR) chemical imaging, in which molecular content is visualized using spectroscopy and images are formed using microscopy, is an emerging area to characterize cells and tissues. We first present here results from a Fourier transform IR (FT-IR) imaging approach that permits a rapid and simultaneous fingerprinting of inherent biologic content, extraneous materials and metabolic state without the use of labeled probes. We describe results to automate histopathology without dyes or human input in four classes of problems that are relevant to clinical pathology. Further, applied to engineered 3D tissue models for breast tumors, we show that the imaging technology is useful in rapidly assessing culture quality and that the model systems can act to inform researchers about the involvement of different cell types in cancer progression.

An emerging understanding of the biological characterization process with IR imaging lies in a combination of theory, novel instrumentation and signal processing forms an integrated approach to biochemical analyses.[1] Theory informs instrumentation that can be built for optimal data recording [2]. The requirements imposed by the optimal imaging configurations necessitate the use of novel light sources, which may include a broadband synchrotron [3] or narrowband quantum cascade lasers [4]. While the first approach leads to novel FT-IR configurations, the use of the latter has led to the emergence of the discrete frequency IR (DFIR) approach.[5] The former approach requires a better understanding of coherence and image formation, which is available now in great detail.[6] The latter approach not only requires the same but also needs computational approaches that lead to identification of specific spectral metrics [7] or sparse sampling approaches [8] to realize full advantages of the DFIR approach.

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FTIR IMAGING OF COPPER ZINC SUPEROXIDE DISMUTASE AGGREGATION IN LIVING CELLS FOR THE STUDY OF FAMILIAL ALS

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Amyotrophic Lateral Sclerosis (ALS) is a debilitating neurological disease affecting the motor neurons of the spinal cord. The discovery of novel effective treatments for ALS is made difficult from by the lack of known pathologies for sporadic cased of the disease, and a poor understanding of the mechanisms causing inherited or familial ALS (FALS). The most prevalent form of familial ALS, accounting for 20% of known cases, is caused by mutations in the anti-oxidant metalloprotein copper-zinc superoxide dismutase 1 (SOD1) resulting in the formation of SOD1 aggregates within spinal cord tissue. Through development and application of *in vivo* time resolved Fourier transform infrared (FTIR) imaging, we are elucidating secondary structural changes to FALS-SOD1 during aggregation as a function of time. Our data studying the D125H SOD1 mutation suggests a unidirectional aggregation pathway for this variant, involving the formation of parallel β-sheet rich fibrils. In combination with prior studies of the G36R mutation, this data suggests multiple pathways for SOD1 aggregation exist in vivo.

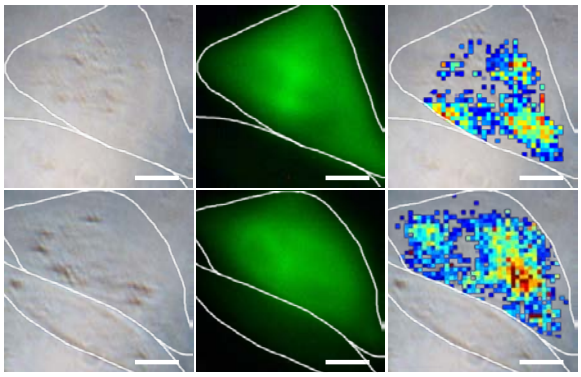

Fig 1: Visible, Fluorescent, and overlay of antiparallel to parallel β-sheet ratio (1695/1630 cm^{-1}) color map (left to right) for aggregation of D125H SOD1 mutant after 12 (top) and 24 hours (bottom). Scale bar is 10 microns.

ACKNOWLEDGMENTS

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SYNCHROTRON WIDEFIELD FTIR IMAGING OF DIABETIC RETINA TISSUE

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Retinal layers (photoreceptors, bipolar cells and ganglion cells) have distinct chemical signatures, and can be easily detected with chemical imaging [1]. Hyperspectral imaging using the synchrotron source and focal plane array detector produces a 3-D cube of data (x,y,Abs(λ); # of pixels) that contains spatial and spectral information, where each pixel in the image plot contains a high signal-to-noise spectrum. Hyperspectral datasets of eye sections obtained from wild type (non-diabetic) and Akita/+ (diabetic) mice provide insight into specific chemical signatures associated with diabetic retinopathy, a major complication of diabetes. Male Akita/+ mice spontaneously develop diabetes by 4-weeks of age due to a mutation in their insulin gene. Retinas from 6-week-old, and 6-month-old mice were evaluated for detection of chemical changes as a function of the disease.

To evaluate the hyperspectral data we use Principal Component Analysis (PCA) to compare chemical information and detected biomarkers employing both the spectral and spatial information. For example, it is known that the photoreceptors are affected early in the progression of diabetes. Thus, the chemical signatures (individual pixel spectra) from the photoreceptor layers are compared as a function of disease (WT vs. Akita) to detect potential biomarkers of the disease pathology. The PC loadings and scores reveal the spectral and spatial chemical variation, respectively. The PC loadings [2] are well known to give insight into the spectral components that are major contributors for that PC. An image representation of the PC scores associated with each pixel reveals which areas of an image are highly linked to the features in the loading. Significant differences attributed to glycation process in diabetes, the spectral regions related to lipid and nucleic acids and DNA bands are highlighted from PC loadings. From pixel to pixel comparison of image representation of the PC scores higher variations for diabetic samples were observed.

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SINGLE CONTACT ATR MAPPING OF SOFT MATERIALS BY SYNCHROTRON FTIR

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Attenuated Total Reflection (ATR) is a sampling method frequently used for FTIR microanalysis of samples which cannot be prepared as thin sections for transmission analysis [1]. Generally, an ATR prism is attached to the front of the microscope objective and 2D mapping achieved by repeated contacts with the ATR crystal. The method is more suited to harder materials, since the multiple ATR contacts may lead to damage of softer materials. We have developed ATR devices for the purpose of analysing softer materials, where only gentle contact can be made with the sample surface, in which the ATR crystal is attached to the microscope stage rather than the objective. Figure 1A shows our latest ATR device which is similar in principle to the "Macro" ATR devices offered by some manufacturers, but employs more precise piezoelectric sample alignment and ATR contact control. A modified micro-compression cell in which a ZnSe ATR prism is brought gradually into contact with the surface of the sample has also been used to study the hydration water in chitosan-hyaluronic acid model biolubricant, as a function of pressure [2]. Figure 1B shows the OH spectral shift between bulk water (plot 3) and less strongly hydrogen bonded hydration water within the film (plot 2).

As part of a study of the resistance of insect wings to biofilm formation, the same ZnSe ATR has been used to map the surface of structured fatty acid films. Figure 1C shows a map of the relative peak position of νCH_2 absorption of a textured stearic acid film on graphite, being studied as an analogue to the dragonfly wing epicuticle.

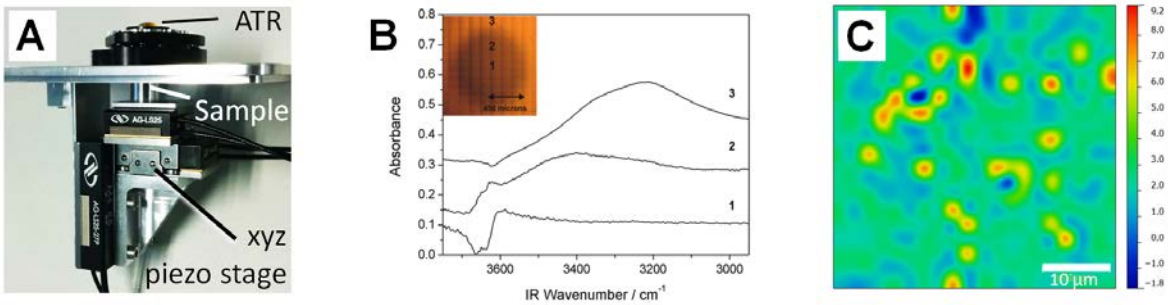

Fig 1: A. Piezo controlled sample mount with ATR crystal attached to stage, B. OH absorption in chitosan-hyaluronic acid model biolubricant, C. νCH_2 relative peak position of a textured stearic acid film.

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SOFT X-RAY MICROSCOPY RADIATION DAMAGE ON FIXED CELLS INVESTIGATED WITH SYNCHROTRON RADIATION FTIR MICROSCOPY

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Radiation damage of biological samples remains a limiting factor in high resolution X-ray microscopy (XRM) [1]: the extent to which the lateral resolution can be pushed without unacceptable sample degradation is still an open question. The present work [2] reports on a novel study performed at Elettra - Sincrotrone Trieste where the impact of soft X-rays (1KeV) on formalin fixed Human Embryonic Kidney 293 cells exposed to different doses has been assessed not only with XRM, as often reported in relevant literature on the topic, but by coupling it with two additional independent non-destructive microscopy methods: Atomic Force Microscopy (AFM) and SR-FTIR Microscopy (FTIRM). The results reveal that cell morphology is not substantially affected even at higher exposure doses (~$6\cdot10^8$ Gy), while indeed nanometric pits and bulges increase in number and size when increasing the exposure time (See Fig.1, panels e-g). On the contrary, the biochemical response changes significantly also at the lower radiation dose (~$2\cdot10^6$ Gy), resulting in a progressive breakdown of the covalent bonding network (See IR chemical images in Fig. 1, panels b-d). Overall, FTIRM suggests that low-energy X-rays on formalin fixed cells primarily induce the oligomerization of bio-macromolecules and then affect their constitutive monomers down to the formation of small, and possibly volatile compounds. Consequently, unnatural ultrastructural details and modifications in elemental distribution could be induced by the X-ray probing source. Therefore special attention needs to be devoted to improve preparation techniques and acquisition strategies that minimize the risks of artifacts, especially when more radiation-sensitive hydrated species are imaged.

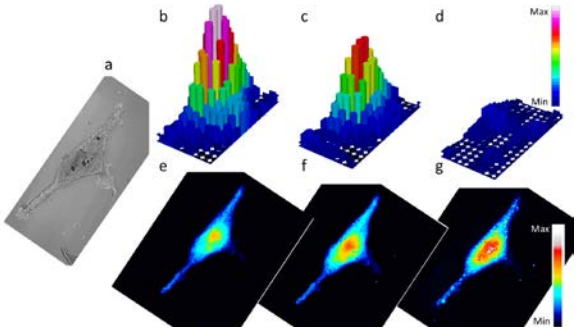

Fig 1: a) Optical image of a formalin-fixed HEK293T cell; b-d) Chemical images of the asymmetric stretching of phosphate moieties (area integral of the spectral band 1270-1190 cm^{-1}) for the same cell in a) upon air-drying and exposure to $2\cdot10^6$ Gy (compatible with low resolution STXM mapping) and $6\cdot10^8$ Gy (compatible with XRF mapping); e-g) AFM images of the same cell in a) following the same scheme of b-d.

