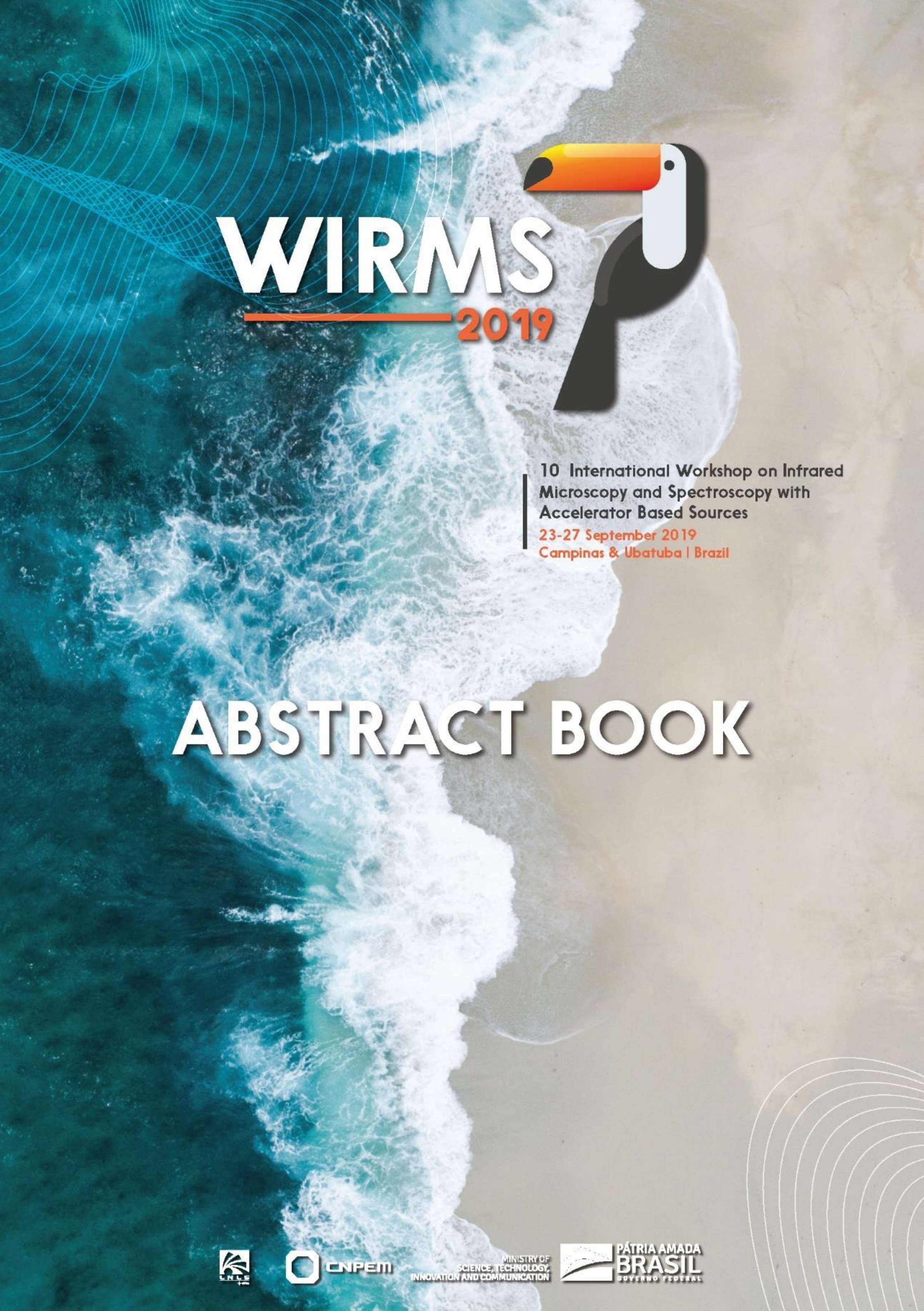

WIRMS 2019

10 International Workshop on Infrared
Microscopy and Spectroscopy with
Accelerator Based Sources

23-27 September 2019
Campinas & Ubatuba | Brazil

ABSTRACT BOOK

LNLS

CNPEM

MINISTRY OF
SCIENCE, TECHNOLOGY,
INNOVATION AND COMMUNICATION

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Shift the spectrum of fiber femtolasers

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FOREWORD

We are glad to announce and host the 10th edition of International Workshop on Infrared Microscopy and Spectroscopy with Accelerator Based Sources – WIRMS 2019.

Promoted by the Brazilian Synchrotron Light Laboratory (LNLS/CNPEM), the WIRMS 2019 will be held in Brazil from the 23rd to 27th of September 2019. During the first day schedule – 23rd of September – it is included a visit tour to Sirius, the brand new brazilian synchrotron light source. The workshop will highlight the latest advances in infrared spectroscopy and imaging inside synchrotron and free electron laser facilities.

The event will gather around 100 participants including infrared spectroscopy experts in several modalities such as ultra-resolved chemical imaging, vibrational analysis at extreme environments, THz spectroscopy, new infrared sources and detectors, time-resolved chemical analysis, infrared spectral-tomography among others.

In an overwhelming environment that mixes tropical rainforest, rocks and beautiful beaches, we expect WIRMS 2019 to be a great occasion for connecting ideas and for discussing future perspectives of the community in the context of new light sources, including the arrival of 4th generation storage rings.

We look forward to welcoming you to Brazil in September!

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PROGRAM

	Monday (Sept/23)		**Tuesday (Sept/24)**		**Wednesday (Sept/25)**
08:45	Registration at CNPEM	**08:45**	Welcome	**08:45**	Anouncements
		09:00	**Oppening talk - Harry Westfahl**	**09:00**	**Markus Raschke**
09:30	Opening Talk **Yves Petroff**	**09:30**	**Hans Bechtel**	**09:35**	Bernd Kaestner
10:00	Coffee break and Sirius facility tour	**10:05**	Mark Frogley	**09:55**	Ingrid Barcelos
		10:25	Francisco Maia	**10:15**	Marcio Soares
		10:45	**Coffee Break**	**10:35**	**Coffee Break**
		11:05	**Hoi-Ying**	**10:55**	**Sponsor 1 - Neaspec**
		11:40	Christoph Sandt	**11:15**	**Eglof Ritter**
		12:00	Jitraporn (Pimm) Vongsvivut	**11:50**	Per Uvdal
		12:20	Tomasz Wrobel	**12:10**	Jitraporn (Pimm) Vongsvivut
12:50	Departure to Ubatuba	**12:40**	**Lunch**	**12:30**	**Lunch**
		14:00	**Jan-Christophe Deinert**	**14:00**	**Lawrence Carr**
		14:35	**Lukas Wehmeier**	**14:35**	Gihan Kamel
		15:10	Akinori Irizawa	**14:55**	Yuka Ikemoto
		15:30	**Coffee Break**	**15:15**	Tim May
		15:50	**Andrea Perucchi**	**15:35**	**Coffee Break**
		16:30		**15:55**	**Christophe Szwaj**
			Posters Session	**16:30**	Ferenc Borondics
				16:55	Carsten Cleff
		19:00	**Regular dinner**	**19:00**	**Conference Dinner**
					Mike Martin + Lisa Vaccari

PROGRAM

	Thursday (Sept/26)		**Friday (Sept/27)**		Saturday (Sept/28)
08:45	Anouncements	**08:45**	Anouncements	**07:30**	Breakfast + check out
09:00	**Rainer Hillenbrand**	**09:00**	**Pascale Roy**	**08:00**	Transfer to Airports
09:35	Miriam Unger	**09:35**	Matthew Ryder		
09:55	Barbara Souza	**09:55**	**M. C. Martin**		
10:15	**Mengkun Liu**	**10:30**	Coffee Break		
10:50	**Coffee Break**	**10:50**	**Lisa Vaccari**		
11:10	**Alex McLeod**	**11:25**	**Paul Dumas**		
11:45	Stephanie Gilbert Corder	**12:00**	Closing Remarks		
12:05	Julian Barnett				
12:25	**Lunch**				
14:00	Francesco Capitani	**14:00**	Trip to Anchieta's Isle (optional)		
14:20	Tyler Huffman				
14:40	Mustafa Kansiz				
15:00	Eugenio Calandrini				
15:20	**Coffee Break**				
15:40	Jean-Blaise Brubach				
16:00	**Sponsor 2 - Bruker Nano**				
16:20	**IAC meeting + free time**				
19:00	**Tropical Cocktail Party**	**19:00**	**Regular dinner**		

ORAL PRESENTATIONS

IR sources, detectors and facility developments

IR spectro-microscopy and imaging

Nanoscale resolved synchrotron IR analysis

Special IR Techniques

Special Session: Why all the fuzz about synchrotron IR/THz now?

POSTER PRESENTATIONS

IR sources, detectors and facility developments

IR spectro-microscopy and imaging

Nanoscale resolved synchrotron IR analysis

Special IR Techniques

ORAL PRESENTATION

ACCELERATOR BASED INFRARED SOURCES AND DETECTOR SATURATION

Y. Ikemoto[1]*, H. Zen[2]

[1]*Japan Synchrotron Radiation Institute (JASRI), SPring-8, 679-5198, Hyogo, Japan;*
[2]*Kyoto University, Institute of Advanced Energy, 611-0011, Kyoto, Japan.*
**ikemoto@spring8.or.jp*

In order to perform various investigations by infrared synchrotron radiation, infrared detectors are important as well as source characteristics. In the next generation low emittance synchrotron plans, it is hard to expect that the infrared light becomes stronger than the current status. Therefore, detector systems become more important. In this study, characteristics of detector saturation are investigated by infrared synchrotron radiation (IR-SR) at infrared beamline BL43IR in SPring-8 and infrared free electron laser (IR-FEL) at KU-FEL in Kyoto University. HgCdTe (MCT) detector is an infrared semiconductor detector, which is most frequently used for mid-infrared spectroscopy measurements. A high sensitivity and a high response speed are the prominent features of MCT detector. However, the linearity is not good and the saturation causes serious problems to infrared spectra. The electron energy and the storage ring current of SPring-8 are 8 GeV and 100 mA, respectively. The Photon flux of the infrared light at SPring-8 is not higher than that at the other facilities. The problem of detector saturation, however, is serious. A photoconductive MCT detector mounted on BRUKER HYPERION2000 was used to evaluate the saturation. SPring-8 has eight types of bunch modes. The time structures are different in each bunch mode. We find that the detector saturation causes a decrease of the signal intensity and a deterioration of the signal-to-noise ratio, and degree of the saturation depends on the bunch mode. In order to exclude the time structure parameters and investigate the saturation effect in detail, we used IR-FEL. The macro pulse time width is about 2 microseconds at KU-FEL, that is similar to the train part duration time of IR-SR at SPring-8. Fig. 1 shows output voltage of photoconductive MCT detectors. The IR-FEL beam was split into two and they were injected into two detectors, MCT-1 and MCT-2. The intensity of the light into MCT-2 was enough low not to saturate. The intensity of the light into MCT-1 was increased from (a) to (c). The curve (a) shows a linear dependence, which means the detector is not saturated. The curve (b) has a flat part at the high voltage region, which is a typical saturation behavior. The injected intensity of the curve (c) is the highest among three, but the output voltage is found to be suppressed than that of (b). At the deep saturation condition, care must be taken in the analysis of the signal intensity. In order to reveal the mechanism of the saturation, we also observed response curves at various injection intensities and pre-amp gains using photoconductive and photovoltaic MCT detectors. Based on the results, appropriate use of MCT detector will be discussed.

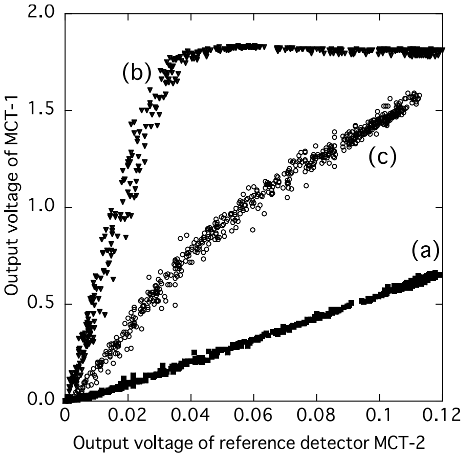

Fig. 1 Output voltage of MCT detector at various intensities of the light.

Keywords: infrared synchrotron radiation, infrared free electron laser, HgCdTe detector, saturation

INFRARED SYNCHROTRON RADIATION WITH 2020 VISION

G.L. Carr

National Synchrotron Light Source II, Brookhaven Nat'l Laboratory, Upton, NY 11973 USA
carr@bnl.gov

This presentation will survey our current understanding of infrared synchrotron radiation sources and beamline designs, using the 1st infrared beamline at NSLS-II as an example. Aspects of source dimension, waveguide cutoff effects and motivation for the overall optical design will be discussed, along with performance results (including coherent emission during normal accelerator operations at 400 mA). While infrared spectromicroscopy remains the dominant measurement method, other techniques continue to develop and evolve, placing additional demands on the source as well as detectors. A particular example is near-field infrared nanospectroscopy for spanning the far-infrared spectral region where a ~1 MHz response bandwidth is needed to match harmonics of the AFM oscillation frequency. The potential for fast bolometers with custom long-pass filters will be described.

Acknowledgements:
This work supported by the U.S. Dep't, of Energy through contracts DE-SC0012704 at NSLS-II.

Keywords: IR sources, detectors, facility developments

IR sources, detectors and facility developments

MATERIAL SCIENCE USING THz-FEL

A. Irizawa[1]*, S. Suga[1], T. Nagashima[2], A. Higashiya[2], M. Hashida[3], S. Sakabe[3], T. Kawasaki[4], K. Tsukiyama[4]

[1]The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan; [2]Setsunan University, 17-8 Ikedanaka-machi, Neyagawa, Osaka 572-8508, Japan; [3]Graduate School of Science, Kyoto University, Kyoto, 6110011 Japan; [4]IR Free Electron Laser Research Center, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan.
**irizawa@sanken.osaka-u.ac.jp*

The free electron laser in the terahertz region (THz-FEL) at the Institute of Scientific and Industrial Research (ISIR) in Osaka University is based on the stimulated radiation from compressed high-energy electron pulses. The natures of FEL are, short pulse, high intensity, variable wavelength, monochromatic, polarization, and coherency in time and space. THz and/or FIR is the electromagnetic wave locating on the boundary between radio waves and photons. It behaves as a high-frequency oscillating electric field and also as low-energy photons against for the electrons in materials. Thus, the THz-FEL can be used not only as a brilliant probe light source for spectroscopy but also as a pump light source that enables novel excitations in materials. Recently, nonlinear interactions between semiconductors and the intense THz wave from FEL (frequency: 2.5-7.5 THz, electric field: >3 MV/cm) have been investigated [1]. Under irradiation of focused THz-FEL, a periodic structure so called LIPSS was observed on the surface of semiconductor Si as an irreversible phenomenon. The periodicity of LIPSS by THz-FEL is ~1/25 of the wavelength, which is small enough to exceed the diffraction limit. A scaling law was found between the LIPSS periodicity and the pulse number, which also might be seen in case of LIPSSs with other materials, by other wavelengths (e.g. NIR). These results possibly be understood in a framework of self-organized criticality phenomena shown in nonequilibrium open system [2]. As another irradiation experiments, we will touch in the talk about a remarkable performance in processing of biomolecular aggregate structure.

References:

[1] A. Irizawa, S. Suga, T. Nagashima, A. Higashiya, M. Hashida, and S. Sakabe, Appl. Phys. Lett. 111, 251602 (2017).
[2] N. Gregoire and I. Prigogine, Self-Organization in Nonequilibrium Systems (Wiley, New York, 1977), Vol. 191977.

Acknowledgements:

This work was supported by JSPS KAKENHI Grant No. JP17K18989, by the research program “Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials,” and by “Executive Program of Cooperation in The Field of Science and Technology between The Government of Italy and The Government of Japan (2017–2019).” The authors would like to thank Dr. K. Kawase, Dr. M. Fujimoto, Mr. K. Furukawa, Ms. K. Kubo, and Mr. Y. Okada supporting us with the operation of THz-FEL. The authors also would like to thank Dr. S. Kashiwagi, Prof. S. Okuda, Prof. K. Sakamoto, Prof. S. Kimura, and Prof. T. Hosokai for useful discussions. Prof. A. Maecelli, Prof. S. Lupi, and Prof. S. Dabagov have encouraged us through the international collaboration.

Keywords: FEL, THz, FIR, nonlinear

MID-IR GENERATION BASED ON DIFFERENCE FREQUENCY GENERATION (DFG) AND FEMTOSECOND FIBER LASER SYSTEMS

Carsten Cleff*, Peter Adel, Marc Fischer, and Ronald Holzwarth

Menlo Systems GmbH, Am Klopferspitz 19a, D-52152 Martiensried, Germany
**c.cleff@menlosystems.com*

Difference frequency generation-based laser systems provide great flexibility for applications in infrared microscopy and spectroscopy. In contrast to light generation in an active laser medium, the DFG process is not limited to specific wavelength ranges [1, 2]. Thus, DFG systems can provide access to a large spectral domain starting in the near infrared and extending to THz radiation. Furthermore, DFG systems can operate at low repetition rates of a few kHz as well as at high repetition rates of several hundreds of MHz, or even GHz. Depending on the pump laser system and nonlinear crystals used, DFG systems can provide output power levels of hundreds of mW and narrow spectral bandwidths of a few wavenumbers as well as a large spectral bandwidth of hundreds of wavenumbers [1, 2]. Additionally, the DFG process inherently generates carrier envelope offset frequency free radiation (f_{ceo}=0) providing easy access to vibrational spectroscopy with extremely high precision. Here, we present multiple system designs for DFG-based offset-free MID-IR laser systems in the 3 - 15 µm range. Our system designs utilize two-color femtosecond fiber laser systems based on Menlo Systems' highly reliable and low noise figure 9^{TM} laser technology. Starting with either an Yb-based or Er-based fiber laser system, we use frequency shifting in nonlinear fibers to generate a second wavelength output between 1 µm and 2.2 µm, which is overlapped with the fundamental wavelength for DFG generation in different nonlinear crystals. Menlo Systems' DFG system designs can cover various repetition rates, output power levels, and spectral bandwidths for MID-IR radiation (see Figure 1). We demonstrate MID-IR generation between 3 µm and 15 µm with output power levels of up to 200 mW and spectral bandwidths between 40 cm^{-1} and 400 cm^{-1} with repetition rates between 100 MHz and 250 MHz. The presented DFG systems are versatile tools for infrared microscopy and spectroscopy. Furthermore, Menlo Systems' offset-free DFG systems allow to increase precision and simplify detection without requiring an FTIR spectrometer when used in a dual-comb configuration [3].

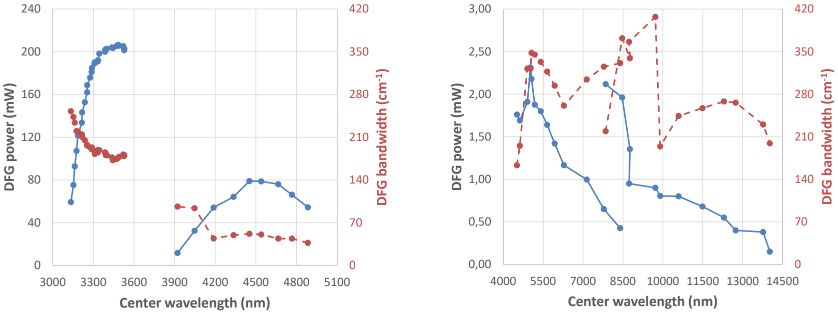

Figure 1: Wavelength range, output power levels, and spectral bandwidths covered by Menlo Systems' DFG sources.

References:

[1] G. Sobon et al., Opt. Letters 42(9), 1748-1751 (2017).
[2] C. Gaida et al., Light: Science & Applications 7(94), 1-8 (2018).
[3] F. Keilmann, C. Gohle, and R. Holzwarth, Opt. Letters 29(13), 1542-1544 (2004).

