WIRMS 2013

CONFERENCE PROGRAM

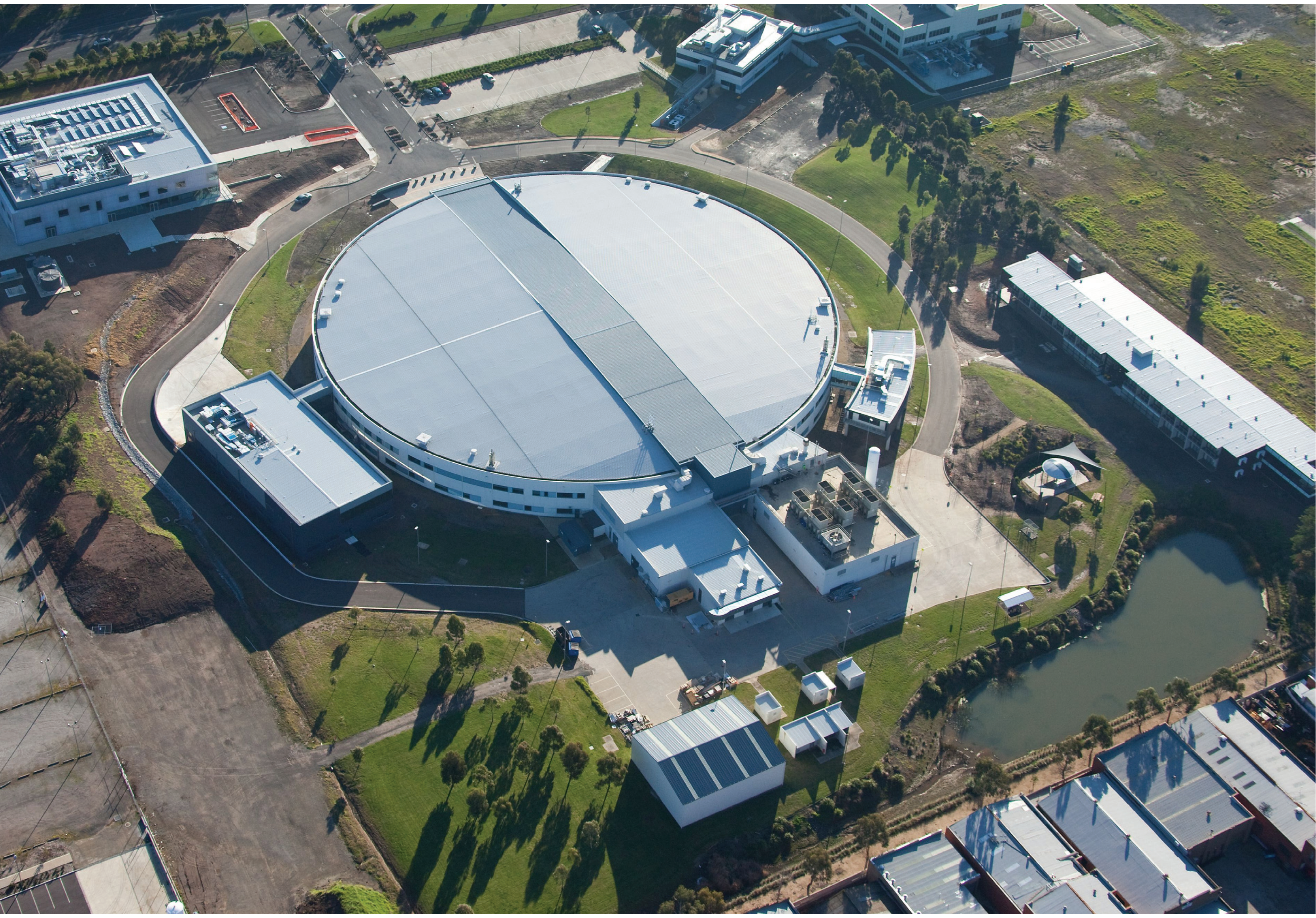
10-14 NOVEMBER 2013
MANTRA / LORNE VICTORIA

BRUKER

MASSIVE

HOSTED BY
Australian Synchrotron

www.wirms2013.com.au



Welcome

As host of the 7th International Workshop on Infrared Microscopy and Spectroscopy with Accelerator Based Sources, WIRMS, the Australian Synchrotron welcomes you in joining scientists from Australia and around the globe for what promises to be a stimulating event at the Mantra Erskine Resort, Lorne, on the Great Ocean Road.

In the tradition of previous WIRMS conferences, we will be joined by staff and users from many of the Synchrotron and Free Electron Laser IR facilities around the world, including some new facilities represented for the first time at WIRMS. The conference will provide a great opportunity to meet and exchange ideas with IR scientists from a range of scientific fields, and we look forward to joining you in a beautiful location.

Mark Tobin

Australian Synchrotron

On behalf of the WIRMS Local Organising Committee

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Committees

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Conference organiser

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U. Schade (BESSY, Germany)
L. Vaccari (Elettra, Italy)
G.P. Williams (Jefferson Lab, USA)

General Information

Conference Satchel

All WIRMS 2013 delegates will receive a conference satchel including conference materials and other sponsor inserts.

Conference venue contact details

Mantra Lorne
Mountjoy Parade
Lorne, VIC 3232
Telephone: +61 3 5228 9777

Dietary requirements

If you have advised the Conference Secretariat of special dietary requirements, please speak to a member of catering staff at the commencement of each meal break / social function.

Emergency details

In an emergency telephone 000 for Ambulance, Fire Service or Police.

Exhibition opening times

The exhibition will be held in the Foyer and will be open at the following times.

Monday 11 November	9.00am – 5.00pm
Tuesday 12 November	9.00am – 8.00pm
Wednesday 13 November	9.00am – 3.30pm

Lanyards

Sponsored by SWINBURNE UNIVERSITY OF TECHNOLOGY

Lanyards should be worn at all times during WIRMS 2013 for security purposes and to assist the organisers with identifying participants.

Mobile phones and electronic devices

As a courtesy to speakers and your fellow delegates, please switch off your phones and electronic devices during presentations and whilst in session.

Registration desk

The registration desk is located in the main foyer of the Mantra Lorne Conference Centre and will be open at the following times.

Sunday 10 November	11.30am – 8.00pm
Monday 11 November	8.30am – 2.00pm

Smoking

Smoking is not permitted indoors at Mantra Lorne. Smokers must always remain at least 4m from any doorway when smoking. Fines can be imposed for smoking in prohibited places.

Social Program

Welcome Reception

Sponsored by DEAKIN UNIVERSITY AUSTRALIA Worldly; DEAKIN UNIVERSITY AUSTRALIA Worldly Centre for Chemistry and Biotechnology

Sunday 10 November
6:00pm – 8:00pm
Seagrass Lawn, at the Mantra (subject to weather!)

Relax after the journey down to Lorne with colleagues in an informal atmosphere.

One ticket is included with full conference registration.

Additional tickets may be purchased in advance for $45 each.

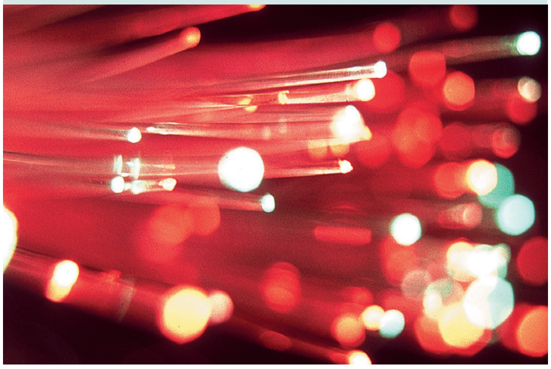
Conference Dinner

Wednesday 13 November
7:00pm – 10:00pm
Lorne Surf Live Saving Club

The social highlight of the conference is the dinner. Enjoy a night of fine food and wine and the opportunity to bond and network.

One ticket is included with full conference registration.

Additional tickets may be purchased in advance for $120 each.



Student Awards

Congratulations to our student award winners:

- Juliane Raasch, Insitute of Micro- And Nanoelectronic Systems, Karlsruhe Institute of Technology GERMANY
- Padraig Minihane, Advanced Light Source USA
- Johanna Howes, University of Technology Sydney AUSTRALIA
- Ken O'Neal, University of Tennessee USA
- Himal Bhatt, Bhabha Atomic Research Centre INDIA

Invited Speakers

Dr Hans Bechtel

Advanced Light Source, Berkeley, USA

Hans Bechtel has over 15 years of experience in spectroscopic methods and analysis. Before joining the ALS infrared beamline staff in 2007, he received his B.S. in Chemistry and Computer Science/Mathematics from Furman University, his PhD in Physical Chemistry from Stanford University, and was a postdoctoral researcher in the Spectroscopy Laboratory at the Massachusetts Institute of Technology. He has co-authored over 50 scientific papers.

Hans will address the conference on: Ultra-broadband infrared nano-spectroscopy with a synchrotron source.

Dr Jean-Blaise Brubach

Synchrotron SOLEIL, France

Jean-Blaise Brubach is a beamline scientist on the AILES beamline at the Synchrotron SOLEIL. He obtained his PhD on the dynamics of water molecules in bulk and in confined systems from the University Paris-Sud, Orsay (Essonne, France), after which he obtained a postdoctoral position at the University of Pharmacology of Châtenay Malabry (Val de Marne, France) for the society Gattefossée S.A., where he studied lipid excipient for drug targeting for drug delivery. In 2005, Jean-Blaise joined the synchrotron SOLEIL (Essonne, France) for the development and the building of the AILES beamline devoted to infrared spectroscopy, in particular in the THz range. Since 2008, he has supported experiments on this beamline and has personal research projects in biochemistry and soft matter.

Jean-Blaise will address the conference on: Recent results on material research using the AILES Beamline.

Dr Paul Dumas

Synchrotron SOLEIL, France

Paul Dumas is responsible for the SMIS beamline at SOLEIL. He has been in the synchrotron field, especially exploiting infrared radiation, since 1990. Together with Gwyn Williams and Carol Hirschmugl, he was involved, in the early 90's in surface science studies using the synchrotron infrared source at NSLS. He was initiated to microscopy by Gwyn Williams and G.L. Carr, and soon after was responsible for the design and construction of a synchrotron infrared micro-spectroscopy beamline at LURE (France). The facility was closed in 2003, and he was charged to design and built an infrared beamline at SOLEIL (SMIS).

His main scientific activity concerns application in biology and biomedical, high pressure research and beamline design.

Talk title in the Extreme Condition session: High Pressure Science using synchrotron infrared microscopy at the SMIS beamline (SOLEIL).

Prof Carol Hirschmugl

University of Wisconsin – Milwaukee, USA

Carol Hirschmugl is a Professor of Physics at the University of Wisconsin – Milwaukee, having obtained degrees from SUNY StonyBrook and Yale University. She has been an Alexander von Humboldt postdoctoral fellow at the Fritz Haber Institute der Max Planck Gesellschaft, and a University of California Presidential postdoctoral fellow at the Lawrence Berkeley National Laboratory. She has pioneered the use of synchrotron based infrared sources for a variety of applications, spending time at the National Synchrotron Light Source (Brookhaven, NY), Advanced Light Source (Berkeley, CA), Synchrotron Radiation Center (Stoughton, WI), ANKA (Karlsruhe, Germany) and European Synchrotron Radiation Facility (Grenoble, France). In particular, her developments have led to using these bright sources for reflection absorption IR spectroscopy to study adsorbate/substrate interactions, and most recently, high definition wide-field infrared imaging at a new NSF-MRI funded facility at the SRC that is called IRENI (Infrared ENvironmental Imaging).

Carol will address the conference on: Three dimensional spectral imaging with synchrotron FTIR spectro-micro-tomography.

Invited Speakers

Dr Yao-Chang Lee

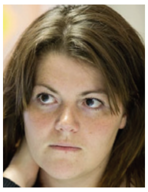
National Synchrotron Radiation Research Center, Taiwan

Yao-Chang Lee, beamline scientist at the BL14A1 beamline of National Synchrotron Research Center, received his Ph.D. in physical chemistry from National Tsing Hua University in Taiwan. He focuses on development of innovative method using multi-cancer marker for early cancer detection by employing FTIR-based imaging methods since joining NSRRC of Taiwan in 2004. Recently, he has successfully demonstrated novel cancer screening methods based on the variance of membrane glycoconjugates, using wax physisorption kinetics (WPK) and FTIR imaging methods, for screening colorectal cancer, oral cavity cancer, gastric cancer, cervical cancer, prostate cancer, and sarcoma. With the help of the fast screening method of WPK, he is further working on the Electric-field-assisted WPK for grading cancers to establish a digital cancer grade system to further aid cancer treatment. Moreover, he is also establishing novel cancer therapies using infrared spectral tip for improving the efficiency of cancer treatments using alternative electric field.

Presentation title under Biomedical Applications session 1: An innovative study of electrostatically-assisted Wax Physisorption Kinetics for Grading Oral Cavity Cancer using Synchrotron-based FT-IR Imaging.

Ms Emeline Pouyet

ESRF, France



Emeline Pouyet is a Ph.D. student at the ID21 beamline at the European Synchrotron Radiation Facility (Grenoble, France). She received her M.S. Degree in Archeometry in 2010 with a project focused on the study of ancient glassmaking processes. At the ID21 beamline, her current activity aims at providing an efficient combination of the synchrotron based techniques: infrared and X-Rays micro-spectroscopy, for the study of artistic paintings prepared as thin sections. As infrared and X-Rays based techniques offer complementary information, the achievement of molecular, elemental and structural characterization on a single complex and heterogeneous sample is a real asset in the Cultural Heritage field. In this context, the interests and challenges of such a combination are evaluated. An important part of her research is focused on optimizing thin section preparation: one of the objectives is to limit any analytical interferences from external materials, in particular for infrared spectroscopy. Moreover, new technical developments are implemented with a particular focus on full-field approach giving full 2D information.

Emeline will address the conference on: Cultural Heritage applications at the European Synchrotron Radiation Facility.

Dr Evan Robertson

La Trobe University, Australia

Dr Evan Robertson qualified for his PhD at Monash University, working with Prof. Don McNaughton in the area of high resolution FTIR spectroscopy from 1993-1995. He then worked as a post-doctoral researcher in laser spectroscopy with Prof John Simons at the University of Oxford from 1996-2000. In 2001, he returned to the School of Chemistry at Monash University to take up simultaneous Logan and ARC research fellowships, which was followed by a lectureship from 2006. In 2009, he moved to La Trobe University where he leads a research group in optical spectroscopy manifested in two major areas: (1) laser-based spectroscopy directed towards understanding gas phase conformation and clusters of biomolecules; and (2) FTIR spectroscopy relevant to planetary atmospheric and interstellar chemistry. His research has led to over 80 journal publications, and is supported by ARC grants, the Australian Synchrotron and National Computing Infrastructure.

Evan will address the conference on: Aerosol nanoparticles and the Far-side of IR spectroscopy.

Prof Peter Weightman

University of Liverpool, UK

Peter Weightman is a surface scientist whose initial research focused on studies of the electronic structure of materials using a variety of laboratory and synchrotron techniques. In particular he developed and applied the techniques of Auger spectroscopy and Reflection Anisotropy Spectroscopy. He played a leading role in establishing the Interdisciplinary Research Centre in Surface Science in Liverpool and became its Director in 1998. He has been an active proponent of the case for a new UK light source, chairing the scientific committee of the 4GLS proposal and developing the biological case for the NLS proposal. Together with Elaine Seddon and Wendy Flavell he achieved funding for a prototype accelerator, ALICE, at Daresbury which is now operating. He constructed and commissioned a terahertz beamline on ALICE and has recently commissioned a scanning near field optical microscope (SNOM) on the infrared free electron laser on ALICE. Peter is using the terahertz beamline [1] and SNOM [2] in studies of biological systems.

Peter will be addressing the conference on: The Daresbury ALICE accelerator and research on the ALICE THz and infrared beamlines.

Dr Gwyn P. Williams

Deputy Director of the Free Electron Laser facility at Jefferson Lab, USA

Gwyn P. Williams is the Deputy Director of the Free Electron Laser facility at Jefferson Lab, and manages the lab's research programs in photon science. He has co-authored 260 research publications and is a Fellow of the American Physical Society. Gwyn was born in England, and has spent all 42 years of his career using synchrotron radiation, first at Daresbury Lab in England, then at Tantalus in Wisconsin, then Brookhaven National Lab in New York, and, for the past 13 years, at Jefferson Lab. Gwyn's research has used particle accelerators as light sources to help understand the fundamental physical behaviour of materials and surfaces. He was the 1990 recipient of an R&D 100 Award for developing a wavefront dividing interferometer for use with such sources. His research has motivated a lifelong parallel development of these ultra-bright light sources as probes, the main focus being in the infrared spectral region. Gwyn currently serves on a number of scientific advisory committees for large facilities around the world. He was on the editorial board of Synchrotron Radiation News for 25 years and is currently a reviewer for Nature, Physical Review and Physical Review Letters.

The topic of his talk will be "40 Years at the NSLS - an IR Footpath to WIRMS 2013".