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FTIR STUDY OF THE BIOCHEMICAL EFFECTS IN F98 GLIOMA CELLS INDUCED BY X-RAY IRRADIATIONS COMBINED WITH GD NANOPARTICLES: FIRST STUDIES AT THE INFRARED EMIRA BEAMLINE OF SESAME SYNCHROTRON (JORDAN)

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Radiotherapy (RT) plays a key role in the treatment of cancer. However, its main limitation is to reach curative doses in the tumor while sparing the surrounding healthy tissue. One strategy to improve the clinical outcome in RT is to increase the dose effects in the tumor. This can be achieved by using specific nanoparticles (NP). Numerous studies have shown an enhanced effectiveness of tumor cell killing when NP were associated to irradiation [1-3]. However, the mechanisms of action are not yet clear. In addition to the damage due to a possible local dose enhancement, the interaction of NP with essential biological macromolecules could lead to changes in the cellular function, such as cell arrest at radiosensitive phases [4]. These effects, which could be amplified with a subsequent irradiation, might increase their anticancer effectiveness. Along this line, in this study we used F98 glioma rat cells as an *in vitro* model to evaluate the intracellular biochemical changes induced by x-ray irradiations in combination with Gadolinium NP by using Fourier transform infrared microspectroscopy (FTIR). FTIR allows *in situ* chemical structure determination of intracellular biomolecules. In addition, this technique has significantly contributed to study apoptosis, as well as cell cycle and cell death modes. In this work, FTIR measurements were performed using the internal source of infrared radiation at SESAME synchrotron. Principal Component Analysis (PCA) was performed to show the variances between the different sets of spectra. Preliminary results are very encouraging. Fig. 1 shows the PCA in the sugar and DNA region of the infrared spectral range. Differences in the presence of Gd NP are clearly observed for a tumor dose of 10 Gy, indicating changes in the cellular function. PCA reveals also differences in the proteins region, where a shift of Amide I band to the lower frequency range is observed in the presence of NP. This shift has been previously related to the hallmark characteristics of cell death [5]. Clear differences are also observed in the lipids region of the infrared spectral range.

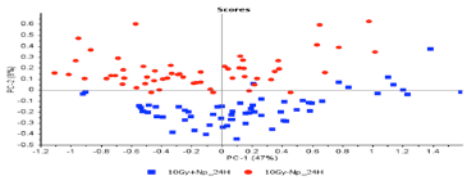

Fig 1: PCA in the sugar and DNA region of the infrared spectra of F98 glioma cells for a dose of 10 Gy. Blue points correspond to the presence of Gd NP and red points to the absence of Gd NP. PCA reveals also differences in the protein and lipids region of the infrared spectral range.

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SPECTROELECTROCHEMISTRY USING SYNCHROTRON INFRARED RADIATION

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The high brilliance of synchrotron infrared radiation (SIR) provides unique opportunities for electrochemists to spatially and temporally map electrochemical interfaces. To assess the temporal resolution benefit of SIR, an external reflectance cell containing a 25 µm radius ultramicroelectrode has been employed to achieve an electrochemical time constant less than one microsecond [1]. The use of a prototypical electrochemical system, i.e. the mass-transport controlled reduction of ferricyanide, allows for a proof of principle evaluation of the viability of SIR for step-scan spectroelectrochemistry. Modelling of the material flux in the restricted diffusion space afforded by the external reflectance cell allows the quantitative SIR results to be compared to model predictions. The results provide a detection limit of 36 fmol for step-scan SIR measurements of ferrocyanide.

SIR has also been employed to map the diffusion layer in the vicinity of a working electrode. A thin-cavity transmission cell is employed to generate a two-dimensional diffusion space. The use of simple redox couples allows for a proof of principle evaluation of the viability of SIR for simultaneous mapping (in time and space) of the concentrations of species in the diffusion layer. Deviations between measurement and modeling are attributed to heterogeneity in the beam intensity profile, spurious convection, as well as difficulties in accurately accounting for the working electrode's edge effects. The method has recently been extended to map catalytic "hotspots" in binary metal alloys used for methanol fuel cell reactions. Implications for future IR spectroelectrochemical studies will be presented.

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DYNAMIC OF THE HEAT-SHOCK RESPONSE IN LIVE CELLS FOLLOWED BY FTIR MICROSPECTROSCOPY

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Heat-Shock (HS) Response is a highly conserved mechanism by which cell respond to injuries like sudden temperature variations, oxidative and osmotic stresses. Specifically, the cellular response to temperature increase involves the activation of HS factor genes and the synthesis of HS proteins, chaperons that counteract the misfolding/aggregation of native proteins promoted by the temperature rise [1]. In this contribution, we propose the use of FTIR Microspectroscopy (FTIRM) as an analytical methodology to investigate the dynamics of HS response in unlabelled cells [2]. Repeated spectra of live MCF-7 and MDA-MB 231 breast cancer cells subjected to severe HS (T = 42.5±0.5 °C) were collected for two hours and compared with the ones retrieved from a control population (T = 37±0.5 °C) monitored for the same period of time. Through the study of the temporal evolution of the second derivatives of the spectra and by 2D correlation analysis of absorbance data, we were able to identify a common sudden HS response among the two cell lines. Within the first 10 minutes after the HS application, we observed the hyperfluidization of cell membranes, the transient increment of signal lipids, and an alteration of proteome profile. Persistent intracellular accumulation of extended β-folded protein aggregates was instead monitored after 40 minutes of stress. Moreover, we noticed that a lower resistance to heat shock characterizes MCF-7 cells, since only their spectra showed at the end of the two hours signals of pre-apoptosis. Several diseases, like age-on-set disorders and cancer, involves the alteration of HSR pathways; therefore, the possibility to identify and monitor intermediates of protein aggregation on live cells can offer great advantages for biomedical studies, suggesting FTIRM as a tool for the early diagnosis of cellular stress conditions.

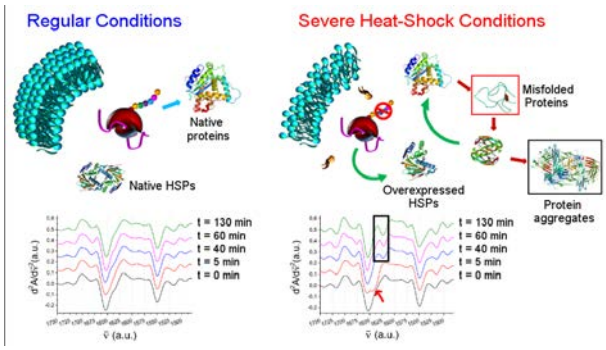

Fig 1: On the right, sketch of the steps of the protein misfolding and subsequent aggregation induced by severe HS (T=42°C) applied for 2 hours, as deduced by FTIRM data. Second derivatives of the spectra of a representative group of T-shocked cells at selected time points are presented on the lower panel. On the left, second derivative of the spectra of cells kept at 37 °C and normal cellular protein synthesis pathways are shown.

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INFRARED SPECTROSCOPY IN 3D: FTIR SPECTRO-MICROTOMOGRAPHY

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Synchrotron infrared beamlines use the diffraction-limited beam properties to enable a variety of cutting edge science at the micron length scale in both reflection and transmission. It has enabled a wide variety users to perform science across numerous fields.

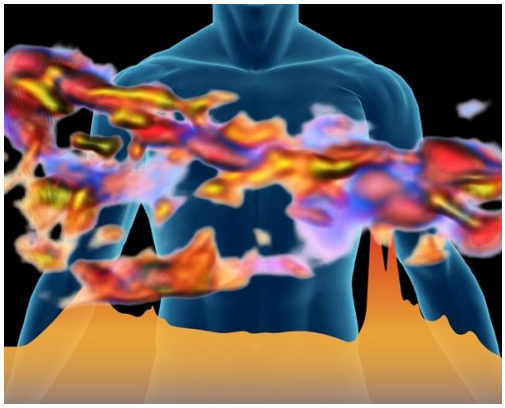

Fig 1: 3D visualization of a one day old mouse embryonic stem cell culture protein and lipid distrubution.

In this talk, I will describe a new technique we have recently developed and demonstrated. 3D FTIR tomography [1] provides spectrally rich, label-free, nondestructive visualizations of distinctive chemical compositions throughout intact biological or materials samples. The technique has combined Fourier Transform Infrared (FTIR) spectroscopy with computed tomography (CT) to create a non-destructive 3D imaging technique that provides molecular-level chemical information of unprecedented detail on biological and other specimens with no need to stain or alter the specimen. We are installing a new IR imaging and tomography endstation at beamline 2.4 of the Advanced Light Source (ALS). I will describe how the technique works and present application examples spanning a variety of scientific disciplines.

ACKNOWLEDGMENTS

- The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.
- This work was performed together with Hans Bechtel, Carol Hirschmugl, Dilworth Parkinson, Charlotte Dabat-Blondeau, Martin Ashford, Michael Tang, Michael Nasse, Julia Sedlmair, Barbara Illman, Miriam Unger, Marco Keiluweit, Jonathan Castro, David Buschke, Brenda Ogle.