Keywords: difference-frequency-generation, laser, fiber-laser, ultra-short pulses

IR sources, detectors and facility developments

PROGRESS OF MID AND FAR IR BEAMLINES AT CANADIAN LIGHT SOURCE

Tim May*, S. Rosendahl, B. Billinghurst

Canadian Light Source, University of Saskatchewan, 44 Innovation Blvd., Saskatoon, Canada.
**tim.may@lightsource.ca*

Since the 2017 WIRMS at Diamond, the CLS Infrared beamlines have been progressing despite all odds. The year 2018 saw operations cut in half when the ring shut down due to electron gun problems, and most of the first half of 2019 for extended maintenance. Despite this, several improvements occurred. Notable for the Mid IR were installation of a dedicated horizontal ATR microscope interface on the beamline along with an improved PID control on the Active Optics chicane, and enclosure of the Mid IR hutch. A new Agilent spectrometer and Cary 620 microscope with FPA and a new IRSweep QCL IR spectrometer were installed offline. The Far IR most notably hired a new Associate Scientist with a high-pressure science background. The Diamond Anvil Cell microscope had objective/viewing and sample stages motorized and a gas pressure filling station purchased to expand condensed phase work. We installed a new QMC detector and cryostat with closed-cycle helium cooler to good effect. This provides a TES Bolometer for 5-600 cm^{-1} and a Ge:Cu for 300-1300 cm^{-1} ranges. A new layout of the Mid IR optics is developing with optics for the Far IR started. This will employ the minimum divergence optics for wide aperture ports of T. Moreno's design [1,2]. These will apply to both the current and a new ring. An emerging vision of a next-generation ring has motivated work on possible methods for extracting IR from a new ring. A concept is being explored we call "Gentle Bends". It utilizes a long-radius bending chicane in a straight section of the ring. It can provide a long wavelength source but is complex with multiple edge sources overlapping and extracting the light from the small ring chamber. Many different ring and port parameters need to be determined to see which approach works best for either optics upgrades on the current ring or a future low-emittance lattice ala NSLSII, Soleil, Sirius etc. The Canadian IR Community interest in the new ring has to guide these new developments.

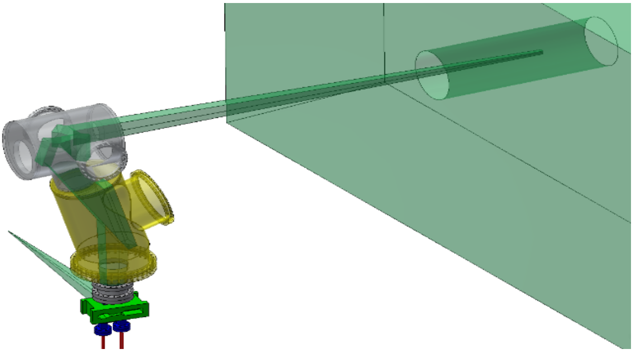

Figure 1: Concept of new "front end" for the Mid IR beam port. Four added mirrors shape the beam after M1 for minimum divergence. Beam is constrained to go through existing tunnel in shield wall.

References:

[1] T. Moreno, J. Synchrotron Radiation 22, 1163 (2015).
[2] T. Moreno, J. Synchrotron Radiation 24, 386 (2017).

Acknowledgements:

Thanks to T. Moreno, R.Oliveira Fritas, L. Dallin and R. Chernikov for good discussions.

Keywords: Synchrotron Infrared Spectroscopy Microspectroscopy

IR sources, detectors and facility developments

SRIR UNLIMITED

Ferenc Borondics

SOLEIL Synchrotron, BP48, L'Orme des Merisiers, 91192 Gif sur Yvette Cedex, France.
ferenc.borondics@synchrotrons-soleil.fr

Infrared spectromicroscopy has been a well-established technique for many decades and still, it doesn’t fail to bring new surprises. The variety of techniques, accessing information both above and beyond the diffraction limit is ever-growing and combined with new generation accelerator sources it offers the possibility of the highest quality data. In this talk, I will cover recent development at the SMIS beamline of the SOLEIL synchrotron focusing on new developments, new challenges, and future plans.

Keywords: infrared, diffraction limit, instrumentation development

TERAHERTZ COHERENT SYNCHROTRON RADIATION: RECENT RESULTS ON HIGH REPETITION-RATE MEASUREMENTS AND STABILITY CONTROL AT SOLEIL

C. Evain[1], C. Szwaj[1]*, E. Roussel[1], J. Rodriguez[1], M. Le Parquier[1],
S. Bielawski[1], M.-A. Tordeux[2], F. Ribeiro[2], M. Labat[2],
N. Hubert[2], J.-B. Brubach[2], L. Manceron[2], P. Roy[2]

[1]Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers, Atomes et Molécules, Centre d'Étude Recherches et Applications (CERLA), F-59000 Lille, France; [2]Synchrotron SOLEIL, Saint Aubin, BP 34, 91192 Gif-sur-Yvette, France.
**christophe.szwaj@univ-lille.fr*

Coherent synchrotron radiation (CSR) occurs when small structures are formed inside an electron bunch, as the result of either the so-called microbunching instability, or short bunch operation. CSR is known as an intense source of terahertz radiation, with an interesting potential in user applications. However, specificities of the sources still required dedicated work in order to understand and master the dynamics of the emission. Here we present recent results obtained at SOLEIL, on ultrafast measurements, modeling [1] and control. In particular, we will show how new techniques (time-stretch) potentially allow time-domain spectroscopy to be performed in single-shot at high (multi-MHz) repetition rates. We will also show how feedback strategies inspired from chaos control enables to suppress the so-called microbunching instability, thus opening the way to stable CSR sources in a broad range of operation modes.

References:

[1] C. Evain et al. Phys. Rev. Lett. 118, 054801 (2017).
[2] C. Evain et al. Nat. Phys. 15, 635 (2019)

Acknowledgements:

This work was supported by LABEX CEMPI, CPER P4S.

Keywords: Coherent Synchrotron Radiation, Electro-Optic sampling

IR sources, detectors and facility developments

THE TERAFERMI BEAMLINE AS A POWERFUL TOOL FOR NONLINEAR STUDIES ON DIRAC MATERIALS

A. Perucchi

Elettra – Sincrotrone Trieste, Italy.
andrea.perucchi@elettra.eu

TeraFERMI is the THz beamline of the FERMI Free Electron Laser. The beamline is based on a Coherent Transition Radiation source providing intense and broadband THz pulses in the MV/cm range. These fields are used to achieve THz control of matter and to push materials well into their nonlinear regime. A class of materials particularly studied at TeraFERMI is that of topological insulators. Thanks to their Dirac massless carriers, topological insulators show nonlinear THz behavior, similarly to the case of graphene. I will discuss in this presentation our most recent results on the THz control of plasmons in the Bi_2Se_3 topological insulator, and more in general, on the study of quantum materials with THz synchrotron sources.

Keywords: Free Electron Lasers, Plasmons, Topological Insulator

IR spectro-microscopy and imaging

AMPLITUDE TUNING AND PROPAGATION MODULATION OF HYPERBOLIC PLASMON PHONON POLARITONS IN GRAPHENE-HBN HETEROSTRUCTURES

Francisco C. B. Maia[1]*, Brian T. O Callahan[2], Alisson R. Cadore[3], Ingrid D. Barcelos[1], Leonardo C. Campos[3], Kenji Watanabe[4], Takashi Taniguchi[4], Christoph Deneke[5], Alexey Belyanin[6], Markus B. Raschke[2], Raul O. Freitas[1]

[1]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970 Campinas, Sao Paulo, Brazil; [2]Department of Physics, Department of Chemistry, and JILA, University of Colorado, Boulder, Colorado 80309, USA; [3]Department of Physics, Federal University of Minas Gerais, 30123-970 Belo Horizonte, Minas Gerais, Brazil; [4]National Institute for Materials Science, Namiki 305-0044, Japan; [5]Applied Physics Department, Gleb Wataghin Physics Institute, University of Campinas (Unicamp), 13083-859 Campinas, Sao Paulo, Brazil; [6]Department of Physics Astronomy, Texas AM University, College Station, Texas 77843-4242, United States.
**francisco.maia@lnls.br*

Subwavelength polaritons are an important topic in Nanophotonics of van der Waals materials. Here we present a study of the hybrid hyperbolic plasmon-phonon polaritons (HP^3) in the graphene-hexagonal Boron Nitride (G-hBN) heterostructure using synchrotron infrared nanospectroscopy (SINS). By electric gating and by engineered micro-structured metasurfaces (air-Au patterned substrate), we establish control of the amplitude of HP^3 modes. It is shown that the amplitude depends on the interaction between mid-infrared plasmons of graphene and Au with discrete hyperbolic phonon-polaritons (HPhP) of the hBN. Such effect is described by a Fano model (eq. 1). Regulation of polaritonic flow is demonstrated in the vicinity of air-Au in-plane heterointerface. In this region, there is an abrupt discontinuity of the dielectric permittivity, i.e. transition from air to Au, leading to momenta mismatch of polaritons. Hence, in-plane polaritonic waves travelling from air to Au present a higher reflection coefficient that waves propagating in the opposite directions (Au to air). The asymmetry in reflection/transmission features unprecedented HP^3 anisotropic regulation of the flow of polariton waves [1]. The impact of our findings will be relevant for designing novel nanophotonic devices using polaritons as information carriers.

References:

[1] Nano Lett., 2019, 19 (2), pp 708–715

Acknowledgements:

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Keywords: graphene plasmon-polaritons, hyperbolic phonon-polaritons, hybrid heterostructures, graphene, hBN

FOUR-ANGLE POLARISATION-RESOLVED TRANSMISSION FTIR MAPPING FOR MATERIALS ORIENTATION ANALYSIS

Jitraporn (Pimm) Vongsvivut[1]*, M. J. Tobin[1], R. Honda[2], M. Ryu[2],
P. Takkalkar[3], N. Kao[3], S. Juodkazis[4], J. Morikawa[2]

[1]Infrared Microspectroscopy (IRM) Beamline, Australian Synchrotron, 800 Blackburn Road, Clayton, Victoria 3168, Australia; [2]Tokyo Institute of Technology, Meguro-ku, Tokyo, 152-8550, Japan; [3]School of Engineering, RMIT University, Melbourne, Victoria 3001, Australia; [4]Swinburne University of Technology, Hawthorn, Victoria 3122, Australia.
**jitrapov@ansto.gov.au*

Molecular orientation in polymeric and composite materials can play a significant role in overall mechanical performance and chemical properties. Infrared absorption by specific functional groups occurs preferentially when the electric vector of the probing beam is aligned with the dipole oscillation corresponding to the absorbing frequency and can therefore be used to gain information on the molecular orientation of selected molecules. The team at the Tokyo Institute of Technology has developed a method whereby the dipole orientation angle (θ) for each pixel of a hyper-spectral image can be determined from Eq. 1, where $A_{\phi_{1,2,3,4}}$ are absorbances at the four polarisation azimuths separated by $\pi/4$ [1]. The dipole orientation angle and strength are then plotted as “vectors” over each pixel within the spectral map, enabling the visualisation of molecular orientation. We have applied this method in the analysis of molecular re-orientation in silk fibres [2] and in the study of the effects of additives to poly-lactic acid (PLA) composite materials. Figure 1 shows an example of the orientation vector map of spherulites formed in a PLA solvent cast film, showing the absorption strength (colour) and dipole orientation (vector line) for the C=O absorption at 1759 cm^{-1}. More recently, the method has also been applied to reveal molecular orientation inside the micro-domains of the paracetamol form II, which has a better water solubility and compressibility compared to the commercially used forms I [3], and to analyse polymeric patterns using focal plane array IR detectors [4].

$$\theta = \frac{1}{2}\tan^{-1}\left(\frac{A_{\phi_3} - A_{\phi_1}}{A_{\phi_4} - A_{\phi_2}}\right) \text{....... (Eq. 1)}$$

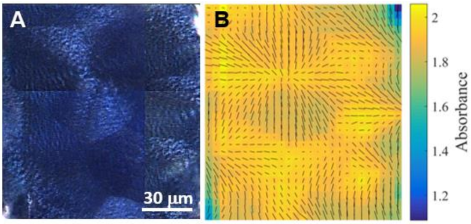

Figure 1: (A) Polarised light image and (B) the correponding polarisation vector map of PLA spherulites, showing direction and strength of dipole orientation for each pixel of the absorbance map.

References:

[1] Y. Hikima, J. Morikawa and T. Hashimoto, Macromolecules. 44, 3950 (2011).
[2] M. Ryu, A. Balčytis, X. Wang, J. Vongsvivut, Y. Hikima, J. Li, M.J. Tobin, S. Juodkazis and J. Morikawa, Scientific Report. 7(1), 7419 (2017).
[3] R. Honda, M. Ryu, A. Balčytis, J. Vongsvivut, M.J. Tobin, S. Juodkazis and J. Morikawa, Applied Surface Science. 473, 127 (2019).
[4] R. Honda, M. Ryu, M. Moritake, A. Balčytis, V. Mizeikis, J. Vongsvivut, M.J. Tobin, D. Appadoo, J. Li, S.H. Ng, S. Juodkazis and J. Morikawa, Nanomaterials. 9, 732 (2019).

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Keywords: synchrotron infrared, polarisation, molecular orientation

IR spectro-microscopy and imaging

MONITORING THE KINETIC OF CELLULAR UPTAKE OF MOLECULES TAGGED WITH AN INFRARED ACTIVE PROBE IN SINGLE LIVING CELLS. A FEASIBILITY STUDY

C. Sandt[1]*, S. Clède[2], P. Dumas[1], C. Policar[2]

[1]SMIS beamline, synchrotron SOLEIL, Gif sur Yvette, France; [2]LBM, Ecole normale supérieure, Sorbonne université, Paris, France.
**sandt@synchrotron-soleil.fr*

Measuring the transport kinetics of small molecules across membranes in living cells is important for both biology and medicine, for evaluating pharmacokinetics or for optimizing intracellular drug delivery. Many methods (fluorescent labeling and radiolabeling) and models (cellular, vesicular or artificial lipid bilayers) have been developed. Single cell methods give information not attainable with population wide studies. We evaluated the use of rhenium-tris-carbonyl ($Re(CO)_3$) infrared active probes that show absorption in the IR transparent windows of the cells coupled with synchrotron IR microspectroscopy in a microfluidic device. In the past few years, we have developed these probes to perform static evaluations of the accumulation and distribution of several biomolecules (lipids, peptides, polysaccharides) in various cells and tissues by synchrotron IR microspectroscopy at the single cell level and at subcellular resolution. Monitoring the kinetic of the cellular uptake in living cells is even more challenging, since water necessary for live cell measurements absorbs strongly infrared radiations. Considerations of detection threshold, measurement speed, and signal to noise ratio can also be limiting factors. We showed that using an in-house microfluidic device compatible with synchrotron infrared microspectroscopy, it was possible to monitor the uptake of 2 medium-chain alkanes (C_8H_{17} and $C_{12}H_{25}$) tagged with $Re(CO)_3$ in single, fully-hydrated, living MDA-MB231 cells over the course of several hours. High cell survival rates were observed with a live/dead fluorescent test. Strong variations in the penetration kinetics were observed between individual cells. The $Re(CO)_3$ tagged molecules were detected at milli-absorbance unit and shown to enter the cell on the hour time scale. The kinetic data were fitted to Hill and Fick diffusion models and were best fitted by the Hill model suggesting that active transport could be the primary cell penetration mechanism. The use of synchrotron radiation source allowed for relatively fast measurements at subcellular resolution and high signal to noise ratio. However, only one single cell could be measured for each run resulting in limited statistical significance. FPA imaging could potentially be used to measure statistically relevant numbers of cells while still providing single cell resolution. FPA detectors being inherently slower than conventional MCT detectors would be of limited use for fast kinetics. Coupling of a synchrotron radiation source and a FPA detector could allow measuring fast kinetics over a large number of cells simultaneously.

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Keywords: rhenium carbonyl probes, living cells, microfluidic, cellular uptake

IR spectro-microscopy and imaging

REAL-TIME SYNCHROTRON-BASED FTIR SPECTROMICROSCOPY OF MOLECULAR SIGNALING DURING ELECTROTAXIS INITIATION

Zhiqiang Zhao[1], Liang Chen[2], Yao-Hui Sun[1],
Kevin Loutherback[2], Min Zhao[1], Hoi-Ying N. Holman[2]*

[1]Department of Dermatology, Institute for Regenerative Cures, University of California Davis, Sacramento, California, USA; [2]Molecular Biophysics & Integrated Bioimaging (MBIB) Division, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, California, USA.
**hyholman@lbl.gov*

Electrotaxis is an important cellular function for translocation during many cellular and developmental processes, such as wound healing, tumor cell metastasis, or tissue development. Current imaging approaches of studying signal transduction during electrotaxis often requires fluorescent tags. Here we present an experimental platform combining synchrotron infrared spectromicroscopy and a novel microfluidic electrotaxis chamber to allow label-free infrared spectroscopy study of live-cell electrotaxis in well-defined direct-current electric fields (dcEFs). We demonstrated that this novel approach enables us to measure the evolution of multiple molecular signaling events at sub-cellular resolutions, simultaneously, in live human corneal epithelial cells during their early response to dcEFs. Spatio-temporarily resolved spectra revealed both gradations of asymmetric patterns of protein phosphorylation and lipid-phase modification with an EF-guided directional preference, providing new insights into multi-molecular coordination during cellular signal transduction. We anticipate this powerful multiplex and label-free method will provide new opportunities and perspectives in understanding complex biological processes.

Keywords: synchrotron FTIR, Infrared imaging, molecular signaling, electrotaxis

IR spectro-microscopy and imaging

SESAME IR BEAMLINE: THE FIRST IN THE MIDDLE EAST AND NEIGHBOURING REGIONS

Gihan Kamel[1,2]*, Giorgio Paolucci[1], Paul Dumas[3]

[1]*SESAME, Allan, Jordan;* [2]*Department of Physics, Faculty of Science, Helwan University, Cairo, Egypt;*
[3]*Soleil Synchrotron, France.*
gihan.kamel@sesame.org.jo

SESAME is the only synchrotron light facility in the Middle East. It aims at promoting advanced research capabilities and technology within its Members, and considered as the region's bridge to peace and mutual understanding. Current Members are Cyprus, Egypt, Iran, Israel, Jordan, Pakistan, Palestine and Turkey. Whereas, Brazil, Canada, China, the European Union, France, Germany, Greece, Italy, Japan, Kuwait, Portugal, the Russian Federation, Spain, Sweden, Switzerland, the United Kingdom and the United States are the Observers. SESAME came into operation by the year 2016 with its first operational beamline (XAFS/XRF) hosting users in 2017. In the context of beamlines selection of the potential end stations at SESAME, infrared microspectroscopy was identified as one of the most demanded techniques as shown by various scientific communities. It is the first new designed beamline at SESAME realized in collaboration with the French Synchrotron, SOLEIL. The IR beamline came into operation late 2018. As the WIRMS workshop is considered one of the most important meetings concerning the IR spectroscopy and imaging in synchrotron radiation facilities, it will be an excellent opportunity to present the current status and progress of the SESAME IR beamline in such a relevant meeting with many experts in the field. Some examples of SESAME Users' first experiments together with the future opportunities will be presented.

Keywords: sesame, synchrotron IR, infrared microspectroscopy

IR spectro-microscopy and imaging

SISSI BEAMLINE UPGRADES: NEW SCIENTIFIC OPPORTUNITIES FOR THE USER COMMUNITY

L. Vaccari[1]*, G. Birarda, A. Surowka, A. Matruglio,
N. Cefarin, C. Stani, M. Pachetti, P. Zucchiatti

[1]Elettra *Sincrotrone Trieste, SISSI-Chemical and Life Sciences, S.S. 14 Km 163.5, I-34149, Basovizza, Trieste. Italy.*
**lisa.vaccari@elettra.eu*

SISSI (Synchrotron Infrared Source for Spectroscopy and Imaging) is the Infrared spectroscopy and microscopy beamline at Elettra, open to users since 2006 and jointly managed by Elettra (SISSI-Chemical and Life Sciences branch, SISSI-Bio) and IOM-CNR (SISSSI-Material Science, SISSI-Mat). During the years of operation, the beamline had host users covering a large variety of scientific fields, including surface and material science, cellular biology, and cultural heritage, among the others.

At SISSI-Bio, the user community requests become more and more challenging in recent years, and they drove beamline changes in both instrumentation and sampling approaches. In 2018, a new optical coupling at low-vacuum for the two branches has been implemented at SISSI, that will allow the simultaneous operation of the two branches and at the same time cleared an IRSR port for a new end- station. In January 2019, an IR s-SNOM from NeaSpec GmbH has been installed, and it is now operational with broadband DFG laser, while the coupling with IRSR is planned for the end on 2019. The beamline upgrade will be presented, along with selected examples highlighting the potentiality of multiscale FTIR analysis, from macro to nanoscale, in the fields of biology and cultural heritage.