List of Delegates

Last Name	Title	First Name	Organisation	Country
Allioux	Mr	Francois-Marie	Deakin University	AUSTRALIA
Amarie	Dr	Sergiu	Neaspec GmbH	GERMANY
Appadoo	Dr	Dominique	Australian Synchrotron	AUSTRALIA
Bales	Mr	Andrew	Bruker Biosciences	AUSTRALIA
Bambery	Dr	Keith	Australian Synchrotron	AUSTRALIA
Banas	Dr	Agnieszka	Singapore Synchrotron Light Source	SINGAPORE
Banas	Dr	Krzysztof	Singapore Synchrotron Light Source	SINGAPORE
Bechtel	Dr	Hans	Advanced Light Source	USA
Bhatt	Mr	Himal	Bhabha Atomic Research Centre	INDIA
Billinghurst	Dr	Brant	Canadian Light Source	CANADA
Borondics	Dr	Ferenc	Canadian Light Source	CANADA
Brubach	Dr	Jean-Blaise	Synchrotron SOLEIL	FRANCE
Carr	Dr	G. Lawrence	Brookhaven National Laboratory	USA
Chen	Prof	Xin	Fudan University PRC	CHINA
Cinque	Dr	Gianfelice	Diamond Light Source	UNITED KINGDOM
Cojocari	Dr	Oleg	ACST GmbH	GERMANY
Constable	Mr	Evan	University Of Wollongong	AUSTRALIA
Dillon	Dr	Carolyn	University Of Wollongong	AUSTRALIA
Dredge	Dr	Paula	Art Gallery Of New South Wales	AUSTRALIA
Dumas	Dr	Paul	Synchrotron SOLEIL	FRANCE
Dumee	Dr	Ludovic	Deakin University	AUSTRALIA
Engdahl	Dr	Anders	MAX IV Laboratory, Lund University	SWEDEN
Ennis	Dr	Courtney	Australian Synchrotron	AUSTRALIA
Freitas	Dr	Raul	Brazilian Synchrotron Light Laboratory	BRAZIL
Frogley	Dr	Mark	Diamond Light Source Limited	UNITED KINGDOM
Gasharova	Dr	Biliana	Institute Of Photon Science And Synchrotron Radiation, Karlsruhe Institute Of Technology	GERMANY
Goodall	Dr	Rosemary	Museum Victoria	AUSTRALIA
Hackett	Dr	Mark	University Of Saskatchewan	CANADA
Hawksworth	Ms	Emma	University Of Wollongong	AUSTRALIA
Heimdal	Dr	Jimmy	MAX-Lab	SWEDEN
Hellwig	Prof	Petra	University Of Strasbourg	FRANCE
Heraud	Dr	Philip	Monash Universiy	AUSTRALIA
Hermann	Mr	Peter	Physikalisch-Technische Bundesanstalt	GERMANY
Hirschmugl	Ms	Carol	UW-Milwaukee	USA
Höhne	Dr	Gernot	Bruker Optics Germany	GERMANY
Howes	Miss	Johanna	University Of Technology, Sydney	AUSTRALIA
Huxley	Mr	Derek	Warsash Scientific	AUSTRALIA
Ikemoto	Dr	Yuka	JASRI/SPring-8	JAPAN
Kimura	Prof	Shin-Ichi	Osaka University	JAPAN
Kondyurin	Dr	Alexey	University Of Sydney	AUSTRALIA
Koshiba	Mr	Yuya	Waseda University	JAPAN
Kuroda	Dr	Ryunosuke	National Institute Of Advanced Industrial Science And Technology (AIST)	JAPAN
Lee	Dr	Yao-Chang	National Synchrotron Radiation Research Center	TAIWAN
Lepodise	Mrs	Lucia	University Of Wollongong	AUSTRALIA
Martin	Dr	Michael	Lawrence Berkeley National Laboratory	USA
Martin	Dr	Danielle	Australian Synchrotron	AUSTRALIA
Mathis	Dr	Yves-Laurent	ANKA Synchrotron Radiation Facility, Karlsruhe Institute Of Technology	GERMANY

Last Name	Title	First Name	Organisation	Country
May	Mr	Tim	Canadian Light Source	CANADA
McNaughton	Prof	Donald	Monash University	AUSTRALIA
Minihane	Mr	Padraig	Advanced Light Source	USA
Moens	Prof	Luc	Ghent University	BELGIUM
Moyle	Mrs	Melissa	Australian Synchrotron	AUSTRALIA
Muscat	Ms	Delina	University Of Ballarat	AUSTRALIA
Naiker	Ms	Dini	Leica Microsystems Pty Ltd	AUSTRALIA
Nasse	Dr	Michael	Karlsruhe Institute Of Technology	GERMANY
Nguyen	Ms	Song Ha	Swinburne University Of Technology	AUSTRALIA
Nieuwoudt	Dr	Michel	University Of Auckland	NEW ZEALAND
Okamura	Prof	Hidekazu	Kobe University	JAPAN
O'Neal	Mr	Kenneth	University Of Tennessee	USA
Perucchi	Dr	Andrea	INSTM-UdR Trieste-ST	ITALY
Plathe	Ms	Ruth	Australian Synchrotron	AUSTRALIA
Pouyet	Miss	Emeline	ESRF	FRANCE
Puskar	Dr	Ljiljana	Australian Synchrotron	AUSTRALIA
Qi	Dr	Zeming	National Synchrotron Radiation Laboratory PR	CHINA
Raasch	Miss	Juliane	Insitute Of Micro- And Nanoelectronic Systems, Karlsruhe Institute Of Technology	GERMANY
Reis	Ms	Rackel	Victoria University	AUSTRALIA
Rieger	Mr	Peter	Institute Of Photon Science And Synchrotron Radiation, Karlsruhe Institute Of Technology	GERMANY
Robertson	Dr	Evan	La Trobe University	AUSTRALIA
Sadler-Moyes	Ms	Wendy	BOC	AUSTRALIA
Sakaue	Dr	Kazuyuki	Waseda University	JAPAN
Sali	Mr	Diego	Bruker Optics Italia	ITALY
Schade	Dr	Ulrich	HZB, BESSY II	GERMANY
Silvester	A/Prof	Ewen	La Trobe University	AUSTRALIA
Spiers	Dr	Kathryn	Australian Synchrotron	AUSTRALIA
Taira	Dr	Yoshitaka	National Institute Of Advanced Industrial Science And Technology (AIST)	JAPAN
Takahashi	Dr	Toshiharu	Research Reactor Institute, Kyoto University	JAPAN
Tan	Mr	Eugene	Australian Synchrotron	AUSTRALIA
Tobin	Dr	Mark	Australian Synchrotron	AUSTRALIA
Tuck Lee Augustine	A/Prof	Tan	National Institute Of Education, Nanyang Technological University	SINGAPORE
Uvdal	Prof	Per	MAX-IV Laboratory, Lund University	SWEDEN
Vaccari	Dr	Lisa	Elettra-Sincrotrone Trieste	ITALY
Van Bronswijk	Prof	Wilhelm	Curtin University	AUSTRALIA
Vongsvivut	Dr	Jitraporn (Pimm)	Deakin University	AUSTRALIA
Wallace	Mrs	Leanne	Australian Synchrotron	AUSTRALIA
Webb	Dr	Hayden	Swinburne University Of Technology	AUSTRALIA
Weightman	Prof	Peter	University Of Liverpool	UNITED KINGDOM
Whelan	Miss	Donna	Monash University	AUSTRALIA
Williams	Prof	Gwyn	Jefferson Lab	USA
Wong	Mr	Andy	Monash University	AUSTRALIA
Wood	A/Prof	Bayden	Monash University	AUSTRALIA
Yousef	Dr	Ibraheem	SESAME Synchrotron	JORDAN
Zen	Dr	Heishun	Institute Of Advanced Energy, Kyoto University	JAPAN

Conference Program

Day 1 Sunday 10 November

12:30	Lunch
1:00	**Bruker Opus 7 Workshop**
6:00	Welcome Reception

Sponsored by DEAKIN UNIVERSITY AUSTRALIA Worldly; DEAKIN UNIVERSITY AUSTRALIA Worldly Centre for Chemistry and Biotechnology

Day 2 Monday 11 November

08:50	**Welcome** *Mark Tobin*
09:00	**Introduction** *Session Chair: Mark Tobin*
	Gwyn Williams, Jefferson Lab, USA PLENARY – The IR Footpath to WIRMS 2013
09:30	**THz Facility Development** *Session Chair: Yves-Laurent Mathis*
	Peter Weightman, Liverpool University, UK The Daresbury ALICE accelerator and research on the ALICE THz and infrared beamlines
10:00	*Andrea Perucchi, ELETTRA Synchrotron, Italy* TeraFERMI – The THz beamline of the FERMI Free-Electron-Laser
10:20	*Peter Rieger, ANKA KIT, Germany* Simulations of photon intensity distributions to facilitate design of beamlines at accelerator-based IR/THz sources
10:40	Morning Coffee
11:10	**Coherent Synchrotron Radiation and FELs** *Session Chair: Larry Carr*
	Gianfelice Cinque, DIAMOND Light Source, UK Coherent Synchrotron Radiation in bursting low-α and top-up mode at Diamond: a unique source for spectroscopy in the THz gap 5 to 100 cm^{-1}
11:30	*Jean-Blaise Brubach, Synchrotron SOLEIL, France* Broadband THz spectroscopy using Coherent Synchrotron Radiation (CSR): recent results for high resolution molecular physics and condensed matter studies on the AILES Beamline
11:50	*Juliane Raasch, KIT, Germany* 15 ps temporal resolution of the electric field of Coherent Synchrotron Radiation using a high-Tc $YBa_2Cu_3O_{7-x}$ real-time detection system
12:10	*Brant Billinghurst, Canadian Light Source, Canada* The effect of fill pattern on superradiant synchrotron radiation in the Terahertz region
12:30	Lunch

Sponsored by HiQ; BOC A Member of The Linde Group

2:00 **Cultural Heritage**
Session Chair: Ljiljana Puskar

Emeline Pouyet,ESRF, France
Cultural Heritage applications at the European Synchrotron Radiation Facility

2:30 *David Thurrowgood, National Gallery of Victoria, Australia*
Synchrotron Infrared Microscopy and rediscovering a hidden painting by Edgar Degas

2:50 *Rosemary Goodall, Melbourne Museum, Australia*
Investigation of Historical Dart and Arrow Poisons Using Synchrotron Based Infrared Microscopy and Spectroscopy

3:10 *Per Uvdal, MAX IV Lab, Sweden*
54-Million years old bio-molecules observed in pigment particles in a fossil fish eye

3:30 *Paula Dredge, Art Gallery of New South Wales, Australia*
Examination of Ripolin enamel house paint as used by the artist Sidney Nolan, with synchrotron sourced Infrared microscopy and spectroscopy

3:50 Afternoon Tea

4:20 **Extreme Conditions**
Session Chair: Shin-Ichi Kimura

Paul Dumas, Synchrotron SOLEIL, France
High Pressure Science using synchrotron infrared microscopy at the SMIS beamline (SOLEIL)

4:50 *Hidekazu Okamura, Kobe University*
High Pressure Infrared Studies of Strongly Correlated Electron Systems at SPring-8

5:10 *Himal Bhatt, Bhabha Atomic Research Centre, India*
Optical Conductivity studies on Copper doped Ru1212 at High Pressure

5:30 *Biliana Gasharova, ANKA KIT, Germany*
Phase transformations in the $CaO\text{-}SiO_2\text{-}H_2O$ system: synchrotron IR microscopy at ANKA helps decoding unusual transformation mechanisms

Conference Program

Day 3 Tuesday 12 November

09:00	**Sub-diffraction limit spectroscopy** *Session Chair: Gianfelice Cinque*
	Hans Bechtel, Advanced Light Source, USA Ultra-broadband Infrared Nano-spectroscopy with a Synchrotron Source
09:30	*Yuka Ikemoto, SPring-8, Japan* Infrared Near-field spectroscopy by synchrotorn radiation source at SPring-8 BL43IR
09:50	*Peter Hermann, PTN, Germany* High-resolution imaging and nano-FTIR spectroscopy by using a broadband synchrotron radiation source
10:10	*Sergiu Amarie, Neaspec, Germany* *Sponsored by* neaspec Introducing nano-FTIR – imaging and spectroscopy at 10nm spatial resolution
10:30	Morning Coffee
11:00	**IR Microscopy – Facility Developments** *Sponsored by* BRUKER *Session Chair: Mike Martin*
	Carol Hirschmugl, University of Wisconsin, Madison, USA Three dimensional spectral imaging with synchrotron FTIR spectro-micro-tomography
11:30	*Shin-Ichi Kimura, UVSOR Facility, Japan* Infrared micro-spectral imaging using a linear array detector at UVSOR-III
11:50	*Raul Freitas LNLS synchrotron, Brazil* Synchrotron-based a-SNOM IR endstation at the LNLS: beamline installation and commissioning details
12:10	*Yves-Laurent Mathis, ANKA KIT, Germany* Status of the Infrared Microscopy station at ANKA
12:30	*Ibraheem Yousef, SESAME Synchrotron, Jordan* An Infrared Synchrotron Radiation beamline EMIRA at the Third Generation Light Source SESAME
12:50	Lunch

2:20	**Biomedical Applications 1** *Session Chair: Pimm Vongsvivut*
	Yao-Chang Lee, NSRRC, Taiwan An innovative study of electrostatically-assisted Wax Physisorption Kinetics for Grading Oral Cavity Cancer using Synchrotron-based FT-IR Imaging
2:50	*Lisa Vaccari, ELETTRA Synchrotron, Italy* IRMS and Flow Cytometry: uniqueness and complementarity of these techniques for live cell analysis
3:10	*Phil Heraud, Monash University, Australia* Synchrotrom FTIR spectroscopy discriminates very early differentiation stages in living human stem cells
3:30	Afternoon Tea
4:00	**Biomedical Applications 2** *Session Chair: Carolyn Dillon*
	Donna Whelan, Monash University, Australia Detecting Cell Cycle Related Changes to the Concentration and Conformation of DNA in Single Live Cells at the Australian Synchrotron
4:20	*Mark Hackett, University of Saskatchewan, Canada* A "Stroke of Insight": Coupling Synchrotron Infrared Light, Wide-Field Focal Plane Array Detectors and Stroke Research
4:40	*Keith Bambery, Australian Synchrotron, Australia* Evaluating the resonant Mie scattering extended multiplicative signal correction algorithm (RMieS-EMSC) on synchrotron FTIR spectra of single cells
5:00	*Bayden Wood, Monash University, Australia* Synchrotron FTIR spectroscopy of malaria infected erythrocytes

Conference Program

Day 4 Wednesday 13 November

09:00	**Atmospheric and Environmental Science** *Session Chair: Brant Billinghurst*
	Evan Robertson, La Trobe University, Australia Aerosol nanoparticles and the Far-side of IR spectroscopy
09:30	*Don McNaughton, Monash University, Australia* Synchrotron high-resolution FTIR spectroscopy sorts out the ground state and low wavenumber modes of ketenimine.
09:50	*Johanna Howes, University of Technology Sydney, Australia* Assessing metabolic variation of endosymbiotic and cultured *Symbiodinium microadriaticum* using Synchrotron imaging FTIR spectroscopy
10:10	*Ewen Silvester, La Trobe Unversity, Australia* Investigation of fungal decomposition of leaf lignin using synchrotron infrared microspectroscopy
10:30	*Michel Nieuwoudt, University of Auckland, New Zealand* Imaging the Chemical environments of individual Fluid Inclusions using Synchrotron Fourier Transform Infrared microscopy
10:50	Morning Coffee
11:20	**Far-IR Condensed Phase** Session Chair: Dominique Appadoo
	Jean-Blaise Brubach, Synchrotron SOLEIL, France Recent results on material research using the AILES Beamline
11:50	*Larry Carr, NSLS Brookhaven, USA* Photo-Induced spectroscopy of GaAs in a magnetic field: time-resolved circular dichroism
12:10	*Petra Hellwig, University of Strasbourg, France* Hydrogen bonds and protonation reactions in membrane proteins: a far infrared spectroscopic approach
12:30	*Gernot Hoehne, Bruker Optik, Germany* *Sponsored by* BRUKER Instrumental Developments in Molecular Spectroscopy: New Components, Accessories and Technologies
12:50	Lunch

1:50	**Materials Applications** *Session Chair: Andrea Perucchi*
	Bill van Bronswijk, Curtin University, Australia Detection of Water in Radiation damaged zircon using Synchrotron FTIR-ATR
2:10	*Alexey Kondyurin University of Sydney, Australia* Synchrotron IR imaging of protein coating on vascular stents
2:30	*Song Ha Nguyen, Swinburne University of Technology, Australia* Correlation between the proportion of epicuticular waxes and wettability among various species of dragonfly wing
2:50	*Mark Frogley, DIAMOND Light Source, UK* Infrared Microanalysis of Molecular Deformations in Graphene Oxide Based Materials During Nanomechanical Tensile Tests
3:10	**Time Resolved Studies** *Session Chair: Danielle Martin*
	Ulrich Schade. Helmholtz-Zentrum Berlin, BESSY II, Germany A Fèry Prism based Mid-IR Spectrometer with µs Time Resolution in Single-Shot Mode
3:30	*Ferenc Borondics, Canadian Light Source, Canada* Electrochemical reaction kinetics followed by FTIR spectromicroscopy – Approaching the diffraction limit

Day 5 Thursday 14 November

09:30	Travel To Synchrotron	
12:00	Welcome Talk At Synchrotron	
12:15	Lunch	*Sponsored by* ezzi vision™
1:00	Tour of The Australian Synchrotron	
3:00	Bus Departs Synchrotron	

Conference Abstracts

Welcome and Introduction

08:50 – 09:30

Session Chair – Mark Tobin

08:50

WELCOME

09:00-09:30

GWYN P. WILLIAMS ***Invited Speaker***

The IR Footpath to WIRMS 2013

0900-0930

THE IR FOOTPATH TO WIRMS 2013

GWYN P. WILLIAMS *Invited Speaker*

Jefferson Lab, Newport News, Virginia, 23606 USA

I will look back at the 40-year roadmap that led to the development of IR synchrotron radiation and the large and highly collaborative community that it supports today. The story will be embellished by personal experiences and peppered with surprising coincidences, all of which were critical in building the structure that we have today. The striking birth and early evolution of the IRSR field would not have been possible without the energy and persistence of many individuals from around the world. The continued growth, diversification, and impact of the IRSR field is attributable to an increasingly large number of highly innovative and energetic scientists, and as this meeting unfolds I look forward to learning the many exciting stories that will determine the future.

Work supported by the Office of Naval Research, the Joint Technology Office, the Commonwealth of Virginia, the Air Force Research Laboratory, the US Army Night Vision Lab, and by DOE under contract DE-AC05-06OR23177.

THz Facility Development

09:00 – 10:40

Session Chair – Yves-Laurent Mathis

09:30-10:00

PETER WEIGHTMAN ***Invited Speaker***
The Daresbury ALICE accelerator and research on the ALICE THz and infrared beamlines

10:00-10:20

ANDREA PERUCCHI
TeraFERMI - The THz beamline of the FERMI Free-Electron-Laser

10:20-10:40

PETER RIEGER
Simulations of photon intensity distributions to facilitate design of beamlines at accelerator-based IR/THz sources

10:40-11:10

MORNING COFFEE

0930-1000

THE DARESBURY ALICE ACCELERATOR AND RESEARCH ON THE ALICE THz AND INFRARED BEAMLINES

PETER WEIGHTMAN *Invited Speaker*

Physics Department, University of Liverpool, Oxford Street, Liverpool L69 3BX UK

The ALICE accelerator at Daresbury is an energy recovery linear accelerator. It is equipped with a terahertz (THz) beamline and associated tissue culture facility and an infrared free electron laser (FEL). The FEL has recently been equipped with a scanning near filed optical microscope. The structure and operation of ALICE will be described and brief accounts given of recent research on the Frohlich hypothesis with the THz beamline [1] and a search for a diagnostic of oesophageal cancer using the SNOM [2].

References

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1000-1020

TERAFERMI - THE THz BEAMLINE OF THE FERMI FREE-ELECTRON-LASER

A. PERUCCHI[1], P. DI PIETRO[1] AND S. LUPI[2]

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[2] CNR-IOM and Department of Physics, Sapienza University of Rome, P.le A. Moro 2, 00185 Rome, Italy

TeraFERMI is the THz beamline for pump-probe studies on the femtosecond time-scale, to be constructed at the FERMI Free Electron Laser (FEL) facility. The beamline will make use of the coherent radiation emitted by the electrons already spent from the FEL undulators, before being damped. TeraFERMI will uniquely use passive optical elements and will work in parasitic mode during normal user FERMI-FEL operation. This will result in short, coherent, high power THz pulses to be used as a “pump” beam, in order to modulate structural properties of matter, thereby inducing phase transitions. The intense THz pulses are also associated with a remarkably large transient magnetic field, to be used for controlling and manipulating magnetic states of matter. The modifications produced to the ionic and magnetic structures and the corresponding changes induced in the electronic properties will be probed by means of infrared spectroscopy from THz to visible. The domains of application of TeraFERMI will cover very different fields from solid-state physics to biochemistry.

We discuss here relevant scientific cases, the choice of the source, and the expected performances of TeraFERMI. Through electron beam dynamics simulation we show that the installation of the THz source in the beam dump section provides a new approach for compressing the electron bunch length without affecting FEL operation. Thanks to this further compression of the FEL electron bunch, the TeraFERMI facility is expected to provide THz pulses with 10’s µm wavelength.

Acknowledgement

We acknowledge all the Elettra-Sincrotrone Trieste staff presently contributing to the TeraFERMI design.

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SIMULATIONS OF PHOTON INTENSITY DISTRIBUTIONS TO FACILITATE DESIGN OF BEAMLINES AT ACCELERATOR-BASED IR/THz SOURCES

P. Rieger[1], Y.-L. Mathis[2], B. Gasharova[1] and D. A. Moss[2]

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[2] ANKA Synchrotron Radiation Facility, Karlsruhe Institute of Technology, P.O. Box 3640, Karlsruhe, 76021, Germany

At ANKA we have used the software Synchrotron Radiation Workshop (SRW) [1] as an essential tool for diagnostic of our infrared beamline IR1 and the design of IR2 [2]. The simulations showed that the far-IR/THz edge radiation (ER) can interact with the vacuum chamber walls already inside the bending magnet and thus very close to the electron beam. Unfortunately SRW can't compute wavefronts at large angles of observation and at a close vicinity of the source. As we need to take into account these perturbations for the propagation of the radiation through the entire beamline optics, we started to develop our own code.