REFERENCES

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OPEN CHANNEL MICROFLUIDIC MEMBRANE DEVICE FOR LONG-TERM FTIR SPECTROMICROSCOPY OF LIVE ADHERENT CELLS

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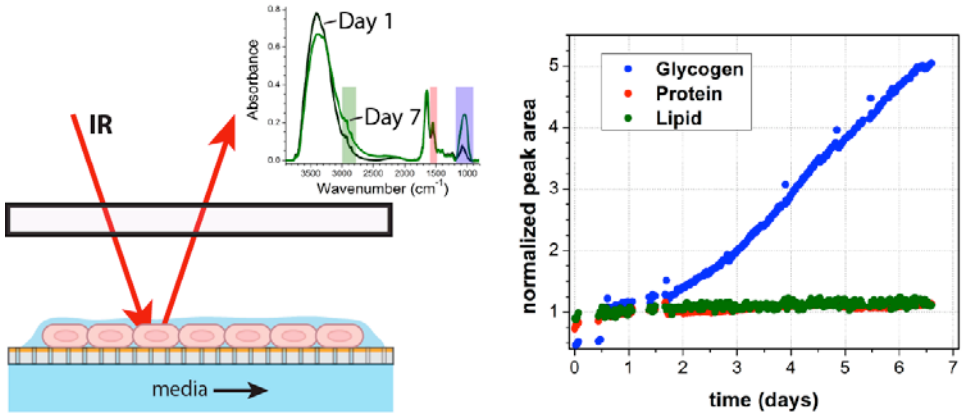
Spatially resolved infrared spectroscopy is a label-free and nondestructive analytical technique that can provide spatiotemporal information on functional groups in biomolecules of a sample by their characteristic vibrational modes. One difficulty in performing long-term FT-IR measurements on live cells is the competition between the strong IR absorption from water and the need to supply nutrients and remove waste. Here, we developed an open-channel membrane device that allows long-term continuous IR measurement of live, adherent mammalian cells. Composed of a gold-coated porous membrane between a feeding channel and a viewing chamber, it maintains on the upper membrane surface in a thin layer of fluid while media is replenished from the feeding channel below. Using this device, we monitored the spatiotemporal chemical changes in live colonies of PC12 cells under nerve growth factor (NGF) stimulation for up to 7 days using both conventional globar and high-resolution synchrotron radiation-based IR sources. We identified the primary chemical change cells undergo is an increase in glycogen that may be associated with secretion of glycoprotein to protect the cells from evaporative stress at the air–liquid interface. Analyzing the spectral maps with multivariate methods of hierarchical cluster analysis (HCA) and principal component analysis (PCA), we found that the cells at the boundary of the colony and in a localized region in the center of the colony tend to produce more glycogen and glycoprotein than cells located elsewhere in the colony and that the degree of spatial heterogeneity decreases with time. This method provides a promising approach for long-term live-cell spectromicroscopy on mammalian cell systems.



ACKNOWLEDGEMENTS: This work was performed under the BSISB Program funded by the U.S. Department of Energy, Office of Science, and Office of Biological and Environmental Research. The Advanced Light Source is supported by the Director, Office of Science, and Office of Basic Energy Sciences. Both were supported through Contract DE-AC02-05CH11231.

SR-FTIR AS A TECHNOLOGY FOR ARCHAEAL/BACTERIAL IDENTIFICATION AND FUNCTIONAL PROFILING

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Microbes living collectively in an environmental ecosystem like the subsurface or even on the human skin often thrive as thousands of different species. In either case, the community structure, function and cell-cell relationship can reach a dynamic equilibrium, which plays a key role in biogeochemical cycling or in human health. Archaea are well-recognized components in both ecosystems, yet many studies focus on bacteria only, because of conventional approaches. Conclusions regarding the microbiome function can thus be misleading. Here we demonstrate that SR-FTIR could open a new window into the microbiome world of entire communities including archaea. SR-FITR is a rapid and non-destructive screening method capable of providing chemical and microbial information from a sample with little sample preparation. We used SR-FTIR spectral features in the 2800-3000 cm^{-1} and 900-1280 cm^{-1} regions to distinguish entire microbial communities from different geographic locations, to reveal co-localizations of archaea and bacteria within their environment [1, 2] (Figure 1a), and to classify and quantify community members as archaea, bacteria, or ultra-small bacteria via comparison to established standards (Figure 1b) [3]. We also demonstrate that the high brightness and spatial resolution achievable with SR-FTIR spectromicroscopy allowed linking geochemical processes to archaea and bacteria. Our findings suggest that SR-FTIR is a useful tool for gaining insights into microbiome and microbiome-host interactions of various environments.

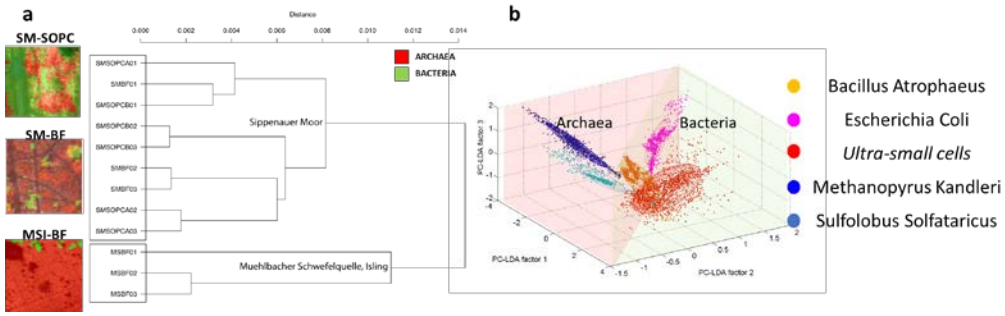

Fig 1: a. SR FTIR profiling of the archaeal and bacterial communities in biofilms collected from different sites in Germany. b. Confirmation of unknown ultra-small bacterial species by comparing their spectra in the PC space with the reference samples.

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MOLECULES AS DOCUMENTS OF THE PAST: WERE DINOSAURS REALLY BLACK?

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Melanosome-like microbodies, preserved in e.g. fossil plumage and skin, have been used to reconstruct original colours. Color plays an essential role, while often in a complex manner, in how many animals interact with both the surrounding environment (UV-protection and thermal regulation) and socially. Feathers are amongst the most complex epidermal structures known, and they have a well-documented evolutionary trajectory across non-avian dinosaurs and basal birds. Now these supposedly ancient melanosomes have also been interpreted as microorganismal residues, a conflict mostly driven by the lack of conclusive spectroscopic data. By combining the imaging facilities at D7, MAX-IV laboratory with the high brilliance of SMIS at SOLEIL we have recorded both single point data as well as image data for a new specimen of the Jurassic paravian *Anchiornis* from Tiaojishan Formation of Liaoning Province in China[1]. We show that the microbodies indeed are eumelanosomes and fibril-like microstructures preserved as endogenous eumelanin and authigenic calcium phosphate. Additional techniques were necessary to utilized to support these findings, most importantly ToF-SIMS and SEM. These results provide novel insights into the early evolution of feathers at the sub-cellular level, and demonstrate unequivocally that melanosomes can be preserved in fossil feathers.

ACKNOWLEDGMENTS

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NEW LIGHT ON MATERIALS IN EXTREME CONDITIONS

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The development of laboratory techniques for generating extreme P-T conditions on materials together with the refinement of probes of material behavior continue to lead to discoveries across a broad range of the sciences. At multimegabar pressures and temperatures and from millikelvins to thousands of degrees, novel electronic, magnetic, superconducting, and superhard phases are being discovered. New insight into dense hydrogen has been obtained from high P-T measurements as well as studies of alloys and compounds of hydrogen, leading to the creation of new metallic and superconducting phases. High-pressure studies of oxides, silicates, carbonates, and metal alloys have led to new materials and phases with remarkable properties important for Earth and planetary science. In each of these studies, synchrotron radiation, including synchrotron infrared light, has played a key role.

SPATIAL DISTRIBUTION OF CARRIER DENSITY OF YTTRIUM-DOPED SMS

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Physical properties of some materials are drastically changed at the first-order phase transition by tuning external parameters of temperature, pressure, magnetic field, and chemical pressure. At the first-order transition, phase separations as well as phase coexistence are sometimes observed [1]. Since the phase separation is strongly related to the origin of the first-order transition, the origin of the phase separations is under debate in some materials.

Samarium monosulfide SmS is known to be a material with a pressure-induced first-order insulator-to-metal transition accompanied with the color change from black to golden-yellow, namely black-golden phase transition (BG transition), at the critical pressure of about 0.7 GPa [2]. The origin of the BG transition is known as the valence transition from Sm^{2+} with larger ionic radius to Sm^{3+} with smaller radius owing to the external pressure. At the BG transition, carrier density suddenly increases, i.e., an insulator-to-metal transition (IM transition) occurs. However, the relation between the BG and IM transitions has not been revealed. When a part of Sm^{2+}-ions are replaced to Y^{3+}-ions of smaller ionic radius, namely $Sm_{1-x}Y_xS$, a similar BG transition is realized at ambient pressure [3]. At the border of the BG transition of x ~ 0.17, the black and golden phase separation is observed. Here, we discuss the relation between the BG phase separation and the carrier density distribution detected by using the synchrotron IR imaging at UVSOR and an X-ray fluorescence imaging.

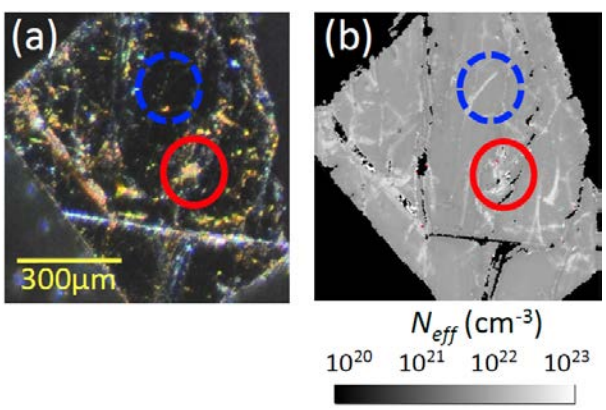

Fig 1: (a) Visible image of a measured sample of $Sm_{0.83}Y_{0.17}S$. (b) Spatial distribution of the effective carrier density (N_{eff}) from the Drude and Lorentz fitting of reflectivity spectra. Open solid (red) and dashed (blue) circles indicate the points of a typical golden phase area and a black phase area with different carrier density, respectively.