For what it concerns sampling methodologies, it will be presented the latest results obtained in the optimization of a new type of liquid cells, suitable for both ambient-pressure and in-vacuum measurements of biological specimens, made by confining in a controlled way ultrathin water layers by few-layers graphene [1]. And furthermore, after that, the implementation of a tomo-IR setup and suitable algorithms for the analysis of totally natural tannin rigid foams, viable alternative to petrol- derived thermo-insulating materials [2], will be introduced.

References:

[1] A. Matruglio et al., Journal of Instrumentation, 13, C05016 (2018)
[2] S. Donato et al., Proceedings of the 9th Conference on Industrial Computed Tomography, Padova, Italy (2019).

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Keywords: beamline upgrade, Multi-scale analysis, Graphene Liquid Cells, IR-tomography

IR spectro-microscopy and imaging

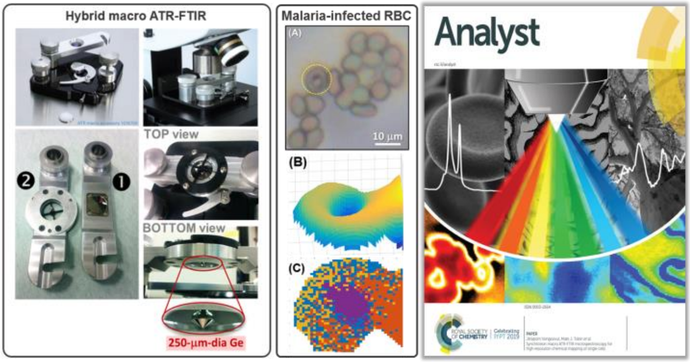
SYNCHROTRON MACRO ATR-FTIR MICROSPECTROSCOPY FOR HIGH-RESOLUTION CHEMICAL MAPPING OF SINGLE CELLS

Jitraporn (Pimm) Vongsvivut[1]*, D. Pérez-Guaita[2], B. R. Wood[2], P. Heraud[2], K. Khambatta[3], D. Hartnell[3], M. J. Hackett[3], M. J. Tobin[1]

[1]Infrared Microspectroscopy (IRM) Beamline, Australian Synchrotron, 800 Blackburn Road, Clayton, Victoria 3168, Australia; [2]Centre for Biospectroscopy, Monash University, Clayton, Victoria 3168, Australia; [3]Curtin Institute for Functional Molecules and Interfaces, School of Molecular and Life Sciences, Curtin University, GPO Box U1987, Perth, Western Australia 6845, Australia.

**jitrapov@ansto.gov.au*

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy has been used widely for probing the molecular properties of materials. Coupling a synchrotron infrared (IR) beam to an ATR element using a high numerical aperture (NA) microscope objective enhances the spatial resolution, relative to transmission or transflectance microspectroscopy, by a factor proportional to the refractive index (*n*) of the ATR element. This work presents the development of the synchrotron macro ATR-FTIR microspectroscopy at Australian Synchrotron Infrared Microspectroscopy (IRM) Beamline, and demonstrates that high quality FTIR chemical maps of single cells and tissues can be achieved at an enhanced spatial resolution [1]. The so-called "hybrid" macro ATR-FTIR device was developed by modifying the cantilever arm of a standard Bruker macro ATR-FTIR unit to accept germanium (Ge) ATR elements with different facet sizes (*i.e.* 1 mm, 250 µm and 100 µm in diameter) suitable for different types of sample surfaces (Figure 1). We demonstrated the capability of the technique for high-resolution single cell analysis of malaria-infected red blood cells, individual neurons in a brain tissue and cellular structures of a *Eucalyptus* leaf. The ability to measure a range of samples from soft membranes to hard cell wall structures demonstrates the potential of the technique for high-resolution chemical mapping across a broad range of applications in biology, medicine, environmental science and more.



References:

[1] J. Vongsvivut, D. Perez-Guaita, B.R. Wood, P. Heraud, K. Khambatta, D. Hartnell, M. Hackett and M.J. Tobin, Analyst. 144, 3161 (2019).

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The development of the macro ATR-FTIR device used was funded as part of the Science Projects at the Australian Synchrotron. The authors wish to acknowledge Mr. Alan Easdon from the Australian Synchrotron, for his substantial contribution to the design and mechanical works associated with the development of this device.

Keywords: synchrotron infrared, ATR FTIR, spatial resolution, red blood cell, neuron, plant leaf

IR spectro-microscopy and imaging

TRANSFLECTION INTERFERENCE INFLUENCE ON SPECTRAL QUALITY AND HISTOPATHOLOGIC CLASSIFICATION OF INFRARED IMAGING DATA

Tomasz P. Wrobel[1]*, Danuta Liberda[1], Michael Hermes[2], Paulina Koziol[1],
Nick Stone[2], Czeslawa Paluszkiewicz[1], Wojciech M. Kwiatek[1]

[1]Institute of Nuclear Physics Polish Academy of Sciences, PL-31342, Krakow, Poland; [2]School of Physics and Astronomy, University of Exeter, Exeter EX4 4QL, United Kingdom.
**tomasz.wrobel@ifj.edu.pl*

Infrared (IR) Imaging can be used for fast, accurate and non-destructive pathology recognition of biopsies when supported by machine learning algorithms. Transflection mode of measurements is the most probable one to be translated into the clinic due to economic reasons of large-scale imaging with expensive transmissive substrates (CaF_2, BaF_2). A typical procedure after collection of a biopsy from the patient is embedding the sample within paraffin wax. This has an impact on sample optical properties on one hand minimizes scattering, but on the other increases interference (so called Electric Field Standing Wave effect) and distorting spectra, by creating a flat, thin film. Moreover, interference has been shown to be more prominent in a coherent IR source, such as Quantum Cascade Laser (QCL) [2] and is expected to be also high using a synchrotron source. The question, whether lower scattering but higher interference in a paraffin-embedded sample will provide better spectral quality over dewaxed sample, with higher scattering and lower interference, remains open. In this work we will investigate this aspect by evaluating classification performance of a Random Forest classification of two tissue types (pancreas, esophagus) measured in transmission/transflection, FT-IR vs two QCL microscopes and with and without paraffin.

References:

[1] M. Hermes, R. B. Morrish, L. Huot, L. Meng, S. Junaid, J. Tomko, G. R. Lloyd, W. T. Masselink, P. Tidemand-Lichtenberg, C. Pedersen, F. Palombo, and N. Stone, *Journal of Optics*, 20(2), 1-21 (2018).
[2] B. M. DeVetter, S. Kenkel, S. Mittal, R. Bhargava, and T. P. Wrobel, *Vib. Spectrosc.*, 91, 119–127 (2017).

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Keywords: infrared imaging, histopathology, interference, cancer

Nanoscale resolved synchrotron IR analysis

COMPUTATIONAL SCATTERING-TYPE NEAR-FIELD OPTICAL MICROSCOPY

Bernd Kästner[1]*, Franko Schmähling[1], Andrea Hornemann[1], Georg Ulrich[1], Arne Hoehl[1], Mattias Kruskopf[1], Klaus Pierz[1], Gerd Wübbeler[1], Clemens Elster[1], Samuel Johnson[2], Markus B. Raschke[2]

[1]Physikalisch-Technische Bundesanstalt (PTB), Berlin and Braunschweig, Germany; [2]Department of Physics, Department of Chemistry, and JILA, University of Colorado, Boulder, USA.
**bernd.kaestner@ptb.de*

Near-field scanning optical microscopy circumvents the diffraction limit known from classical optics and provides diffraction unlimited spatial resolution. Among those techniques infrared (IR) scattering-type scanning near-field optical microscopy (s-SNOM) has become a powerful imaging and spectroscopy tool. Ultra-broadband synchrotron radiation from the Metrology Light Source (MLS) provides IR-radiation suited for performing nano-FTIR spectroscopy [1]. However, for many applications nano-imaging of soft matter or quantum materials requires hyperspectral imaging, resulting in a large number of spectral data sets and therefore long acquisition time. Here we will present results from applying novel computational imaging methods to the s-SNOM for enhanced spatio-spectral imaging speed.

(1) In the application of compressed sensing (CS), this provides improvement in the spatio-spectral acquisition time by reducing the number of sampling points to 1/9th [2]. Fig. 1(a) and (b) show the principle of CS: The measured interferogram (a) and its Fourier transform (b) are shown in blue. CS is demonstrated by randomly selecting a much reduced number of points of the interferometer positions. CS is able to reconstruct from this limited set of measurements the complete interferogram (red curve). The saved measurement time may be used to increase the integration time for each of the measurements, thereby increasing the signal-to-noise ratio.

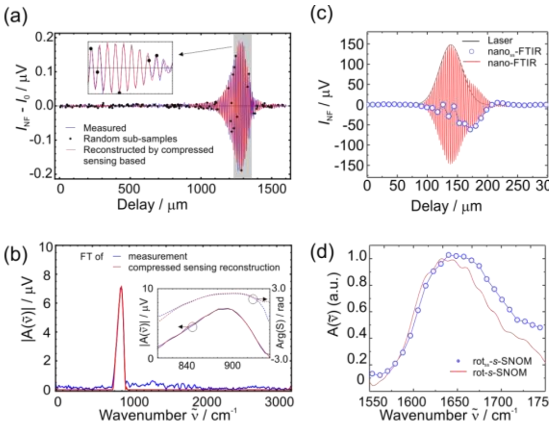

Figure 1: (a) Interferogram of measured (red), randomly sampled (black dots) and CS reconstructed (blue) data, in (b) the corresponding spectra. (c) Conventional (red) interferogram with Laser envelope (black) and sub-sampled (blue) data points for use in rotating frame. (d) Spectral response of rotated data for conventional (red) and subsampled (blue) case.

(2) For light sources with intermediate bandwidth an approach involving shifting the spectroscopic carrier frequency into the rotating frame also reduces the number of data points required [3]. This approach complements CS *s*-SNOM, yet is fully deterministic and still Nyquist limited and particularly advantageous for limited bandwidth and broad vibrational resonances as typically encountered in biological systems. We show the result of this novel approach in Fig. 1(c) and (d) where, by transforming into the rotating frame of the carrier frequency in combination with utilizing prior knowledge of the vibrational resonances to be probed, IR excitation spectrum, and other general sample characteristics, we are able to accelerate IR *s*-SNOM data collection by *more than 10-fold for each spatial and spectral dimension.* We apply this to chemical nano-imaging of protein sheets which reveals multi-scale spatial heterogeneities in the prismatic region in oyster shells. Rotating frame *s*-SNOM (rot-*s*-SNOM) is particularly powerful for chemical nano-imaging of systems with broad resonances (~50 cm^{-1}) as is common in biological materials.

References:

[1] P. Hermann, A. Hoehl, P. Patoka, F. Huth, E. Rühl, and G. Ulm, "Near-field imaging and nano-Fourier-transform infrared spectroscopy using broadband synchrotron radiation.," Opt. Express 21, 2913–9 (2013).
[2] B. Kästner, F. Schmähling, A. Hornemann, G. Ulrich, A. Hoehl, M. Kruskopf, K. Pierz, M. B. Raschke, G. Wübbeler, and C. Elster, "Compressed sensing FTIR nano-spectroscopy and nano-imaging," Opt. Express 26, 18115 (2018).
[3] S. C. Johnson, E. A. Muller, O. Khatib, E. A. Bonnin, A. C. Gagnon, and M. B. Raschke, "Infrared nanospectroscopic imaging in the rotating frame," Optica 6, 424–429 (2019).

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Nanoscale resolved synchrotron IR analysis

CONTROLLING ELECTRONIC PHASE SEPARATION ON THE NANOSCALE

S. N. Gilbert Corder[1,2]*, H. A. Bechtel[2], M. C. Martin[2], M. Liu[1]

[1]*Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY 11794, USA;* [2]*Advanced Light Source Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.*
**SGilbertCorder@lbl.gov*

I will discuss recent work from the Liu group to elucidate the nature of electronic phase transitions in strongly correlated and heavy fermion systems VO_2, Ca_2RuO_4, and $Sm_{1-x}Y_xS$ [1-3]. These studies rely on a combination of nano-FTIR and s-SNOM imaging to acquire the knowledge necessary to both answer open questions in long-studied materials and to explore potential device applications. In VO_2/TiO_2 $(110)_R$ thin films, substrate patterning causes the local strain environment and intrinsic phase separation lengths compete, enabling selective control of the anisotropy, metallic phase fraction, and transition temperature without sacrificing VO_2 film quality [1]. This understanding of the VO_2/TiO_2 interface could pave the way for improved opto-electronic devices. In marked contrast to the filamentary metallization typical of oxides, the Ca_2RuO_4 phase boundary exhibits spontaneous orientation-dependent metal-insulator microstripes when the transition is electrically induced [2]. The comparably low currents required to electrically switch Ca_2RuO_4 make this an appealing material for energy-efficient devices. In $Sm_{1-x}Y_xS$ single crystals, manipulation of the nanoscale strain environment and phase diagram allows independent control of two plasmonic resonances (visible and IR) in a particular sample; enabling creation of a novel dual-band metamaterial [3]. I will relate the critical importance of nano-FTIR and s-SNOM imaging for understanding electronic phase separation, and also discuss the benefits of a multimodal approach to materials characterization.

References:

[1] S. N. Gilbert Corder, et. al. PRB 96, 161110(R) (2017).
[2] J. Zhang, et. al. PRX 9, 011032 (2019).
[3] S. N. Gilbert Corder, et. al. Nat. Comm. 8, 2262 (2017).

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Keywords: Nano-FTIR, Phase-change Material, s-SNOM

Nanoscale resolved synchrotron IR analysis

EXPANDING THE FRONTIERS OF SYNCHROTRON INFRARED NANOSPECTROSCOPY

Hans A. Bechtel[1]*, Stephanie N. Gilbert Corder[1,2], Omar Khatib[1,3],
Jonathan M. Larson[1], Yi-Hsien Lu[1], Ziheng Yao[1,2], Samuel C. Johnson[3],
Robert Kostecki[1], Miquel Salmeron[1], Mengkun Liu[2], G. Lawrence Carr[4],
Markus B. Raschke[3], Michael C. Martin[1]

[1]Lawrence Berkeley National Laboratory, Berkeley, CA USA; [2]Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY USA; [3]Departments of Chemistry, Physics and JILA, University of Colorado, Boulder, CO USA; [4]National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY USA.
**habechtel@lbl.gov*

The development of near-field infrared techniques has enabled infrared analysis to surpass the diffraction-limit and probe chemical and physical heterogeneities at the nanoscale. In one such technique, called infrared scanning near-field optical microscopy (IR s-SNOM), IR light is focused onto and scattered by an atomic force microscope (AFM) tip, and detected interferometrically in the far-field with an IR detector. When combined with the broad bandwidth, spatial coherence, and high brightness of synchrotron infrared radiation, IR s-SNOM enables vibrational spectroscopy spanning the infrared region with a wavelength-independent spatial resolution equivalent to the tip-apex radius, which is typically less than 25 nm. The Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory operates two of these synchrotron infrared nanospectroscopy (SINS) instruments that are available for general users to address fundamental questions that can only be answered with a chemically selective nanoscopic probe. In this talk, I will describe the technical aspects of the SINS technique and highlight representative examples of the rapidly growing range of applications in physics, chemistry, biology, materials science, geology, and atmospheric and space sciences. While most of the applications to date have been measured under ambient conditions in the mid-IR, many in situ / in operando measurements require additional environmental control (i.e. variable cryogenic temperatures, gas/vacuum, liquids) and/or increased spectral range in the far- and near- IR that push the current boundaries of our instruments and technique. I will describe efforts at the ALS to address some of these challenges and offer perspectives for the future of SINS.

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Keywords: infrared, nanospectroscopy, synchrotron

EXTRACTING THE ELECTRONIC PROPERTIES OF AN OXIDE TWO-DIMENSIONAL ELECTRON GAS BY SCANNING NEAR-FIELD OPTICAL MICROSCOPY AND PHONON MODELING

Julian Barnett[1]*, Martin Lewin[1], Georg Ulrich[2], Bernd Kästner[2],
Marc Rose[3], Felix Gunkel[3], Regina Dittmann[3], Thomas Taubner[1]

[1]Institute of Physics (IA), RWTH Aachen, 52056 Aachen, Germany; [2]Physikalisch-Technische Bundesanstalt, 12489 Berlin, Germany; [3]Peter Gruenberg Institute, Forschungszentrum Juelich and JARA-FIT, 52425 Juelich, Germany.
**barnett@physik.rwth-aachen.de*

In the family of functional oxide materials one interesting system is the interface between $SrTiO_3$ and $LaAlO_3$ (LAO/STO), which are large-bandgap insulators in their bulk state: combining the two insulating materials gives rise to a confined and highly conductive two-dimensional electron gas (2DEG) close to the interface [1], if the number of LAO unit cells is larger than three. This 2DEG exhibits remarkable properties such as superconductivity and gate tunability, and displays the possibility for future transistor applications. However, its investigation was thus far limited to non-local methods, that average over larger areas.

Here, scanning near-field optical microscopy (SNOM) in a nano-FTIR setup is used in conjunction with synchrotron radiation to obtain nanoscale IR spectra of LAO/STO interfaces in the range of their near-field phonon resonances, as the local electronic properties of complex oxides can be quantified by exploiting plasmon-phonon coupling [2].

Interestingly, both LAO and STO exhibit near-field phonon resonances in the spectral region of interest, leading to a non-trivial scattering spectrum that strongly depends on the number of LAO unit cells deposited on top. Additionally, growth strain and confinement effects of these ultra-thin films need to be taken into account, as their dielectric function deviates significantly from the bulk case [3].

The SNOM spectral response of different samples was predicted by using a combination of the transfer matrix method and the finite dipole model [4] and systematically compared to synchrotron nano-FTIR measurements. As a result, local electronic properties of the interfacial 2DEG could be extracted quantitatively, enabling the possibility of its nanoscale lateral mapping in the future.

References:

[1] A. Ohtomo et al., Nature 427, 423 (2004).
[2] M. Lewin et al., Adv. Funct. Mater. 28, 1802834 (2018).
[3] K. L. Kostov et al., Phys. Rev. B 94, 075438 (2016).
[4] B. Hauer et al., Optics Express 20, 13173 (2012).

Keywords: two-dimensional electron gas, LAO/STO, nano-FTIR, ultrathin-layer phonons

Nanoscale resolved synchrotron IR analysis

IR AND THz NEAR-FIELD NANO-IMAGING AND NANO-SPECTROSCOPY OF CORRELATED ELECTRON MATERIALS

Mengkun Liu

Stony Brook University, Stony Brook, NY, USA.
mengkun.liu@stonybrook.edu

Over the past decade, optical near-field techniques, especially the scattering-type scanning near-field optical microscope (s-SNOM), have undergone tremendous development. This is partly due to the ever-increasing demand for the exploration of the nano-world and partly due to the many technical advances in laser and scanning probe technologies. I will use this opportunity to report the recent advances in the IR and THz near-field microscopy and spectroscopy technology and discuss their applications in complex correlated electron materials. I will also report on how to extract complex dielectric constants from near-field experiments and discuss the future development of s-SNOM including the cryogenic capabilities and its coupling to ultrafast pump-probe spectroscopy. These new developments set the stage for future spectroscopic investigations to access the fundamental properties of complex materials at the nanoscale.

Keywords: s-SNOM, correlated electron materials, THz near-field imaging

Nanoscale resolved synchrotron IR analysis

IR NEAR-FIELD NANOSCOPY AND NANOSPECTROSCOPY

Rainer Hillenbrand

CIC nanoGUNE and Ikerbasque, San Sebastian, Spain
r.hillenbrand@nanogune.eu

Scattering-type scanning near-field optical microscopy (s-SNOM) and nanoscale Fourier transform infrared spectroscopy (nano-FTIR) open a new era in modern nanoanalytics, including the chemical identification of organic and inorganic materials, protein secondary structure mapping, free-carrier profiling in semiconductors, or mapping of plasmon polaritons in 2D materials such as graphene, all with a spatial resolution of about 10 - 20 nm. s-SNOM and nano-FTIR are based on elastic light scattering at an atomic force microscope tip, employing either monochromatic laser illumination or broadband illumination from a glow bar, a supercontinuum laser or a synchrotron. Acting as an optical antenna, the tip converts the illuminating field into a strongly concentrated near field at the very tip apex (nanofocus), which provides a means for local excitation of molecule vibrations, plasmons or phonons in the sample surface. Recording of the tip-scattered field as a function of sample position (employing monochromatic illumination) yield nanoscale-resolved IR and THz images, while Fourier-transform spectroscopy of the tip-scattered field (employing broadband illumination) allows for nanoscale IR point spectroscopy and IR hyperspectral nanoimaging. In this talk, recent developments, trends and applications in materials sciences and nanophotonics will be discussed.