The new code makes no approximations and it delivers unaffected solutions of Maxwell equations, like SRW does. However, it can generate the electric and magnetic field vectors for situations like near-field infrared ER, as close to the source as necessary, and calculate the corresponding photon intensity distribution. We can now place an observer plane inside the bending magnet and thus calculate a wavefront at large observation angles prior to the interactions with the chamber, and then use it for further propagation calculations.

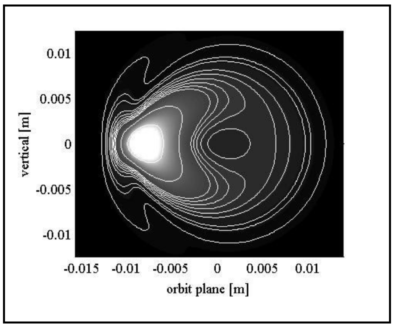

Fig. 1. Spectral energy density of ANKA ER at 300 µm inside the bending magnet vacuum chamber together with the coulomb field of the passing electron.

The new code is not limited to synchrotrons but can be also used for the development of new kinds of IR/THz facilities like our linac-based coherent IR/THz source FLUTE [3]. In this case we can simulate the production and the extraction of ER from a bending magnet exit edge by a mirror placed on the particle's trajectory. In a next step we want to study the interference of this radiation with the transition radiation produced by the electron bunch interacting with the mirror (Fig. 1). Our preliminary results on this new IR/THz source will be also presented.

Acknowledgement

We thank very much Oleg Chubar (NSLS) for his support with SRW and his advice on simulations as well as development of the new code and we would like to thank Markus Schwarz (ANKA) for helpful discussions.

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Coherent Synchrotron Radiation and FELs

11:10 – 12:30

Session Chair – Larry Carr

11:10-11:30

GIANFELICE CINQUE
Coherent Synchrotron Radiation in bursting low-α and top-up mode at Diamond: a unique source for spectroscopy in the THz gap 5 to 100 cm-1

11:30-11:50

JEAN-BLAISE BRUBACH
Broadband THz spectroscopy using Coherent Synchrotron Radiation (CSR): recent results for high resolution molecular physics and condensed matter studies on the AILES Beamline

11:50-12:10

JULIANE RAASCH
15 ps temporal resolution of the electric field of Coherent Synchrotron Radiation using a high-Tc $YBa_2Cu_3O_{7-x}$ real-time detection system

12:10-12:30

BRANT BILLINGHURST
The effect of fill pattern on superradiant synchrotron radiation in the Terahertz region

12:30-14:00

LUNCH

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COHERENT SYNCHROTRON RADIATION IN *BURSTING* LOW-α AND TOP-UP MODE AT DIAMOND: A UNIQUE SOURCE FOR SPECTROSCOPY IN THE THz GAP 5 TO 100 cm^{-1}

G. CINQUE AND M. D. FROGLEY

MIRIAM beamline, Diamond Light Source, Harwell Campus, Chilton-Didcot, OX11 0DE, Oxfordshire, UK

At DIAMOND, the UK Synchrotron Radiation Facility in Oxfordshire, the Multimode InfraRed Imaging And Microspectroscopy (MIRIAM) beamline is operational since December 2009. MIRIAM exploits Diamond Synchrotron Radiation (SR) brightness from a bending magnet source for diffraction-limited IR absorption microanalysis and IR imaging mostly in the mid-IR range. By means of Fourier Transform IR interferometry (FTIR), vibrational absorption spectroscopy is also performed from the visible up to the sub-THz region. Due to the uniquely wide front end and optical design MIRIAM long wavelength cut off is circa 4 mm, and its performances have been used so far up to 2 mm wavelength (i.e. 0.15 THz).

From the initial observation of Coherent SR in storage rings [1], operation in *stable* low-alpha mode has been privileged at SR facilities for boosting the IR photon flux quadratically with the bunch current, i.e. with the idea that the e- bunch length compression close to one millimetre can stimulate CSR emission at that wavelength scale and beyond. Diamond yearly experience in low-alpha mode started for time-resolved X-ray experiments and is summarized in [2]. A first report of the performances achieved via CSR in the Far-IR/THz at MIRIAM is also published [3]. This work refers to an initial characterization of Diamond IR CSR in both *stable* low-alpha mode - like most SR facilities - as well as in the so-called *bursting* mode at higher current density per bunch. The last one is rather unique because broadens the IR spectral range accessible from the 2 mm up to 100 μm wavelength.

This contribution is focused on the actual use of *bursting* versus *stable* CSR (see Figure 1) for FTIR spectroscopy, and to show the performances experimentally achieved at MIRIAM for stable FTIR spectroscopy in the 0.15-3 THz/5-100 cm^{-1} domain, including stability/ reproducibility considerations following the latest upgrade of top-up injection during low-α operation. Applications in condensed matter studies as well as in a broader range of research applications are thus possible via IR dedicated CSR at MIRIAM and beamtime allocation twice a year.

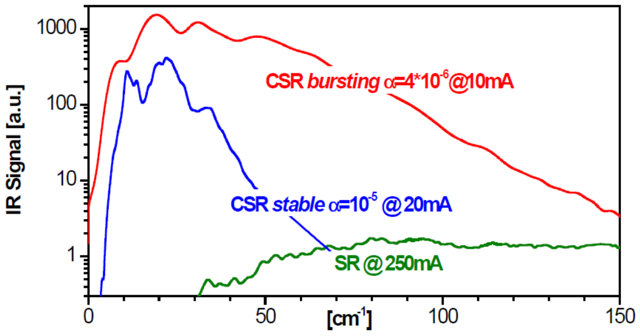

Fig. 1. CSR IR Signal from MIRIAM FTIR shown in scale for different Diamond operation modes.

Acknowledgement

A special thanks to Riccardo Bartolini and Ian Martin from the Accelerator Physics group of Diamond for their invaluable contribution with the e- beam setting in low alpha and top up.

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1130-1150

BROADBAND THz SPECTROSCOPY USING COHERENT SYNCHROTRON RADIATION (CSR): RECENT RESULTS FOR HIGH RESOLUTION MOLECULAR PHYSICS AND CONDENSED MATTER STUDIES ON THE AILES BEAMLINE

P. Roy, [1], J. Barros[1], C. Evain[2], L. Manceron[1], J. B. Brubach[1], M. A Tordeux[1], P. Brunelle[1], L. Nadolski[1]. A. Loulergue[1], M. E. Couprie[1], S. Bielawski[2], C. Szwaj[2], L. Chaix, S. de Brion[3], V. Simonet[3], R. Ballou[3] S. Petit[4], C. Thompson[5], D. Appadoo[6] and D. McNaughton[5]

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On numerous Synchrotron Radiation facilities, THz Coherent Synchrotron emission is exploited as a broadband source for Fourier Transform spectroscopy. For this purpose, the spectral range of the Coherent Synchrotron Radiation (CSR) is widened by reducing the bunch length. In particular coherent emission up to 1 THz is reached with a bunch length equivalent to a few picoseconds emission. The bunch length in a storage ring varies with the current, but in a first approximation, it depends on the energy of the electrons, on the radiofrequency cavity voltage, and on the momentum compaction factor α. This latter parameter defines the relationship between the relative momentum deviation δ of the electrons in the bunch, and the longitudinal spread of the electrons (L) over the average length of one complete orbit of the ring (L_0): $L/L_0=\alpha\delta$. Reducing the momentum compaction factor α is therefore an efficient way to shorten the electron bunches.

The flux of this emission in the sub THz range (up the 10000 times the regular synchrotron emission) is very advantageous for spectroscopy, but when the electron bunch current reaches a threshold, the bunch undergo a self-amplified instability with an irregular evolution in space and time of the electron distribution. The resulting intensity fluctuations lead to artifacts on the FT-based measurements, which strongly limit the use of CSR in particular for high-resolution measurements.

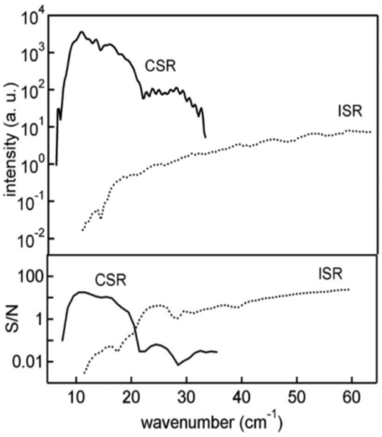

Fig. 1. *Top:* intensity profile of the CSR compared to incoherent synchrotron radiation (ISR). The intensity was normalized for the same current per bunch.
Bottom: signal-to-noise obtained by dividing two successive spectra (10 scans, 1 h, 10^{-3} cm^{-1} resolution) with the same conditions as described above for ISR and CSR.

At SOLEIL however, by screening different currents and bunch lengths, we defined stable CSR conditions for which the signal-to-noise ratio (S/N) allows for measurements at high resolution. The stable CSR allowed us to perform both high resolution spectroscopy as well as optical studies on condensed matter. We will present the source performance as well as various applications such as the study of electromagnons in Langasite, and a high-resolution investigation of the rotational spectrum of the Propynal molecule.

Acknowledgement

The authors acknowledge SOLEIL machine group, and in particular A. Nadji, M. Labat, L. Cassinari, R. Nagaoka, as well as J.-M. Ortega from LCP, ANR, DYNACO, and RASY-COH contract of Triangle de la Physique. This work received support from Egide (Contract No. 24152 QE).

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1150-1210

15 ps TEMPORAL RESOLUTION OF THE ELECTRIC FIELD OF COHERENT SYNCHROTRON RADIATION USING A HIGH-T_C $YBa_2Cu_3O_{7-X}$ REAL-TIME DETECTION SYSTEM

J. Raasch[1], P. Thoma[1], A. Scheuring[1], K. Ilin[1], M. Siegel[1], A.-S. Müller[2], N. Smale[3], E. Roussel[4], C. Evain[4], C. Szwaj[4], S. Bielawski[4], T. Konomi[5], S. Kimura[5], M. Katoh[5], M. Hosaka[6], N. Yamamoto[6], H. Zen[7], K. Iida[8] and B. Holzapfel[8]

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[7] Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan
[8] Leibniz Institute for Solid State and Materials Research Dresden, IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany

The time resolved measurement of single Coherent Synchrotron Radiation (CSR) pulses requires a detection system with picosecond time resolution, a broad spectral range and linear response over a large range of radiation power [1,2].

We have developed an ultra-fast direct detection system for the THz frequency range. Combining the picosecond scaled response mechanism of the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ (YBCO) to THz excitations with broad-band readout we reach a temporal resolution of 15 ps full width half maximum (FWHM). This detection system has shown to fulfil all of the above mentioned requirements. The use of a log-spiral broad band THz antenna enables the detection of CSR signals from 30 GHz up to 3 THz. The dynamic range of YBCO excited with CSR accounts for at least 30 dB [3]. Real-time resolution of CSR single shots was observed at the ANKA and UVSOR-III storage rings. The experimental results are in good agreement with simulations. Figure 1 shows a CSR pulse recorded at ANKA with a FWHM of 17 ps which is above the temporal resolution of our detection system [4].

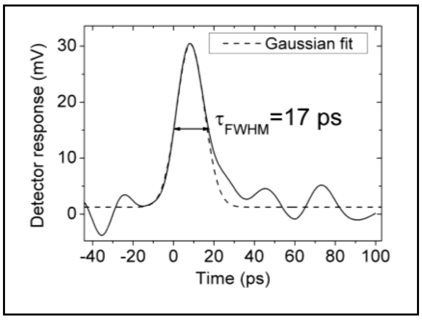

Fig. 1. First observation of real-time evolution of CSR pulse.

In contrast to conventional superconducting bolometers [5], in YBCO detectors the CSR THz spectrum corresponds to sub-gap excitations of magnetic quanta (vortices) typical for type-II superconductors. Therefore the YBCO detector responds to the electrical field of THz radiation while the response of bolometers is determined by the absorbed radiation power. Moreover due to self-generation of vortices the YBCO detector does not require any bias which reduces the noise level of the detector. These properties enable us to follow oscillations of CSR electric fields on a picosecond scale as demonstrated in recent experiments at the UVSOR-III facility.

In this contribution the author will present experimental results acquired at ANKA and UVSOR-III pointing out the high performance of the developed detection system. Furthermore examples of measurements that are feasible only through the vortex-movement based detection of THz radiation will be shown.

Acknowledgement

The authors thank Agilent Technologies and Tektronix for supplying broad-band real-time oscilloscopes for the measurements at ANKA and UVSOR-III.

This work was supported by the German Federal Ministry of Education and Research (Grant No. 05K2010), the French National Research Agency (Grant No. 2010 blanc 042301), the Ministry of Education, Culture, Sports, Science & Technology in Japan (Quantum Beam Technology Program) and the Institute for Molecular Science (International Collaboration Program).

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THE EFFECT OF FILL PATTERN ON SUPERRADIANT SYNCHROTRON RADIATION IN THE TERAHERTZ REGION.

B.E. BILLINGHURST, J.C. BERGSTROM , L. DALLIN, M. DE JONG, T. E. MAY, J. M. VOGT AND W.A.WURTZ

Canadian Light Source Inc., 44 Innovation Boulevard., Saskatoon, S7N2V3, Saskatchewan, Canada

We report high-resolution measurements of superradiance, using coherent synchrotron radiation in the terahertz region from the Canadian Light Source synchrotron and a Michelson interferometer with a nominal frequency resolution of 0.00096 cm^{-1}.

Superradiance arises when a high degree of phase coherence exists between the radiation fields of the individual electron bunches, and manifests itself as a series of narrow spectral peaks at harmonics of the bunch frequency. These conditions were achieved at the Canadian Light Source by operating the synchrotron at an energy of 1.5 GeV, with the momentum compaction adjusted to produce a bunch length of a few picoseconds. Here we focus on the effect of changing the fill pattern of the bunches in the ring. Three fill patterns were used; an uninterrupted fill pattern with 210 buckets filled (denoted as 111111…), a fill pattern with a filled bucket followed by two empty buckets (1001001…) and two filled buckets followed by an empty bucket (11011 …). Each fill pattern produced a unique interferogram and spectrum. A full account of this work can be found in our recent paper in Physical Review Special Topics Accelerators and Beams [1].

Acknowledgement

Research described in this paper was performed at the Canadian Light Source, which is funded by the Canada Foundation for Innovation, the Natural Sciences and Engineering Research Council of Canada, the National Research Council Canada, the Canadian Institutes of Health Research, the Government of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan.

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Cultural Heritage

14:00 – 15:50

Session Chair – Ljiljana Puskar

14:00-14:30

EMELINE POUYET ***Invited Speaker***
Cultural Heritage applications at the European Synchrotron Radiation Facility

14:30-14:50

DAVID THURROWGOOD
Synchrotron Infrared Microscopy and rediscovering a hidden painting by Edgar Degas

14:50-15:10

ROSEMARY GOODALL
Investigation of Historical Dart and Arrow Poisons Using Synchrotron Based Infrared Microscopy and Spectroscopy

15:10-15:30

PER UVDAL
54-Million years old bio-molecules observed in pigment particles in a fossil fish eye

15:30-15:50

PAULA DREDGE
Examination of Ripolin enamel house paint as used by the artist Sidney Nolan, with synchrotron sourced Infrared microscopy and spectroscopy

15:50-16:20

AFTERNOON TEA

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1400-1430

CULTURAL HERITAGE APPLICATIONS AT THE EUROPEAN SYNCHROTRON RADIATION FACILITY

EMELINE POUYET *Invited Speaker*

European Synchrotron Radiation Facility (ESRF), Grenoble, France

As Infrared and X-Ray based techniques offer complementary information, the achievement of molecular, elemental and structural characterization on a single complex and heterogeneous sample is a real asset in the Cultural Heritage field. In this context, the interests and challenges of such a combination are evaluated. An important part of Emeline's research is focused on optimizing thin section preparation: one of the objectives is to limit any analytical interferences from external materials, in particular for Infrared spectroscopy. Moreover, new technical developments are implemented with a particular focus on full-field approach giving full 2D information.

1430-1450

SYNCHROTRON INFRARED MICROSCOPY AND REDISCOVERING A HIDDEN PAINTING BY EDGAR DEGAS

D.THURROWGOOD[1], L. PUSKAR[2], N. TSE[3], E. MULVIHILLE[3], D. HOWARD[2] AND M. TOBIN[2]

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The study of high value artworks is restricted by a strong preference that examination is non-destructive. Where sampling is permitted, usually following extended negotiation, researchers face a difficult task of obtaining as much information as possible from small and precious samples. Results from paint samples from a painting by French Impressionist Edgar Degas (1834-1917), belonging to the National Gallery of Victoria have been examined by transmission measurements at the Australian Synchrotron infrared beamline using AgCl thin section sample preparation techniques. In addition, data obtained from these experiments can further be compared to complementary Synchrotron X-ray Fluorescence microscopy techniques on the same cross sections, providing elemental distributions. The information obtained using this technique has been critical in revealing and understanding a hidden Degas under painting.

Presented here, is a development of greatly improved preparation pathway for examining paint samples from historic paintings, in conjunction with synchrotron based Fourier-transform infrared microscopy. We demonstrate high quality spectra obtained from samples where good data were previously been difficult to obtain. Embedding paint samples in polyester resin is a standard preparatory technique, to retain the spatial integrity of paint films when they are polished or microtomed for materials analysis. We have optimised an alternative preparation technique that relies on embedding small paint samples in silver chloride (AgCl), which are then microtomed into very thin cross sections (~3 µm) suitable for transmission measurements. The significant advantage of AgCl as an embedding material is that it is infrared transparent, and therefore no infiltration or chemical change due to the heat of curing resins is observed in the spectra. Where a conventional bock mount ATR technique reveals one study surface, this technique enables many thin sections to be taken from a sample, giving more representative sample information. This is an important advance in the context of the limited availability of study material. This preparation technique has strong potential for application to other samples, outside of the art conservation field.

This work will detail the refinement of a methodology of AgCl thin section paint sample preparation, give examples of the spectral data quality which has been achieved, and discuss our initial attempts to interoperate these data sets. We will demonstrate how it may be used to encourage alternative practices in paint sample examination for researchers working with both synchrotron and conventional laboratory instrumentation. This work will encourage new avenues for technical study of cultural heritage, and demonstrate its effectiveness in the form of new understandings about and artwork by Degas.

1450-1510

INVESTIGATION OF HISTORICAL DART AND ARROW POISONS USING SYNCHROTRON BASED INFRARED MICROSCOPY AND SPECTROSCOPY

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Museum Victoria holds in its Indigenous Collection a number of poison darts and arrows from South East Asia and Africa. The focus of this investigation is the stained tips of three sets of small wooden darts from Southeast Asia and residues on the iron heads of six arrows from Africa, covering three collection periods between 1873 and 1971. Information about the possible poisons was either not available or not recorded when the items were collected and the identity of the residues on these items has therefore remained unknown. As part of an on-going identification of hazardous substances in the collection we wished to identify if poisons are present on these items, if they are still active and whether they pose a risk to staff working with the collection. Ethnographic information indicates that the residues are toxins and are probably from the Antiaris, Stychnos or Strophanthus plants, the active ingredient being contained in the sap, bark or seeds[1].

The 25 cm thin wooden darts have a thick coating of poison on the tip and the residue material is highly desiccated. The nature of these items precludes sampling so the dart tips and arrow heads require analysis by non-destructive analysis techniques. The high spatial and spectral resolution of the synchrotron system was utilised because the toxic component of the residues which is bound in a mixture of plant proteins and carbohydrates is present in very low levels. The experimental setup used the Bruker Hyperion 2000 microscope with Bruker V80v Spectrometer on the Infrared Beamline at the Australian Synchrotron Facility. Measurements were made in reflectance mode as any contact with the items could cause damage to the desiccated residues. Small dislodged fragments from the darts in two different quivers were collected for transmission analysis using a micro diamond cell. Both IR maps and point analysis were used to analyse these two samples.