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REVEALING THE PRESSURE-INDUCED BREAKDOWN PATHWAY IN WS_2 NANOTUBES

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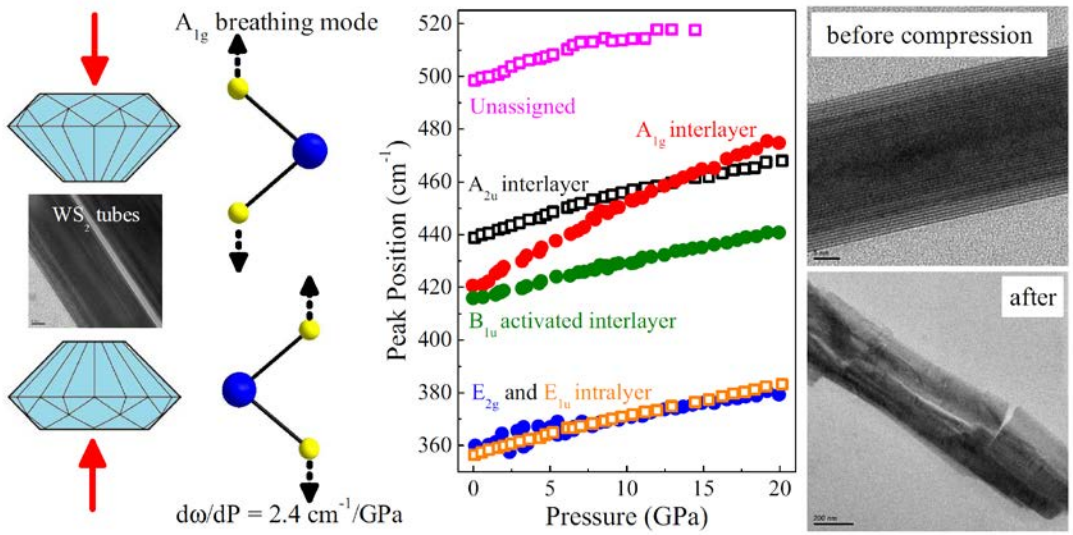
We bring together synchrotron-based infrared and Raman spectroscopies, diamond anvil cell techniques, and an analysis of frequency shifts and lattice dynamics to unveil the pressure-induced breakdown mechanism of multiwall WS2 nanotubes. While most of the vibrational modes display similar hardening trends, the Raman active *A*1*g* interlayer breathing mode is almost twice as responsive, suggesting that the nanotube breakdown pathway proceeds through this displacement. Suppression of this vibration, for instance with a filler or nanoscroll geometry, could prevent the breakdown and extend the range of solid state lubrication applications. At the same time, the high pressure infrared measurements provide unexpected insight into the electronic properties of the multiwall WS2 tubes. The rising spectral background is fit to a percolation model, indicating that the nanotubes display a modest macroscopic conductivity.



ACKNOWLEDGMENTS

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PRESSURE EVOLUTION OF AN EXCITONIC INSULATOR STUDIED BY SYNCHROTRON INFRARED SPECTROSCOPY

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We have made high-pressure infrared (IR) study of Ta_2NiSe_5, which has been suggested to be an "excitonic insulator" (EI), using synchrotron radiation source at SPring-8. An EI refers to an exotic insulating state caused by strong excitonic correlation between electrons and holes. The EI was first predicted theoretically in the 1960s [1], but the identification of an actual material as EI was not established for a long time. Recently, however, the layered chalcogenide Ta_2NiSe_5 has been strongly suggested to be an EI, on the basis of anomalous band dispersion found in photoemission data [2]. Ta_2NiSe_5 has also shown strongly pressure-dependent electrical resistivity [3]. It is theoretically expected that an external pressure is an important parameter to control the properties of an EI [1]. Therefore, we have studied the pressure evolution of energy gap and the excitation spectrum with IR spectroscopy, to better understand the electronic structures in Ta_2NiSe_5.

In our experiment, an IR microscope at BL43IR of SPring-8 was used to measure both the far-IR and mid-IR reflectance [R(ω)] of a Ta_2NiSe_5 single crystal, which was mounted in a diamond anvil cell to apply high pressure up to 6.5 GPa. Details of the high pressure IR studies with DAC [4,5] and the data analysis to obtain the optical conductivity [σ(ω)] [6] have been already discussed.

The measured σ(ω) data show that Ta_2NiSe_5 at ambient pressure is an insulator with an energy gap of about 0.1 eV at 300 K, which increases to about 0.2 eV at 10 K. With cooling, in addition, a sharp peak centered at about 0.3 eV grows in σ(ω), which should result from a flat dispersion of the valence band due to strong excitonic correlation. With increasing pressure, the energy gap in σ(ω) is quickly suppressed. At 5 GPa, the energy gap is completely suppressed, but the excitonic peak still survives, indicating that the excitonic correlation is still present. We will discuss in more detail the pressure evolution of the electronic structures in Ta_2NiSe_5.

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INFRARED SIGNATURES OF PRESSURE-INDUCED TOPOLOGICAL PHASE TRANSITIONS IN SELECTED NARROW-GAP SEMICONDUCTORS

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Topological insulators have been recently established as a new state of matter, hosting metallic surface states on insulating bulk. Such intriguing properties originate from an inverted bulk band structure, endowing the electronic wavefunctions with a nontrivial topology. Pressure has been proposed to drive band inversion and topological phase transitions in many normal insulators [1]. Combining infrared micro-spectroscopy with the diamond anvil cell technique, we uncovered robust bulk signatures consistent with pressure-induced band inversion in narrow-gap semiconductors BiTeI [2] and $PbSn_{1-x}Se_x$ [3]. We anticipate these results to be useful for identifying a variety of candidate pressure-induced topological insulators.

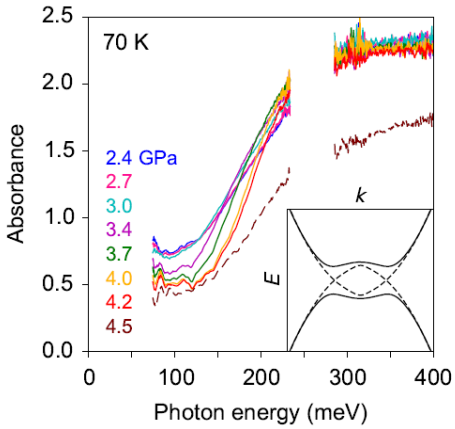

Fig 1: Pressure-dependent mid-infrared absorbance of PbSe measured at 70 K. The tilting of the absorption edge towards higher photon energy with increasing pressure indicates band gap reopening. (Band gap closing occurs at pressure less than 2.4 GPa). A structural phase transition occurs at 4.5 GPa. The inset illustrates hybridization opens up a band gap when the bands cross and invert.

ACKNOWLEDGMENTS

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SYNCHROTRON IINFRARED AND RAMAN SPECTROSCOPIC STUDIES of DENSE SOLID HYDROGEN

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High-pressure synchrotron infrared (IR) and Raman spectroscopic techniques have been employed to investigate the I-III-IV phase transitions in dense solid hydrogen at room temperature as well as variable temperatures at selected pressures. The I-III phase transition is constrained to be near 202 GPa at room temperature. The new constraints are based on the slope changes of pressure dependence on peak width of the Raman vibron band and peak intensity of the principal IR vibron band. The III-IV phase transition is clearly observed at 221 GPa and room temperature using the diagnostic of the principal IR vibron band splitting and the concomitant of intensity change and the appearance of the high-frequency sharp IR band of phase IV. This gives rise to two main IR vibron bands (v_1 and v_2). The frequency of the ν_1 band is remarkably temperature independent. Its large negative shift with pressure at room temperature provides not only additional information at variable temperatures in phase IV but also a more reliable pressure marker above 200 GPa. These measurements constrain the I-III-IV triple point to be 208 GPa and 315 K based on current implementation of the diamond anvil Raman scale. Complementing Raman measurements are fully consistent with the analysis of the IR vibrational spectrum in the region of the phase diagram corresponding to the I-III-IV transitions. IR measurements generally provide a more precise determination of the phase boundaries, particularly at higher temperatures. More important is the information of the electronic properties provided by the IR measurements, particularly at lower wavenumbers. Regions of the spectrum show transparency down to 0.07 eV at 242 GPa and room temperature (*i.e.* for phase IV). The results place bounds on both the transition to a highly conducting phase as well as on the mechanism of metallization, including the formation of a semimetallic phase, consistent with recent calculations.

ACKNOWLEDGMENTS

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COMMISSIONING OF A SINGLE-SHOT MID-INFRARED SPECTROMETER

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The mid-infrared (mid-IR) spectral region is widely used to obtain structural information on matter. When dynamic systems are to be investigated, time-resolved IR-spectroscopy utilizing the fourier-transform infrared (FTIR) method is commonly applied. This allows time-resolutions down to nanoseconds but an essential prerequisite is that the experiment can be repeated in exactly the same way thousands of time, connoting that the systems under investigation are cyclic. However, many systems in chemistry and biology are either non-cyclic, like the vertebrate photoreceptor rhodopsin, or they exhibit a very long cycling period, like the optogenetic tool channelrhodopsin, which then makes measurements slow and complicated. Here, first commissioning results from a different approach are reported, where a highly brilliant synchrotron light source, a dispersive Féry-spectrograph and a modern focal-plane array detector are utilized for single-shot measurements in the microsecond time-regime.

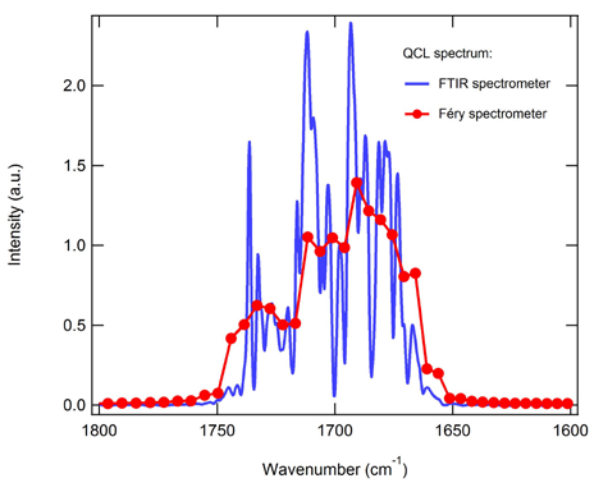

Fig 1: Emission spectrum of a mid-infrared quantum cascade laser, obtained with a FTIR spectrometer (*blue line,* Bruker Vertex 80v, 1 cm^{-1} spectral resolution) and with the dispersive Féry-spectrometer (*red line*, 6 cm^{-1} spectral resolution).