Keywords: infrared nanoimaging, infrared nanospectroscopy, s-SNOM, nano-FTIR

NANOSCALE ANALYTICS ON ORGANIC MATERIALS USING NANO-FTIR

Adrian Cernescu

neaspec GmbH, Munich, Germany.
adrian.cernescu@neaspec.com

Scattering-type scanning near-field optical microscopy (s-SNOM) has become a key technology to study the chemical composition of organic materials at the nanoscale. This AFM-based technology exploits the strong confinement of light at the end of a sharp, metallic AFM tip to generate a nanoscale optical hotspot at the sample surface. Importantly, the amplitude and phase of the light within the optical hotspot correlates with the absorption and reflectivity properties of the sample directly below the tip.

With the development of Fourier transform infrared spectroscopy on the nanoscale (nano-FTIR) and hyperspectral nano-spectroscopy, we have successfully extended s-SNOM towards a complete spectroscopic analysis tool that is capable of analyzing complex polymer nanostructures with <10 nanometer precision. With tremendous nanoscale sensitivity, the nano-FTIR spectroscopy enables not only nano-chemical identification and to explore local distribution of polymer blends but it also offers information about local orientation of polymer chains in crystalline organic semiconductors and in polymer monolayers. Various examples of s-SNOM measurements on different polymer and biomaterial samples will be presented.

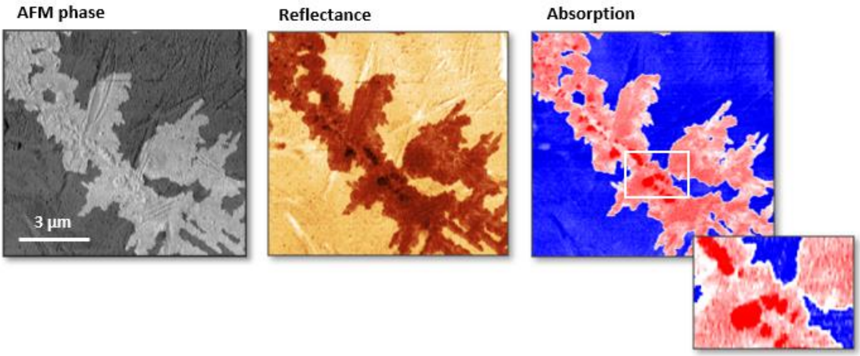

Figure 1: *Imaging of a 10 nm thin PEO monolayer at 1123 cm^{-1} (asy. C-O-C stretching) shows self-assembled nanostructures and areas of different material thickness. High contrast absorption images allow to clearly distinguish between mono- and bilayer film areas.*

Acknowledgements:
This work was done in collaboration with Dr. Georgievski Ognen Pop from Academy of Sciences of the Czech Republic

Keywords: nano-FTIR, nanoscale analytics, polymers, biomaterials

Nanoscale resolved synchrotron IR analysis

NEAR-FIELD NANOSCOPY WITH INFRARED-TO-THz ACCELERATOR-BASED PHOTON SOURCES

Lukas Wehmeier[1]*, S.C. Kehr[1], T. Nörenberg[1], F. Kuschewski[1], Th. de Oliveira[1,3],
J.M. Klopf[3], S. Winnerl[3], S. Kovalev[3], M. Gensch[3,4,5], M. Helm[3], L.M. Eng[1,2]

[1]Institute of Applied Physics, School of Science, TU Dresden, 01062 Dresden, Germany; [2]ct.qmat: Würzburg-Dresden Cluster of Excellence – EXC 2147, 01062 Dresden, Germany; [3]Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstraße 400, 01328 Dresden, Germany; [4]Deutsches Zentrum für Luft und Raumfahrt, Rutherfordstr. 2, 12489 Berlin, Germany; [5]Institut für Optik und Atomare Physik, TU Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany.
**lukas.wehmeier@tu-dresden.de*

We advertise scattering-type scanning near-field infrared nanoscopy (s-SNIM) in the spectral range of 75 to 1.3 THz [1], using the narrow-band free-electron laser FELBE at the Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Germany [2], for illumination (see Fig. 1). When combining s-SNIM with FELBE, we demonstrate the λ-independent optical resolution of a few 10 nm only, by exploring structured Au samples [1], meta-materials [3,4], nanowires [5], minerals [6] and ferroic phase-transitions [7,8] down to LHe temperatures [7-9]. Notably, the intense radiation pulses from FELBE enable investigations of non-linear effects and optically excited samples on the nanometer scale [5]. Moreover, HZDR recently extended the wavelength range down to 100 GHz radiation employing the novel super-radiant TELBE light source [10,11]. We are adapting our s-SNIM to this TELBE photon source as well, aiming for equally high spatial resolution as with FELBE. The unique combination of infrared-to-THz spectroscopy and microscopy with a resolution of a few 10 nm enables near-field probing of polaritons based on plasmons, phonons, cooper pairs, and magnons, which dominate the materials' optical response in this frequency regime and with that enable the fundamental characterization of light-matter interaction down to nanometer and molecular length scales.

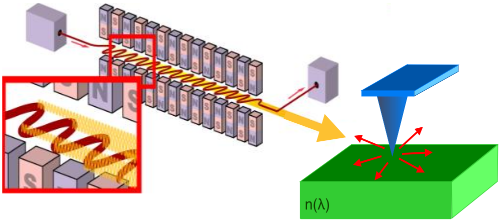

Figure 1: Near-field microscopy and spectroscopy utilizing the infrared-to-THz free-electron laser FELBE.

References:

[1] F. Kuschewski, H.-G. von Ribbeck, J. Döring, et al., Appl. Phys. Lett. 108, 113102 (2016).
[2] S.C. Kehr, J. Döring, M. Gensch, et al., Synchr. Rad. News 30, 31 (2017).
[3] S.C. Kehr, R.G.P. McQuaid, T. Kämpfe, et al., ACS Photonics 3, 20 (2016).
[4] M. Fehrenbacher, S. Winnerl, H. Schneider, et al., Nano Lett. 15, 1057 (2015).
[5] D. Lang, L. Balaghi, S. Winnerl, et al., Nanotechn. 30, 084003 (2019).
[6] T. Firkala, F. Kuschewski, T. Nörenberg, et al., Minerals 8, 118 (2018).
[7] J. Döring, H.-G. von Ribbeck, M. Fehrenbacher, et al., Appl. Phys. Lett. 105, 053109 (2014).
[8] J. Döring, D. Lang, L. Wehmeier, et al., Nanoscale 10, 18074 (2018).
[9] D. Lang, J. Döring, T. Nörenberg, et al., Rev. Sci. Instrum. 89, 033702 (2018).
[10] B. Green, S. Kovalev, V. Asgekar, et al., Sci. Rep. 6, 22256 (2016).
[11] S. Kovalev, B. Green, T. Golz, et al., Struct. Dyn. 4, 024301 (2017).

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Keywords: IR-to-THz nanospectroscopy, Cryogenic IR nanospectroscopy, Polaritons, Free-electron laser

OPTICAL NANO-IMAGING OF DIRAC PLASMONS AT THE GRAPHENE-TALC HETEROSTRUCUTURE

I. D. Barcelos[1]*, A. R. Cadore[2], F. C. B. Maia[1], F. Feres[1,3],
R. F. de Oliveira[4], C. C. B. Bufon[4], R. Freitas[1]

[1]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM) 13083-970, Campinas, São Paulo, Brazil; [2]Cambridge Graphene Centre, The University of Cambridge CB3 0FA, Cambridge, United Kingdom; [3]Physics Department, Institute of Geosciences and Exact Sciences, São Paulo State University (UNESP) 13506-900, Rio Claro, São Paulo, Brazil; [4]Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970, Campinas, São Paulo, Brazil.
**ingrid.barcelos@lnls.br*

Plasmonics as a separate branch of nanophotonics has recently attracted intensive attention driven by both emerging applications with strong interaction between light and free electrons. Plasmonics also allow breaking the diffraction limit to confine light into subwavelength volumes with high field enhancements. In general, the investigation of these effects requires the use of scattering-scanning near field optical microscopy (s-SNOM), since its probe bridges the momentum mismatch between free-space excitation and high-momenta polaritons. For instance, s-SNOM can be used to launch and map the interference fringes of propagative surface plasmon polaritons (SPPs) in graphene. In this context, with the rise of graphene, new scientific and technological opportunities are appearing for optoelectronics and photonics applications, i.e. highly doped graphene is a promising plasmonic material to operate in the mid-infrared and terahertz (THz) spectral window. Here, we describe and present propagating graphene plasmons atop of atomically flat Talc substrates in the real space using synchrotron infrared nano-spectroscopy (SINS)[1]. Our observation demonstrates remarkably strong light confinement, in situ gate tunability and relatively low intrinsic losses. All these phenomena are directly attributed to its two-dimensionality and its unique band structure. Moreover, we show that the graphene dispersion relation is indeed modified due to substrate phonons polaritons, with extra modes appearing caused by the strong coupling between Graphene-plasmons and Talc-phonons[2] (plasmon-phonon coupling). Our comparison between the model and the experimental data shows clear evidence of splitting of the plasmon dispersion due to the hybridization of the graphene-plasmon mode with Talc-phonons polaritons. Therefore, we demonstrate a new 2D platform for studies of plasmonics phenomena.

References:

[1] Freitas RO, Deneke C, Maia FCB, et al. Low-aberration beamline optics for synchrotron infrared nanospectroscopy. Opt Express. 26, 11238 (2018).
[2] Barcelos ID, Cadore AR, Alencar AB, et al. Infrared fingerprints of natural 2D talc and plasmon-phonon coupling in graphene-talc heterostructures. ACS Photonics. (2018).

Keywords: hybrid heterostructures, graphene plasmon-polaritons, SINS

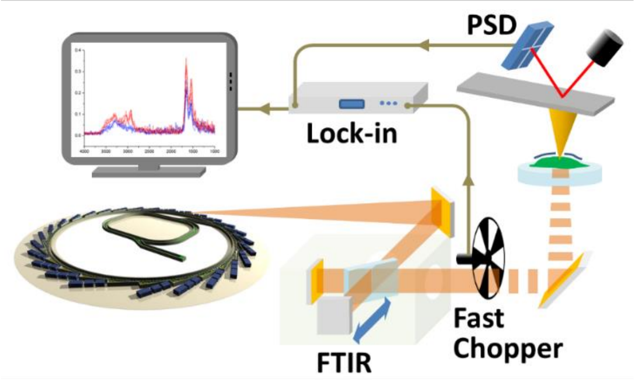
Nanoscale resolved synchrotron IR analysis

PHOTOTHERMAL INFRARED NANOSPECTROSCOPY WITH SYNCHROTRON RADIATION AT DIAMOND LIGHT SOURCE

M.D. Frogley*, I. Lekkas, C.S. Kelley, G. Cinque

Diamond Light Source Limited, Harwell Science and Innovation Campus, Didcot, Oxon, OX11 0DE, UK
**mark.frogley@diamond.ac.uk*

Since the first demonstration of broadband resonance-enhanced AFM-IR with Synchrotron Radiation at the MIRIAM beamline of Diamond in 2016 [1], the nanospectroscopy system has undergone significant technical developments and has been available to users in commissioning mode since January 2018. Continuous FTIR spectra are achieved with useful signal-to-noise in the 4000 – 800 wavenumber region at around 0.5 micron spatial resolution, limited by thermal diffusion and the modulation frequency of the SR beam, for soft materials like single biological cells and polymers [2]. A summary of recent results will be presented. Obtaining good quality data at rates required for IR nanoimaging, or for thin samples below a few hundred nm remains challenging in the current, normal incidence/bottom illumination geometry (shown in the figure) and investigations into the signal and noise performances will be discussed in comparison with theoretical expectations. Finally, planned future development of the instrument will be outlined. Optics adaptations will push towards theoretical performances and allow routine top or bottom illumination. A novel fast optical chopper, planned for implementation in autumn 2019, will allow access to higher cantilever resonances up to 200 kHz for higher spatial resolution, reduced thermal noise and greater spectral bandwidth below 500 wavenumbers.



References:

[1] P.M. Donaldson, C.S. Kelley, M.D. Frogley, J. Filik, K. Wehbe and G. Cinque, Optics Express 24 (3), 1852 (2016).

[2] C.S. Kelley, M.D. Frogley, A. Fitzpatrick, K. Wehbe, P.M. Donaldson and G. Cinque, Spectroscopy Europe 28 (6), 18 (2016).

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Keywords: Infrared, Near-field, Nanospectroscopy, Synchrotron

Nanoscale resolved synchrotron IR analysis

PROBING THE NANOSCALE CHEMICAL COMPOSITION OF ORGANIC-INORGANIC HYBRID PEROVSKITE FILMS THROUGH SYNCHROTRON INFRARED NANOSPECTROSCOPY

R. Szostak[1,2], M. M. Soares[2]*, R. O. Freitas[2], H. C. N. Tolentino[2], A. F. Nogueira[1]

[1]University of Campinas (UNICAMP), Laboratório de Nanotecnologia e Energia Solar, Chemistry Institute, 13083-970, Campinas, Brazil; [2]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970, Campinas, Brazil.
**marcio.soares@lnls.br*

Lead-based organic-inorganic hybrid perovskites (OIHP) materials have dramatically changed the photovoltaic scenario with power conversion efficiencies (PCE) over 20% [1] in only six years. Despite this rapid development, stability issues related to ion mobility and/or organic depletion, structural changes and segregation under operating and illumination conditions still hinder their real-world scale application. At room temperature, the presence of moisture (> 50% RH) leads to an irreversible degradation of the perovskite, where the main product is lead iodide (and lead bromide in mixed halide perovskites) [2]. Degradation has direct impact on the power conversion efficiency of OIHP solar cells. Despite degradation mechanisms being normally expressed as a bulk property, they are more likely to take place in the scale of single grains and between their boundaries. The recent advances in efficiency attained by compositional engineering have enabled devices to operate with improved stability [3]. However, the question on how the different structural phases are distributed in the structure, influencing the structural-optical properties and device's performance is still open. Hence, the development of analytical tools for accessing the grain-to-grain OIHP chemistry is of great relevance. Here, we employed synchrotron infrared nanospectroscopy (nano-FTIR) to map individual nanograins in OIHP films. Our results reveal a spatial heterogeneity of the vibrational activity associated to the nanoscale chemical diversity of isolated grains. For the first time, it was possible to map the chemistry of individual grains in CsFAMA ($Cs_{0.05}FA_{0.79}MA_{0.16}Pb(I_{0.83}Br_{0.17})_3$) and FAMA ($FA_{0.83}MA_{0.17}Pb(I_{0.83}Br_{0.17})_3$) films, providing information on their local composition. In association with synchrotron x-ray diffraction investigations of fresh and degraded samples, the nanograins with stronger nano-FTIR activity in CsFAMA and FAMA films could be assigned to PbI2 and hexagonal polytypes phases, respectively. We observe that despite the narrow morphological dispersion of the grained film, specific grains feature such stronger vibrational activity, associated to degraded grains, in clear contrast to the homogeneous overall response of the cubic black phase perovskite. The analysis herein can be extended to any OIHP films where organic cation depletion/accumulation can be used as a chemical label to study composition.

References:

[1] D. Bi et al., Efficient luminescent solar cells based on tailored mixed-cation perovskites. Sci. Adv. 2, e1501170–e1501170 (2016).
[2] J. M. Frost et al., Atomistic origins of high-performance in hybrid halide perovskite solar cells. Nano Lett. 14, 2584–2590 (2014).
[3] M. Saliba et al., Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. Energy Environ. Sci. 9, 1989–1997 (2016).

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Keywords: solar cells, organic-inorganic hybrid perovskite, synchrotron infrared nanospectroscopy, x-ray diffraction

Nanoscale resolved synchrotron IR analysis

REAL-TIME *IN SITU* MONITORING OF DRUG RELEASE FROM METAL ORGANIC FRAMEWORK NANOCOMPOSITES VIA SYNCHROTRON MICROSPECTROSCOPY

Barbara E. Souza[1]*, Kirill Titov[1], Zhixin Zeng[1], Arun S. Babal[1],
Yang Zhang[1], Annika Möslein[1], Magda Wolna[2], Mark D. Frogley[2],
Gianfelice Cinque[2], Jin-Chong Tan[1]

[1]Multifunctional Materials & Composites (MMC) Laboratory, Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, United Kingdom; [2]Diamond Light Source, Harwell Campus, Chilton, Oxford OX11 0DE, United Kingdom
**barbara.souza@eng.ox.ac.uk*

Nanocomposites formed by metal-organic frameworks (MOFs) embedded into biocompatible polymer matrices are an emergent new class of pharmaceutically suitable carriers for sustained drug release. Chemical transformations of MOFs during the release of the desired entrapped guest molecules are central to better understand ways of triggering and controlling the progressive release of these therapeutic agents. The microscopic understanding of the release of guest molecules from host frameworks is, generally, carried out using *in vitro* techniques (e.g. sample and separate, continuous flow, dialysis membranes)[1] that are primarily interested in fashioning the drug release kinetics. However, gaining deep comprehension of the drug release process requires observing and monitoring both chemical and physical changes in the drug-loaded samples. Even though the conventionally applied stepwise approaches allow understanding the drug release kinetics, it overlooks the ongoing transformation of the MOF chemical structure during the guest release process. These changes represent the key in correlating the guest-host interactions underpinning different triggered release strategies. To circumvent these limitations, herein we have applied an *in situ* strategy for the real time studying of the release of anti-cancer drug 5-FU from HKUST-1/PU membrane composites *via* Fourier transform infrared microspectroscopy (microFTIR) in Beamline B22 at the Diamond Light Source, (United Kingdom) [2,3]. Synchrotron irradiation allows *in situ* broadband measurements to be conducted in a less-than-a-minute timescale (per FTIR spectrum), and with a high signal-to-noise ratio, ideal for tracking the transformations of host framework through the evolution of vibrational bands. We performed microFTIR spectroscopy experiments in different fluid-cells (i.e. static and flow Harrick liquid cells) to examine the composites behavior to the molecular structure changes of the host-guest assembly during the dynamic release of the guest molecules. The study uniquely reveals that HKUST-1 creates hydrophilic “channels” within the polyurethane (PU) membrane allowing the slow release of the drug molecules. We found that the 5-FU molecules, encapsulated into HKUST-1 pores, covalently coordinated to the unsaturated copper site simultaneously interact with the carboxylate groups present in the organic linker. We have unraveled that the combination of the porous framework with the polymeric matrix is a promising strategy to overcome the “burst effect” [4] (fast release of the guest in large quantities within the first minutes), an outstanding limitation to the practical use of many porous host structures as drug delivery systems.

References:

[1] S. D’Souza, A Review of In Vitro Drug Release Test Methods for Nano-Sized Dosage Forms. Opt Express, 2014. 22(24): p. 29304-13.
[2] J. Doherty, et al., Live single cell analysis using synchrotron FTIR microspectroscopy: development of a simple dynamic flow system for prolonged sample viability. Analyst, 2019. 144(3): p. 997-1007.
[3] H. M. Elsheikha, et al., Label-free characterization of biochemical changes within human cells under parasite attack using synchrotron based micro-FTIR. Analytical Methods, 2019.
[4] X. Huang and C.S. Brazel, On the importance and mechanisms of burst release in matrix-controlled drug delivery systems. Journal of Controlled Release, 2001. 73(2-3): p. 121-36.

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Keywords: microspectroscopy, metal-organic frameworks, nanocomposites.

Nanoscale resolved synchrotron IR analysis

RECENT INNOVATIONS IN NANOSCALE IR SPECTROSCOPY: A TUNABLE BROADBAND IR LASER SOURCE FOR NEAR-FIELD IMAGING AND SPECTROSCOPY

Miriam Unger[1]*, Qichi Hu[2], Honghua Yang[2]

[1]Bruker Nano Surfaces Division, 76186 Karlsruhe, Germany; [2]Bruker Nano Surfaces Division, Santa Barbara, CA 93117, USA.
**miriam.unger@bruker.com*

The properties of chemically or structurally heterogeneous materials are often determined by intermolecular interactions over nanometer length scales. Measurement tools that can access these length scales with chemical specificity are thus highly desirable in understanding and engineering many advanced materials.