The level of degradation of the residues was assessed using the characteristic bands for plant proteins, carbohydrates and amino acids. The presence of strong amide I and amide II bands in the protein components of the poisons suggests that little degradation of the protein has occurred. Similarly strong clear carbonyl bands for amino acids were found in the mapped area of one dart sample. Protein material will breakdown with time and studies of archaeological material by infrared and Raman techniques has shown that the amide bands, in particular the amide II band, reduce in intensity with breakdown[3]. The spatial resolution achieved on the synchrotron based infrared microscope enabled the identification of particles within the plant matrix with high intensity carbonyl bands at 1723 and 1704 cm^{-1}. These have been reported for antiarin the toxin from the Antiaris plant reported to have been used in dart poisons in the South East Asia[2]. Second derivative spectra were used to identify further bands relating to antiarin. Further analysis of sap and seed material for other toxic plants was also undertaken and is on-going.

Acknowledgement

We acknowledge the support of the Australian Synchrotron for the user grant in funding this research and the staff of the infrared beamline for their assistance, in particular Lauren Hyde.

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1510-1530

54-MILLION YEARS OLD BIO-MOLECULES OBSERVED IN PIGMENT PARTICLES IN A FOSSIL FISH EYE

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The definition of fossil species is normally based on morphological characters and physical structure but there are several problems with this approach. Recent advances in ultra-sensitive molecular spectroscopy have made it possible to analyze fossil materials to demonstrate that bimolecular traces, originating from the species when it was still alive, can survive over deep time. That is we are now starting to obtain molecular data from multi-million-years old species that potentially will reveal new things about the life and behavior of these extinguished animals based on hard-core spectroscopic data. This realization is about to revolutionize the field of paleontology and transfer paleontology in to the realms of modern molecular biology/chemistry/physics. The announcement of the coloration of dinosaurs is an example where the results are all based on morphology rather than on chemistry or physics. The color is inferred form the observation of micrometer size bodies assumed to be pigment particles, melansomes, in fossil feathers (1). The size and shape of these structures, however, makes them indistinguishable from bacteria making the assumptions about coloration tentative at best. In some recent work (2) we demonstrate that melanosome-like microbodies in a 54 million-years-old fish eye indeed contains high concentrations of melanin. This is accomplished by combining a set of spectroscopies, FTIR-microscopy and Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) and modern reference materials.

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1530-1550

EXAMINATION OF RIPOLIN ENAMEL HOUSE PAINT AS USED BY THE ARTIST SIDNEY NOLAN, WITH SYNCHROTRON SOURCED INFRARED MICROSCOPY AND SPECTROSCOPY

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The artist Sidney Nolan (1917-1992), inspired by Pablo Picasso's use of the ready-made paint manufactured by the Ripolin company, began painting with this commercial paint product in 1943. Ripolin® became Nolan's paint of choice for the following decade and was the principal medium used in his series on the Ned Kelly subject 1946-1947 (Figure 1). Although the brand name has been applied to Nolan's Ripolin paintings since they were first exhibited in 1948[1], it has not been understood what the components of the paint were. This has created difficulties in cataloguing his paintings while using the usual generic terms for paint, oil or synthetic. It has not been understood how these non-artists' paints may have aged and what might be safe and effective conservation treatments for this types of paint film.

Fig. 1. Sidney Nolan *First-class marksman*, 1946, Ripolin enamel on hardboard. Art Gallery of New South Wales. Purchased with funds provided by the Gleeson O'Keefe Foundation 2010.

The gift by Nolan's daughter Jinx Nolan in 2006 to the Art Gallery of New South Wales of the contents of Nolan's studio dating from the early 1950s in Wahroonga Sydney, included a large amount of Ripolin paint in cans. Fourier Transform Infrared spectroscopy identified that all of the Ripolin paints from the studio cans were oil-based, and zinc oxide was the principal white pigment. Although zinc oxide does not exhibit spectral features in the infrared region 600-4000 cm^{-1}, when mixed with oil it typically develops infrared spectral features in the carboxylate region 1500-1650 cm^{-1}. The development of zinc carboxylates is of concern for the stability of the paint films. It has been observed that zinc soap species in paint films can aggregate into lumps that in some cases have migrated through dry and hardened paint films causing disruptions to the surface of paintings[2].

Ripolin paint from the Nolan studio cans was found to contain visible lumps when painted out and air dried. Samples were prepared for infrared mapping studies to examine these lumps and their distribution within the dry paint films on the Infrared Beamline at the Australian Synchrotron. Samples were prepared as cross-sectional studies mounted in polyester resin and microtomed as 5-10 micron thin-sections. These were supported on a diamond window and examined in transmission mode. Infrared spectra were collected at 5 x 5 micron aperture at 5 micron steps following custom defined grid positions. Spectra were the sum of 32 scans at a resolution of 4 cm^{-1}.

The 'lumps' were found to have distinctive carboxylate features with sharp spectral absorbance peaks at 1533 and 1551 cm^{-1} with a shoulder at 1597 cm^{-1}. Similar spectral peaks have been observed in zinc oxide-based oil paint films associated with zinc oleate (zinc 9-octadecenoic acid)[3]. The paint matrix surrounding these zinc oleate features gave a broad non-specific carboxylate feature with no sharp peaks. This suggested that aggregation of oleate species of the zinc carboxylates had occurred in the Ripolin paint in cans and could therefore be a concern for Nolan's paintings in Ripolin.

Acknowledgement

This research formed part of the Australian Research Council Linkage Project, The twentieth century in paint. The Australian Synchrotron funded the use of the Infrared Beamline through its merit based application system.

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Extreme Conditions

16:20 – 17:50

Session Chair – Shin-Ichi Kimura

16:20-16:50

PAUL DUMAS ***INVITED SPEAKER***
High Pressure Science using synchrotron infrared microscopy at the SMIS beamline (SOLEIL)

16:50-17:10

HIDEKAZU OKAMURA
High Pressure Infrared Studies of Strongly Correlated Electron Systems at SPring-8

17:10-17:30

HIMAL BHATT
Optical Conductivity studies on Copper doped Ru1212 at High Pressure

17:30-17:50

BILIANA GASHAROVA
Phase transformations in the CaO-SiO_2-H_2O system: synchrotron IR microscopy at ANKA helps decoding unusual transformation mechanisms

17:50

SESSION CLOSE

1620-1650

HIGH PRESSURE SCIENCE USING SYNCHROTRON INFRARED MICROSCOPY AT THE SMIS BEAMLINE (SOLEIL)

PAUL DUMAS[1] *Invited Speaker*
F. OCCELLI[2], S. LEFRANCOISE[1] AND P. LOUBEYRE[2]

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[2] CEA-DAM-DIF, Arpajon, 91297, France

High Pressure research is expressing an increasing interest in exploiting the brightness advantage provided by synchrotron infrared sources. The number of articles in this field has increased markedly over the recent years. Often, Diamond Anvil Cells (DAC) of small dimension accommodate the short working distance constraints of the commercially available focusing metallic optics (of Schwarzschild-type) (maximum around 25 mm). However, high pressure studies requires more and more the use of larger sample environments to couple high pressure to variable temperature or to achieve multi-Megabar pressures with strengthened DACs (as those used for X-ray Studies),. The need for increase the working distance, while keeping the same optical parameters as the commercially available objective, guided us to design home-made infinity corrected Schwarzschild, (x15, N.A. 0.5), with working distance of 43 mm, and producing a FWHM beam of 22±5 µm, the mid-IR range. The horizontal microscope as we designed allows a simultaneous study in IR and Raman/Fluorescence, Mid- and Far-IR, either in transmission or reflection modes (Fig1). Recently, we carried out a study of the phase transformations under pressure at 296 K in solid H_2 and D_2 by combining synchrotron infrared and Raman spectroscopy measurements [1].

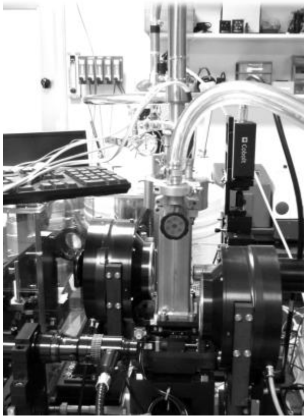

Fig. 1. Side view of the home-made horizontal microscope, with a cryostat, and the Raman head beside the collecting IR optics.

Synthetic diamond anvils were used to offer a good transparency below 1800 cm^{-1}. The very good stability of the bench enables to perform measurements on 4 µm sample with a good signal to noise ratio. The study of solid hydrogen (deuterium) under very high pressures and ultimately the observation of metal hydrogen is one of the most challenging problem of high pressure science The IR absorption measurement is the primary diagnostic that can evidence this insulator metal transition. We have shown that there is no sign of metallic character up to 290 GPa, contrarily to what was published in a recent article [2]. A more detailed phase diagram has been obtained, pointing to the conditions of potential metallic character of H_2 at higher pressure and at lower temperature.

The details of the microscope and optics will be shown, as well as several other important results obtained so far with this microscope.

Acknowledgement

We would like to acknowledge the Optics Group at SOLEIL, for the alignment of the Schwarzschild, as well as collaborators at the beamline: Jean Paul Itie, Gunnar Weck, Agnes Dewaele, Sandra Ninet, Wren Montgomery, Philippe Lerch and Frederic Datchi

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1650-1710

HIGH PRESSURE INFRARED STUDIES OF STRONGLY CORRELATED ELECTRON SYSTEMS AT SPRING-8

H. OKAMURA[1], Y. IKEMOTO[2] AND T. MORIWAKI[2]

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[2] Japan Synchrotron Radiation Institute and SPring-8, Sayo, Japan

IR spectroscopy under high pressure has been one of the major applications of IR synchrotron radiation [1]. With the use of a diamond anvil cell (DAC), one can perform IR spectroscopy of a material at a high pressure of 10 GPa (~ 100 kbar) and above [2]. Since only a small sample with a typical size of 0.2 mm or smaller can be used in a DAC, the high brilliance of IR synchrotron radiation is quite advantageous. At the beamline BL43IR of SPring-8, we have performed IR spectroscopy of various strongly correlated electron systems, such as YbS [3] , $CeRu_4Sb_{12}$ [4] , and $PrRu_4P_{12}$ [5]. In these previous studies, the pressure evolutions of a band gap [3], heavy electron state [4], and unconventional charge-density-wave gap [5] were investigated at pressure up to 20 GPa, at temperatures down to 9 K, in both far-IR and mid-IR ranges. In addition, we have proposed a simple method for performing Kramers-Kronig analysis on the reflectance data measured with DAC, taking into account the large refractive index of diamond [6].

In this presentation, we will discuss our recent works on $SrFe_2As_2$ [7] and $CeXIn_5$ (X=Co, Rh). $SrFe_2As_2$ at ambient pressure is an antiferromagnetic metal with a Neel temperature of T_N ~ 195 K, but with increasing external pressure, T_N decreases and superconductivity with T_c ~ 34 K appears above 4 GPa. We have observed marked pressure-evolution of optical conductivity [$\sigma(\omega)$], as shown in Fig. 1. It is seen that the clear depletion of spectral weight (pseudogap) in $\sigma(\omega)$, which is due to spin density wave in the antiferromagnetic state at ambient pressure, is rapidly suppressed with increasing pressure. On the other hand, $CeRhIn_5$ and $CeCoIn_5$ are well-known heavy electron superconductors with T_c=2 K. While $CeCoIn_5$ is already superconducting at ambient pressure, $CeRhIn_5$ becomes superconducting at pressure of 2 GPa. We have measured their $\sigma(\omega)$ at 6 K under pressure, therefore probing their normal state electronic structures. The measured $\sigma(\omega)$ spectra show strong pressure dependencies, which suggest a broadening and shifting of *f* electron band with pressure. Such a result is well expected since a stronger hybridization of *f* electron with conduction band is theoretically expected with increasing pressure. However, an explicit demonstration of such a result based on $\sigma(\omega)$ had not been reported previously. We will discuss these results more in detail.

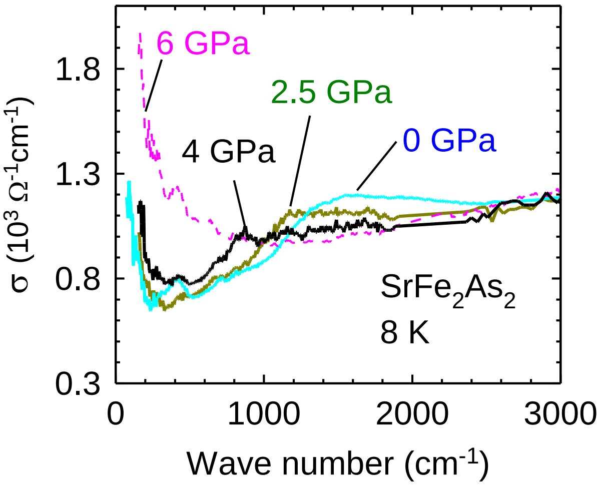

Fig. 1. Optical conductivity (σ) of $SrFe_2As_2$ at high pressure and low temperature measured with diamond anvil cell [7].

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1710-1730

OPTICAL CONDUCTIVITY STUDIES ON COPPER DOPED RU1212 AT HIGH PRESSURE

H. BHATT[1], M. N. DEO[1], S. KARMAKAR[1], M. R. GONAL[2], N. PATEL[1]
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$RuSr_2GdCu_2O_8$ (Ru1212) system has drawn attention due to its remarkable property of coexistence of superconductivity (T_c ~45 K) and magnetism (T_m ~130 K) [1]. Its tetragonal lattice structure is similar to the well known high T_c superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO) [1]. The RuO_2 planes are responsible for its magnetic properties. Cu doping for Ru has shown to raise the T_c at the expense of magnetism which remains preserved up to ~20% doping [2]. On application of high hydrostatic pressures, T_c hardly varies, but T_m increases, which is saturated at pressures higher than 1.6 GPa [3]. For undoped Ru1212 sample, optical conductivity studies at low temperature have shown the evidence of electron-phonon coupling, in particular the broadening of the Cu-O bending mode near 300 cm^{-1} near T_c, shift in the broad mid IR polaron band and suppression of spectral weight at low frequencies [4]. The present work is aimed at understanding the underlying effects of pressure, particularly at lower pressures, which influence the magnetic ordering in Ru1212, with 10% copper doping for ruthenium.

High pressure IR reflectivity measurements on polycrystalline sample of $Ru_{0.9}Sr_2GdCu_{2.1}O_8$ up to ~5 GPa were carried out using Diamond Anvil Cell (DAC) and IR microscope. LHe bolometer and LN_2 MCT detector for FIR (250-700 cm^{-1}) and MIR (600-12000 cm^{-1}) respectively were used, where the diffraction limited spot size on to the sample was made ~90 μm and ~45 μm respectively. The bright and broad band IR source at the SISSI beamline at Elettra synchrotron was utilized to record the spectra in the complete spectral range. CsI was used as pressure transmitting medium. Ruby fluorescence was monitored at each pressure for pressure estimation. All the reflectivity data were normalized for background and diamond contribution. The reflectivity data have been fitted using the Drude-Lorentz model to calculate the optical parameters. A continuous low frequency Hagen Rubens extrapolation for normal state up to ω=0 was carried out. For extrapolation to higher frequencies above the measured frequency range, it was assumed that there still is some contribution due to inter/intra band transitions.

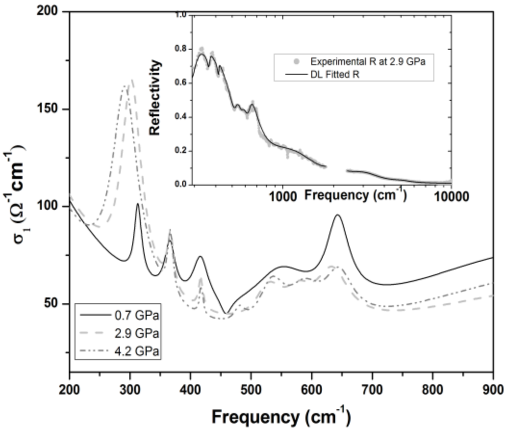

Fig. 1. Far IR optical conductivity spectra of Cu doped Ru1212 at high pressure. Inset: Drude Lorentz fitting of reflectivity data.

In the title compound, the apical oxygen, surrounded by Sr in plane atoms, connects CuO_2 plane on one side and the RuO_6 octahedra on the other side. The phonon modes related to apical oxygen vibrations (~ 650 cm^{-1}), CuO_2 bending mode (~ 300 cm^{-1}) and RuO_6 octahedral vibrations (~ 190 cm^{-1}) have shown marked changes in the optical conductivity spectra across magnetic and superconducting transitions in Ru1212 [4]. Our IR reflectivity data show a sharp fall in reflectivity up to nearly 800 cm^{-1} at all pressures, which is consistent with its undoped parent compound. Although, the RuO_6 vibrations could not be checked in the current investigations, due to diffraction limitations at high pressure, we could probe the apical oxygen vibration and CuO_2 bending mode. It can be seen in figure that the peak intensity of the CuO_2 bending mode near 300 cm^{-1} in the optical conductivity spectrum at 0.7 GPa is comparable to the peak intensity of the apical oxygen mode near 650 cm^{-1}. As the material is compressed beyond 2 GPa, the spectral contribution of the bending mode increases, whereas that of the apical oxygen mode decreases. Interestingly, this is also accompanied with slight red shift in the position of the bending mode with pressure. Softening as well as gain in the intensity with pressure of this mode on and above a distinctive rise in the peak width indicates an increase in anharmonicity and interactions with the surrounding system. Further compression has very little effect on this mode up to the measured pressure value of ~ 5 GPa.

An electronic background of ~ 100 Ω^{-1} cm^{-1} in the measured spectral range 250-12000 cm^{-1} is consistent with the dc conductivity value at room temperature. However, slight reduction in the spectral weight contribution from the interband part in the mid IR region is also noticed at higher pressures. Further, in

the MIR data, we also observe a shift in the polaronic band position near 3000-4000 cm^{-1} region accompanied with slight shift of spectral weight from higher to lower frequencies between 0.9 GPa and 1.5 GPa. The Cu-Cu distance defining the thickness of CuO_2 double layers, and the buckling angle of CuO_2 planes are the structural parameters primarily responding to the magnetic ordering at lower temperatures [1]. Our results indicate that pressure has strong effects on the Cu related phonon mode and overall structure up to nearly 2 GPa, thus influencing the magnetic properties in this compound. The overall implications of pressure on phonons and crystal structure; interband and free electron Drude behaviour corroborated with high pressure X-ray diffraction results shall be discussed.

Acknowledgement

We thank Dr. Andrea Perucchi for his support at the SISSI beamline.

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1730-1750

PHASE TRANSFORMATIONS IN THE CAO-SIO$_2$-H$_2$O SYSTEM: SYNCHROTRON IR MICROSCOPY AT ANKA HELPS DECODING UNUSUAL TRANSFORMATION MECHANISMS

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Calcium-silicate-hydrates (C-S-H phases, C = CaO, S = SiO_2, H = H_2O) are a very interesting group of silicates. On the one hand, they have a huge technical importance since they are the essential product of the cement hydration and therefore responsible for the chemical and mechanical properties of construction materials. On the other hand, the large diversity of their structures makes them an ideal object for basic crystallographic and mineralogical research. A fundamental scientific discovery could potentially become an important mean for society in achieving global climate protection objectives without suffering economic losses.

In the institute for technical chemistry at KIT, a new family of cementitious materials was designed as a promising, environmentally friendly, and cost-effective alternative to standard concrete. Complementary to other techniques like XRD, Raman spectroscopy, DTA/TG, SEM, etc., synchrotron infrared microspectroscopy helps decoding the mechanisms of phase transformations upon heating, changing chemistry or pressure. A deeper understanding of these mechanisms is needed in order to manipulate the materials properties. Compared to X-ray diffraction, IR spectroscopy is very sensitive to the structural short-range order, to the presence of protons and to the degree of polymerization of silicate tetrahedra in crystalline as well as amorphous materials, which is a valuable advantage for the study of cement phases.