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SPECTRAL WEIGHT REDISTRIBUTION IN $(LaNiO_3)_n/(LaMnO_3)_2$ SUPERLATTICES FROM OPTICAL SPECTROSCOPY

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In the last years there has been a great interest in the novel electronic and magnetic properties observed at the interfaces between different complex oxides materials. These properties arise from both the character of oxygen ions and the correlation of electrons. At the interfaces of these structures a charge redistribution and a resulting reconstruction of the orbital and spin degrees of freedom (electronic reconstruction) produces a new two-dimensional state [1].
Here, we have studied the optical properties of four films of $(LaNiO_3)_n/(LaMnO_3)_2$ superlattice (SL) (n=2, 3, 4, 5) on $SrTiO_3$ substrates. $LaNiO_3$ (LNO) is the only member of the perovskite rare-earth nickelate series that does not undergo a metal to insulator transition at low temperatures; while $LaMnO_3$ (LMO) is an antiferromagnetic insulator, known for being the parent compound of colossal magnetoresistance manganites. X-ray spectroscopy shows that in the SLs the Mn oxidation state is converted from 3+ to 4+, while Ni is intermediate between 2+ and 3+ [2].
We have measured the reflectivity of the four SLs and of a pure LNO at different temperatures from 20 K to 400 K, and extracted the optical conductivity through a Kramers-Kronig consistent Lorentz-Drude model of the reflectivity. The two compounds of the alternated layers in the SL show a very different conductivity. LMO is an insulator since its conductivity is almost zero in the IR range. LNO, on the contrary, is a metal displaying a sharp Drude peak and a background conductivity in the mid-IR. For increasing n, the LNO/LMO SL undergoes an insulator-to-metal transition. The presence of a broad mid-IR band shows that the LNO/LMO SL is not a pure combination of the LMO and LNO conductivities, and confirms the mixing of the valence on Mn and Ni sites [2]. The piling up of spectral weight in the mid-IR range can be explained by the presence of both electronic correlation and polaronic effects (or even more likely, a mixture of the two) [3].

ACKNOWLEDGMENTS

This work was partially supported by Italian Ministry of Research (MIUR) program FIRB Futuro in Ricerca Grant No. RBFR10PSK4. J. D. H and A. B. acknowledge support from Department of Energy, Office of Basic Energy Science, Materials Science and Engineering Division. Work at Argonne National Laboratory, including the use of the Center for Nanoscale Materials and Advanced Photon Source, was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357.

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MUELLER MATRIX SPECTROSCOPIC ELLIPSOMETRY OF MAGNONS AND MAGNETO-ELECTRIC MODES IN MULTIFERROICS USING SYNCHROTRON RADIATION

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Far-IR optical spectra of complex materials, such as magneto-electric (ME) and multiferroic (MF) crystals, materials with chirality, and metamaterials, are in the focus of modern experimental and theoretical studies. For the light propagation analysis in bi-anisotropic crystals, dielectric susceptibility $\hat{\varepsilon}(\omega)$, magnetic permeability $\hat{\mu}(\omega)$, and ME $\hat{\alpha}(\omega)$ and $\hat{\alpha}'(\omega)$ tensors should be included into consideration. The theoretical representation of bi-anisotropic optical phenomena can be done using Mueller matrices (MM). Correspondingly, one of the most appropriate experimental techniques for studies of elementary excitations in bi-anisotropic materials is Mueller matrix spectroscopic ellipsometry (MM-SE). Application of MM-SE at the National Synchrotron Light Source, Brookhaven National Laboratory (NSLS-BNL) for MF, ME, and ferrimagnetic materials with $\mu \neq 1$ is illustrated with several experimental examples for RFeO$_3$, RMnO$_3$, RFe$_3$(BO$_3$)$_4$ and R_3Fe$_5$O$_{12}$ single crystals (R=rare earth). We demonstrate how magnetic and electric dipoles, such as magnons and phonons, can be distinguished from a single MM measurement without adducing any modeling arguments. In another example the parameters of ME components of electromagnons have been determined using MM spectra of TbMnO$_3$. Recent MM measurements of TbFeO$_3$ in a permanent magnetic field of ±0.45 T will be presented. The experimental spectra have been simulated and fitted using 4×4 Berreman's matrix formalism. The related activity of our team in the MM-SE instrument development, theory of the data analysis and operations, and simulations of the light propagation in materials with $\mu \neq 1$ is published in Refs. [1-5].

ACKNOWLEDGMENTS

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ULTRAFAST DIMENSIONALITY-DEPENDENT DYNAMICS OF MAGNETIC CORRELATIONS IN PHOTO-DOPED MOTT INSULATOR Sr_2IrO_4

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Time and energy-resolved spectroscopy using modern light sources is providing us ever more sensitive probes of electron-dynamics. This talk will describe the first implementation of time-resolved resonant inelastic X-ray scattering (tr-RIXS) at a free electron laser. We explain how tr-RIXS allows us to study the magnetic and orbital dynamics in a way that is highly complementary to infra-red spectroscopy and apply this to the photo-doped Mott insulator Sr_2IrO_4. We find that the non-equilibrium state 2 ps after photo-excitation has strongly suppressed long range magnetic order, but hosts photo-carriers that induce strong, non-thermal magnetic correlations. The magnetism recovers its two-dimensional (2D) in-plane N´eel correlations on a timescale of a few ps. The three dimensional (3D) long-range magnetic order, however, recovers over a far longer timescale of a few 100 ps. More broadly, we argue that characterizing the magnetic, as well as the charge, properties of ultra-fast transient states is a crucial part of our efforts to understand these systems and that tr-RIXS is a uniquely powerful way of accessing this degree of freedom.

TIME-RESOLVED SINGLE NANOCRYSTAL MICRO PHOTOLUMINESCENCE STUDIES OF 0D AND 0D-2D SEMICONDUCTING NANOMATERIALS

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The Center for Functional Nanomaterials at BNL is a user focused DOE nanoscience facility. Within the large palette of available facilities and techniques, the Advanced Optical Microscopy facility incorporates a suite of time-resolve confocal PL, Raman and hyperspectral microscopes with diffraction limited resolution and with detection in the Visible (VIS) and Near Infrared (NIR) spectral ranges, some of these with single nanocrystal/nanoparticle detection sensitivity, and also non-linear optical microscopy capabilities like two photon micro-PL and Second Harmonic Generation Microscopy.

In this talk I will describe how time-resolved single nanoparticle PL methods can be useful at probing exciton dynamics in type I core/shell semiconducting nanocrystals like CdSe/ZnS emitting in VIS and PbS/CdS emitting in NIR and dynamics in charge transfer in hybrids incorporating such 0D nanomaterials [1-3]. I will discuss in particular how such methods can unravel heterogeneity in exciton radiative recombination in these nanocrystals and how such heterogeneity can be suppressed by charge transfer with external acceptor nanomaterials. Finally I will introduce a recently developed hybrid nanomaterials in our group, a 0D-2D hybrid based on CdSe/ZnS-layered SnS2 which shows high potential for photo sensing. I will show how single nanocrystal optical methods can uniquely discriminate between charge and energy transfer as possible interaction mechanisms between CdSe/ZnS and layered SnS_2 and discuss the evolution of the rate for 0D-2D interaction with the number of layers of SnS2, starting with single layer SnS2. [4]

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SYNCHROTRON INFRARED NANO-SPECTROSCOPY AND -IMAGING

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Near-field mid-infrared nano-imaging and -spectroscopy has recently emerged as a frontier in imaging science, for local probing of molecular, biological, or quantum matter with nanometer spatial resolution and with vibrational chemical, low-energy electronic, or polaritonic resonant contrast [1]. With synchrotron infrared nano-spectroscopy (SINS), we take advantage of the low-noise, broadband, high spectral irradiance, and coherence of synchrotron infrared radiation for scattering type, scanning near-field optical microscopy (*s*-SNOM) [2]. We will describe our development of SINS, initiated at IRIS/BESSY (Germany) [3], and leading to the development of a full nano-spectroscopic and –imaging endstation at the ALS [2], with concurrent efforts at Spring-8 (Japan), SOLEIL, ANKA and PTB (Germany), and LNLS (Brazil). We will provide a perspective to further extend sensitivity, imaging speed, and spectral content by implementing adaptive, correlative, and prior-knowledge/compressive imaging and spectroscopy techniques. In addition the use of advanced scanning probe microscope platforms will allow for spectroscopic SINS nano-imaging under controlled temperature, *in situ,* and in liquid environments and the multi-modal combination with advanced electron and X-ray imaging techniques.

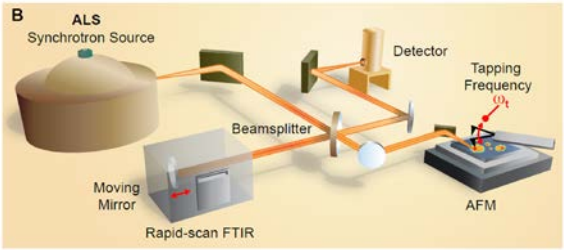

Fig 1: Synchrotron infrared nano-spectroscopy (SINS) and nano-imaging at ALS taking advantage of high spectral irradiance and bandwidth from 300 – 5000 cm^{-1} (λ= 30 – 2 μm) for vibrational chemical, electronic Drude response, phonon or plasmon polaritonic nano-imaging and –spectroscopy.

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ADAPTION OF BROADBAND SYNCHROTRON RADIATION FOR NANO-FTIR SPECTROSCOPY

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Near-field optical techniques such as scanning near-field infrared microscopy and nano-FTIR spectroscopy enable imaging and spectroscopic characterization of samples with a high sensitivity and a spatial resolution at the nanoscale. For mapping the chemical composition of the sample surface preferably monochromatic light sources are used. In contrast, for enabling the acquisition of nano-FTIR spectra radiation sources with a relatively broad emission spectrum are advantageous e.g. thermal, synchrotron or laser-based sources. Successful nano-FTIR experiments utilizing ultra-broadband synchrotron radiation (SR) [1, 2] have been recently demonstrated by several groups. In order to exploit the full potential of this technique we report on the adaption of storage ring optics at the Metrology Light Source (MLS) for reducing the size of the electron bunches. This results not only in a reduced beam diameter but also improves the coherence properties of the SR. In combination with appropriate spectral filters the sensitivity of SR-based near-field spectroscopy can be increased significantly, thus enabling also the spectroscopic characterization of thin organic layers.

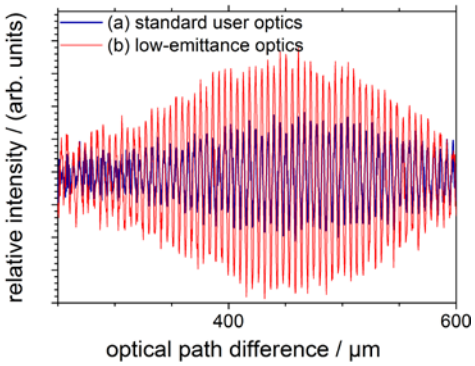

Fig 1: Interferograms recorded from a SiC sample using two different storage ring optics: (a) standard user optics and (b) low-emittance optics with reduced electron bunch dimension.