Broadband infrared scattering scanning near-field optical microscopy (IR s-SNOM) is one of such technique that can perform chemical imaging and nanoFTIR spectroscopy with the desired spatial resolution and chemical specificity. Based on the scattering response of a sample coupled in the near-field to the plasmonic enhancement of a metalized scanning probe tip, IR s-SNOM is broadly compatible with a variety of laser sources (like QCLs, broadband lasers etc.) and detection modalities.

In the presentation we demonstrate an ultra-broadband (6 octave) nano spectroscopy platform by combining a high-power mid-IR OPO/DFG laser source with an IR s-SNOM system. Due to the architecture of the broadband laser source, it allows the unique combination to perform 200 cm^{-1} broadband emission over a wavenumber range from 4000-670 cm^{-1} and 20 cm^{-1} narrowband operation over the 2000-670 cm^{-1} wavenumber range. Apart from the quasi-cw operation of the broadband IR source which is required for s-SNOM measurements, additionally a triggered pulsed mode is available for photothermal AFM-IR investigations. Therefore, in terms of flexibility and tuning range the OPO/DFG laser source sets a new standard for the complementary nanoscale IR techniques, especially IR s-SNOM spectroscopy (nano-FTIR) and imaging and photothermal AFM-IR.

In this context, we will also highlight the laser performance and will demonstrate its use on several samples which will achieve promising new insights in the understanding of a multitude of different materials.

Keywords: nanoscale IR spectroscopy, IR s-SNOM, broadband laser, nano-FTIR

Nanoscale resolved synchrotron IR analysis

STATE OF THE ART IN CRYOGENIC INFRARED NANO-IMAGING

A. S. McLeod[1,2]*, J. D. Zhang[2], K. W. Post[3], E. van Heumen[4], J. Rondinelli[5], W. Wu[6], R. D. Averitt[2], I. K. Schuller[2], and D. N. Basov[1,2]

[1]*Columbia University, New York, NY 10027, Dept. of Physics*
[2]*University of California San Diego, La Jolla, CA 92093, Dept. of Physics*
[3]*Los Alamos National Laboratory, Los Alamos, NM 87544.*
[4] *University of Amsterdam, 1012 WX Amsterdam, Netherlands.*
[5]*Northwestern University, Evanston, Illinois 60208, Dept. of Materials Science and Engineering*
[6]*University of Science and Technology of China, Hefei 230026, China, Hefei National Laboratory for Physical Sciences at the Microscale*
** am4734@columbia.edu*

Bypassing the diffraction limit of conventional limit of light, near-field microscopy has emerged as an invaluable tool for nanometer-resolved optical investigations of inhomogeneous materials. Recent instrumental developments have brought this technique to cryogenic temperatures (down to T=20K), a regime where quantum phase transitions such as the insulator-to-metal transition (IMT) can emerge among so-called correlated electron materials. Using external stimuli including temperature, strain, and even light, here I explore universal phenomenologies and the opportunities for nano-scale control over the IMT among representative correlated electron materials. I first reveal how spatial morphologies of insulator and metal domains provide clues to short-ranged interactions between coupled order parameters in the rare-earth nickelate NdNiO3, selectively driving the IMT at nanometer scales [1]. On the other hand, I demonstrate how long-ranged interactions with strain produce nano-textured percolation and growth of striped insulator and metal domains in thin films of the “canonical Mott insulator” V2O3 [2]. By tuning the energetic landscape controlling the transition, I demonstrate active manipulation of these textures through nano-imaging of the IMT in layered ruthenate single-crystals under in situ application of uniaxial strain and electrical current. Lastly, nano-imaging of an epitaxial manganite reveals how a unique combination of coupled order parameters and strain susceptibility create conditions for a metastable IMT both “activated” through optical excitation and “deactivated” through locally applied pressure [3]. These examples highlight the singular capabilities of infrared nano-imaging deployed at cryogenic temperatures, promising expansive opportunities for the future investigation of quantum phase transitions in correlated electron materials.

References

[1] K.W. Post*, A.S. McLeod*, M. Hepting, M. Bluschke, Y. Wang, G. Cristiani, … & D.N. Basov. Coexisting first- and second-order electronic phase transitions in a correlated oxide. Nature Physics, 1–6. (2018). doi: 10.1038/s41567-018-0201-1. *These authors contributed equally.

[2] A.S. McLeod, E. Van Heumen, J.G. Ramirez, S. Wang, T. Saerbeck, S. Guenon, … I.K. Schuller, & D.N. Basov. Nanotextured phase coexistence in the correlated insulator V2O3. Nature Physics. (2017). doi: 10.1038/nphys3882

[3] A.S. McLeod*, J.D. Zhang*, M.Q. Gu, … W.B. Wu, J. Rondinelli, R.D. Averitt, & D.N. Basov. Multi-messenger nano-probes of hidden magnetism in a strained manganite. Nature Materials. To appear (2019) *These authors contributed equally.

Special IR Techniques

EXPLORING THz-DRIVEN DYNAMICS ON SUB-CYCLE TIMESCALES AT THE TELBE FACILITY

Jan-Christoph Deinert[1]*, Bertram Green[1], Igor Ilyakov[1], Nilesh Awari[1],
Zhe Wang[1], Semyon Germanskiy[1], Min Chen[1], Mohammed Bawatna[1],
Michael Gensch[1,2,3], Sergey Kovalev[1]

[1]Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany; [2]DLR e.V., Rutherfordstraße 2, 12489 Berlin, Germany; [3]Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany
**j.deinert@hzdr.de*

The TELBE Terahertz (THz) facility at Helmholtz-Zentrum Dresden-Rossendorf (HZDR) offers narrowband high-field high-repetition rate THz radiation for driving low-energy excitations in matter in the spectral region between 0.1 THz and 1.5 THz [1]. In combination with our pulse-resolved data acquisition and the numerous available probing techniques based on table-top laser systems, we can resolve THz-driven dynamics with few 10 fs time resolution and high dynamic range of up to 120 dB [2]. This makes TELBE a unique facility for exploring low-energy THz excitations offering (resonant) access to a multitude of fundamental modes, e.g., lattice vibrations, molecular rotations, spin precession and the motion of free electrons [3]. Recently, we demonstrated THz high harmonic generation (HHG) in the model 2D material graphene [4]. Here, the ultrafast collective thermal response of free background electrons near the Dirac point [5] enables very efficient generation of harmonics in the technologically relevant THz frequency range. We further show that the underlying principle of the collective response can be generalized to other 2D and 3D Dirac materials, such as CdAs. The crucial role of doping in graphene can be exploited by, e.g. electrochemical gating, which allows tuning of the HHG efficiency by almost two orders of magnitude. The corresponding setup for phase-resolved nonlinear THz spectroscopy further enables a novel technique: Higgs spectroscopy, which offers new ways for understanding unconventional superconductivity. Using this technique, we recently discovered a new collective mode distinct from the heavily damped Higgs mode in different families of cuprates [6]. Our results establish Higgs spectroscopy as a new approach to uncover interactions directly relevant to superconductivity.

In this contribution, I will also discuss experiments on the selective THz control of magnetic properties in a number of different materials [7], which is enabled by probing techniques, such as Faraday Rotation or MOKE, using the NIR and UV output from our table-top sources.

References:

[1] B. Green et al., Sci. Rep. 6, 22256 (2016).
[2] S. Kovalev et al., Struct. Dyn. 4, 024301 (2017).
[3] T. Kampfrath et al. Nat. Photonics 7, 680–690 (2013).
[4] H. Hafez et al., Nature 561, 507 (2018).
[5] Z. Mics et al., Nature Communications 6, 7655 (2015).
[6] H. Chu et al., arXiv preprint, arXiv:1901.06675 (2019).
[7] S. Kovalev et al., J. Phys. D: Appl. Phys. 51, 114007 (2018).

Keywords: Terahertz, ultrafast, nonlinear dynamics, pump-probe

Special IR Techniques

INFRARED STUDY OF THE 2H-$MoTe_2$ ELECTRONIC STRUCTURE UNDER PRESSURE

F. Capitani[1]*, E. Stellino[2], F. Ripanti[3], A. Celeste[1,4], M. Verseils[1], J.-B. Brubach[1],
P. Roy[1], F. Borondics[1], C. Petrillo[2], P. Postorino[4], P. Dore[4]

[1]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192 Gif-sur-Yvette, France; [2]Department of Physics and Geology, University of Perugia, Via A. Pascoli, 06123 Perugia, Italy; [3]Department of Physics, "Sapienza" University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy; [4]Institut de Chimie et des Materiaux Paris-Est, CNRS UMR 7182, UPEC, 2-8, rue Henri Dunant, 94320 Thiais, France.
**francesco.capitani@synchrotron-soleil.fr*

Transition Metal Dichalcogenides (TMDs) are a well-known class of layered materials with stoichiometry MX2, where M is a transition metal atom and X is a chalcogen element [1]. Among TMDs, molybdenum-based compounds with a 2H hexagonal lattice and semiconducting nature with bandgaps in the infrared region are of particular interest for a wide range of electronic and optoelectronic applications [2,3]. This stimulated several investigations pointing out the strong dependence of the electronic structure on the number of layers and on their interaction, as witnessed by an indirect to direct bandgap transition when the crystal sample is reduced down to monolayer [4,5]. The application of pressure, which mainly acts on the inter-layer distance, thus represent a powerful and clean tool to tune and study the electronic properties of these systems.

Here, we report the infrared spectroscopic study of the electronic properties of bulk 2H-$MoTe_2$ under pressure up to about 20 GPa. Infrared transmission measurements have been performed from the far to the near infrared range at the synchrotron SOLEIL on the SMIS and AILES beamlines. The pressure dependence of the bandgap and the pressure-induced increase of the spectral weight in the far infrared range indicate that a semiconductor to insulator transition takes place at 13±1 GPa. This result is in well agreement with theoretical predictions based on the density functional theory [6]. We also propose a simple method based on the Drude model, which in the metallic phase associates the integral of the far-infrared absorption to the free electron density. This allows us to provide a semi-quantitative description of the slow pressure-induced increase of the electron density that characterizes the metallization process in bulk 2H-$MoTe_2$.

Finally, this study shows the importance of performing broadband infrared spectroscopy at high pressure at synchrotron facilities. For this reason, an upgrade of the high-pressure optical setup available the SMIS beamline is currently under commissioning. The main features of this upgraded setup are also presented.

References:

[1] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis. Nat. Rev. Mater., 2:17033, 2017.
[2] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano. Nat. Nanotechnol., 7:699 EP, 2012.
[3] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, and M. C. Hersam. ACS Nano, 8:1102, 2014.
[4] W. S. Yun, S. W. Han, I. G. Hong, S. C.and Kim, and J. D. Lee. Phys. Rev. B, 85:033305, 2012.
[5] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz. Phys. Rev. Lett., 105:136805, 2010.
[6] M. Riflikova, R. Martonak, and E. Tosatti. Phys. Rev. B, 90:035108, 2014.

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Keywords: transition metal dichalcogenides, spectroscopy, metallization

Special IR Techniques

INFRARED/THz SPECTROSCOPY OF MATERIALS AT EXTREME PRESSURES AND TEMPERATURES

Jean-Blaise Brubach[1], Benjamin Langerome[1], Francesco Capitani[1], Kelly Rader[1], Thomas Souske[1], Thomas Timusk[2], Pascale Roy[1]*

[1]*Synchrotron Soleil, Saint-Aubin, 91190, France;* [2]*Department of Physics and Astronomy, McMaster University, Hamilton and The Canadian Institute for Advanced Research, Toronto, ON M5G 1Z8 Canada.*
**pascale.roy@synchrotron-soleil.fr*

Spectroscopic probes are among the most important techniques for characterizing new physical states induced by changes of temperature and/or pressure. In link with its high brightness and wide spectral coverage, synchrotron infrared radiation is ideally suited for such studies. The AILES beamline on the SOLEIL Synchrotron Light Source is an integrated facility for infrared/THz spectroscopy allowing to measure transmission or reflectivity from ambient to multi-megabar pressures and sub-Kelvin temperatures [1]. Materials analyzed include both inorganic and organic systems, where pressure effects on vibrational, electronic and magnetic excitations have been investigated. These investigations complement x-ray studies, Raman and transport measurements carried out on the same materials. An overview of recent examples will be presented, including:

i) Low temperature studies of ultrathin layers materials, with superconducting transitions at sub-kelvin temperatures.

ii) Pressure induced superconducting materials, for which the low-frequency dynamics of record high temperature H3S compounds reveals the mechanism responsible for the superconducting transition [2].

References:

[1] A. Voute et al., Vib. Spectrosc. 86, 17-23 (2016).
[2] F. Capitani et al., Nat. Phys. 13, 859-863 (2017).

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Keywords: Superconductivity, High Pressure, Sub Kelvin temperatures.

Special IR Techniques

IONIZATION, HYDRATION AND INTERMOLECULAR H-BONDING IN FUEL CELL MEMBRANES

J.B. Brubach[1]*, P. Roy[1], Iojoiu[2], J. Peet[2], S. Lyonnard[2]

[1]Synchrotron SOLEIL, AILES beamline, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex; [2]Laboratoire Léon Brillouin, CNRS -CEA- UMR 12, CEA–Saclay, 91191 Gif sur Yvette cedex, France.
**brubach@synchrotron-soleil.fr*

Proton exchange membrane fuel cell (PEMFC) is a promising technology for powering automobiles and small portable electronics. One major challenge is to improve the proton-conducting polymers that constitute the heart of the fuel cell, the membrane-electrode assembly. Antagonist properties are desired: thermal and mechanical stability on the one side, excellent proton conductivity on the other side. The current technical standard of choice for these materials is the family of polymers known as perfluorosulfonic acid (PFSA) ionomers, among them the benchmark material, Nafion [1]. Recently new original aromatic multi-blocs copolymers functionalized with the same ionic function as the one in Nafion have been synthetized [2,3]. The combination of the AILES beamline and the home-made hydration cell allow to perform in situ hydration sequences (hydration/dehydration including drying) of mesoporous samples, with real-time acquisition of FIR and MIR spectra. It has allowed to i) elucidate the mechanism of sulfonic acid ionization and concomitant hydronium ion formation, ii) establish the state and properties of adsorbed water molecules, iii) probe the existence of hydration thresholds related to the solvation of SO3-/H3O+ species and formation of a multi-connected H-bond network and iv) to highlight the mechanism which govern the proton conductivity.

References:

[1] S. D. Bernardina et al, J. Phys. Chem. C, , 118 (44) 25468-25479, (2014)
[2] Assumma, L. et al., J. Polym. Sci. A, 53, 1941-1956, (2015)
[3] Assumma, L. et al., Appl. Mat. Interfaces, 7, 13808-13820, (2015)

Keywords: Nafion, H-Bond, Hydronium, proton conductivity.

Special IR Techniques

MULTIPHONON ANHARMONICITY IN CUBIC IONIC CRYSTALS

E. Calandrini[1]*, L. Paulatto[1], F. He[1], R. P. S. M. Lobo[2], A. Bosak[3],
L. Paolasini[3], P. Roy[4], D. Antonangeli[1], P. Giura[1]

[1]Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC), UMR CNRS 7590, Sorbonne Universités – UPMC; [2]École Supérieure de Physique et de Chimie Industrielles (ESPCI), 10 Rue Vauquelin, 75005 Paris; [3]European Synchrotron Radiation Facility (ESRF), Grenoble, France; [4]Synchrotron Soleil, L'Orme des Merisiers Saint Aubin, BP 48 91192, Gif-sur-Yvette , France.
**eugenio.calandrini@upmc.fr*

Long observed anomalies in the reststrahlen region of reflectivity spectra of cubic ionic crystals cause the failure of the harmonic scenario and find clear explications in the multi-phonon scattering processes [1,2]. Indeed, anharmonic effects are responsible for the finiteness of the phonon linewidths as well as the temperature and pressure dependence of the phonon frequencies. The need of an advanced description of the normal modes multiphonon interactions is not only of fundamental interest but also has an impact on many physical macroscopic properties such as electric, thermal conductivity and thermoelectricity [3,4]. For these reasons, in the last two decades, theoretical and numerical tools have been dramatically improved and now require a combined approach with the experimental side to accomplish an effective confirmation[5,6]. These macroscopic quantities under investigation depend on the entire phonon spectrum and are sensitive to the approximations used in the ab-initio simulations and to the quality of individual samples, jeopardizing the possibility to draw easy comparison. Combined experimental techniques are required to probe the entire phonon dispersion: Raman and infrared spectroscopy at zero wavevector and neutron or x-ray scattering at finite wavevector. Despite the simplicity of cubic ionic crystal systems, they will allow to frame the problem and present practical advantages from both the theoretical and experimental standpoints: they require modest computational efforts, they present enhanced anharmonic effects, they dispose phonons as unique heat carriers, they have direct interest for geological sciences and technological applications. To our best knowledge, most of the results of this research field are based on numerical studies, few on experiments and even fewer on the combination of the two approaches[7,8]. Here we present a comprehensive study of the optical phonon dispersion in the whole Brillouin zone of MgO single crystal as a function of temperature and pression, by combining ab-initio calculations, synchrotron based IR reflectivity and inelastic x-ray scattering experiments. For the first time, the outcomes of experiments and numerical results are systematically compared for the determination of the anharmonic contribution to the normal modes energy and lifetime.

References:

[1] J. R. Jasperse, A. Kahan, J. N. Plendl, S. S. Mitra, Phys. Rev. 146, 526 (1966).
[2] G.A. Adebayo, Y. Liang, C.R. Miranda, and S. Scandolo J. Chem. Phys. 131, 014506 (2009).
[3] Q. Yin and S. Y. Savrasov, Phys. Rev. Lett. 100, 225504 (2008).
[4] N- K. Ravichandran and D. Broido, Nat. Com 10, 827 (2019).
[5] L Paulatto, I Errea, M Calandra, F Mauri, Physical Review B 91 (5), 054304 (2015).
[6] G. Fugallo, B. Rousseau and M. Lazzeri, Phys. Rev. B 98, 184307 (2018).
[7] P. Giura, N. Bonini, G. Creff, J. B. Brubach, P. Roy, and M. Lazzeri, Phys. Rev. B 86, 121404(R), 2012.
[8] P-F. Lory et al. Nat. Comm. 8, 491 (2017).

Keywords: Density Functional Perturbation Theory, Infrared Spectroscopy, Phonon anharmonicity

Special IR Techniques

NOVEL CONCEPTS IN INFRARED NANO-IMAGING – COMPETING, CONFUSING, CONTROVERSIAL, OR COMPLEMENTARY?

Markus Raschke

University of Colorado, Department of Physics, Department of Chemistry
mara6442@colorado.edu

Over the past decade a number of infrared scanning probe techniques have matured, and new ones emerged, that can extend the spatial resolution of infrared spectroscopy into the nanometer regime. They take advantage of different contrast mechanisms, through the optical or mechanical response of a scanning probe tip under infrared resonant interaction with the sample. Specifically, near-field enhanced light scattering based on a tip-sample coupled polarization makes infrared scattering scanning near-field optical microscopy (IR s-SNOM) an all optical technique, providing the full optical response function of a material, and widely applied for the study of vibrational, phonon, polariton, and other low-energy excitations in molecules, 2D materials, and quantum materials. In addition, associated with the resonant absorption of the sample a thermal expansion, even as small as picometers, gives rise to an opto-mechanical force response of the scanning probe tip in photo-thermal induced resonance (PTIR) or AFM-IR, providing a direct measure of the nanoscale spectral absorption. In addition, albeit controversial, an optical gradient force between the tip and the sample was proposed as the underlying contrast in a method termed photo-induced force microscopy (PiFM). However, as the number of demonstrations and applications grew, showing in part impressive contrast, spatial resolution, and sensitivity, a in part confusing picture emerged with regards to the respective contrast mechanisms, notably in tip-force detection in PiFM and PTIR. In this talk we will compare and quantify the responses from the different techniques, applied to different sample systems and materials excitations, and based on their multimodal implementation in a single instrument. We will discuss possible cross-talk and super-position of the different signal channels and their sensitive dependence on AFM operation. We will conclude with a perspective for the optimization of the different techniques for different applications, their fundamental limits, and a proposal for a more general approach to the exploration of infrared nano-spectroscopy based on optical, opto-thermal, and opto-mechanical principles for the study of molecular, quantum, and bio-systems.