In the present study a sequence of phase transformations in the CaO-SiO_2-H_2O system upon heating will be presented. Possible mechanisms will be discussed based on synchrotron infrared images and a modular crystal structure approach.

Acknowledgement

We gratefully acknowledge the excellent support of Yves-Laurent Mathis and Michael Süpfle at the infrared beamline of the ANKA synchrotron facility, Karlsruhe, Germany.

Sub-Diffraction Limit Spectroscopy

09:00 – 10:30

Session Chair – Gianfelice Cinque

09:00-09:30

HANS BECHTEL ***INVITED SPEAKER***
Ultra-broadband Infrared Nano-spectroscopy with a Synchrotron Source

09:30-09:50

YUKA IKEMOTO
Infrared Near-field spectroscopy by synchrotron radiation source at Spring-8 BL43IR

09:50-10:10

PETER HERMANN
High-resolution imaging and nano-FTIR spectroscopy by using a broadband synchrotron radiation source

10:10-10:30

SERGIU AMARIE
Introducing nano-FTIR - imaging and spectroscopy at 10nm spatial resolution

10:30-11:00

MORNING COFFEE

0900-0930

ULTRA-BROADBAND INFRARED NANO-SPECTROSCOPY WITH A SYNCHROTRON SOURCE

HANS BECHTEL[1] *Invited Speaker*
M. C. MARTIN[1], R. L. OLMON[2], E. A. MULLER[2], B. POLLARD[2], AND M. B. RASCHKE[2]

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Synchrotron infrared radiation is 100-1000 times brighter [1] than conventional thermal sources, and when combined with an infrared microscope, it enables infrared spectroscopy and imaging with enhanced sensitivity and spatial resolution limited by diffraction (typically 2-10 μm) [2]. Although synchrotron infrared micro-spectroscopy is an extremely powerful technique for material characterization [3] and the study of living cells [4] and tissues [5,6], the μm-sized wavelengths of infrared radiation have limited its application in areas where chemical information at the nanoscale is desired.

Here, we overcome this limitation by combining synchrotron infrared radiation with scattering-type scanning near-field optical microscopy (s-SNOM). In an s-SNOM experiment, incident light is scattered off the tip of an atomic force microscope (AFM) positioned next to the probed sample. The conductive tip effectively acts as an antenna and localizes the electric field in the near-field region of the nanoscopic tip apex. Consequently, the spatial resolution of s-SNOM is determined only by the size of the tip apex, which is typically 10-20 nm. Laser-based infrared s-SNOM measurements have demonstrated chemical contrast in samples considerably smaller than the wavelength of light [7], but nano-spectroscopic measurements have been limited by the narrow tuning range of most infrared laser sources [8]. The high spectral irradiance provided by synchrotron infrared radiation spans a much wider spectrum, and enables broadband infrared nano-spectroscopy based on s-SNOM. In this talk we will demonstrate our implementation of synchrotron IR s-SNOM at the Advanced Light Source (ALS) (Fig 1, upper panel) and its application for nano-scale spatio-spectral investigations of a range of hard and soft matter systems.

Fig. 1 (lower panel) shows as one example the spatial and spectral characterization of microscopic SiO_2 microstructures on Si. Synchrotron s-SNOM spectra spanning the full mid-infrared (700 cm^{-1} – 4000 cm^{-1}), including the fingerprint absorption region, are rapidly acquired from sub-100 nm spatial regions with the frequency range limited only by the choice of beamsplitter and detector [9]. Using a rapid-scan asymmetric FTIR s-SNOM technique, we directly obtain both spectral s-SNOM amplitude and phase, from which the frequency-dependent optical constants can be determined.

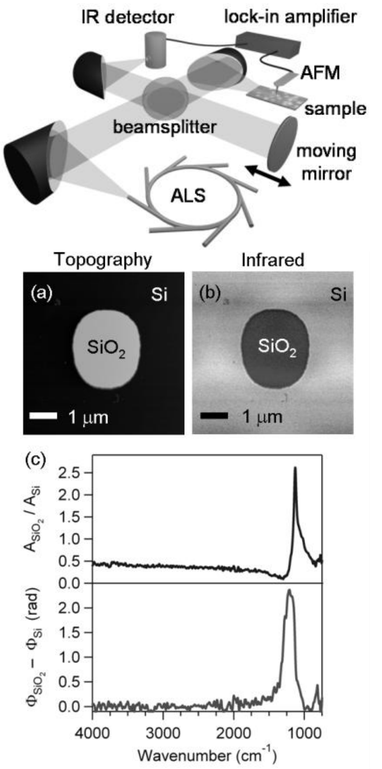

Fig. 1. Upper Panel: Schematic of the ALS synchrotron nano-spectroscopy setup. Lower Panel: (a) Topography and (b) IR s-SNOM image of SiO_2 microstructure on silicon with 20 nm spatial resolution. (c) Near-field amplitude and phase spectra of SiO_2 patch referenced to Si.

Acknowledgement

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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0930-0950

INFRARED NEAR-FIELD SPECTROSCOPY BY SYNCHROTRON RADIATION SOURCE AT SPRING-8 BL43IR

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An infrared synchrotron radiation (IR-SR) is a broadband white light source, and it has an advantage of a high brilliance. In this study, we have developed near-field spectroscopy by IR-SR source at BL43IR/SPring-8, and achieved a near-field spectral measurement with 200 nm spatial resolution.

Scanning near-field optical microscopy (SNOM) is a technique to get higher spatial resolutions than the diffraction limit. We have already constructed infrared near-field spectroscopy apparatus for the IR-SR source[1]. It was composed of a SNOM system and a commercial FTIR spectrometer, and achieved 300 nm spatial resolution. However, the S/N ratio of the near-field spectrum was not high enough, and it was difficult to perform various experiments by our apparatus. In order to improve the S/N ratio, in the present study, we have modified the optical configuration into an asymmetric interferometer configuration, as shown in Fig. 1. It utilizes basically the same optical configuration as that developed by Keilmann and Hillenbrand [2]. Compared to their light sources such as an infrared laser or a thermal radiation source, the IR-SR has a higher brilliance in wide infrared regions, so a broadband near-field spectroscopy can be expected. In the previous configuration of our system, the light after passing through the interferometer was focused onto the probe tip, and scattered light from the probe was detected by an MCT [1]. In the present configuration, the probe is placed at one side of the interferometer. In this asymmetric configuration, the near-field signal is expected to be enhanced because of an interferometric gain.

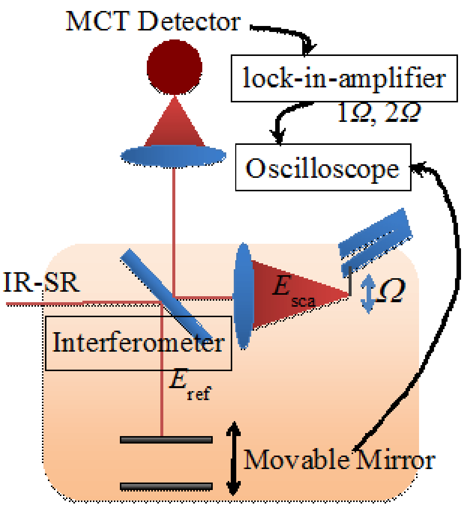

Fig. 1. Schematic illustration of near-field spectroscopy apparatus at BL43IR.

In Fig. 1, the IR-SR injected into the interferometer is split by ZnSe beam-splitter. One beam goes to a movable mirror, and the other is focused onto the tip of the SNOM probe. We use platinum coated tungsten tip as a SNOM probe. The radius of curvature is 100 nm. The movable mirror is controlled by a piezo stage. The scattered light from the probe tip and the reference beam reflected by the movable mirror interfere each other. The signal is detected by an MCT (HgCdTe) detector. In order to eliminate background signal other than the near-field one, modulation spectroscopy is performed by a frequency of probe oscillation, 32 kHz. We extract 1st and 2nd harmonic components (n_1, n_2) by the lock-in-amplifier and record them by the oscilloscope. The position of the movable mirror is also recorded by the oscilloscope.

The spectra of n_1 and n_2 were observed while the probe is moved perpendicularly away from the sample. The intensity of n_2 spectrum rapidly decreased with increasing the distance between the probe and the sample, and almost vanished when the distance was larger than about 100 nm. The intensity of n_1 didn't change much up to 100 nm. From these observations, n_2 signal was shown to be spatially localized adjacent to the probe tip, and signal of n_2 was recognized as a near-field signal. The spatial resolution was estimated by Au film on Si substrate. The probe was scanned across the edge of Au film, and the near-field spectra were observed at every 50 nm step. The spectral intensities at 910, 920 and 940 cm^{-1} (11.0, 10.9 and 10.6 µm) are plotted against the probe position in Fig.2. The intensities rapidly decrease at the edge of the Au film. The decrease is observed over an about 200 nm, which is much shorter than the wavelength. The spatial resolution of our system is estimated to be 200 nm. We also measured the near-field spectrum of ink on the Au film. In the conference, we will discuss examples of the near-field spectroscopy experiments.

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0950-1010

HIGH-RESOLUTION IMAGING AND NANO-FTIR SPECTROSCOPY BY USING A BROADBAND SYNCHROTRON RADIATION SOURCE

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A widely used method for chemical recognition is Fourier transform infrared (FTIR) spectroscopy which provides specific information about the absorption properties of samples in the spectral range from 300 cm^{-1} to 4000 cm^{-1}. The spatial resolution of FTIR microscopy is limited by diffraction thus preventing a spectroscopic characterization of individual nanostructures. Near-field infrared microscopy circumvents this limitation by using a sharp metallic probe which acts as a nano-scale light source when irradiated by a focused photon beam [1]. However, the use of conventional radiation sources, such as tunable gas lasers, for the acquisition of near-field infrared spectra requires time consuming subsequent measurements at different wavelengths providing only optical information in a relatively narrow spectral range. Radiation sources with a broad emission spectrum, such as thermal sources [2] or synchrotron radiation [3], represent therefore an attractive alternative to overcome these limitations.

In the following, we report on the use of broadband synchrotron radiation provided by the Metrology Light Source (MLS) [4] for near-field imaging and acquisition of nano-Fourier transform infrared spectra in a wide spectral range. For demonstrating the high spatial resolution by using synchrotron radiation, scans are performed on thin Au layers deposited on a silicon-carbide (SiC) substrate and at Au/SiC edges. In the nano-FTIR spectra recorded from the SiC surface the characteristic phonon resonance band at 927 cm^{-1} appears confirming the near-field signal detection from SiC [3]. The resolution limit is estimated to be <100 nm, which is far below the diffraction limit. Additionally, further results obtained from soft and hard matter samples are presented.

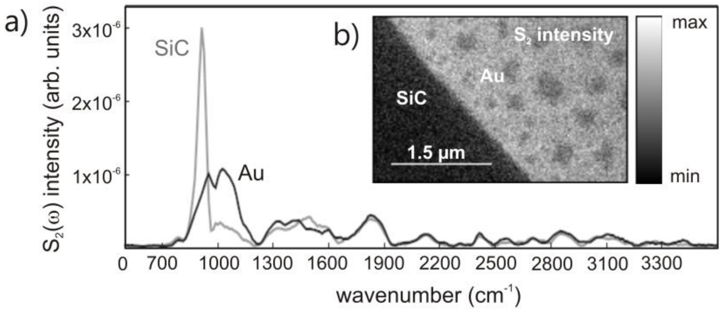

Fig. 1. a) Nano-FTIR spectra acquired from SiC and Au surfaces. The phonon resonance at 927 cm^{-1} confirms near-field detection. b) Near-field image (2nd harmonic (S2-signal)) of the sample surface recorded by using broadband synchrotron radiation.

Acknowledgement

The authors thank the MLS-team and the associates from the X-ray and IR-Spectrometry group for their great support and fruitful discussions.

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1010-1030

INTRODUCING NANO-FTIR – IMAGING AND SPECTROSCOPY AT 10 nm SPATIAL RESOLUTION

S. AMARIE

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The optical spectral region and in particular the “material fingerprint region in infrared”, allows the investigation of a large variety of material properties. Neaspecs patented broad-band illumination and background suppression technique eliminates the diffuse light and thus allows a spatial resolution of 10 nm throughout the infrared spectrum. nano-FTIR is equally suited for organic and inorganic sample and requires only standard AFM sample preparation. An outlook of several application potential of nanoscale chemical mapping by local infrared imaging and spectroscopy will be presented elsewhere:

- Quantitative measurement of local infrared absorption and dielectric function;
- Semiconductor free carrier distribution;
- Nanoscale phase transition;
- Chemical characterization of polymer blends;
- Bio-medical nano-imaging.

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IR Microscopy – Facility Developments

11:00 – 12:50

Session Chair – Mike Martin

Session Sponsor

11:00-11:30

Carol Hirschmugl ***Invited Speaker***
Three dimensional spectral imaging with synchrotron FTIR spectro-micro-tomography

11:30-11:50

Shin-Ichi Kimura
Infrared micro-spectral imaging using a linear array detector at UVSOR-III

11:50-12:10

Raul Freitas
Synchrotron-based a-SNOM IR endstation at the LNLS: beamline installation and commissioning details

12:10-12:30

Yves-Laurent Mathis
Status of the Infrared Microscopy station at ANKA

12:30-12:50

Ibraheem Yousef
An Infrared Synchrotron Radiation beamline EMIRA at the Third Generation Light Source SESAME

12:50-14:20

Lunch

1100-1130

THREE DIMENSIONAL SPECTRAL IMAGING WITH SYNCHROTRON FTIR SPECTRO-MICRO-TOMOGRAPHY

CAROL HIRSCHMUGL *Invited Speaker*

University of Wisconsin-Milwaukee, E. Kenwood Blvd, Milwaukee, WI, USA

Non-destructive three-dimensional imaging with rich spectral information reveals distributions of distinctive chemistry throughout an intact sample. FTIR spectro-micro-tomography combines mid-infrared absorption contrast with computed tomographic data acquisition and reconstruction that significantly enhances chemical and morphological localization by determining a complete spectrum for every voxel.

These millions of spectra across the sample volume will be a boon for advanced spectral segregation techniques leading to powerful segmentation and identification algorithms. Spectro-micro-tomography will become a quantitative, spectrally rich, analytical 3D micro imaging method for a wide variety of scientific, industrial, materials, energy, and medical applications.

1130-1150

INFRARED MICRO-SPECTRAL IMAGING USING A LINEAR ARRAY DETECTOR AT UVSOR-III

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Since synchrotron radiation (SR) in the infrared (IR) and terahertz (THz) regions is higher brilliance than internal light sources of laboratorial FTIRs, SR is widely accepted in the world as an advance IR/THz source. Recently, IR imaging with diffraction limit resolution has been performed by using IR-SR combined with a focal plane array (FPA) detector [1]. The covering wavenumber range of FPA detector, however, is limited down to the wavenumber as much as 950 cm^{-1}. To exceed the wavenumber limitation of FPA, a linear array MCT detector is one of candidates because the covering wavenumber range is down to 600 cm^{-1} even though the number of pixels is less than that of FPA. So, we try to check the performance to combine a linear array IR imaging system (FT/IR6100 + IRT7000, JASCO Ltd.) with the IR/THz beamline 6B of UVSOR-III. In this paper, we report the results of the performance test and discuss the possibility of the IR imaging using the linear array MCT detector.

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1150-1210

SYNCHROTRON-BASED A-SNOM IR ENDSTATION AT THE LNLS: BEAMLINE INSTALLATION AND COMMISSIONING DETAILS

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Infrared (IR) beamlines are present in the most of the synchrotron facilities worldwide. The use of IR radiation extracted from synchrotron sources brings major advantages compared to black body IR sources such as higher brilliance (up to 1000 times higher), pulsed time structure (allowing pump-probe studies) and well defined polarization states. In consequence, IR beamlines, often designed with micro-spectroscopy capability, are nowadays among the topmost demanded beamline at synchrotron facilities. The wide energy range source extending from visible to far-IR light is applied in a large variety of research fields like mineralogy, biomedicine, cultural heritage, petroleum prospection, high pressure science, surface science or astrophysics.

Although Fourier Transform IR spectroscopy (FTIR) using synchrotron sources is indeed the ultimate tool for IR analysis in many fields, there is an increasing demand for conducting FTIR with lateral resolution in the nanometer range (nano-FTIR), i.e., way beyond the Abbe diffraction limit. IR imaging and nano-FTIR using appertureless scanning near-field optical microscopy (a-SNOM) has recently achieved a lateral resolution below 100 nm [1,2]. These results indicate the need for high brilliance IR continuum sources with a large spectral range for a-SNOM. IR synchrotron facilities would offer such a source meeting all requirements of a-SNOM instruments.

This contribution presents the new IR beamline of the Brazilian Synchrotron Light Laboratory (LNLS). The beamline is in advanced stage of construction and will have an a-SNOM setup as its first endstation. Details of the beamline optics and preliminary results from the current commissioning phase of the a-SNOM endstation will be exposed in this presentation.

Acknowledgement

The authors strongly acknowledge Yves Petroff for idealizing this project.

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1210-1230

STATUS OF THE INFRARED MICROSCOPY STATION AT ANKA

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The IR microscopy station at ANKA was part of ANKA's original complement of beamlines [1], entering service in early 2003 as Germany's first and Europe's third IR microscopy beamline, following those of Paul Dumas at LURE and Mark Tobin at Daresbury. It was the first beamline at ANKA to observe synchrotron light, the first to produce a scientific publication, and following the general opening of ANKA it immediately became the facility's most heavily oversubscribed beamline. In particular the use of edge radiation as the source has proved highly influential for the design of later IR beamlines at many other synchrotron facilities.

In 2009 ANKA the IR microscopy station was closed in order to move it to its own dedicated beamline, with a number of improvements compared to the original beamline. The most important are: an increased number of thermocouples monitoring the heat load pattern on the extraction mirror; the efficiency of the extraction mirror cooling; motorized screens and cameras after each mirror for remote optimization of the beam alignment in the front-end section; a window changer with four different window materials to maximize transmittance for a given spectral range; a fast feedback system for beam stabilization based on the ALS design [2] in front of each of the two experimental stations.

This beamline is now providing photons to our existing experimental station for IR microscopy consisting of a Bruker IFS 66v/S spectrophotometer equipped with beamsplitters for all spectral ranges, with a Bruker IRscope II modified with structural reinforcement for greater mechanical stability, smaller apertures, motorized condenser holder, objectives for transmission/reflection (15x and 36x), grazing incidence and ATR (Ge/Si), a superior purge box, and focal plane array and an FIR bolometer in addition to the standard MCT detector.

This ambitious design was not without its problems in the realization, so that the project took significantly longer than we originally envisaged. Therefore we're now especially happy to present this report on the progress and status of the new beamline ANKA-IR2.

Acknowledgement

We are indebted to Johannes Steinmann for his invaluable assistance in commissioning the fast feedback system.

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1230-1250

AN INFRARED SYNCHROTRON RADIATION BEAMLINE EMIRA AT THE THIRD GENERATION LIGHT SOURCE SESAME

I.YOUSEF

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SESAME is a third generation synchrotron facility which is being constructed in Jordan. Nine countries from the Middle East region are contributing to this project, SESAME is still under construction, it is located at around 30 kilometers to the North West of the capital Amman. The aim of this project is to provide the Middle East region with the intense light of the synchrotron radiation which strongly recommended for many applications that demands the brightness and other beam properties of the synchrotron radiation in the energy range extending from X-rays to infrared.

Thanks to the initial motivation and interest expressed by SESAME directorate and users, the Infrared beamline has been selected as one of the three day-1 beamline at SESAME. Other beamlines are mainly part of donation of beamlines from Daresbury, Swiss Light Source, and LURE. The IR beamline will be the first and only one brand new beamline, entirely designed.

The main objective of the IR beamline is to provide the Middle East scientific community of SESAME with the high brilliant Infrared synchrotron light, dedicated to spectroscopy and Microspectroscopy. Accounting for the construction details and space constraint of the storage ring in construction, the beamline has been designed to produce beams into the experimental floor, with minimum of aberrations. The optimized optical set up, the details of the mirrors mounting, and the location of all instruments in the ground floor have been designed with the assistance of softwares such as SRW, Rays and SolidWorks. Infrared Microspectroscopy will be the main objective of the initial operation of the beamline.