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SINGLE PLASMONIC METAL OXIDE NANOCRYSAL CHARACTERIZATION UTILIZING SYNCHROTRON INFRARED NANOSPECTRSOCPY

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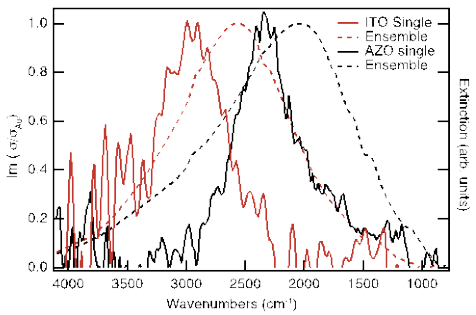
The localized surface plasmon resonances (LSPR) achieved in metal oxide nanocrystals through doping are currently under investigation due to their tunable resonance energies: visible to mid-IR. Unlike in metal nanocrystals where LSPR optical features are manipulated through complex shape and size synthesis, metal oxide systems instead change material and dopant in order to achieve desired linewidth and energy. Inhomogeneity between crystals introduced by dopant concentration,



Ensemble FTIR (dashed lines) measurements of ITO and AZO nanocrystals compared to their narrowest single particle spectra collected by synchrotron infrared nanospectroscopy (SINS)

and internal distribution causes ensemble measurements through typical spectroscopies to only reveal an average since LSPR are influenced greatly by dopant integration in their damping and carrier concentration, which has previously obscured the quality of plasmons in metal oxides. Single nanocrystal absorption measurements performed using a broadband synchrotron IR light source coupled to a conductive AFM tip[1] reveal nanocrystals of aluminum doped zinc oxide (AZO) and tin doped indium oxide (ITO) LSPR linewidths as narrow as 600 cm^{-1} can occur which is less than half of what their ensemble spectra have indicated. This can be explained through single nanocrystal LSPR energies varying over a range of 700 cm^{-1} due to dopant integration fluctuations during synthesis. These LSPR linewidths are in fact narrower than those measured for single noble metal nanoparticles of similar size and shape, indicating that metal oxide LSPR are a strong candidate for plasmonic applications in the infrared.

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INFRARED NEAR-FIELD SPECTROSCOPY SYSTEM AT SPRING-8 BL43IR

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We are developing an infrared near-field spectroscopy system with a high brilliant IR-SR light source at SPring-8 BL43IR. In this study, we introduce the present status of our system. We made various improvements to the system and the data qualities enhanced.

The near-field spectroscopy system comprised an atomic force microscope (AFM) and Fourier transform infrared (FTIR) spectrometer [1,2]. The configuration of the FTIR interferometer is an asymmetric one, in which one beam split by a beamsplitter is focused onto the tip of an AFM probe, and the other beam goes to a movable mirror. The scattered light from the probe and the light reflected by the movable mirror interfere with each other. The near-field signal is extracted by a modulation method with an AFM oscillation frequency.

The beam fluctuation raises the noise level of the near-field spectra. We addressed large fluctuation caused by upper stream beam transport system, and are constructing feedback system to reduce a relatively small beam fluctuation. Characters and types of each instrument components influence the performance of the whole system. We changed a type of detector, AFM probe and beamsplitter to the appropriate ones. The purge cover was also made to prevent the influence the atmosphere to the spectra. Owing to these improvements, the signal-to-noise and signal-to background ratios of the near-field spectra have been improved more than 6-fold and 8-fold, respectively, compared with those observed in the previous system. The spectral range expanded to 800 ~ 2500 cm^{-1}. The phonon structures such as SiC and SiO can be stably measured. The spatial resolution was estimated to be about 200 nm.

ACKNOWLEDGMENTS

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NANOSPECTRAL IMAGING OF PHONON POLARITONS WITH SINS

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By combining scattering-type-scanning near-field optical microscopy (*s*-SNOM) with infrared light from a synchrotron source, synchrotron infrared nano-spectroscopy (SINS) enables sensitive vibrational chemical imaging, spanning the mid- and far-infrared regions (300-5000 cm^{-1}) with < 25 nm spatial resolution [1]. The spatial field localization at the tip apex results in a large near-field momentum sufficient to optically excite phonon polaritons (PhPs), which are quasiparticles resulting from the strong coupling of photons with optical phonons. Here, we use SINS to image the PhP spectral response in thin hexagonal boron nitride (hBN) crystals. The large spectral bandwidth of the synchrotron source enables the simultaneous measurement of both the out-of-plane (780 cm^{-1}) and in-plane (1370 cm^{-1}) hBN phonon modes. In contrast to the strong and dispersive in-plane mode, the out-of-plane mode PhP response is weak. Measurements of the PhP wavelength reveal a proportional dependence on sample thickness for thin hBN flakes [2].

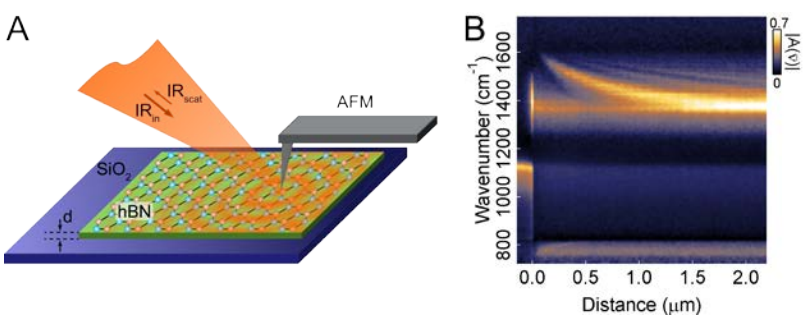

Fig 1: (A) Synchrotron IR light illuminates the conductive AFM tip, which launches polariton waves that propagate radially outward from the tip along the hBN surface and reflect off the edges. (B) SINS amplitude spatio-spectral linescan obtained perpendicular to the edge of a 147 nm-thick hBN flake.

ACKNOWLEDGMENTS

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Synchrotron Infrared Near-Field Spectroscopy of Antenna-Coupled Molecular Vibrations

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Infrared optical antennas promise high sensitivity detection and sub-wavelength control with chemical specificity to molecular vibrations. However, engineering nanoscale optical antennas and analyzing the frequency-dependent spatial distribution of electric fields within the antenna have proven difficult. Scattering-scanning near-field optical microscopy (s-SNOM) [1] has been used to investigate the vector electric field distribution with nanoscale resolution [2]. We extend this with the development of an ultra-broadband infrared spectrum analyzer utilizing synchrotron infrared nanospectroscopy (SINS) [3]. Spectroscopic investigations spanning the full mid-IR (700-5500 cm^{-1}) reveal enhancement of hybridized antenna-vibrational modes, coupling-induced spectral shifts, and both bright and dark overtone modes. These results offer new insight into the mechanism of near-field antenna enhancement of molecular vibrations.

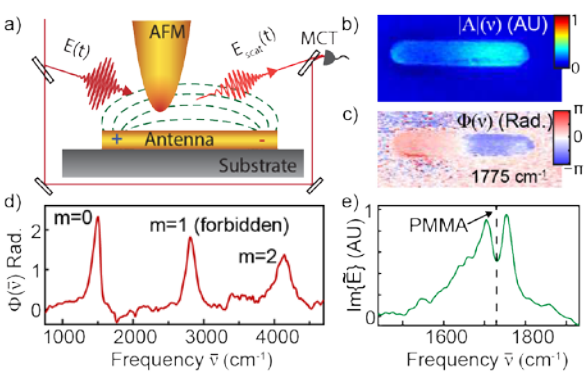

Fig: 1 (a) Scattering-scanning near-field optical microscopy of an optical antenna. Single-wavelength imaging measures near-field optical magnitude (b) and (c) phase images resonant with the antenna response. Synchrotron infrared nanospectroscopy spectrum of a single optical antenna, showing (d) fundamental and overtone modes and (e) hybridized modes of an antenna resonant with molecular vibrations.

ACKNOWLEDGMENTS

Beamline 5.4 of the ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences and the Office of Biological and Environmental Research, both of the U.S. Dept. of Energy under Contract No. DE-AC02-05CH11231. M.B.R. thanks DoE, Office of Basic Energy Sciences, for support under Award DE-FG02-12ER46893.

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SYNCHROTRON INFRARED NANO-SPECTROSCOPY BY SELF-REFERENCED INTERFEROMETRY

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Infrared scattering near-field optical microscopy (s-SNOM)[1,2] has emerged as a new frontier in imaging science due to its potential to provide nanoscale spatially resolved chemical spectroscopy for the investigation of molecular, soft-matter, and biological materials. Recently, s-SNOM has extended its reach by using ultra-broadband infrared sources from synchrotron accelerators (SINS) for a wide range of a nano-scale electronic and vibrational spectroscopy applications [3,4]. Originally developed on the basis of asymmetric interferometry, s-SNOM is an intrinsically phase-sensitive technique able to yield the complex dielectric function of materials. In this work we present an alternative approach for extracting nano-scale optical constants of materials by employing a symmetric detection scheme that uses the spatially coherent scattered background field from the tip-sample region as a reference field for both signal amplification and interferometry. We demonstrate the benefits of this approach of near-field self-referenced interferometry in terms of interferometric stability and improved signal-to-noise level [5] in both self-heterodyne broadband interferometry and self-homodyne detection using a narrow-band CW laser. Based on a simple model for tip-sample scattering and interferometric detection, we extract fundamental optical constants and infrared vibrational spectra of a variety of hard-matter and molecular materials in good agreement with established values.

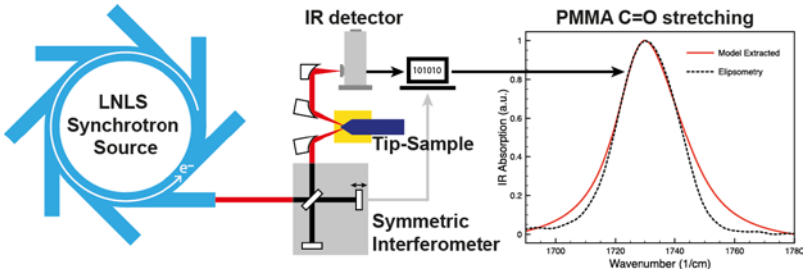

Fig 1: Schematic of of self-referenced SINS developed at LNLS. Right panel: C=O stretching mode measured from 80 nm thick PMMA/Au film by self-reference SINS (red curve) and far-field ellipsometry (black dashed curve).

ACKNOWLEDGMENTS

– The authors thank Neaspec GmbH, Y. Petroff, P. Dumas, I. Craig and K. Hinrichs. This research was supported by the Brazilian MCTI and by the U.S. DOE under award No. DE-FG02-12ER46893.