Keywords: IRs-Snom, PTIR, PiFM

Special IR Techniques

OPTICALLY SUPER-RESOLVED INFRARED IMAGING MICRO-SPECTROSCOPY

T.J. Huffman[1]*, Robert Furstenberg[1], Christopher A. Kendziora[1], R.A. McGill[1]

[1]*U.S. Naval Research Laboratory, 4555 Overlook Ave SW, Washington, DC 20375, USA.*
**tyler.huffman.ctr@nrl.navy.mil*

Broadband spectroscopy is antithetical to microscopy. This concept, articulated in the diffraction limits of Abbe and Rayleigh, has traditionally stood as the fundamental limiting factor of the imaging disciplines. For spectroscopy, this implies that the spatial resolution of a hyperspectral image is limited by the longest wavelength of the spectrum. While broadband spectroscopy has established itself as perhaps the most useful technique for chemical identification and analysis, the superior resolution of optical microscopy has allowed it to persist as the canonical technique in Biology and an invaluable tool in Materials Science, despite most interesting chemical information lying in the longer wavelength – lower resolution – infrared region of the spectrum. Here we present a novel technique to break the correspondence between wavelength and spatial resolution. Optically Super-resolved InfraRed Imaging micro-Spectroscopy (OSIRIS) permits the collection of *fully broadband* hyperspectral images at the maximum optical spatial resolution. Modulated long wavelength light is directed onto the sample, while a short wavelength probe beam senses the resultant modulation in local temperature. A spectrum is collected by varying the wavelength of the modulated light. Thus, OSIRIS constitutes the full generalization of color vision to full spectral bandwidth with spatial resolutions up to the maximum achievable with super-resolution and coherent microscopy ($\lambda_{probe}/4NA \geq 70$ nm). The non-contact nature of OSIRIS permits deep tomography and real-time imaging via multiplexing of the probe beam, while preserving the versatility and ease of use of optical microscopy. The impact of a mature OSIRIS microscope combining the versatility, speed, and spatial resolution of optical microscopy with the analytical power and chemical specificity of infrared spectroscopy cannot be understated.

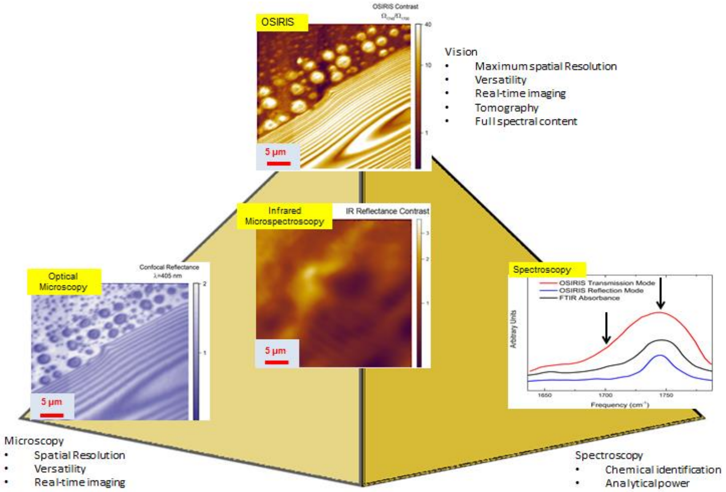

Figure 1: Study of olive oil droplets on a gold mirror, demonstrating how OSIRIS unifies microscopy and spectroscopy.

Keywords: sub-diffraction, hyperspectral imaging, infrared spectroscopy

Special IR Techniques

SUBMICRON SIMULTANEOUS IR AND RAMAN MICROSCOPY (IR+RAMAN): BREAKTHROUGH DEVELOPMENTS IN OPTICAL PHOTOTHERMAL IR (O-PTIR) COMBINED WITH RAMAN PROVIDE NEW CAPABILITIES

Mustafa Kansiz[1]*, Curt Marcott[2]

[1]Photothermal Spectroscopy Corp, 325 Chapala St, Santa Barbara, CA, 93101, USA; [2]Light Light Solutions, 2558 High Hammock Rd, Seabrook Island, SC, 29455, USA.
**mkansiz@photothermal.com*

Both Infrared (IR) and Raman Spectroscopies are well established, relatively mature technologies and are typically present as separate stand-alone instruments in most laboratories, since each technique offers unique analytical capabilities with complimentary spectroscopic information. The recent advent of Optical Photothermal IR (O-PTIR), which has enabled for the first time, submicron infrared microscopy in reflection mode (far-field) providing “FTIR transmission-like” spectral quality, without the typical reflection spectral artefacts and distortions associated with traditional FTIR or other emerging QCL based IR microscopy systems.

The fundamental basis for the technique, the “IR Photothermal Effect” is not new and has been exploited for decades with techniques such as PhotoAcoustic Spectroscopy (PAS) and more recently with AFM-IR (nano-IR). Where O-PTIR differs to these other Photothermal techniques is that it uses an optical (green laser) probe for detection, being analogous to the microphone in PAS and the AFM tip in AFM-IR. The use of this optical probe is the key enabling breakthrough in O-PTIR allowing for non-contact, far-field measurements, which provides for numerous benefits in instrument capabilities relative to traditional FTIR/QCL microscopy but also in instrument architecture, thus allowing, in a world first, a combined IR and Raman (IR+Raman) platform that provides for simultaneous IR and Raman spectral information at the same time, from the same spot with the same spatial resolution.

Figure 1 demonstrates the well-known complementarity of the IR and Raman, where certain bands are active or strong with one technique and not in the other, thus a simultaneous collection provides for significantly more information and better sample characterisation and also opens up new data analysis strategies for these two correlative techniques. Polymeric examples as well as examples from life sciences, pharmaceutical and industrial failure analysis will be presented.

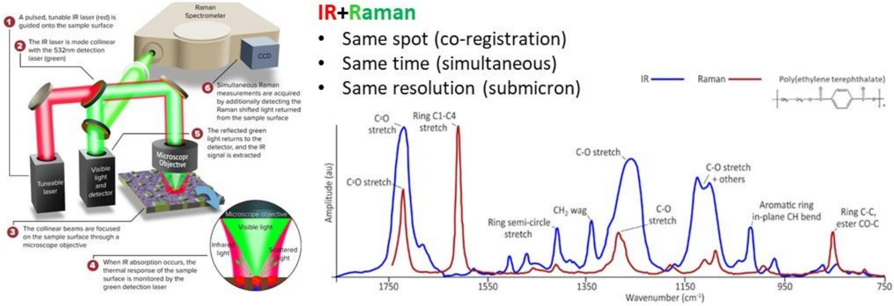

Figure 1: Left, Instrument schematic design showing IR (red) and Probe (green) laser beam paths and detection. Right, Example simultaneous IR and Raman spectrum of PET.

Keywords: O-PTIR, Infrared Microscopy, Raman, Submicron, Instrumentation Development, IR+Raman

SYNCHROTRON-BASED SINGLE-SHOT INFRARED SPECTROSCOPY AT BESSY II

Eglof Ritter[1]*, Ljiljana Puskar[2], So Young Kim[3], Jung Hee Park[3], Klaus-Peter Hofmann[4], Franz Bartl[5], Peter Hegemann[1], Ulrich Schade[2]

[1]Humboldt-Universität zu Berlin, Institute of Biology, Experimental Biophysics, 10115 Berlin; [2]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Department of Locally Sensitive and Time-Resolved Spectroscopy, 12489 Berlin, Germany; [3]Chonbuk National University, Division of Biotechnology, Advanced Institute of Environment and Bioscience, 54596 Iksan, Republic of Korea; [4]Charité-Universitätsmedizin Berlin, Institute for Medical Physics and Biophysics, 10117 Berlin, Germany; [5]Humboldt-Universität zu Berlin, Institute of Biology, Biophysical Chemistry, 10115 Berlin, Germany

**eglof.ritter@hu-berlin.de*

Proteins are among the key players in the cells of living organisms, and one of the most important techniques to study their structure and function is infrared (IR) spectroscopy. State-of-the-art time- resolved IR spectroscopy methods employed to follow protein kinetics at a timescale of milliseconds and below are often limited to cyclic systems in which exactly the same reaction can be triggered in quick succession and multiple times, without any substrate loss [1]. However, the majority of systems in nature is either not cyclic or has a long cycling time, making time-resolved IR measurements either impossible or very demanding. For example, vertebrate rhodopsin, the protein that initiates vision in our eyes, undergoes an irreversible activation cascade after light absorption. Although this protein is in the focus of scientific interest in pharmacology and medicine because it constitutes the prototype of a huge family of protein receptors mediating basic functions of life such as vision, smell, taste and drug reception [2], no time-resolved IR spectra of its activation cascade have been published so far. We developed a mid-IR spectrometer with microsecond time resolution specifically tailored for such irreversible processes. It uses the brilliant synchrotron radiation source of BESSY II [3] in combination with a fast linear detector array in a unique diffraction limited dispersive spectrometer concept [4].

Here we present the first results using this novel spectrometer on several light-activated protein systems, amongst others, vertebrate rhodopsin.

References:

[1] Ritter E., Puskar, L., Aziz, EF., Hofmann, KP., Hegemann, P. & Schade, U., Time-resolved infrared spectroscopic techniques as applied to channelrhodopsin. *Front. Mol Biosci.* **2**, 38 (2015).
[2] Hilger, D., Masureel, M. & Kobilka, BK., Structure and dynamics of GPCR signaling complexes. *Nat. Struct. Mol. Biol.* **25,** 4–12 (2018)
[3] Peatman WB. & Schade U., A brilliant infrared light source at BESSY. *Rev Sci Instrum.* **72**, 1620 (2001).
[4] Schade U., Ritter, E., Hegemann, P., Aziz, EF. & Hofmann, KP., Concept for a single-shot mid-infrared spectrometer using synchrotron radiation. *Vib. Spectrosc.* **75**, 190 (2014).

Keywords: Time-resolved spectroscopy, Dispersive techniques, Protein structure/ function relations, single-shot spectroscopy

Special session: Why all the fuzz about synchrotron IR/THz now?

LATTICE DYNAMICS OF HIGHLY POROUS MATERIALS

Matthew Ryder

Neutron Scattering Division, Neutron Sciences Directorate, Oak Ridge National Laboratory, USA
rydermr@ornl.gov

Highly porous materials such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and hydrogen-bonded organic frameworks (HOFs) have recently been suggested to have promising electronic and dielectric properties.[1-3] However, high levels of porosity often couple with low structural and mechanical stability.[4, 5] Therefore, the low-frequency lattice dynamics of porous framework materials can reveal a diversity of valuable information relating to the structural flexibility and stability and can explain the mechanistic origins of anomalous mechanical phenomena.[6-8] Spectroscopic techniques such as Raman and synchrotron infrared (IR) spectroscopy and inelastic neutron scattering (INS) in conjunction with density functional theory (DFT), can be used to study the terahertz (THz) vibrations of various porous framework materials. Intriguing structural motions and transitions are revealed, including gate opening and breathing dynamics,[6] 'trampoline-like' mechanisms and molecular rotors reminiscent of negative thermal expansion (NTE),[7, 8] and buckling of 2D layers.[9] The work has also recently advanced to investigate the effect of external stimuli (pressure and temperature) and has revealed the nature and underlying mechanisms behind stimuli-induced phase changes and amorphization.[9-11]

References

[1] M. R. Ryder et al., ChemPlusChem, 83, 308-316 (2018).
[2] P. Li et al., Angew. Chem., Int. Ed., 58, 1664-1669 (2019).
[3] M. R. Ryder et al., J. Phys. Chem. Lett., 9, 2678-2684 (2018).
[4] M. R. Ryder and J. C. Tan, Dalton Trans., 45, 4154-4161 (2016).
[5] M. R. Ryder et al., Phys. Chem. Chem. Phys., 18, 9079-9087 (2016).
[6] M. R. Ryder et al., Phys. Rev. Lett., 113, 215502 (2014).
[7] M. R. Ryder et al., Phys. Rev. Lett., 118, 255502 (2017).
[8] M. R. Ryder et al., CrystEngComm, 18, 4303-4312 (2016).
[9] A. M. Evans et al., Ind. Eng. Chem. Res., Accepted, DOI: 10.1021/acs.iecr.9b01288.
[10] M. R. Ryder et al., ChemRxiv, Submitted, DOI: 10.26434/chemrxiv.8097818.
[11] M. R. Ryder et al., Chem. Commun., 53, 7041-7044 (2017).

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Keyrords: Lattice Dynamics, Density Functional Theory, Porous Materials, Terahertz

Special session: Why all the fuzz about synchrotron IR/THz now?

INFRARED SCIENCE AT FUTURE LIGHT SOURCES

Michael Martin

Advanced Light Source, Lawrence Berkeley National Laboratory, Advanced Light Source, USA
mcmartin@lbl.gov

In this talk, I will look at the overall directions of our accelerator-based infrared field, and how it will change as a new generation of multi-bend achromat synchrotrons and upgraded machines become world leading for x-ray science. Nearly 25 years ago, Carr, Reffner and Williams demonstrated that a synchrotron beamline coupled with an IR microscope performs at the diffraction limit in much of the mid-IR [1]. High brightness at the diffraction-limit was a hallmark of synchrotron IR beamlines for the next decades. Diffraction limited storage rings (DLSR) allows the emittance of the electron-beam to be comparable or smaller than the emittance of the x-ray photon beams produced, meaning the diffraction limit is moving well beyond the IR and into the soft- and hard-x-ray energy range. A number of new and upgraded facilities are under construction or planned to take advantage of the significant increase in brightness (brilliance) which will allow new x-ray science and a greater use of coherence-based imaging and time-based spectroscopies [2].

The synchrotron infrared community also has greater perceived competition from single wavelength and broadband laser sources, and improved detectors allowing high quality spectra and images from conventional IR sources. I will show typical characteristics of a DLSR for the infrared, look at how lasers have improved, and discuss both challenges and opportunities for the future of IR from synchrotron and FEL sources. I will use the planned ALS Upgrade [3] to a DLSR as a detailed example but will also discuss other facilities.

References

[1] "Performance of an infrared microspectrometer at the NSLS," GL Carr, JA Reffner, GP Williams, Review of Scientific Instruments, 66 (2) 1490-1492 (1995). DOI: 10.1063/1.1145951
[2] "The next ten years of X-ray science," Makina Yabashi & Hitoshi Tanaka, Nature Photonics 11, 12–14 (2017). DOI: 10.1038/nphoton.2016.251
[3] "A New Light for Berkeley Lab—the Advanced Light Source Upgrade," Ashley White, Kenneth Goldberg, Stephen Kevan, Daniela Leitner, David Robin, Christoph Steier & Lynn Yarris, Synchrotron Radiation News, 32:1, 32-36 (2019). DOI: 10.1080/08940886.2019.1559608

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Keywords: diffraction limit, source, synchrotron, future

POSTER PRESENTATION

IR sources, detectors and facility developments

CHARACTERIZATION OF SYNCHROTRON TERAHERTZ EMISSION AT LNLS

William I. Depetri[1]*, Flavio C. Cruz[1], Raul de O. Freitas[2]

[1]Universidade Estadual de Campinas, Instituto de Física Gleb Wataghin, 13083-859, Campinas, Brazil;
[2]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970 Campinas, Sao Paulo, Brazil.
**wdepetri@gmail.com*

The infrared (IR) beamline at the Brazilian Synchrotron Light Laboratory (LNLS) is particularly interesting for studying the interaction of low energy radiation with matter, such as in surface physics [1] and 2D materials [2]. Infrared beams are extracted from the core of bending magnets or at the entrance or exit (“edge sourced”) with the optics optimized to bypass shorter wavelengths, such as x-rays [3], and extract mid and far-infrared (terahertz) radiation. The present work describes the first characterization of terahertz radiation at the LNLS by using a bolometric camera, combined with terahertz bandpass filters [4]. We measured beam profiles and spectral response from both bending magnet and edge sources in the frequency range from 10THz (30µm) to 400GHz (750µm).

References:

[1] I. D. Barcelos, A. R. Cadore, L. C. Campos, A. Malachias, K. Watanabe, T. Taniguchi, F. C. B. Maia, R. Freitas and C. Deneke. Nanoscale, 27, 2015.
[2] I. D. Barcelos, A. R. Cardore, A. B. Alencar, F. C. B. Maia, E. Mania, R. F. Oliveira, C. C. Bufon, A. Malachias, R. O. Freitas, R. L. Moreira and H. Chacham. ACS Photonics, 5, 5, 2018.
[3] R. O. Freitas, C. Deneke, F. C. B. Maia, Y. Petrof and H. Westfahl, Optics Express, 26, 9 (2018).
[4] A. M. Melo, A. L. Gobbi, M. H. O. Piazzetta and A. M. P. A. da Silva, Adv. Opt. Tech, 530512, 2012.

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Keywords: synchrotron, terahertz, spectroscopy, detection

IR sources, detectors and facility developments

DESIGN AND DEVELOPMENT OF A FAST, FAR-INFRARED BOLOMETER FOR NEAR-FIELD NANOSPECTROSCOPY

G.L. Carr[1]*, H.A. Bechtel[2]

[1]*National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973 USA;*
[2]*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, USA.*
**carr@bnl.gov*

The high brightness of infrared synchrotron radiation reaching into the far-infrared makes it a compelling source for broadband near-field nanospectroscopy to photon energies approaching 10 meV, thus filling the spectral range for which laser-type sources are challenged. Spanning this spectral range covers the majority of phonons in solids as well as other low energy excitations of scientific and technical interest that stem from ordered behaviors. The already successful scattering type scanning nearfield optical microscopy (s-SNOM), combined with a fast Ge:Cu photoconductor, now allows for measurements down to 40 meV [1]. Though extending the spectral range to lower frequencies using other photoconductive materials (e.g. gallium doped germanium) is a plausible approach, the limited spectral range for such detectors is unattractive given the very broadband synchrotron source. Therefore, we are developing a custom bolometer system intended to span the spectral range from just below 100 cm^{-1} to over 800 cm^{-1}. A typical bolometer for the far-IR has a time constant on the order of 1 millisecond, which is inadequate for matching AFM tip modulation frequencies of 100 kHz and higher. Our basic approach is to reduce the system heat capacity by operating at a lower temperature and reducing the bolometer dimensions while increasing the thermal conductance. Background noise is reduced using a cold aperture at the Winston cone entrance. Other issues for achieving a fast response include the readout electronics, which can be a challenge due to the very high impedance of the detector element (~ 40 MOhm). This presentation will report our results to-date using the 2.4 infrared beamline at the Advanced Light Source.

References:

[1] Omar Khatib, Hans A. Bechtel, Michael C. Martin, Markus B. Raschke, and G. Lawrence Carr, ACS Photonics 5, 2773 (2018).

Acknowledgements:

This work supported by the U.S. Dep't, of Energy through contracts DE-SC0012704 at NSLS-II and DE-AC02-05CH11231 at the ALS.

Keywords: near-field, far-infrared, detector

IR sources, detectors and facility developments

DEVELOPMENT OF VARIABLE POLARIZED COHERENT THz SOURCE

S. Kashiwagi[1]*, H. Saito[1], H. Zen[2], A. Irizawa[3], F. Hinode[1], Y. Ishizuki[1],
K. Kanomata[1], S. Miura[1], N. Morita[1], T. Muto[1], I. Nagasawa[1], K. Nanbu[1],
K. Takahashi[1], K. Terada, H. Yamada[1], H. Hama[1]

[1]*Research Center for Electron Photon Science (ELPH), Tohoku University, Sendai, 982-0826, Japan*; [2]*Institute of Advanced Energy (IAE), Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*; [3]*The Institute of Scientific and Industrial Research (ISIR), Osaka University, Ibaraki, 8-1 Osaka 567-0047, Japan.*
**kashiwagi@lns.tohoku.ac.jp*

Terahertz (THz) radiation sources have attracted considerable interests recently, because of their potential applications in material science, medical imaging, high speed communications, etc. Vibrational circular dichroism (VCD) measurements in the THz region are extremely sensitive to conformational changes in proteins. In particular, a THz source capable of switching the left and right circularly polarization with high speed is very useful for biological analysis. One of the most efficient terahertz sources is the electron pulse of relativistic energy produced by an accelerator. A short electron pulse can produce coherent radiation at wavelength longer than electron pulse length with the intensity proportional to the square of the number of electrons contained in a pulse. Electron population in the pulse is typically the order of 10^7–10^{10} electrons, therefore high intense terahertz radiation can be produced form the short electron pulse. We have already succeeded in producing coherent undulator radiation employed the electron beam shorter than 100fs in a test-Accelerator as Coherent Terahertz Source (t-ACTS) at Tohoku University [1]. Variable polarized coherent THz source, which is realized by utilizing a coherence of the undulator radiation, is under development. The polarization state of the coherent undulator radiation is manipulated using Martin-Puplett interferometer as shown in Figure 1. The linearly polarized coherent undulator radiation is split into two perpendicular waves using a wire-grid polarizer, and they are superimposed after adjusting their relative phase. The polarization control system is capable of generating arbitrary polarization states at high speed for each pulse. Demonstration of variable polarized THz source is conducted using a short undulator with 7 periods at t-ACTS. The results of this experiment will be shown in this workshop.