References

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Biomedical Applications - 1

14:20 – 15:30

Session Chair – Pimm Vongsvivut

14:20-14:50

YAO-CHANG LEE ***Invited Speaker***
An innovative study of electrostatically-assisted Wax Physisorption Kinetics for Grading Oral Cavity Cancer using Synchrotron-based FT-IR Imaging

14:50-15:10

LISA VACCARI
IRMS and Flow Cytometry: uniqueness and complementarity of these techniques for live cell analysis

15:10-15:30

PHIL HERAUD
Synchrotron FTIR spectroscopy discriminates very early differentiation stages in living human stem cells

15:30-16:00

AFTERNOON TEA

1420-1450

AN INNOVATIVE STUDY OF ELECTROSTATICALLY-ASSISTED WAX PHYSISORPTION KINETICS FOR GRADING ORAL CAVITY CANCER USING SYNCHROTRON-BASED FT-IR IMAGING

YAO-CHANG LEE *Invited Speaker*

PEI-YU HUANG, AND CHING-IUE CHEN

National Synchrotron Radiation Research Center, No. 101, Hsin-Ann road, Hsinchu Science Park, Hsinchu 30076, Taiwan

The paraffin-beeswax pair of diagnostic agent has been successfully demonstrated for discriminating malignancies from normal of oral cavity cancer based on the method of wax physisorption kinetics (WPK) using synchrotron-based FT-IR imaging [1, 2]. In this study, the correlation between breakdown electrostatic voltage (BEV) and cancer grading of oral cavity cancer was established according to cell surface losing its capability of physisorption with diagnostic wax agent as applying an external electrostatic voltage onto cancer cells in different grades. The result of electrostatically-assisted wax physisorption kinetics of oral cavity cancer cells displayed that the relative amount of paraffin and beeswax residue onto paraformaldehyde-fixed cancer cells seeded on conducted substrate presented a quasi-Gaussian behavior as applying an increasing electrostatic voltage, and the maximum voltage of maximum amount of wax residue was found at 30 V, 30 V, 70 V, 50 V and 70 V for SCC-25, SCC-15, OC-2, OC-3, and OEC-M1, respectively was shown as in the table 1. Moreover, the breakdown bias for SCC-25, SCC-15, OC-2, OC-3, and OEC-M1, is 85 V, 90 V, 165 V, 167 V, and 183 V, respectively, and the result is consistent with pathological cancer grading for oral cavity cancer [3]. Based on our finding, we suggested the breakdown electrostatic voltage is strongly related with the degree of induced membrane polarization of variant grade of cancer due to the alternation of glycoconjugates of cell surface during the course of cancer progression.

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1450-1510

IRMS AND FLOW CYTOMETRY: UNIQUENESS AND COMPLEMENTARITY OF THESE TECHNIQUES FOR LIVE CELL ANALYSIS

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Flow cytometry (FC) is among the techniques mostly employed by the biomedical community for a variety of purposes, from cell counting to biomarker identification and cell sorting. This laser-assisted technique allows the simultaneous analysis of morphological and biochemical properties of thousands of cells per second and its multiparametric nature relies on the use of fluorochromes, most of them exclusively suitable for fixed cells, although the number of dyes compatible with cell life is constantly growing.

IRMS is intrinsically a multiparametric technique, able to provide a comprehensive information on the cellular status: non-damaging and label-free, it already demonstrated great potentialities for *in vitro* analyses and nowadays a new dimension of the method has been opened thanks to the optimization of devices and methodologies for live cell investigation [1,2].

However, in order to disseminate IRMS use across the bio-community, we need to highlight its advantages in relation to standardized approaches such as FC. This presentation will focus on this topic.

The interplay between cellular proliferation, transformation and death is of paramount importance for hindering diseases occurrence, progression and eventually guarantee successful therapy. For example, tumorigenesis is associated with several changes that alter cellular susceptibility to apoptosis while drug sensitivity is often dependent on the cell cycle stage. The knowledge of cell cycle phase distribution as well as of early apoptotic markers are of great importance for understanding cellular behaviour under normal and stressed conditions. These tasks are usually assessed using Flow Cytometry (FC) or immunohistochemistry. In this presentation, the results and information obtained by FC and IRMS analysis of live cells for the evaluation of the cell cycle stage distribution and apoptosis induction will be compared.

In particular, asynchronous, S- and G0-synchronized B16 mouse melanoma cells were studied by running parallel experiments based on MD-IRMS and FC using Propidium Iodide (PI) staining of cellular DNA. Hierarchical Cluster Analysis (HCA) of cellular microspectra in the 1300–1000 cm^{-1} region pointed out a distribution of cells among clusters, which was in good agreement with FC results among G0/G1, S and G2/M phases. The differentiation was mostly driven by the intensity of PhI and PhII bands. In particular, PhI almost doubled from the G0/G1 to G2/M phase, in agreement with the trend followed by nucleic acids during cellular progression [3]. The ability of IRMS to differentiate between G1-progressive and G0-resting phases will also be shown, a result proven by immunohistochemistry and achievable by FC only by using a multi-probe approach.

The induction of apoptosis in U937 monocyte cell line by serum starvation and CCCP (carbonyl m-chlorophenylhydrazone) exposure was also followed by IRMS and FC. The percentage of viable, early and late apoptotic as well as necrotic cells was assessed first by biparametric PI-DiOC6 FC analysis and results were compared with IRMS ones. Once again both techniques were concordant, but complementary: IRMS got details that FC could not easily reveal and vice versa. As an example, IRMS analysis establishes that the apoptotic progression of U937 due to growth factor withdrawal is associated to the accumulation of lipid droplets, a mechanism revealed for other cell lines, leukemic and not, by NMR spectroscopy. In addition, mitochondrial membrane depolarization detected by FC was not revealed by IRMS, which in contrast had the ability to discriminate between reversible and irreversible mitochondrial damage.

Overall, both FC and IRMS are multiparametric techniques that permit the assessment of a broad range of information at the same time. Actually, IRMS is less selective and slower than FC, but it is a label-free technique applicable on live cells and suitable for achieving accurate information of cellular lipids, usually degraded by permeabilization techniques of cell membranes employed for promoting dye penetration.

Acknowledgement

We acknowledge Dr. A. Marcello who kindly allowed the use of FACS at ICGEB - International Centre for Genetic Engineering and Biotechnology, Trieste, Italy

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1510-1530

SYNCHROTRON FTIR SPECTROSCOPY DISCRIMINATES VERY EARLY DIFFERENTIATION STAGES IN LIVING HUMAN STEM CELLS

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Human cells derived from stem cells destined for use in the clinic for regenerative medicine therapies will first need to be differentiated to specific differentiation or lineage commitment states for these treatments to be effective. Conversely, the transplantation of undifferentiated stem cells into the human body presents a danger as it may lead to the formation of cancerous tumours. In this context, we have been investigating using FTIR spectroscopy to define lineage commitment in human stem cells, and envisage spectroscopic approaches may be useful for quality control and selection of differentiated stem cells for use in the clinic. Recently, we have been successful in using FTIR spectroscopy to discriminate living, undifferentiated human embryonic stem cells from those differentiated to commitment stages equivalent to the earliest phases of embryonic development. These measurements used a specialised IR wet chamber and were acquired using the IR microspectroscopy beamline at the Australian Synchrotron [1]. Apart for the obvious practical need to analyse live cells in line with the aim to develop a new modality for cell selection for clinical practice, measurements using living cells had advantages compared to those from dried, fixed cells. Significantly, in terms of detecting changes in differentiation state, bands from DNA and RNA were observed in the FTIR spectra of live cells that were not detected at all or were much less prominent in the FTIR spectra from the dried cells [2]. Indeed, changes in bands assigned to nucleic acids, including the carbonyl stretching band from DNA at ~1720 cm^{-1}, the anti-symmetric phosphodiester stretching band from DNA and RNA at ~1220 cm^{-1}, and stretching bands from C-O groups in DNA and RNA sugars at ~1120 and 1050 cm^{-1}, associated with the differentiation of cells from the stem cell progenitors, were observed in average spectra and loaded prominently in Partial Least Squares Discriminant Analysis (PLS-DA) models used to classify the spectra. Prominent changes in lipid absorbance were also observed as the live stem cells underwent differentiation, matching changes previously observed in the spectra of dried cells [3,4,5]. We will discuss these findings and the potential for FTIR spectroscopy as a quality control tool for cell selection in regenerative medicine practice.

Acknowledgement

Julie Cao was supported by the Australian Synchrotron Postgraduate Award. This work was supported by the Australian Research Council (ARC), Stem Cells Australia and the Australian National Health and Medical Research Council (NHMRC). Andrew Elefanty and Edouard Stanley are Senior Research Fellows of the NHMRC.

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Biomedical Applications - 2

16:00 – 17:20

Session Chair – Carolyn Dillon

16:00-16:20

DONNA WHELAN
Detecting Cell Cycle Related Changes to the Concentration and Conformation of DNA in Single Live Cells at the Australian Synchrotron

16:20-16:40

MARK HACKETT
A "Stroke of Insight": Coupling Synchrotron Infrared Light, Wide-Field Focal Plane Array Detectors and Stroke Research

16:40-17:00

KEITH BAMBERY
Evaluating the resonant Mie scattering extended multiplicative signal correction algorithm (RMieS-EMSC) on synchrotron FTIR spectra of single cells

17:00-17:20

BAYDEN WOOD
Synchrotron FTIR spectroscopy of malaria infected erythrocytes

17:20

SESSION CLOSE

1600-1620

DETECTING CELL CYCLE RELATED CHANGES TO THE CONCENTRATION AND CONFORMATION OF DNA IN SINGLE LIVE CELLS AT THE AUSTRALIAN SYNCHROTRON

D. R. WHELAN[1], K. R. BAMBERY[2], L. PUSKAR[2], D. MCNAUGHTON[1], B. R. WOOD[1].

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[2] Australian Synchrotron, 800 Blackburn Road, Clayton, 3168, Vic, Australia

Single cell spectroscopy using a Synchrotron infrared source yields superior spectral detail due to enhanced signal-to-noise. It also allows detection of disease and abnormality at a single cell level of sensitivity allowing for the detection of spectral differences caused by varied cell age post-mitosis. These differences are otherwise averaged away during population infrared measurements with conventional globar benchtop FTIR instruments. Here we resolve changes to the spectra of cells from one hour post-mitosis through the G_1, S and G_2 phases, to approximately 23 hours post-mitosis. We demonstrate the importance of considering these cell cycle related spectral changes as well as those caused by disease and experimental effects when analysing single cell spectra. Moreover, we show the remarkable sensitivity of FTIR spectroscopy when applied using a synchrotron source to fully hydrated, live cells.

This research follows directly from previous work into the effects of hydration state on the infrared spectra of biological specimens. Using single-cell measurements from the Australian Synchrotron we have previously demonstrated that a change in the hydration state of cells causes a change in the conformation of DNA and that in the hydrated state the absorptions due to DNA are significantly sharper and more easily detected. These results also demonstrate a B-DNA to A-DNA conformational change upon dehydration that is fully reversible upon rehydration in several eukaryotic cell types (1). The biological significance of this result was further shown by detecting the reversible conformational change in live bacteria. The spectroscopic importance of sample hydration was further emphasised by demonstrating the adherence of eukaryotic cells to Beer-Lambert's Law both in the hydrated and dehydrated states. Avian erythrocytes had previously been reported as containing DNA too dense to interact with infrared radiation due to spectra of dehydrated cells that appeared to be missing DNA absorptions (2). This was reported and cited as a constant cause of artefacts that lead to difficulty in disease detection using FTIR spectroscopy. Using regression models built using spectra of hydrated or dehydrated standards containing known concentrations of DNA and protein (haemoglobin) the dry weight percentage of nucleic acid in avian erythrocytes was estimated (3). These results show that DNA absorbs in a Beer-Lambert fashion and further work concluded that previous results were due to the water-mediated conformational transition causing a significant change in the molar extinction coefficient of many of the spectrally important moieties.

Using our understanding of the spectral changes associated with the concentration and conformation of DNA as well as our developed techniques for measuring live, hydrated cells, we obtained the spectra of over 500 cells at known positions in the cell cycle. Principal Component Analysis was used to analyse these spectra utilizing the entire fingerprint and CH_2/CH_3 regions and allowing for detection of spectral changes every two hours (4). Cells that would be indistinguishable using conventional immunocytology were clustered apart successfully and the Loadings Plots demonstrated subtle biochemical changes throughout the cell cycle associated with DNA concentration, lipid ordering and protein structure. The ability to consider DNA absorptions as directly relatable to both concentration and conformation with single cell sensitivity and an understanding of the changes associated with progression through the cell cycle is of great importance to disease detection as well as in fundamental biochemical experiments using FTIR spectroscopy. Moreover, it is anticipated that sensitive spectroscopic detection of DNA in cells will allow for elucidation of changes in cell proliferation and aneuploidy related to cancer.

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1620-1640

A "STROKE OF INSIGHT": COUPLING SYNCHROTRON INFRARED LIGHT, WIDE-FIELD FOCAL PLANE ARRAY DETECTORS AND STROKE RESEARCH

M. J. HACKETT[1], S. CAINE[1], F. BORONDICS[2], T. MAY[2], P. G. PATERSON[1], H. NICHOL[1], I. J. PICKERING[1], AND G. N. GEORGE[1]

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[2] Canadian Light Source, Saskatoon, Saskatchewan, Canada

Stroke is the third leading cause of death to Canadians and Australians, and the second leading cause of adult morbidity in Europe and North America. The major physiological event of a stroke is ischemia, which is the reduction or loss of blood flow (oxygen and energy supply) to all or part of the brain. Despite some neuronal death at the time of ischemic insult, a significant portion of neuronal damage is delayed, occurring days to weeks following stroke. Although the worsening condition of patients who have suffered a stroke due to delayed neurodegeneration is a tragic fact, it highlights that a "therapeutic window in time" may exist for application of a suitable therapy to prevent or minimise delayed neuronal death.

Although considerable research has been performed on the biochemical pathways initiated during and following ischemia, the techniques available to scientists generally provide either a wealth of biochemical information at poor spatial resolution (i.e., tissue micro-dissection and biochemical assay), or very high spatial resolution imaging of a limited number of chemical species (i.e., localisation of a single protein through immuno-cytochemistry in combination with visible light or fluorescence microscopy).

Fourier transform infrared (FTIR) spectroscopy is one technique which provides a wealth of biochemical information (i.e., total protein, aggregated protein, total lipid) at improved spatial resolution relative to tissue micro-dissection and biochemical assay. Further, as recently shown, coupling bright synchrotron sources with high numerical aperture objectives and wide field focal plane array detectors, allows diffraction limited resolution imaging with a large over-sampling factor, in a short time period.[1-3]

Our presentation highlights the coupling of infrared light at the Canadian Light Source with high numerical aperture objectives and a focal plane array detector to provide sub-cellular imaging of individual neurons in situ within brain tissue sections. Using this approach we have been able to image an area of ~30 μm^2 to resolve the location of neuron cell body (~15 μm), and sub-cellular organelles such as the nucleus (~10 μm) and nucleolus (~2-3 μm). With this ability to resolve complex biochemistry at the sub-cellular level we have studied time dependent alterations which occur in the rat hippocampus following global ischemia, to elucidate further the biochemical mechanisms of delayed neurodegeneration.

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1640-1700

EVALUATING THE RESONANT MIE SCATTERING EXTENDED MULTIPLICATIVE SIGNAL CORRECTION ALGORITHM (RMIES-EMSC) ON SYNCHROTRON FTIR SPECTRA OF SINGLE CELLS

K. R. Bambery, D. Martin, L.R. Hyde, L. Puskar and M.J. Tobin

Australian Synchrotron, 800 Blackburn Road, Clayton, 3168, Victoria, Australia.

At the Australian Synchrotron Infrared Microscopy beamline, FTIR spectroscopy provides sensitive molecular fingerprinting for tissues and cells at sub-cellular spatial resolution and without the need for sample pre-treatment with stains or external markers. However, light scattering effects can hamper the analysis of FTIR spectra and this is particularly difficult in the case of spectral imaging of biological cells as these contain many strongly Mie scattering particles (i.e. objects whose size ranges are close to the wavelength of the infrared light). A Resonant Mie Scattering (RMieS) correction algorithm based on Extended Multiplicative Signal Correction (EMSC) [1] has been recently demonstrated to be effective at removing the Mie scatter induced baseline distortions that compromise raw FTIR spectra.

Unfortunately, as RMieS-EMSC is very computationally intensive it can be time consuming to perform this correction on large FTIR data sets. Software has been developed to allow use of the RMieS-EMSC correction algorithm on FTIR images and datasets on the Multi-modal Australian ScienceS Imaging and Visualisation Environment (MASSIVE) high performance computing facility. A user-friendly semi-automated data workflow design allows IR microscopy beamline users to rapidly RMieS-EMSC correct FTIR spectra on MASSIVE. This presentation will give an overview of the application of RMieS-EMSC correction to FTIR microspectroscopic images and datasets of biomedical interest and highlight the advantages of employing a high performance computing facility for this work. The presentation will also describe beamline experiments we have conducted designed to evaluate the performance of the RMieS-EMSC algorithm.

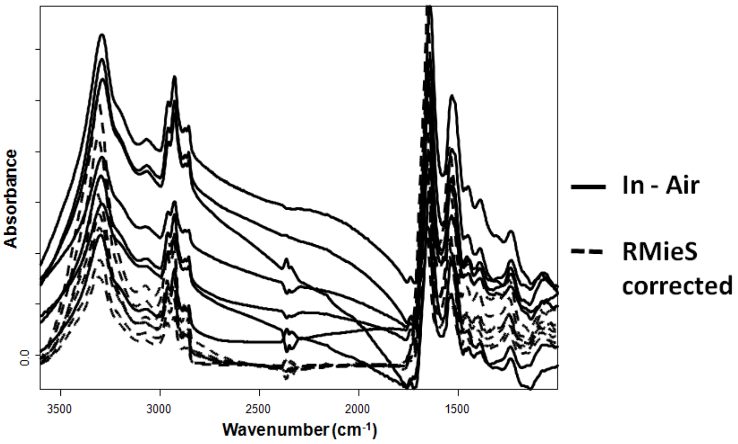

Fig. 1. FTIR spectra of single MCF7 cells before (solid) and after (dashed) RMieS-EMSC correction.

Acknowledgement

This work was supported by the Multi-modal Australian ScienceS Imaging and Visualisation Environment (MASSIVE) (www.massive.org.au).

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SYNCHROTRON FTIR SPECTROSCOPY OF MALARIA INFECTED ERYTHROCYTES

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Previously we have shown that it is possible to differentiate different phases of the malaria parasite as it transgresses through the erythrocytic life cycle using synchrotron FTIR spectroscopy.[1] In that study all of the cells were fixed and the important contributions from the parasitic DNA could not be observed. We have since discovered that the DNA contributions are more readily observed when cells are hydrated.[2] In the hydrated state the B-DNA conformation dominates, whereas in the dehydrated the A-DNA conformation is more prevalent. It appears that the molar extinction coefficient is higher for the B-DNA conformation compared to the A-DNA conformation hence the DNA bands are more intense in the hydrated state.

In this study we have investigated live malaria infected cells using synchrotron FTIR and compared the different stages of parasite throughout the erythrocytic life cycle. We report for the first time the detection of malaria parasite DNA as evinced by the important phosphodiester marker bands including the asymmetric phosphate stretch at 1242 cm^{-1} and the symmetric phosphate stretch at 1082 cm^{-1} along with the base-stacking mode at 1715 cm^{-1}. The appearance of the asymmetric phosphate stretch at 1242 cm^{-1} is particularly interesting as this is consistent with the A-DNA conformation normally only observed in dehydrated cells.