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NEAR-FIELD IR SPECTROMICROSCOPY USING PHOTOTHERMAL PROBES AND BROADBAND SYNCHROTRON RADIATION AT DIAMOND

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At MIRIAM beamline B22 we experimentally tested the use of broadband synchrotron radiation (SR) InfraRed (IR) from Diamond for photothermal near-field infrared spectroscopy by thermal expansion and scanning thermal microscopy (SThM). A custom IR microscope and a fast optical chopper (50-150 kHz) provided sample illumination and modulation of SRIR at rates matching the cantilevers' resonance in an atomic force microscope (AFM). Fourier Transform IR (FTIR) photothermal expansion absorption spectra of polymer samples were recorded in acquisition time of several minutes. Sub-diffraction limited spatial resolution was demonstrated by simultaneously detection of photothermal expansion and topography across micrometric-size samples: this was proven to be better than 500 nm by measurements at fixed wavelength excitation of 6 μm, i.e. λ/12. Using the SThM approach, photothermal FTIR spectra of fixed mammalian cells were recorded for comparison of different near field detection methods.

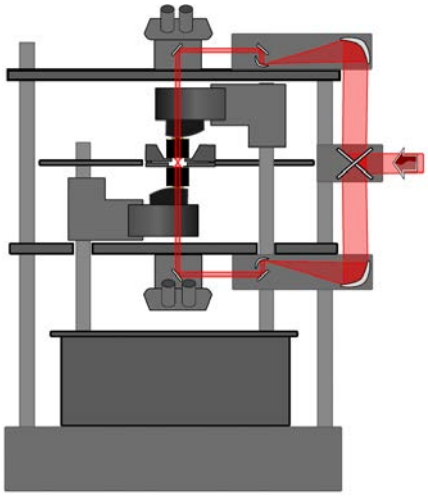

Fig 1: dedicated IR microscope, with illumination paths and AFM location, used for near field spectromicroscopy experiments at MIRIAM beamline B22 of Diamond.

AFM-BASED NANOSCALE INFRARED SPECTROSCOPY OF MONOLAYERS AND ULTRA THIN FILMS

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We have implemented a "resonance enhanced" version of atomic force microscopy-based infrared spectroscopy (AFM-IR), demonstrated recently by Lu, Jin, and Belkin [1]. The resonance enhanced AFM-IR technique uses a tunable infrared laser source that is pulsed synchronously with a resonance mode in an AFM cantilever to detect minute amounts of thermal expansion resulting from absorption of IR radiation. By sweeping the wavelength of the tunable infrared source it is possible to obtain IR absorption spectra from nanoscale regions of a sample on films as thin as a single monolayer. Using resonance enhanced AFM-IR, we have obtained high quality absorption spectra of ultra-thin samples such as single polymer lamellae, self-assembled monolayers, and Purple Membrane protein films.

Because the AFM probe tip can map the thermal expansion on very fine length scales, the AFM-IR technique provides a robust way to obtain interpretable IR absorption spectra at spatial resolutions down to ~25 nm, well below the resolution limit of other techniques used for organic chemical analysis.

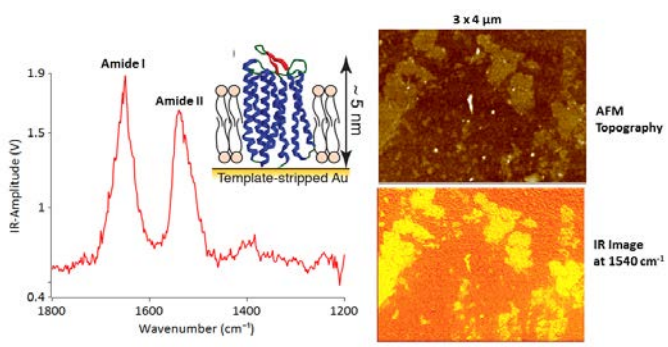

Fig 1: AFM topography image (top right) and IR absorption image collected with the QCL source tuned to the fixed wavenumber of 1540 cm^{-1} (bottom right) of a PM film of Halobacterium salinarium on gold. An AFM-IR spectrum collected at one location on the PM film is shown on the left. A diagram of the 5-nm-thick PM structure adsorbed on the gold surface is also shown.

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DEVELOPMENT OF CANCER DIAGNOSTICS USING THE ALICE IR-FEL FOR IR-SNOM AND AFM-IR IMAGING OF TISSUE

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The scientific programme on ALICE is aimed at developing more accurate and sensitive diagnostic techniques to improve oesophageal, prostate and cervical cancer survival rates [1]. IR-SNOM is being developed and used to obtain images with spatial resolutions down to 0.1 µm [2]. At this level sub-cellular structures can be imaged and identified. IR-SNOM in reflection mode is a well-developed technique; it has been extended to include transmission mode, where the IR radiation is focussed onto the underside of the sample and the fibre collects radiation transmitted through the sample. Images, from biopsies of benign and cancerous tissue, have been obtained using both SNOM techniques. The wavelengths were chosen to differentiate different types of tissue. Computerised algorithms, that have the potential to contribute to rapid analysis of biopsies, are being developed.

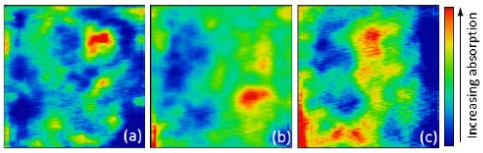

Fig 1: Images of oesophageal tissue recorded with IR-SNOM showing the relative amount of light collected by the fibre tip in reflection mode. (a) 8.05 µm, (b) 7.3 µm, (c) 6.5 µm. Image size is 250µ x 250 µm.

A recently developed atomic force microscopy technique, AFM-IR, which enables images with spatial resolutions of tens of nm to be obtained, was deployed. In this technique the expansion of the sample that results from heating due to the IR pulse is detected. Successful AFM-IR imaging was demonstrated on breast cancer cell cultures and Aβ amyloid fibres [3].

ACKNOWLEDGMENTS

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- We are grateful to the ASTeC staff at Daresbury for upgrading, maintaining and running the ALICE facility.

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SINGLE-SHOT TERAHERTZ SPECTROSCOPY WITH PICOSECOND TIME RESOLUTION

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At synchrotrons operating in low-alpha mode to generate Coherent Synchrotron Radiation (CSR) the appearance of instabilities above a beam current threshold leads to bursting THz signals and thus varying temporal and spectral pulse shapes [1]. We present a novel detection system based on superconducting nano-bolometers that will enable the bunch-by-bunch monitoring of the spectrum of single THz pulses.

Two approaches of a single-shot THz spectrometer are currently investigated: the concept of an on-chip detector array with integrated narrow-band antennas (see Fig. 1) and a quasi-optical setup making use of delay lines and THz bandpass filters. By deploying this second setup simultaneous bunch-by-bunch resolution at 350 GHz and 650 GHz was realized successfully with a niobium nitride hot-electron bolometer exhibiting a response time of less than 165 ps full width at half maximum (FWHM) [2]. Further improvement is achieved through the combination of the ultra-fast intrinsic response time of the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ (YBCO) and broadband readout lines. A temporal resolution of 15 ps FWHM along with real-time resolution of CSR single-shots at the ANKA storage ring have been demonstrated [3].

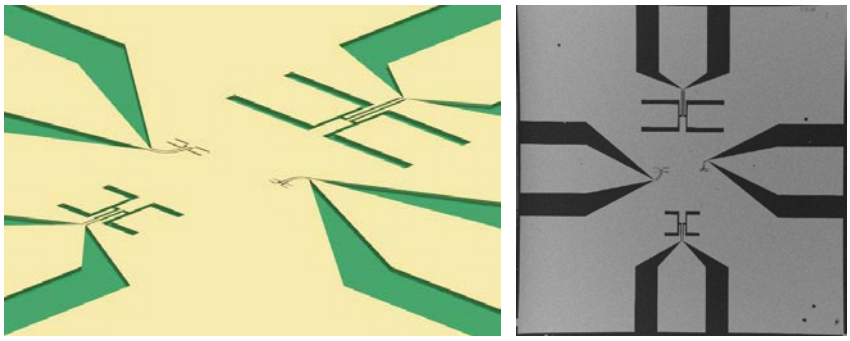

Fig 1: Draft of the detector array with four frequency bands and scanning-electron microscopy picture of the fabricated YBCO detectors.

ACKNOWLEDGMENTS

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TERAFERMI BEAMLINE: FINAL PROJECT AND STATUS OF THE INSTALLATION

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3) CNR-IOM and Dipartimento di Fisica, Università "Sapienza", Roma 00185, Italy

TeraFERMI is the new THz beamline [1] based on the FERMI seeded Free-Electron-Laser facility in Trieste. The beamline takes advantage of the short electron bunch structure of the FERMI LINAC to generate THz pulses in the 100's microjoule range through Coherent Transition Radiation. Thanks to the high peak power (>GW) and electric field (>MV/cm) TeraFERMI will be used to address non-linear THz spectroscopy and to achieve coherent control on material's properties. The TeraFERMI beamline will thus allow extending the Free-Electron-Laser's advantages in terms of coherence, peak power, and ultrafast time structure, into the long wavelengths spectral range.

The mounting of the TeraFERMI beamline and experimental hutch is scheduled for July and August 2015. We discuss here the final project of the beamline and will present updates on the outcome of the TeraFERMI installation and initial commissioning.

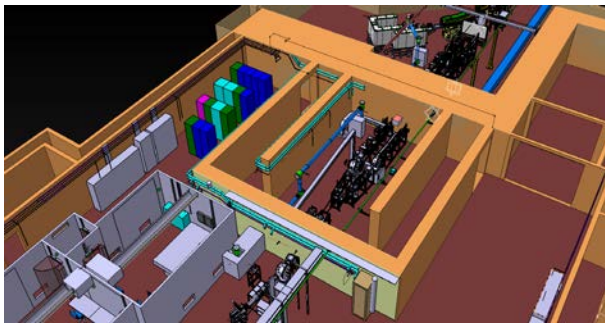

Fig 1: Layout of the TeraFERMI beamline, extending along approximately 30 m from the FERMI undulator hall to the experimental room.