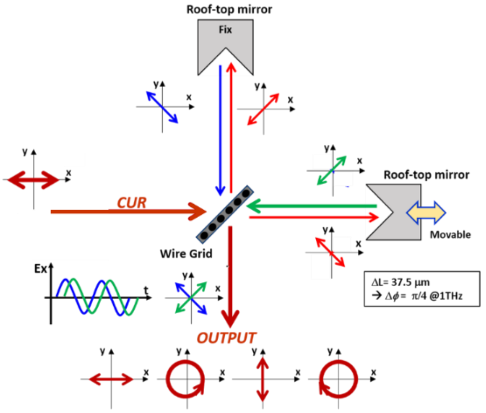

Figure 1: Polarization control system employing a Martin-Puplett type interferometer.

References:

[1] Shigeru Kashiwagi et al., Infrared Physics & Technology 93, 335-339, (2018).

Acknowledgements:

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Keywords: coherent radiation, terahertz wave, short electron pulse, polarization.

IR sources, detectors and facility developments

IMBUIA BEAMLINE: THE INFRARED STATION AT SIRIUS

Thiago M. dos Santos[1,2]*, Francisco C. B. Maia[1], Ingrid Barcelos[1], Raul Freitas[1]

[1]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970 Campinas, Sao Paulo, Brazil; [2]School of Electrical and Computer Engineering, University of Campinas, 13083-852 Campinas, SP, Brazil.
**thiago.santos@lnls.br*

Imbuia is the new infrared beamline planned for Sirius, the Brazilian 4th generation synchrotron source. The name is an acronym for Infrared Micro and nano-spectroscopy Beamline for Ultra-resolved Imaging Applications. This beamline will provide experimental stations dedicated to multiscale opto-chemical analysis of organic and inorganic materials.

The Imbuia infrared beam will cover the range from THz to near-IR, which will enable studies in a variety of areas such as chemistry, physics, geology, paleontology, biology and many others. This broadband beam will be available simultaneously at two branches: The Imbuia-Micro, for infrared multispectral imaging limited by diffraction, and Imbuia-Nano for multispectral imaging with nanometric spatial resolution using s-SNOM (scattering Scanning Near field Optical Microscopy) technique. In this presentation, we present potential scientific goals for the beamline, main details for the optical layout and instrumentation applied to infrared radiation extraction. Beamline supporting labs, samples handling/fabrication and optics lab, will be covered as well as a key point for high level experiments and community service for this station.

Acknowledgements:
The author thanks the Beamline Engineering group (SIL) for assistance with simulations and components design. The Sirius Vacuum group (VAC) is acknowledged for advisement and simulations, in the person of Rafael Molena Seraphim and Thiago Mendes da Rocha.

Keywords: infrared beamline, beamline instrumentation, 4th generation synchrotron.

INTRODUCTION OF INFRARED BEAMLINE AT NATIONAL SYNCHROTRON RADIATION LABORATORY

Chuansheng Hu*, Zeming Qi, Chengxiang Li

University of Science and Technology of China, National Synchrotron Radiation Laboratory, 230029, Hefei, China
**huchsh@ustc.edu.cn*

National Synchrotron Radiation Laboratory (NSRL) owns the first dedicated synchrotron radiation facility in China, Hefei Light Source (HLS). The HLS was fully upgraded to HLS II in 2016. Following the machine upgrade, the infrared beamline was reconstructed to improve its performance. The infrared radiation is extracted from a bending magnet (1 degree port) with an acceptance angle of 60(H) x 55(V) mrad^2, which including edge radiation and constant field radiaton. Two end stations were constructed. One is for spectroscopy experiment covered from far to near infrared, the other one is for microspectroscopy and imaging experiment. In this poster, we introduce the performance of the beamline in detail, including optics, experimental techniques developed at two endstations.

Keywords: infrared beamline, microspectroscopoy, imaging

IR sources, detectors and facility developments

ORANGE INTERFACE PLANS FOR THE SIRIUS IMBUIA BEAMLINE

João Eduardo Levandoski[1, 2] *, Raul Freitas[1]

[1]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970 Campinas, Sao Paulo, Brazil; [2] Federal University of Technology at Parana State (UTFPR), 84016-210, Ponta Grossa, PR, Brazil
**joao.levandoski@lnls.br*

The IMBUIA beamline is the new infrared station to be installed at the Sirius storage ring. This beamline will comprise 2 end stations to be dedicated to multiscale hyperspectral imaging. Since Brazilian Center for Research in Energy and Materials (CNPEM) is an “users open” research complex, researchers from various fields make use of the facilities, so a free and easy-to-use interface is of utmost importance for this beamline. Orange is a powerful interface for data analysis, with many developments' fronts, from image processing to text processing. Currently there is a specific front for spectroscopy, the objective of the work is to assist the synchrotron community in this development. The creation of new widgets aims to develop a complete and fast environment for viewing and post-processing data. In this presentation I will present the planned interface for the IMBUIA beamline and it will be a great opportunity to discuss with the WIRMS audience about the possibilities for inter-facilities developments.

Keywords: Orange, spectroscopy, synchrotron.

IR sources, detectors and facility developments

TOWARDS SINGLE-SHOT TIME-DOMAIN SPECTROSCOPY AT HIGH REPETITION RATES USING PHOTONIC TIME-STRETCH

C. Szwaj[1]*, C. Evain[1], E. Roussel[1], M. Le Parquier[1], S. Bielawski[1],
J.-B. Brubach[2], L. Manceron[2], M.-A. Tordeux[2], M. Labat[2], P. Roy[2]

[1]*Univ. Lille, CNRS, UMR 8523 – PhLAM- Physique des Lasers Atomes et Molécules, F-59000 Lille, France;*
[2]*Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, F-91192 Gif-sur-Yvette, France*.
**christophe.szwaj@univ-lille.fr*

Recording terahertz spectra and electric fields is now possible in single-shot, at high repetition rates [1-3]. In this poster we focus on the so-called spectral encoding and photonic time-stretch methods which has been initially developed for accelerator physics purposes. In particular we detail the present the performances of those systems in terms of achievable repetition rates, sensitivity, resolution, as well as trade-offs. We particular we show that up hundred millions of spectra may be recorded single-shot in the Terahertz domain. This is expected to find applications in new fields where spectra of sources or samples would need to be recorded in single-shot and/or high repetition rates. This opens new spectroscopic possibilities which cannot be achieved using classical methods, as asynchronous optical sampling (ASOPS).

References:

[1] E. Roussel et al. Sci. Rep 5, 10330 (2015).
[2] C. Szwaj et al, Rev. Sci. Instrum 103111 (2016).
[3] C. Evain et al. Phys. Rev. Lett. 118, 054801 (2007).

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Keywords: EOS, photonic time-stretch single-shot

IR spectro-microscopy and imaging

ELECTRON RADIATION DAMAGES TO PORTLANDITE AND BRUCITE STUDIED BY IR MICROSCOPY AND X-RAY DIFFRACTION

E. Garcia-Caurel[1], M.-N. de Noirfontaine[2], M. Courtial[2] , S. Tusseau-Nenez[3], O. Cavani[2], B. Boizot[2], F. Dunstetter[2], D. Gorse-Pomonti[2], F. Borondics[4]*

[1]LPICM, CNRS, Ecole Polytechnique, IP Paris, F-91128, Palaiseau, France; [2]LSI, CEA/DRF/IRAMIS CNRS, Ecole Polytechnique, IP Paris, F-91128, Palaiseau, France; [3]PMC, UMR CNRS 7643, Ecole Polytechnique, IP Paris, F-91128, Palaiseau France; [4]SMIS beam line, Synchrotron SOLEIL, Saint-Aubin, 91192, Gif-sur-Yvette France.
**ferenc.borondics@synchrotron-soleil.fr*

Portlandite $Ca(OH)_2$ and brucite $Mg(OH)_2$ are isomorphous layered hydroxide compounds. Brucite is known to be stable under pressure up to 78 GPa whereas portlandite exhibits a reversible pressure-induced crystalline-amorphous transition at 12 GPa. But decomposition on heating of portlandite occurs at higher temperature than for brucite. Here we study their stability under irradiation by associating IR microscopy and X-ray diffraction. Commercial powders are electron-irradiated at 2.5 MeV, room temperature and high dose rate (~10^8 Gy/h) using the accelerator NEC Pelletron of the SIRIUS platform (Ecole Polytechnique, Palaiseau) [1]. Both compounds are radiation resistant up to the highest dose (~15 GGy for brucite, ~8.5 GGy for portlandite). Only minor radiation effects are detected, essentially in brucite. Radiation damages in portlandite are found to be comparable to the ones observed by heating the powder, at least up to 3.5 GGy for which an effective temperature of 130°C is observed. This is definitely not the case in brucite for which the XRD study reveals i) a net dilatation along the c – axis but at the same time a contraction in the basal plane, ii) some diffuse scattering over a wide angular range compatible with some disorder in the H-sublattice, a result confirmed by the IR study revealing also that the onset of dehydroxylation should be attained at 15 GGy [2]. The results of the XRD and IR microscopy study are detailed. Hypotheses regarding the underlying damage mechanisms are formulated.

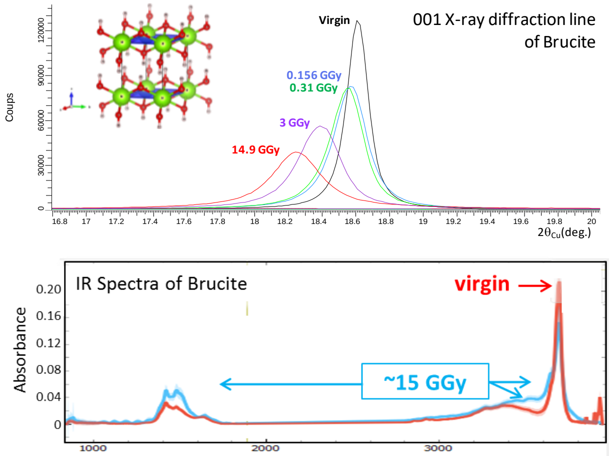

Figure: (top) Evolution of the 001 X-ray diffraction line of brucite with absorbed dose; (bottom) IR spectra of a non-irradiated and an electron irradiated brucite to a very high dose. Results show little chemical modifications of O-H bonding and preservation of the overall crystal structure. The modifications are confined to the H-sublattice.

References:

[1] M.-N. de Noirfontaine et al. J. Nucl. Mater. 509 (2018) 78-93.
[2] M.-N. de Noirfontaine et al. Submitted to Appl. Clay Sci.

Acknowledgements:

The authors would like to thank the EMIR French accelerator network for radiation beam time.

Keywords: Layered hydroxides, Model clay mineral, Radiation damage

IR spectro-microscopy and imaging

EVIDENCE FOR MOLECULAR STRUCTURAL VARIATIONS IN THE CYTOARCHITECTURES OF A JURASSIC PLANT

Yuangao Qu[1,2]*, Nicola McLoughlin[3,4], Mark. A. van Zuilen[5],
Martin Whitehouse[2], Anders Engdahl[6], and Vivi Vajda[2]**

[1]Institute of Deep-Sea Science and Engineering, Chinese Academy of Sciences, Sanya 572000, China; [2]Swedish Museum of Natural History, 114 18 Stockholm, Sweden; [3]Department of Geology, Rhodes University, Grahamstown 6139, South Africa; [4]Albany Museum, Grahamstown 6139, South Africa; [5]Equipe Géomicrobiologie, Institut de Physique du Globe de Paris, Sorbonne Paris Cité, UMR 7154 CNRS, Université Paris Diderot, 75013 Paris, France; [6]MAX IV Laboratory, Lund University, SE-221 00 Lund, Sweden.

*quyg@idsse.ac.cn, **vivi.vajda@nrm.se

In this study, we investigate the molecular structural characteristics of organic remains in various cellular organelles from a 180 Ma Jurassic royal fern belonging to the Osmundaceae family of ferns and compare their carbon isotopic compositions to a now-living species of royal fern (*Osmunda regalis*). We discovered molecular structural variations indicated by Raman and infrared spectral parameters obtained from various fossilized cellular organelles. The organic remains preserved in the chromosomes and cell nuclei show marked structural heterogeneities compared to the cell walls during different stages of the cell cycle. The fossil and extant fern have similar δ13C values obtained from bulk samples, supporting evolutionary stasis in this plant lineage and an unchanged metabolic pathway of carbon assimilation since the Jurassic. The organic remains in the cellular organelles of the fossil seem to be less heterogeneous than those in the extant fern, likely due to the preferential preservation of certain cellular compounds during fossilization. Taphonomic processes appear to have diminished the subcellular isotopic heterogeneities. Our research sheds light on the functioning of ancient plant cellular organelles during mitosis, provides insights to the taphonomic processes operating at molecular and isotopic levels, and shows the practicability of *in situ* techniques in studying the evolution and behaviors of ancient cells.

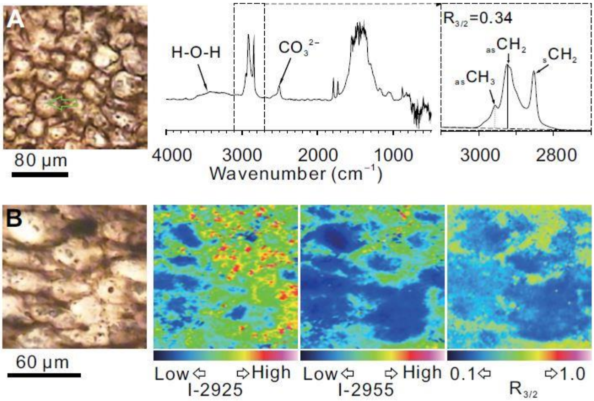

Figure: Examples of micro Fourier-transform infrared spectroscopy spectra and maps obtained from a fossil fern. A: Spectrum obtained from location illustrated by arrow; enlarged parts are used to calculate branching index R3/2 (intensity ratio of the 2955 cm^{-1} band versus 2925 cm^{-1} band) of carbon chains. as—asymmetric, s—symmetric. B: Maps of intensity of 2925 cm^{-1} (I-2925) and 2955 cm^{-1} bands (I-2955) and R3/2, indicating strength of asymmetric vibrations of CH2, CH3, and R3/2, respectively.

References:

[1] Geology 47: 325–329. 2019.

Keywords: Fossil plant, infrared microspectroscopy, cytoarchitecture

IR spectro-microscopy and imaging

IN SITU NANO-FTIR CHARACTERIZATION OF NON-AQUEOUS LITHIUM-O_2 CELLS

Leticia F. Cremasco[1], André N. de Miranda[1], Chayene G. Anchieta[1],
Lorrane C. C. B. Oliveira[1], Julia P. de Oliveira, Bruno A. B. Francisco[1],
Cristiane B. Rodella[2], Gustavo Doubek[1]

[1]*Universidade Estadual de Campinas, Faculdade de Engenharia Química, 13083-852, Campinas, Brazil;*
[2]*Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970, Campinas, Sao Paulo, Brazil.*
doubek@feq.unicamp.br

Batteries are the main technological barrier for the large-scale adoption of electric propulsion. In this scenario, the lithium-air battery system has potential to provide a capacity comparable with fossil fuels like gasoline. However, there is still no scientific consensus that allows the elaboration of a robust project for the system mainly due to the lack of detailed knowledge about the mechanisms involved in its operation[1]. The combination of electrochemical measurements with spectroscopy methods, *in situ* techniques and the integration of multiples characterizations (Raman, XPS, XRD, FTIR) is crucial towards a better understanding of these mechanisms[2]. In situ characterization methods are important tools in the process of explaining some scientific issues regarding Li-O_2 technology and providing a direction to future prospective[2]. Through the data given by the operando nano-FTIR technique, we intended to understand the topographic modifications on the electrode surface while these species are being formed/decomposed, especially concerning electrolyte degradation. It can provide a deeper understanding regarding the electrochemical performance of the working cell and thus insights for material development in device design for the lithium-air technology. A cell was machined especially for the execution of the intended experiments as the cell could not be closed as in the conventional lithium-air systems. The electrode surface was polished until it reached a rugosity of <30 nm and the active carbon nanotubes ink deposited by the spin coating technique. A portable potentiostat/galvanostat (VersaStat 3) was connected to the cell for cycling current and potential control. One of the biggest challenges was to align the practical restrictions of the nano-FTIR technique with the demands of the lithium-air technology. The oxygen reduction reaction takes place in areas where three phases co-exist: solid carbon surface, for the electron transfer to happen; liquid, with the electrolyte that conduces lithium ions and the oxygen to react. Since it is exactly in these areas that the modifications occur, it is necessary that that the AFM tip access regions with certain porosity (electrode carbon matrix) and relative wettability (electrolyte). Despite these technical restrictions, we were able to study some regions. These regions were close to the electrode channels, where we could have a satisfactory amount of the liquid phase, with lithium ions, dissolved oxygen and carbon. Considering that we were working with an open system and aware of the presence of components that are contaminants to the Li-O_2 cells, FTIR spectra show relevant evidence that the system can be studied by this technique, presenting peaks that are consistent with the byproducts expected.

References:

[1] G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, and W. Wilcke. J. Phys. Chem. Lett. 1 (2010).
[2] Feng, N.; He, P.; Zhou, H. Advanced Energy Materials, 6, 9 (2016).

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Keywords: lithium-O_2; batteries; nonaqueous; nano-FTIR

MIE CORRECTION OF SPECTRA FROM SILICA BEADS EMBEDDED IN RESIN MATRIX

J. Solheim[1]*, S. Sirovica[2], O. Addison[3,4], A. Kohler[1]

[1]Faculty of Science and Technology, Norwegian University of Life Sciences, Ås, Norway; [2]Aston Institute of Materials Research and Aston Research Centre for Healthy Ageing, University of Aston, Birmingham, B4 7ET, UK; [3]Biomaterials Unit, School of Dentistry, University of Birmingham, Birmingham, B4 6NN, UK; [4]Faculty of Medicine and Dentistry, University of Alberta, Edmonton, Canada.
**johanne.heitmann.solheim@nmbu.no*

Strong scattering effects affect the in infrared vibrational absorbance spectra of samples where the morphology is changing on a scale comparable to the incident radiation. They have been interpreted as Mie scattering [1] and are particularly strong when the shape of the sample is approximately spherical. Mie scattering introduces broad oscillatory structures in the baseline, as well as peak shifts due to dispersion in the refractive index of the sample. When these features are present in the absorbance spectra, the spectral analysis is severely hampered and it is therefore desirable to remove the Mie scattering signatures from the spectra.

Since the EMSC-based Mie correction approach was introduced in 2008 [2], various methods have been proposed for removing Mie scattering from infrared absorbance spectra [3, 4]. We recently published an open source algorithm that introduced a stop criterion for the number of iterations in the iterative algorithm, and we demonstrated that the new algorithm converges fast [5]. The new algorithm proceeds until an error is minimized. The current state of the art Mie correction algorithm, the ME-EMSC code, has proven to successfully model and remove Mie scattering from infrared spectra of biological samples [5].

In this study, we apply the ME-EMSC code to infrared hyperspectral imaging data of non-biological samples. We demonstrate that strong scatter distortions in wide-field hyperspectral images of silica beads embedded in a resin matrix can be corrected by the ME-EMSC algorithm. The infrared data were acquired with a multi-beam synchrotron source coupled with an IR microscope at the IRENI beamline. The ME-EMSC algorithm takes into account the full extinction efficiency, which is considerably more computationally expensive than the approximation applied in the Mie correction algorithm of Bassan et al. [3]. Although the implementation of the full extinction efficiency increased the model complexity, we were able to decrease the computation time by optimizing the algorithm. Further, we considered practical issues for the treatment of infrared images containing large amounts of spectra, such as filtering of input spectra for the ME-EMSC optimization and a quality test of output spectra. In the present study, we suggest strategies for automated quality control of input and output spectra for the ME-EMSC algorithm.