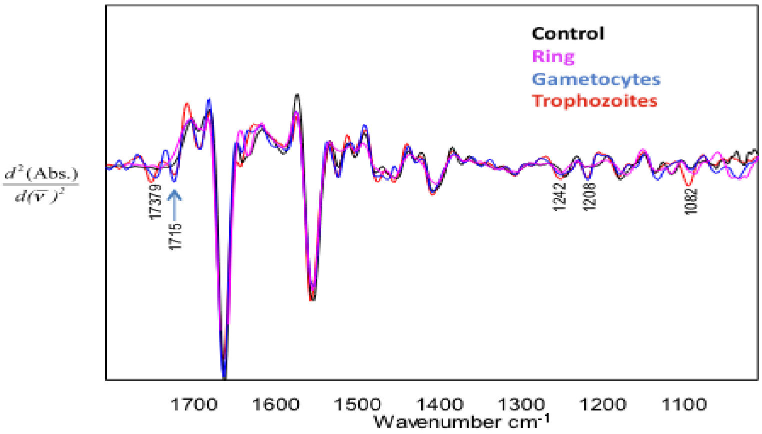

Figure 1. Second derivative spectra of living malaria parasites at different stages of the erythrocytic life cycle highlighting the important haemozoin and DNA marker bands.

More work is required to verify this assignment. Second derivative spectra of the different stages of the parasite are presented and the important bands assigned in Figure 1. The band at 1208 cm^{-1} is assigned to the C-O stretching vibration of the propionate group from hemozoin. This band, along with the DNA marker bands, appear more intense in spectra from trophozoite and gametocyte infected cells compared to the ring stage parasites. None of these bands are observed in the uninfected cells. The results are compared with the analogous spectra recorded of fixed cells. The extremely high throughput and sensitivity of the IR beamline at the Australian Synchrotron has enabled us for the first time to record spectra of living malaria parasites and detect the important DNA and hemozoin marker bands.

Acknowledgement

M.W.A.D is an NHMRC Early Career fellow; LMT is an ARC Australian Professorial Fellow. Dr B. R. Wood is supported by an ARC Future Fellowship grant FT120100926.

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Atmospheric and Environmental Science

09:00 – 10:50

Session Chair – Brant Billinghurst

0900-0930

EVAN ROBERTSON ***Invited Speaker***
Aerosol nanoparticles and the Far-side of IR spectroscopy

0930-0950

DON MCNAUGHTON
Synchrotron high-resolution FTIR spectroscopy sorts out the ground state and low wavenumber modes of ketenimine

0950-1010

JOHANNA HOWES
Assessing metabolic variation of endosymbiotic and cultured Symbiodinium microadriaticum using Synchrotron imaging FTIR spectroscopy

1010-1030

EWEN SILVESTER
Investigation of fungal decomposition of leaf lignin using synchrotron infrared microspectroscopy

1030-1050

MICHEL NIEUWOUDT
Imaging the chemical environments of individual fluid Inclusions using Synchrotron Fourier Transform Infrared microscopy

10:50-11:20

MORNING COFFEE

0900-0930

AEROSOL NANOPARTICLES AND THE FAR-SIDE OF IR SPECTROSCOPY

EVAN G. ROBERTSON[1] *Invited Speaker*

C. MEDCRAFT[2], A. WONG[2], D. MCNAUGHTON[2], C. D. THOMPSON[2], D. APPADOO[3] AND S. BAUERECKER[4]

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Aerosols impact earth's climate both directly through absorption and reflection of light, and indirectly by hosting chemical reactions and influencing cloud formation. They play an important role in interstellar chemistry, particularly those involving molecular ices. When compared to equilibrium conditions for bulk material or even thin films, aerosols display quite different optical properties, structure, phase dynamics, solubilities etc that must be accounted for to accurately model their behaviour.

IR spectroscopy, with its acute sensitivity to the chemical bonding environment, has been widely used to study clusters and aerosols. Recently, a new generation of collisional cooling cell designed by one of our collaborators [Bauerecker 2001] has created new possibilities for systematically studying aerosols generated by pulsed sequences of injections. We have used one of these cells, coupled to the Bruker IFS125HR spectrometer on the High Resolution Infrared Beamline at the Australian Synchrotron, for both high resolution gas phase studies and for aerosol studies. Development work on the cooling cell has made it possible for the first time to extend these types of aerosol measurements to the crucial but hitherto unexplored far IR region. IR Spectra have been measured for aerosols comprised of small organic and inorganic molecules, and aerosols of water ice provide a case study of how much may be learned from such spectra.

Crystalline water ice particles in the nanoscale size regime were generated by rapid collisional cooling at temperatures ranging from 4-209 K. Their spectra have been measured in the far-IR region for the first time, using synchrotron radiation, and also in the mid-IR region. Spectral diagnostics, such as the ratio of surface related dangling OH to interior H-bonded OH stretch bands, reveal the manner in which particle size depends on bath gas temperature and density, and on water molecule concentration. Notably, the aerosol spectra show significant differences compared to previous thin film spectra. The particle size regime (3-150 nm) is such that scattering effects are negligible, and the onset of less crystalline behaviour may be observed for particles smaller than around 5 nm. These measurements provide a means to assess optical constants required for radiative forcing calculations in many contexts, including earth's energy balance.

Acknowledgement

This work was generously supported by the Australian Synchrotron through beamtime allocations and non-beamtime facility access and an Australian Synchrotron Postgraduate Award (C.M.). Financial support from the Australian Government through an Australian Postgraduate Award to C.M. is also gratefully acknowledged. The research was also supported by the Deutsche Forschungsgemeinschaft (Grant BA 2176/3-1).

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SYNCHROTRON HIGH-RESOLUTION FTIR SPECTROSCOPY SORTS OUT THE GROUND STATE AND LOW WAVENUMBER MODES OF KETENIMINE.

D. McNaughton[1], M. K. Bane[1], C. D. Thompson[1], E. G. Robertson[2], D. R. T. Appadoo[3] and C. Medcraft[1]

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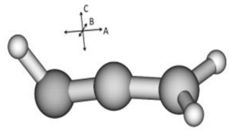
[2] Department of Chemistry, La Trobe University, Victoria, 3083 Australia
[3] Australian Synchrotron, 800 Blackburn Rd, Clayton, 3168, Victoria, Australia



Ketenimine ($H_2C=C=NH$) is a transient molecule that is of interest in interstellar chemistry and apart from its microwave spectrum little is known. This tautomer of acetonitrile has been identified in the star forming region Sagittarius B2(N) by observing microwave emissions. In this work ketenimine was generated by flow pyrolysis of 3-hydroxypropionitrile. Under the experimental conditions formaldehyde, hydrogen cyanide, carbon monoxide and acetonitrile are also present in varying concentrations depending on the precise experimental conditions. Acetonitrile is present from the rapid tautomerization of ketenimine whilst the other species are side products of the pyrolysis. From the microwave studies the half-life of ketenimine in the cell was < 1 second and our flow experiments are consistent with a similar half life. The optimum experimental conditions were found to be an oven temperature of ~1100°C, to ensure the precursor was completely decomposed, whilst pumping the products through a multi-pass White cell at a rate high enough to ensure that the amount of the more stable acetonitrile conformation was minimized. In this study far- and mid-IR high resolution spectra (20-1300 cm^{-1} at nominal resolution 0.001-0.002 cm^{-1}) were recorded using a Bruker HR125 coupled to the far-IR beam line of the Australian synchrotron and both pure ground state rotational transitions and ro-vibrational transitions were recorded using a number of different detectors, beamsplitters, window materials and various pathlengths. DFT calculations at the B3LYP/cc-pVTZ level of theory were used to predict vibration-rotation parameters and Coriolis coupling parameters in order to assist spectral assignment and fitting.

The excited vibrational states exhibit a complex ro-vibrational structure, due primarily to strong Coriolis interactions. As a consequence of this dynamic coupling, some of these modes exhibit a novel intensity sharing effect, with the relatively weak ν_{10} and ν_{12} bands being analyzed completely using perturbation allowed transitions [1], which exhibit intensities independent of their own natural dipole moment derivative. ie. They "steal" intensity from coupled modes.

The analysis of ν_7 [2], ν_{10} and ν_6 [3] were also complicated by the presence of local Fermi and Coriolis resonances with the higher order excitations of ν_{12} and ν_8, which are themselves strongly Coriolis coupled. Analysis of ground state combination differences of ν_7 also uncovered second order Coriolis interactions between the ground state and both ν_{12} and ν_8 at high K_a, and a global fit including the ground state, ν_{12}, ν_8, ν_7, $2\nu_{12}$, $\nu_{12} + \nu_8$, $2\nu_8$, ν_{10} and ν_6 was achieved. The combination and overtones were included in the fit as dark-states, since they were too weak to be observed.

Overall approximately 20000 individual ro-vibrational and ground state transitions were assigned using Loomis-Wood techniques (MacLoomis) and fitted to the appropriate asymmetric top Hamiltonian using Pickett's SPFIT program. A small section of the assigned spectrum together with a spectrum simulated from the fitted parameters is shown in figure 1.

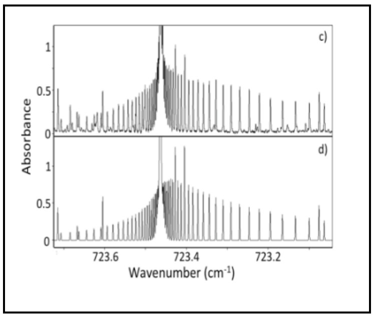


Fig. 1. Experimental (c) and simulated (d) spectrum of a small part of the ketenimine spectrum.

Acknowledgement

We acknowledge the Australian synchrotron for provision of beamtime.

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0950-1010

ASSESSING METABOLIC VARIATION OF ENDOSYMBIOTIC AND CULTURED SYMBIODINIUM MICROADRIATICUM USING SYNCHROTRON IMAGING FTIR SPECTROSCOPY

J. M. HOWES[1], O. SACKETT[1], B.H. STUART[2] AND P. J. RALPH[1]

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The Great Barrier Reef is an ecological hot spot that covers over 200,000 km^2 along the North East coast of Australia and is estimated to be home to at least 27 endangered species, almost 2000 different species of fish and 500 coral species alone. It contributes an estimated $5 billion to Australia's economy per year. The delicate and complicated energy balance within the reef-building coral symbiosis can be severely affected by changes in temperature, salinity, pH and light intensity, all potentially inducing coral bleaching. The cellular mechanism of coral bleaching is not yet known. However, there is a consensus amongst scientists that bleaching involves a disruption of the symbiotic relationship between the zooxanthellae and their coral host. Under stress, the coral will expel the algae, resulting in a loss of pigment and a severe drop in carbon acquisition, the consequences of which are often death.

There is a large amount of research into the photobiology of the coral symbiosis focusing on photosynthetic health of the symbiont and photo-protective mechanisms within the zooxanthellae, as there is evidence to suggest that bleaching is triggered by a breakdown in these systems. Most studies struggle to link the biochemistry of the system with photobiology due to the limitations of the techniques used, such as complicated extraction procedures, spectrophotometric assays and isotopic labelling**.**

Fourier Transform Infrared Spectroscopy has shown promise as an alternative method in the analysis of cultures of the symbiont, *Symbiodinium microadriaticum* and how their macromolecular content changes under environmental stress. However conventional laboratory imaging instruments are not able to visualise the cells with an appropriate resolution. Using the Infrared Environmental beamline (IRENI) at the Synchrotron Radiation Center (University of Wisconsin, Madison) we were able to visualise changes in biochemistry within a single cell. In addition we compared the response of the symbionts in culture and endosymbiotic cells from the scleractinian coral, *Pocillopora damicornis* exposed to thermal stress.

Acknowledgement

This work is based on research conducted at the IRENI beamline whose construction and development was supported by NSF under award #0619759. The project was also supported by the International Synchrotron Access Program (ISAP), Australian Synchrotron.

1010-1030

INVESTIGATION OF FUNGAL DECOMPOSITION OF LEAF LIGNIN USING SYNCHROTRON INFRARED MICROSPECTROSCOPY

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In aquatic ecosystems leaf litter from riparian (bank-side) vegetation can be an important source of carbon and energy to the aquatic food web. Fresh leaves however contain chemical inhibitors (e.g. polyphenols) and are a poor food resource for secondary consumer organisms (shredders and grazers). The initial processing of fresh leaves is therefore via microbial decomposition, rendering the leaf more palatable to secondary consumers, but also removing much of the readily bio-degradable material. In the aquatic environment this decomposition process is termed ‘conditioning’. Aquatic fungi are thought to be important in the conditioning process, likely accessing the carbohydrate content of lignified tissue through lignin oxidation using exo-enzymes (ligninases) [1]. In doing this, fungi are thought to increase the protein and accessible carbohydrate content, and convert the conditioned leaf into a superior food resource.

Infrared (IR) micro-spectroscopy is ideally suited to the study of bio-molecular changes in leaf tissue during fungal leaf decomposition; IR spectra allow the discrimination of leaf tissue composition, and leaf anatomy is reproducible between samples so changes in spatial distributions are readily recognised**.** The coupling of IR micro-spectroscopy with synchrotron light sources offers considerable advantages in terms of spatial resolution, allowing investigation of the interface between fungal tissue and leaf substrate at relevant length scales. In this work we have used focal plane array Fourier transform infrared spectroscopy (FPA-FTIR) and synchrotron light source Fourier transform infrared spectroscopy (S-FTIR) microscopic techniques to map the chemical composition of leaves from two eucalypt species (*Eucalyptus camaldulensis* (River Red Gum) and *Eucalyptus pauciflora* (Snow Gum)) through the terrestrial and aquatic decomposition processes, focusing on changes in the leaf mid-vein anatomy.

In both eucalypt species terrestrial decomposition processes (prior to entering the aquatic system) remove much of the readily bio-degradable leaf tissue, yielding a leaf substrate that is largely composed of lignified vascular tissue, leaf cuticle and fungal material. Further decomposition occurs under aquatic conditions with depletion of lignin-bound carbohydrate (cellulose) immediately adjacent to the fungal tissue. S-FTIR mapping reveals that cellulose depletion is spatially correlated with oxidation (de-polymerisation) of the lignin framework, consistent with the action of fungal exo-enzymes [2]. Seasonal studies of Snow Gum leaf decomposition (with replicate samples) show that cellulose depletion is greater during summer months compared to winter, consistent with seasonal variations in fungal activity.

The work shows that in addition to improving the nutritional value of leaves for macroinvertebrate consumer organisms, fungal decomposition also has a critical role in partitioning leaf carbon into the biodegradable fraction that can be returned to the aquatic carbon cycle, and a recalcitrant fraction that is directed towards long-term carbon storage in sediments.

Acknowledgement

This work was supported by e-Water CRC. We thank Camilla Cohen (Monash University Histology Platform) for assistance in the preparation of leaf sections.

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1030-1050

IMAGING THE CHEMICAL ENVIRONMENTS OF INDIVIDUAL FLUID INCLUSIONS USING SYNCHROTRON FOURIER TRANSFORM INFRARED MICROSCOPY

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Fluid inclusions provide a record of the physical and chemical composition of fluids that form hydrothermal orebodies in the Earth's crust. Microthermometry and *in situ* techniques such as laser ablation inductively coupled plasma mass spectrometry can provide important constraints on the temperature, pressure, apparent salinity, and element concentrations of individual fluid inclusions.

Here, we describe a novel use of synchrotron Fourier Transform Infrared (FTIR) microscopy to map three parameters in in individual fluid inclusions: (1) very low levels of CO_2, (2) variations in dissolved CO_2 and (3) variations in H bonding in the H_2O phase. The intensity of the synchrotron light source allows mapping of individual fluid inclusions, and provides high-resolution images of chemical variability within individual inclusions.

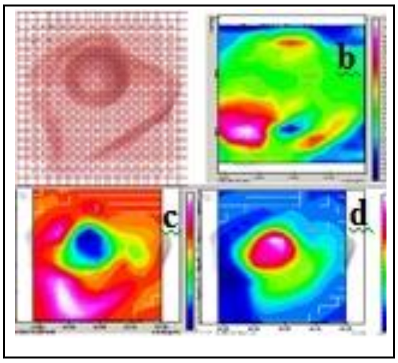

Fig.1 Image of Karangahake 5 inclusion showing grid of spectral collection points. **(b)** Mapping of CO_2 gas (R branch at 2361 cm^{-1}). **(c)** Mapping of higher energy H_2O mode 4101-3379 cm^{-1}. **(d)** Mapping of lower energy H_2O mode (3467-2864 cm^{-1}).

Acknowledgement

This research was undertaken on the Infrared beamline at the Australian Synchrotron, Victoria, Australia and we thank Dr. Mark Tobin for assistance with this. We thank New Talisman Gold Mines Limited for their continuing support of our research, for their assistance with sample collection, and for permission to publish. We thank Professor Bob Bodnar of Virginia Tech for the synthetic CO_2-H_2O fluid inclusions. We also thank the New Zealand Ministry of Business, Innovation and Employment Science and Innovation Group for financial support. We acknowledge travel funding provided by the International Synchrotron Access Program (ISAP) managed by the Australian Synchrotron and funded by the Australian Government.

Far-IR Condensed Phase

11:20 – 12:50

Session Chair – Dominique Appadoo

11:20-11:50

Jean-Blaise Brubach ***Invited Speaker***
Recent results on material research using the AILES Beamline

11:50-12:10

Larry Carr
Photo-induced spectroscopy of GaAs in a magnetic field: time-resolved circular dichroism

12:10-12:30

Petra Hellwig
Hydrogen bonds and protonation reactions in membrane proteins: a far infrared spectroscopic approach

12:30-12:50

Gernot Hoehne
Instrumental Developments in Molecular Spectroscopy: New Components, Accessories and Technologies

12:50-13:50

Lunch **Today's lunch is sponsored by:**

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1120-1150

RECENT RESULTS ON MATERIAL RESEARCH USING THE AILES BEAMLINE

JEAN-BLAISE BRUBACH *Invited Speaker*

SOLEIL Synchrotron, Gif Sur Yvette, 91192, France

In this presentation the infrared beamline AILES of SOLEIL [1] will be briefly introduced and a special emphasis will be placed on its technical specificity. I will then present some examples of measurements covering all the spectral range and using devoted set-up with incoherent and coherent synchrotron emission (which allow an extension to the THz domain).

I will then introduce several studies related to the interaction of water molecules at the interface of various media. These studies aim at probing the properties of water (and ice) next to various types of interface, incorporating both hard and soft substrates. A particular emphasis is put on the study of the hydrogen bond directly observed in the far infrared domain [2], for metalloproteins in solution [3] and mesoporous systems such as Nafion® (polymeric membrane) Vycor® glasses (porous silica glass), and zeolites by following the effect of the hydration level and the temperature.

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1150-1210

PHOTO-INDUCED SPECTROSCOPY OF GaAs IN A MAGNETIC FIELD: TIME-RESOLVED CIRCULAR DICHROISM

XIAOXIANG XI[1], S. N. GILBERT[2], J. J. TU[3], T. STANISLAVCHUK[4], A. A. SIRENKO[4] AND G. L. CARR[1]

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The high brightness, broad spectral coverage and pulsed characteristics of infrared synchrotron radiation enable time-resolved spectroscopy under throughput-limited optical systems, such as high-field cryostats used to study electron dynamics such as cyclotron resonance in the far-infrared. A natural extension for magneto-spectroscopy is to sense circular dichroism, i.e. the difference in a material's optical response for left and right circularly polarized light. A key component is an achromatic ¼ wave retarder for the spectral range of interest. The same type of retarder is used for far-infrared ellipsometry[1] for which achromatic, rhomb-type retarders have been developed that exploit the phase shift between *s* and *p* polarized light upon total internal reflection. We have developed a 4-reflection, in-line retarder using high-resistivity silicon.