ACKNOWLEDGMENTS

- This work is supported by Italian Ministry of Research (MIUR) program FIRB Futuro in Ricerca Grant No. RBFR10PSK4

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EXTREMELY SHORT ELECTRON BUNCH GENERATION FOR PRODUCING THZ SUPERRADIANCE AT T-ACTS, TOHOKU UNIVERSITY

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A test accelerator as a coherent terahertz source (t-ACTS) has been under development at Tohoku University [1], in which a generation of intense coherent terahertz (THz) radiation via an extremely short electron bunch. Superradiance can be emitted from the electron beam when its form-factor is sufficiently large. The bunch length should be 10 times shorter than the wavelength of radiation to obtain the form-factor of 0.7 for Gaussian shape of the electron bunch in longitudinal direction. Since 1 THz radiation's wavelength is 300 μm and the intrinsic photon emittance is $\lambda/4\pi$ ~ 24 μrad, the bunch length less than 30 μm (100 fs) and a normalized transverse emittance less than $24\beta\gamma$ μrad is desirable for superradiance. An injector is consisted with a thermionic RF gun, an alpha-magnet as energy filter, and a 3m-long traveling wave accelerating structure. A long-period undulator has been also installed to provide THz superradiance. Velocity bunching scheme is employed for short electron bunches production. Experiment of short bunch production has been carried out and the bunch length was measured with a streak camera using an optical tradition radiation. We have succeeded in producing a sub-picosecond electron bunch in t-ACTS. The details of the experiment and a future plan for producing THz superradiance using the undulator are described in this workshop.

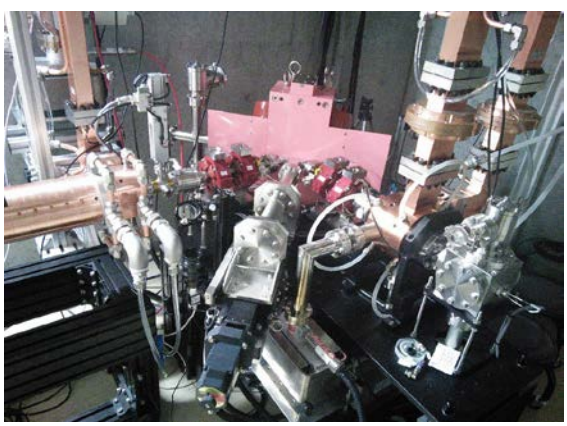

Fig 1: Injector part of t-ACTS.

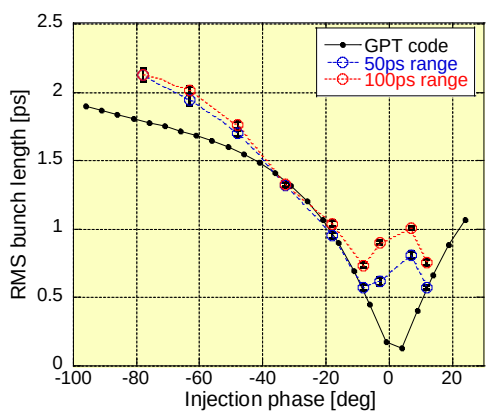

Fig 2: Measured bunch length using streak camera.

ACKNOWLEDGMENTS

- This work is partly supported by Grant-in-Aid for Scientific Research (S) 25790078 and (B) 25286084, MEXT, Japan.

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RAPID-SCAN, STEP-SCAN, AND INTERLEAVED TIME-RESOLVED SPECTROSCOPY SIGNAL-TO-NOISE COMPARIZON

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Step-scan and rapid-scan spectroscopy are traditional ways to collect time-resolved spectra. Scanning mirror of interferometer moves with a constant speed and data are collected „on-fly“ if rapid-scan technique is used. Mirror speed and spectral limit time resolution to 10 ms per spectrum in this technique. Mirror moves stepwise in case of step-scan technique. Experiment is repeated and time-resolved data are acquired at each mirror position. Time-resolution in the step-scan experiment is limited by the response time of the detector (few ns for the current MIR detectors). Unfortunately, noise in the step-scan data is higher compare to the rapid-scan.

Another approach to preform TRS measurements is interleaved spectroscopy. This technique is available recently for the Bruker Vertex series FTIR. Instrument sends multiple triggers to the external setup while interferometer mirror moves continuously. After completion of single scan, data are resorted according to time and time-resolved spectra are calculated. Interleaved TRS method allows to record spectra with ns time resolution and with much less noise in compare to the step-scan technique. Example of time-resolved emission spectra acquired by this technique is shown in fig1.

Details, limitations, and applications of interleaved TRS method will be discussed in this presentation. Time-resolved data on emission of fast infrared LEDs recorded using different techniques will be presented. Signal-to-noise obtained by step-scan, rapid-scan, and interleaved TRS methods will be compared.

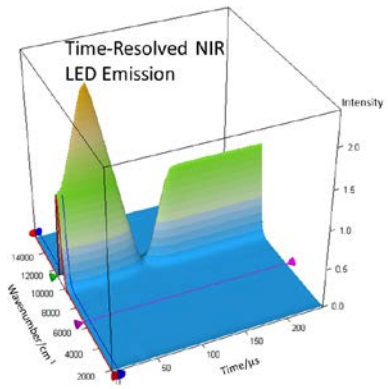

Fig 1. TRS emission spectrum of LED diode measured using interleaved technique.

LASER PHOTOLYSIS ON THE THZ BEAMLINE AT THE AUSTRALIAN SYNCHROTRON

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2) La Trobe University, Bundoora, VIC, 3086

Laser photolysis is a new capability that is presently being added to the THz/Far-IR beamline. This technique will allow our users to perform pioneering spectroscopic studies at ultra-high spectral resolution on gaseous molecules of astrophysical interest; it will also enable our users to study photochemical changes in condensed-phase, solid and biological systems after or during laser irradiation.[1][2]

The addition of lasers will also allow a host of sunlight driven reactions to be studied, providing a source of radicals such as OH or halogens.[3]

We currently have to two lasers: A 40 *W* cw CO_2 laser from Monash University, operating at 10.6 *µm, and, a* 10 *Hz* pulsed 480 *mJ* Nd:Yag Surelite Continuum laser from La Trobe University, operating at 1064, 532, 355 and 266 *nm*

A photolysis gas cell is also available for use. It is suitable for creating steady-state chemical populations with the laser, which can then be probed by the Synchrotron source. We are the only THz beamline with these capabilities.

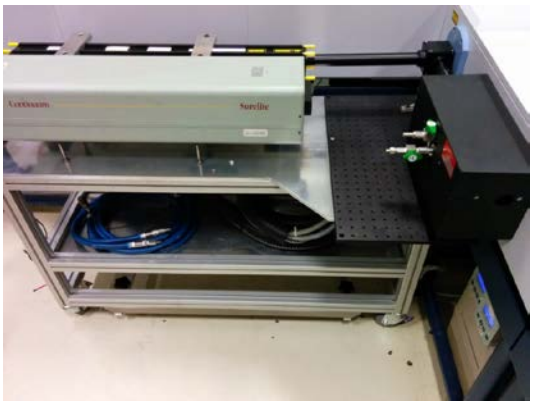

Figure 1. The beam is completely enclosed, making it safe for users

ACKNOWLEDGMENTS

- Australian Synchrotron

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SYNCHROTRON INFRARED STUDIES OF METAL-ORGANIC FRAMEWORKS AT DIAMOND LIGHT SOURCE.

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5) School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

A strong research community has recently emerged using infrared synchrotron radiation (IRSR) at Diamond Light Source to investigate the structure, molecular dynamics and molecular adsorption kinetics of metal-organic frameworks (MOFs). The high brilliance of the source allows high quality polarised absorption spectroscopy of anisotropic single crystals revealing orientation specific information such as alignment of the structure directing template [1], adsorbed molecules [2] and framework structural groups [3]. In-situ single crystal IRSR studies at elevated temperatures elucidate the activation of MOFs via dehydration, decomposition and removal of the organic template [1]. For activated materials, competitive uptake behaviours in controlled flows of gas mixtures in conditions relevant to industrial processes have been quantified, and hydrogen bonding interactions between host and adsorbed species have been determined [3]. The broad spectral bandwidth of IRSR has been exploited in structural studies where the predictions of molecular dynamics simulations can be tuned towards the rich, measured, mid-IR – THz spectra.

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ASPECTS OF DESIGNING AND BUILDING PLASMONIC NANOSTRUCTURED DEVICES FOR USE IN SYNCHROTRON INFRARED SPECTROMICROSCOPY

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The power of synchrotron infrared radiation compared to conventional sources when studying materials at the diffraction limit has been emphasized for years. It is important to note that this advantage is the result of highly focused synchrotron light lowering the noise of the measurement and not by enhancing the signal. Can we do better than the intrinsic limit of signal absorption of an analyte? Metal nanostructures on dielectric substrates can support surface plasmons with resonant frequencies in the infrared spectral region (dependent on metal, substrate, geometry and size). In particular, when the nanostructure size is comparable to infrared wavelengths their resonances occur in the infrared region and are marked by absorption and scattering of infrared radiation. This incident radiation can couple to the metal plasmon and can enhance the magnitude of the electromagnetic field. In the presence of a weak absorber, the plasmonic resonance will be perturbed and manifest as a modulation of the plasmon at the frequency of the molecular vibration. By adjusting the size and geometry of these metal structures, the plasmon can be tuned to coincide with select molecular vibration frequencies (lipids, proteins, etc…). This allows spectroscopic observation of signals arising from concentrations below the detection limit and is the principle behind Surface Enhanced Infrared Spectroscopy (SEIRS). In this talk, aspects of designing and building plasmonic nanostructured devices of varying shape and sizes to achieve maximum plasmonic enhancement for use in synchrotron infrared spectromicroscopy will be discussed. These include computational models, variety of fabrication techniques and several examples on prepared plasmonic devices.

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- Ian Burgess (University of Saskatchewan), Garth Wells (Canadian Light Source) and Francois Lagugne-Labarthet (Western University)

PLASMONIC AND EFFECTIVE MEDIUM BEHAVIOR OF NANOSCOPIC GRANULAR GOLD FILMS

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Using the SINS near-field infrared spectroscopy instrumentation at ALS beamline 5.4, we have measured the near-field response of a set of discontinuous gold films deposited onto sapphire substrate. The spectral range from 400 cm^{-1} to 1500 cm^{-1} spans the sapphire substrate phonon energies, enabled by using a 4.2K Ge:Cu extrinsic photoconductive detector. Features associated with plasmon polaritons appear in the spectra and change character depending on the connectedness of the gold grains. A discussion on these modes and effective medium theories will be presented.

ACKNOWLEDGEMENTS

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