References:

[1] Mohlenhoff, B., Romeo, M., Diem, M., & Wood, B. R. (2005). Biophysical journal, 88(5), 3635-3640.
[2] Kohler, A., Sule-Suso, J., Sockalingum, G. D., Tobin, M., Bahrami, F., Yang, Y., ... & Martens, H. (2008). Appl. Spectrosc., 62(3), 259-266.
[3] Bassan, P., Kohler, A., Martens, H., Lee, J., Byrne, H. J., Dumas, P., ... & Gardner, P. (2010). Analyst, 135(2), 268-277.
[4] van Dijk, T., Mayerich, D., Carney, P. S., & Bhargava, R. (2013). Appl. Spectrosc., 67(5), 546-552.
[5] Solheim, J., Gunko, E., Petersen, D., Großerüschkamp, F., Gerwert, K., & Kohler, A. (2019). J. Biophotonics, e201800415.

Keywords: Mie scattering, infrared images, preprocessing

IR spectro-microscopy and imaging

RESEARCH PROGRESS ON INFRARED BEAMLINE AT NATIONAL SYNCHROTRON RADIATION LABORATORY

Zeming Qi[1], Chuansheng Hu[1], Chengxiang Li[1]

[1]University of Science and Technology of China, National Synchrotron Radiation Laboratory, 230029, Hefei, China; [2]University of Science and Technology of China, Department of Physics, 230029, Hefei, China
[3]Zhejiang University,Institute of Geology and Geophysics, School of Earth Sciences, 310027, Hangzhou, China
**zmqi@ustc.edu.cn*

The Hefei light source (HLS) at National Synchrotron Radiation Laboratory (NSRL),China was fully upgraded to HLS II in 2016. Following the machine upgradtion, the infrared beamline was reconstructed to improve its performance. Experimental techniques like variable temperature reflection spectroscopy, in-situ infrared microspectroscopy and high-pressure infrared spectroscopy have been developed for user researches. Here, we summarize some current scientific research progresses at infrared beamline which covers materials science, physics, chemistry and geoscience. They include: (1). Quantum Control of Graphene Plasmon Excitation and Propagation[1]: Quantum mechanical effects of single particles can affect the collective plasmon behaviors substantially. By combining far infrared spectroscopy and near-field infrared microscopy, the quantum control of plasmon excitation and propagation in graphene is demonstrated by adopting the variable quantum transmission of carriers at Heaviside potential steps as a tuning knob. (2). Oxygen electrocatalysis[2]: High-efficiency and low-cost noble-metal-free NiFe MOF-based bifunctional oxygen electrocatalysts were developed by a facile and controllable strategy based on photoinduced lattice strain. Synchrotron infrared operando microscpectroscopy technique was used to probe the catalytic mechanism. The result reveals the formation of a superoxide intermediate and the structural surface evolutions during oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). (3). Hydrogen sites in olivine at high temperature and high pressure[3]: Fingerprinting hydrogen storage sites in olivine at high temperature and high pressure is fundamental to understand water distribution and its impact on the upper mantle. By in situ high-temperature and high-pressure infrared spectroscopic techniques, hydrogen storage sites in the natural olivine and synthetic Fe-free forsterite were investigated. We find that hydrogen does not transfer between storage sites with increasing temperature, but displays disordering at temperatures over 600°C. In contrast, pressure can induce re-configuration of hydrogen storage sites corresponding to the 3610 and 3579 cm^{-1} bands. Hydrogen storage sites also exhibit disordering at high pressure. The disordering and re-configuration of hydrogen storage sites at high temperature and high pressure favor better understanding of the water effects on physical properties of olivine.

References:

[1] Dongli Wang, Xiaodong Fan, Xiaoguang Li. et al. Nano Letters, 18,1373 (2018).
[2] Weiren Cheng, Xu Zhao, Hui Su, et al. Nature Energy, 4, 115 (2019).
[3] Yan Yang, Wendi Liu, Zeming Qi et al. American Mineralogist, 104, 878 (2019).

Keywords: Graphene Plasmon, in-situ infrared microspectroscopy, high-pressure infrared spectroscopy

IR spectro-microscopy and imaging

SYNCHROTRON MICROSCOPY STATION UPGRADE FOR IRIS BEAMLINE

L. Puskar[1]*, J. Kneipp[2], U. Schade[1]

[1]Helmholtz-Zentrum Berlin, EM-ALTS, 12489 Berlin, Germany; [2]Humboldt-Universität zu Berlin, Department of Chemistry, 12489, Berlin, Germany.
**ljiljana.puskar@helmholtz-berlin.de*

A project proposal for an upgrade of the microscopy station of the IRIS Beamline at Helmholtz-Zentrum Berlin [1] has recently been approved by the German Federal Ministry of Education and Research (BMBF) funding. Here we present the new BMBF project entitled: Connecting Scales in Vibrational Imaging: Synchrotron Microscopy, which is a joint collaborative research effort between Humboldt-Universität-Berlin and HZB.

The aim of this project is the construction of a new Synchrotron Microscopy Station for spatial-, and polarization-resolved infrared spectroscopy at the IRIS beamline of BESSY II with the additional capability to record Raman spectra from the same sample spot. The unique combination of methods will allow to acquire data across a broad range of lateral resolutions to account for broad sample heterogeneity. This is ensured by combining diffraction limited mid-IR microscopy and imaging (providing ~5-10 µm resolution) and near-field IR nanospectroscopy beyond the diffraction limit (10-20 nm resolution). Simultaneous Raman scattering, excited in the visible, and in parallel vibrational linear dichroism (VLD) imaging [2] will provide additional and complementary information on the samples.

Thereby, the new station can connect different levels of understanding of a vast range of complex biological and artificial samples, for example of biomedical origin and new hybrid materials. The approach utilizes new concepts for more sensitive optical spectroscopy and nanoscopy, in particular plasmons and phonons of nanostructures, which will further enhance the performance and range of applications at the beamline.

References:

[1] U. Schade, A. Röseler, E.H. Korte, et al., Review of Scientific Instruments, 73, 1568 (2002).
[2] M. Schmidt, J.S. Lee, U. Schade, Infrared Physics & Technology 53, 157 (2010).

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Keywords: Vibrational Microscpectroscopy, Vibrational Linear Dichroism, Imaging, Nanospectroscopy.

Nanoscale resolved synchrotron IR analysis

HERTZIAN FIELDS AND TUNING SUBDIFFRACTİONAL INFRARED POLARITONS BY ENGINEERED METASURFACE ON BORON NITRIDE

Flávio Feres[1,2]*, Ingrid D. Barcelos[1], Rafael Mayer[1],
Raul de O. Freitas[1], Francisco C. B. Maia[1]**

[1]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970, Campinas, Sao Paulo, Brazil; [2]São Paulo State University, Rio Claro (UNESP/IGCE), Brazil.
**flavio.feres@lnls.br, **francisco.maia@lnls.br*

The light-matter interaction in two-dimensional photonics crystals (2D-PC) occurs, primarily, via formation of polaritons, *quasi*-particules with subdiffractional wavelength originating of the coupling between photon and intrinsic vibrations of the materials, like phonons and plasmons. We use Synchrotron Infrared Nanospectroscopy (SINS) to study hyperbolic phonon polaritons (HP^2) in 2D-PCs crystals of hexagonal boron nitride (h-BN) lying on metallic (Au and Ag), dielectric (SiO_2) substrates and on SiO_2/Au metasurfaces. The HP^2 modes are interpreted as Hertzian dipole waves, which behave differently depending on the substrate type. On metal, the wavelength of in-plane polarized HP^2s is shortened, whereas, for out-of-plane polarized ones, the wavelength is enlarged. On the dielectrics, the opposite is observed. We exploit this property, thus, in the metasurface by varying the thickness of the SiO_2 layer to achieve wavelength tuning over more than 2 micrometers that is a record compared with tuning obtained with devices.

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Keywords: Hexagonal Boron Nitride, hyperbolic phonon-polaritons, SINS

OPTICAL BOW-TIE SLOT ANTENNA AS BROADBAND POINT SOURCE FOR POLARITONS LAUNCHING

Rafael A Mayer[1,2]*, Francisco C. B. Maia[2], Ingrid D. Barcelos[2], Raul O. Freitas[2]

[1]Universidade Estadual de Campinas, Instituto de Física Gleb Wataghin, 13083-859, Campinas, Brazil;
[2]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970, Campinas, Sao Paulo, Brazil.
**rafael.mayer@lnls.br*

Optical antennas, which converts free propagating light into highly confined electromagnetic fields, have been applied to nonlinear optics [1], biochemical sensing [2,3], metamaterials [4], but quite seldom in polaritonics. For instance, nano-infrared-spectroscopy is often used to probe polaritons in 2D crystals, but it offers the difficulty of having multiple polaritonic sources, such as AFM metallic tip, devices metal contacts and the crystal edges. In this work, we propose a bow-tie slot antenna that efficiently launches phonon-polaritons in hexagonal-boron-nitride (hBN). Through finite-difference-time-domain (FDTD) simulations [5], we were able to calculate the antenna's response in the infrared region. The antenna’s geometry was improved by matching its resonance with hBN’s Restrahlen bands, where it exhibits phono-polaritons activity. Simulated polaritonic wavefronts showed circular-like propagation which indicates that polaritons are generated from a single point source.

References:

[1] Palomba, S., Danckwerts, M., & Novotny, L. (2009). Nonlinear plasmonics with gold nanoparticle antennas. Journal of Optics A: Pure and Applied Optics, 11(11), 114030.
[2] Cheng, F., Yang, X., & Gao, J. (2015). Ultrasensitive detection and characterization of molecules with infrared plasmonic metamaterials. Scientific reports, 5, 14327.
[3] van Zanten, T. S., Lopez-Bosque, M. J., & Garcia-Parajo, M. F. (2010). Imaging Individual Proteins and Nanodomains on Intact Cell Membranes with a Probe-Based Optical Antenna. Small, 6(2), 270-275.
[4] Chen, Y., Chen, Y., Chu, J., & Xu, X. (2017). Bridged bowtie aperture antenna for producing an electromagnetic hot spot. Acs Photonics, 4(3), 567-575.
[5] Lumerical, F. D. T. D. (2016). Solutions.

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Keywords: Optical antenna, polaritons, heterostructure

Nanoscale resolved synchrotron IR analysis

ROLE OF METAL IONS IN PROTEIN AGGREGATION RELATED TO ALZHEIMER'S DISEASE

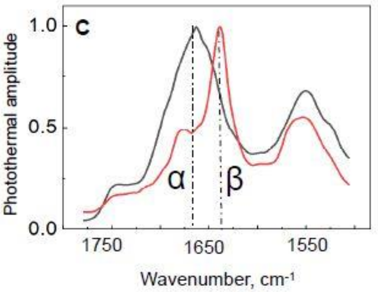
Anders Engdahl[1,2], Nadja Gustavsson[1], IsakMartinsson[1], Angel Rodriguez Fernandez[2], Christophe Sandt[3], FerencBorondics[3], Gunnar Gouras[1], Oxana Klementieva[1].

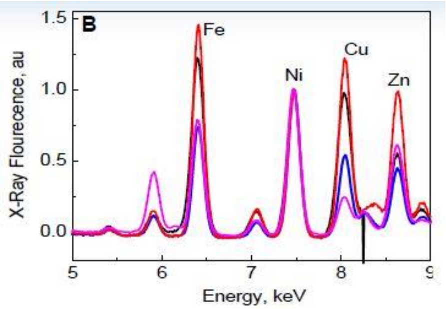
[1]Department of Experimental Medical Science, Lund University, Sweden, [2]MAX IV Laboratory, Lund University, Sweden, [3]Synchrotron SOLEIL, France.
**anders.engdahl@med.lu.*

Alzheimer's disease (AD) is the most common age-related neurodegenerative proteinopathy. Due to lack of understanding of molecular mechanisms behind AD, we do not have effective treatments to cure or prevent this terminal disease. Protein aggregation and metal dyshomeostasis are tightly linked to AD pathology. However, pathological mechanisms have to bee lucidated. We hypothesize that metal dyshomeostasis may trigger aberrantage-related protein aggregation and therefore launch AD development. Our aim is to study accumulation of metal ions (Cu, Fe, and Zn) and Aβ aggregation in primary neurons of AD transgenic mouse models.

Metal ions accumulations were studied by synchrotron-based X-ray fluorescence nanospectrocopy(SR-XRF), scanning of X-ray ptychography, and optical photothermal infrared (OPTIR) spectroscopy. Microspectroscopy was used to locate β-sheet structures directly inprimary neurons at subcellular level.

For the first time, we imaged metal distribution and protein structure at sub-micron resolution in AD transgenic neurons. Our results show changes in metal ions distribution related to AD pathogenesis.However more experiments are required to understand how metal ions might be influenced by β-sheet structures or amyloid-β neurotoxicity.





Keywords: Alzheimer's disease, metals protein aggregation, dyshomeostasis

Nanoscale resolved synchrotron IR analysis

UNRAVELING PHASE SEPARATION AT NANOSCALE IN LIGHT EMITTING ELECTROCHEMICAL CELLS BY IR-SNOM

B. B. M. Torres[1]*, F. C. B. Maia[2], R. O. Freitas[2], D. T. Balogh[1]

[1]Universidade de São Paulo, Instituto de Física de São Carlos,13566-590, São Carlos, Brazil; [2]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970, Campinas, Sao Paulo, Brazil.
**brunobassi@ifsc.usp.br*

Light emitting electrochemical cells (LEC) are luminescent devices similar to light emitting diodes (LED), however their principle of operation is completely different. In LECs, the active layer is composed by at least two different materials: a solid electrolyte and an emissive material. For polymeric LECs, usually the solid electrolyte is based on polyethylene oxide (PEO) and a lithium salt while the emissive material is a semiconducting polymer [1]. As polymers with dissimilar structures and because of the strong crystalline character of PEO, it is expected some phase separation. Due to fast drying imposed by the methods used for thin film production, this phase separation is at nanoscale. In this case, IR-SNOM is a technique that allows us to probe chemical information at this scale. The setup used was assembled at IR1 beamline at UVX LNLS. At first, we investigated only the PEO-Li salts mixture in order to assure if there was any phase separation between pure PEO and PEO-Li salt complex. We found no evidence of such phase separation but it is still an open subject because PEO-Li complex vibration modes are very weak and IR-SNOM signal at the time of the measurement does not had a sufficient noise/signal ratio for this evaluation. After, we analyzed thin films of PEO-Li salt with a polyfluorene derivative, i.e. the actual active layer in a LEC. Despite the complex morphology of such mixture it was possible to precisely correlate structures in the height and AFM phase images with the chemical composition gathered by IR-SNOM. It can be seen that PEO retains its typical fibrillar morphology while the polyfluorene derivative has a more globular one, suggesting that PEO is a continuous phase that limits polyfluorene domains.

References:

[1] Van Reenen, S. et al. J. Am. Chem. Soc. 132, 13776–13781 (2010).

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Keywords: light emitting electrochemical cells, infrared, snom, phase separation

Special IR Techniques

GENETIC ALGORITHMS APPLIED TO THE CONTROL OF MOLECULAR DYNAMICS

Antonio C. P. Neto[1,2]*, Emanuel F. de Lima[1]

1 Universidade Federal de São Carlos, Departamento de Fisica, 13565-905, São Carlos, SP, Brazil; 2 Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970 Campinas, Sao Paulo, Brazil
**netopiccino@gmail.com*

The dynamics of atoms and molecules under time-dependent external fields have been studied extensively in recent decades, due to experimental advances in the production of intense femtosecond-scale laser pulses. Thus, with the proper knowledge of the modulation of these pulses, several intra and intermolecular processes, such as vibrational excitation, dissociation, and even chemical reactions, can be controlled. Among the many possible methods for optimizing the temporal evolution of the initial state density to a desired quantum state configuration, genetic algorithms are among those that most efficiently map the configuration space, looking for global maxima and minima.[1] The space to be mapped by the genetic algorithm consists of numerical solutions of the time-dependent Schrödinger equation due to the presence of an interaction field-dependent Hamiltonian.[2] In the present work, a temporal propagation algorithm was implemented to simulate the vibrational excitation of the OH bond of water through femtosecond laser pulses in the infrared. And a genetic algorithm for the optimization of these pulses was also studied. Measurement techniques used in FELs, such as pump-probe measurements, can benefit from similar algorithms.

References:

[1] Pang, T. (2006). An Introduction to Computational Physics. Cambridge: Cambridge University Press. doi:10.1017/CBO9780511800870

[2] E. F. Lima and J. E. Hornos, The Journal of Chemical Physics, 125, 164110 (2006), https://doi.org/10.1063/1.2364502

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Keywords: genetic algorithms, molecular dynamics, femtosecond laser pulses in IR.

Special IR Techniques

PRESSURE RESPONSE OF THE METAL-ORGANIC FRAMEWORK MIL-101 FILLED WITH METAL NANOPARTICLES

A. Celeste[1,2]*, A. Malouche[2], F. Borondics[1], B. Joseph[3], C. Zlotea[2], F. Capitani[1]

[1]Synchrotron SOLEIL, L'orme des Merisiers, 91192 Saint-Aubin, Gif sur Yvette Cedex, France; [2]Institut de Chimie et des Materiaux Paris-Est, CNRS UMR 7182, UPEC, 2-8, rue Henri Dunant, 94320 Thiais, France; [3]Elettra-Sincrotrone Trieste - S.S. 14-km 163,5, 34149 Basovizza, Trieste, Italy.
**anna.celeste@synchrotron-soleil.fr*

Metal–Organic Frameworks (MOFs) form a versatile class of porous crystalline hybrid materials where metal ions or metallic clusters are connected by organic ligands. Due to the large variety of metals and organic linkers that can be used, MOFs have a large physical and chemical tunability. This allows the design of specific nanometer-scale framework geometries with desired pore structures. For these reasons, MOFs have represented so far the ideal materials for a large number of applications such as gas storage, gas/liquid separation, drug delivery, catalysis, etc [1]. Their tunable and porous nature makes these materials suitable for confining nanometric objects. The insertion of guest nanoparticles (NPs) within porous MOFs represents an effective way to stabilize them and fine-tune the functionality of the host [2]. The porous host can interact with the confined particles due to chemical bonding and steric effects. This interaction can be altered by an external pressure by tuning the balance between weak (i.e. Van der Waals) and strong (covalent) interactions and changing the overall surface-to-volume ratio, thus modifying both the chemical reactivity and the mechanical properties [3]. Among all the MOFs, the mesoporous chromium (III) terephthalate MIL-101 has a rigid zeotype crystal structure with two types of quasi-spherical cages, with pore diameters close to 29 and 34 Å [4]. Recently, we have successfully embedded Pd NPs with an average diameter of 1 nm (around 30-40 atoms per cluster) into MIL-101, for the first time with high metal loadings, up to 20 wt% (i.e. the Pd to sample mass) [5]. Here, we investigate the effect of high pressure on empty MIL-101 and x-Pd@MIL-101with 5 – 20 wt% by synchrotron-based infrared (IR) spectroscopy and x-ray diffraction (XRD) in the 0-10 GPa pressure range. IR spectra were collected in a large energy range to obtain a complete picture of the vibrational dynamics of both the inorganic cluster and the organic linker. To the best of our knowledge, this is the first time the a mesouporous MOF such as MIL-101 is studied at high pressure. We found that, although the large pore diameter, empty MIL-101 shows a high structural stability under compression with the lack of amorphisation in the pressure range explored, although signs of disorder and strain are detected. IR measurements show that the vibrational modes of the organic linker are still present up to 10 GPa, thus confirming the endurance of the local molecular structure. No phase transitions were observed contrary to what reported for the microporous chromium benzenedicarboxylates MIL-53 which shows a phase with collapsed pores [6]. From a preliminary analysis, the presence of Pd nanoparticles inside the MOF pores results in a decreased lattice compressibility but does not alter the overall structural stability in the investigated pressure range. However, the pressure dependence of the Cr-O vibrational frequency is affected by the Pd NPs filling, indicating that local effects are present.

References:

[1] G. Ferey, Chem. Soc. Rev. 37, 191–214 (2008).
[2] C. Roesler, R. A. Fischer, Crystengcomm 17, 199–217 (2015).
[3] P. Ramaswamy et al., J. Mater. Chem. A 5, 11047–11054 (2017).
[4] G. Férey et al., Science 309, 2040 (2005).
[5] A. Malouche et al., J. Mater. Chem. A 5, 23043–23052 (2017).
[6] P. G. Yot et al, Chem. Sci., 7, 446 (2016).

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Keywords: metal organic framework, nanoparticles, high pressure

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