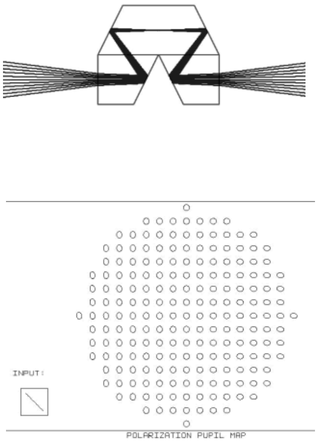

Fig. 1. Beam focus through rhomb retarder and polarization map for 45° linearly polarized incident light.

The performance of such a ¼-wave retarder can be seen in the far-infrared spectra of electrons in GaAs when a magnetic field is applied. At low temperatures, an electron, photo-excited from the valence band, can reside in free electron levels in the conduction band or as an exciton (the bound state of an electron and a hole). In a magnetic field, the conduction band becomes quantized into Landau levels whose spacing increases with field strength. Similarly, excitonic levels are modified by an applied field in a manner analogous to the hydrogen atom. In both cases the far-infrared absorption associated with electronic transitions is affected and becomes dependent on whether the light is in a left or right circularly polarized state. This can be seen in Fig. 2 where the absorption feature near 37 cm^{-1} for B=0 splits into two branches for B≠0. When the photo-excitation is done with a pulsed laser, pump-probe measurements can sense the relaxation through these energy levels[2].

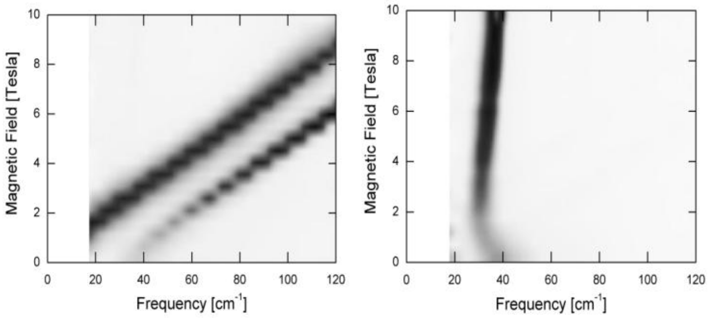

Fig. 2. Photo-induced absorption maps vs. magnetic field for GaAs showing electronic transitions between Landau levels and exciton 1s to 2p levels (at 37 cm^{-1} for B=0). *Left panel*: Right circular polarized light. Right panel: Left circular polarized light. The 2p level splits into $2p^{-1}$ and $2p^{+1}$.

Acknowledgement

This research supported by the U.S. Department of Energy under contract DE-AC02-98CH10886 at Brookhaven National Laboratory. Technical contributions from Randy Smith and Gary Nintzel are gratefully acknowledged.

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1210-1230

HYDROGEN BONDS AND PROTONATION REACTIONS IN MEMBRANE PROTEINS: A FAR INFRARED SPECTROSCOPIC APPROACH

P. HELLWIG

Laboratoire de bioelectrochimie et spectroscopie, UMR 7140, Université de Strasbourg, France,

Energy supply mechanisms are central to life and living cells and are in focus of our research. Although the architectures of several membrane proteins in respiration and photosynthesis as well as the basic chemical reactions have been described, the interactions on molecular level, the curiously high diversity of mechanisms and their high efficiency, need to be clarified.

Conformational changes and protein dynamics play a central role in the catalytic efficiency of enzymes and are crucial to the biological function. Information on large-scale collective molecular motions and the internal hydrogen bonding structure of proteins can be observed in the far spectral region. We have probed the far IR spectral region from 0.06 THz (2 cm-1) to 10 THz (333 cm-1) together with the low frequency region (333-1000 cm-1) with conventional and synchrotron light sources for the study of proteins and membranes and examples of these studies will be described. [1-5]

In order to understand the molecular basis of energy transduction, experiments have been developed which reveal how protons, other ions and water molecules are drawn through proteins and how they are coupled to electron transfer. A combined electrochemical and infrared spectroscopic approach was used for the determination of the pK value of crucial amino acid side chains and for the study of the structural, dynamic and energetic requirements for the proton transferring groups in the proton or sodium pumping enzymes and the cofactor sites that rule them. The technique enables the observation of protein action at the level of single functional groups within large proteins. This reaction induced infrared spectroscopic approach was then further developed for the far infrared spectral range giving access to information from metal ligand vibrations in a redox depended manner. [6]

Acknowledgement

We are grateful to and the CNRS, the FRC and the université de Strasbourg for financial support. Experiments at IR beamlines cited here have been performed at the ANKA in Karlsruhe with the kind support of Dr. David Moss and Dr. Yves-Laurent-Mathis as well as at Berlin with the kind support of Dr. U. Schade.

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INSTRUMENTAL DEVELOPMENTS IN MOLECULAR SPECTROSCOPY: NEW COMPONENTS, ACCESSORIES AND TECHNOLOGIES

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Spectrometers are available from a number of suppliers in USA, Europe, Asia and Japan. The performance of any instrument is usually sufficient for routine analysis. One key differentiation however is the ability to perform specific and sensitive measurements. In this contribution we describe components and features, which enhance the usability and/or add functionality to a spectrometer such as:

1. For molecular vibrational analysis in inorganic and organometallic chemistry as well as for geological, pharmaceutical and physical applications the extension of the mid IR towards the far IR spectral range below 400 cm^{-1} is of general interest. The lower limit of the spectral range is very dependent upon the beamsplitter and is typically limited to 350 cm^{-1} (KBr) or 200 cm^{-1} (CsI). To extend the spectral range further into the far IR and THz spectral ranges one or more additional far IR beamsplitters were required. Today beamsplitters with extended spectral range obviate a frequent exchange are available.

2. ATR spectroscopy using diamond prisms with usually one reflection has revolutionized quality control, however sometimes at the expense of sensitivity. Special applications such as analysis of semiconductors like Silicon or very thin coatings on Silicon require higher sensitivity. A unique ATR accessory enhances the measurement sensitivity for wafer-like semiconductors.

3. Electrochemical analysis is gaining much interest for developments of efficient energy storage devices. Specific accessories support sensitive analysis of electrochemical surface interactions in the external or internal reflection mode which have been adapted for the evacuated sample compartment as well.

4. Analysis or identification of samples, specifically of small samples, is very important e.g. in failure analysis and forensics. Automation features, software guided operation paired with high sensitivity assist the user towards a quick and successful analysis.

THIS TALK SPONSORED BY

Materials Applications

13:50 – 15:10

Session Chair – Andrea Perucchi

13:50-14:10

BILL VAN BRONSWIJK
Detection of Water in Radiation damaged zircon using Synchrotron FTIR-ATR

14:10-14:30

ALEXEY KONDYURIN
Synchrotron IR imaging of protein coating on vascular stents

14:30-14:50

SONG HA NGUYEN
Correlation between the proportion of epicuticular waxes and wettability among various species of dragonfly wing

14:50-15:10

MARK FROGLEY
Infrared Microanalysis of Molecular Deformations in Graphene Oxide Based Materials During Nanomechanical Tensile Tests

.

DETECTION OF WATER IN RADIATION DAMAGED ZIRCON USING SYNCHROTRON FTIR-ATR

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[2] *WA School of Mines, Curtin University, Bentley, 6102, Western Australia*

The purpose of this project was to assess the capability of synchrotron source FTIR microscopy to detect water in radiation damaged zircon mounted on sample holders used for ion microprobe analyses.

Zircon is widely distributed in igneous, metamorphic and sedimentary rocks and is a key component in heavy mineral deposits where it is mined in large quantities mainly for the ceramics industry. In addition, as a result of trace amounts of U and Th incorporated in the crystal structure, zircon has become the most important mineral in U-Pb geochronology and is increasingly being used as a source of fundamental geochemical information based on other trace elements such as the Rare Earth Elements (REE) and Ti, and also Li, Hf and oxygen isotopes. However, over geological time alpha emission from the radioactive decay of U and Th breaks down the zircon structure until it is reduced to the amorphous state. Zircon is nominally anhydrous but as it becomes progressively more radiation damaged, it becomes vulnerable to water penetration through hydrothermal activity or even low temperature weathering. The U-Pb systems in such radiation damaged grains are frequently disturbed and the role of secondary water in facilitating this disturbance and in affecting the concentrations of REE, Ti, Hf and oxygen isotope systems in the zircon grains is the basic problem under investigation in the present project. U, Pb, REE, Ti, Hf and oxygen isotopes are determined on polished zircon grains set in 2.5 cm x 0.5 cm thick resin mounts and it is highly desirable to be able to determine the water content on the same analytical spots used for other element determination on the standard mounts.

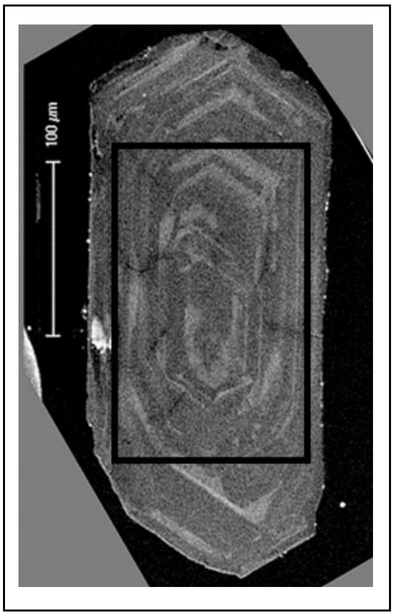

Fig. 1. Complexly zoned Grain 155-31 showing the area mapped for OH using the ~3400 cm^{-1} band.

Conventionally water is measured in zircons by transmission FTIR using thin specially prepared zircon plates. Our purpose in the present project is to explore the possibility of using reflection FTIR to determine water on small areas of the polished surfaces of zircons on the standard mounts. Analyses using FTIR microscopy with a glow bar source were found to have neither the spatial resolution nor sensitivity to produce satisfactory data. However, we have achieved encouraging results using the higher intensity and spatial resolution of the synchrotron IR beam.

Samples investigated by synchrotron FTIR were a set of homogeneous zircons from Sri Lankan gravel deposits and two populations of complexly zoned zircons from Archean granites from Western Australia. We were not successful in detecting water in the zircons using reflected infrared but with FTIR-ATR we observed broad stretching mode OH peaks at around 3400 cm^{-1} in most zircons suspected of containing water. This confirmed previous observations using transmission FTIR [1] that the OH stretch arises primarily from water species in radiation damaged zircon. We were able to map the distribution of OH over selected areas on the polished surfaces of inhomogeneously radiation damaged zircon at 5 micron spatial resolution (Figure 1). The OH content was found to broadly correlate with the degree of radiation damage.

Acknowledgement

We acknowledge support for travel and accommodation from the Australian Synchrotron.

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SYNCHROTRON IR IMAGING OF PROTEIN COATING ON VASCULAR STENTS

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[4] Department of Medicine, University of Sydney, NSW 2006, Australia

All metallic vascular prostheses, including stents and heart valves, exhibit suboptimal biocompatibility that significantly reduces their clinical efficacy. Specifically, while there are more than two million coronary stents deployed worldwide per annum, stent thrombosis and restenosis remain significant unresolved problems. We have recently developed a plasma polymerised polymer coating for covalent binding of proteins to metallic surfaces in their bioactive state; thereby providing a novel platform for vascular biomimicry of metallic implants [1]. The mechanism of attachment is based on reactions between free radicals on the plasma polymer surface and proton-donor groups of the protein molecule [2]. For optimal efficacy, stents need to be completely and uniformly covered with both the plasma polymer and coating protein.

Achieving complete coverage uniformity for the plasma polymer and protein is complex, presenting two significant challenges. First, polymerisation in plasma is a stochastic process and is very sensitive to substrate surface geometry, surface contamination and local plasma density distribution. Therefore, it is critical to analyse the coating on the specific stents in development, as parameters cannot be sufficiently simulated on satellite flat samples. Secondly, the free radicals in the plasma polymer are extremely reactive and can adsorb pollutants from the atmosphere. If non-controlled binding on the surface is prevalent, the surface becomes inactive to proteins. Accordingly, the distribution of the attached proteins on plasma polymer coating should also be analysed on the stent surface.

The FTIR ATR spectroscopy, XPS, AFM, ellipsometry and ELISA assay methods have been successfully used for analysis of plasma polymer and protein attachment for large flat samples [3-6]. However, such methods cannot be used to get information on distribution of the plasma polymer and protein layer on stent struts, which are 70-100 µm thick. The IR beam intensity of modern FTIR spectrometers is not sufficient to get a high signal-to-noise ratio from the expected 5 nm protein layer. A higher intensity IR beam is required to obtain useful protein spectra. We sought to use a high intensity synchrotron IR beam to faciliate the identification of the plasma polymer and protein layers bound to the stent struts.

We carried out experiments at the IR microscopy facility of Australian Synchrotron and determined parameters for measurements which were suitable to obtain spectra of the plasma polymerised coating and protein immobilised on the stents. The amount of protein was analysed using the characteristic lines of protein molecules (Amide A, I and II). The lateral resolution, signal-to-noise ratio and spectral resolution were sufficient to analyse the protein distribution on the stent surface, which has a complicated shape. The results showed that the plasma polymer coating process used at that time, produced a non-uniform protein coating layer on the stent surface despite a complete coating of the metal stent with the plasma polymer. This data directly informs our plasma polymer stent coating conditions, as well as the protein incubation regime. These can be adjusted to provide higher uniformity of bioactive protein coating on whole the surface of the complex shaped stent. Further investigations are underway.

Acknowledgement

We acknowledge funding from the Australian Research Council, National Health and Medical Research Council. This research was undertaken on the far infrared and Infra Red Microscope beamline at the Australian Synchrotron, Victoria, Australia.

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1430-1450

CORRELATION BETWEEN THE PROPORTION OF EPICUTICULAR WAXES AND WETTABILITY AMONG VARIOUS SPECIES OF DRAGONFLY WING

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Insects first evolved the ability to fly at least 400 million years ago and are one of the biggest families, representing half of all living organisms on Earth [1]. In order to adapt to ever-changing environments, they have diverged in different directions to cope with different stresses. Investigation into their mechanisms for coping with these environmental stresses has provided the scientific community with great insights for many useful applications nowadays. Very recently, dragonflies have been gained much attention due to their sophisticated surface structure, and are synonymous with superhydrophobicity, self-cleaning and anti-bactericidal phenomenon. Previously published works revealed that the fundamental components of epicuticular layer of dragonfly wings consisted of peptide linked structural protein components of the bulk of the wing membrane. Waxy components include long chain aliphatic hydrocarbon (C_{14}-C_{30}) together with some carboxylic acid (palmitic acid and stearic acid) made up the outermost layer of insect wing epicuticle. In this work, we compare and contrast the chemical composition of epicuticular waxes presented on the surfaces of aged and fresh dragonfly species. The contribution of their surface chemistry to surface characterisation also evaluated. *Diplacodes melanopsis* and *Austrogumphus guerini* were preserved in Melbourne museum since 1970s and provided for studying. When comparing with fresh dragonfly wings *Diplacodes bipunctata*, *Hemianax papuensis* [2] and *Hemicordulia tau* [3] using FTIR, the fundamental components of the dragonfly wings were found to remain unchanged. However, the amount of waxy components varied between species. The wettability of *Diplacodes melanopsis* which appeared lowest (138°) compare to other species, synchronising with its low waxy quantity. The composition of individual waxy components can be varied qualitative and quantitative which gave substantial differences in their surface chemistry and surface topography.

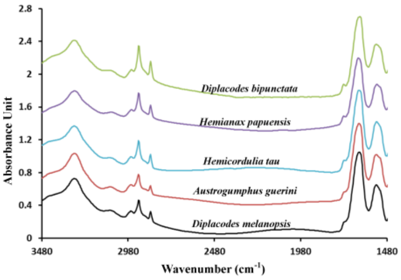

Fig. 1. Chemical profiles of the different dragonfly wings species as inferred from infrared absorption spectra. The spectra were acquired at the Australian Synchrotron.

Acknowledgement

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1450-1510

INFRARED MICROANALYSIS OF MOLECULAR DEFORMATIONS IN GRAPHENE OXIDE BASED MATERIALS DURING NANOMECHANICAL TENSILE TESTS

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An atomic-force microscope tensile testing system, developed for sensitive mechanical testing of micro-nanoscale samples, has been coupled with the high brightness synchrotron infrared microscope at Diamond Light Source, UK, for *in-situ* spectroscopy of molecular deformations under strain.

This technology is being used to investigate the deformations and failure mechanisms in graphene oxide (GO) based materials, whose mechanical properties are important for applications in energy storage systems such as electrical batteries and supercapacitors and in multi-layered composites. In simple GO papers, nanomechanical tensile tests on hydrated and dehydrated samples demonstrate the importance of hydrogen bonding between GO sheets, which fails abruptly at large applied strain [1], and this is compared with GO materials with designed interfaces using cross linking molecules.

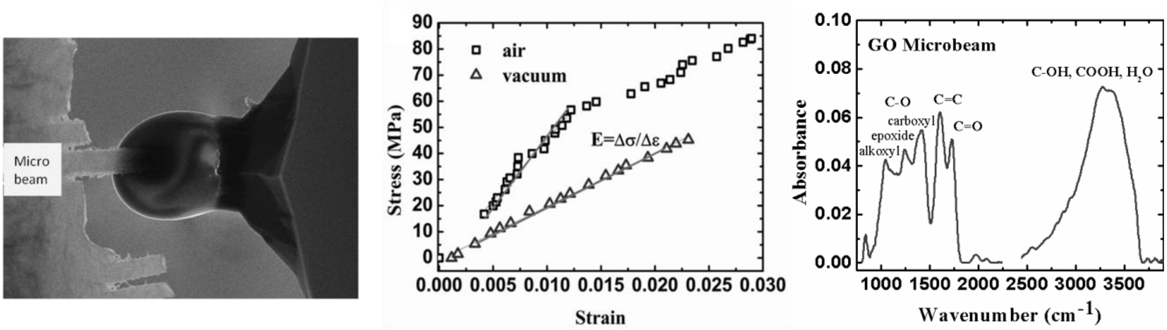

Fig. 1. Left: AFM nanomechanical testing of a GO paper micobeam. Centre: Tensile behaviour of hydrated and dehydrated GO paper microbeams. Right: IR spectrum of a GO microbeam during AFM tensile testing (strain ~0.5%).

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Time Resolved Studies

15:10 – 15:50

Session Chair – Danielle Martin

15:10-15:30

ULRICH SCHADE
A Fèry Prism based Mid-IR Spectrometer with µs Time Resolution in Single-Shot Mode

15:30-15:50

FERENC BORONDICS
Electrochemical reaction kinetics followed by FTIR spectromicroscopy - Approaching the diffraction limit

15:50

CONCLUDING REMARKS

ANNOUNCEMENT OF LOCATION FOR WIRMS 2015

1510-1530

A FÈRY PRISM BASED MID-IR SPECTROMETER WITH µS TIME RESOLUTION IN SINGLE-SHOT MODE

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Several attempts have been made to extend time-resolved mid IR spectroscopy to higher time resolution for non-cyclic measurements. Such methods are either limited to specific samples [1] or lack spectral resolution [2]. Here, we report on a single-shot spectrometer which overcomes the aforementioned limitations. The spectrometer will be applied for the investigation of the irreversible cascade of structural alterations in proteins (e.g. rhodopsin) upon light absorption.

Our spectrometer optics is based on a Fèry prism [3] which not only disperses a beam into a spectrum but also focuses the beam. The design basically follows the optical design of Warren *et al*. [4]. The prism is made of BaF_2 while the elements of the re-imaging optics are made of Ge lenses. The lenses are anti-reflection coated in order to minimize reflection losses in the spectral working range from 5.5 µm to 10 µm. The design has been optimized by non-sequential ray-tracing resulting in a diffraction-limited imaging of the spectrum onto the linear FPA with a usable dispersion of $d\lambda/dx = 25$ nm/ 40 µm.

The array detector is operating in snap-shot mode with photon noise limited performance. All pixels are illuminated simultaneously. This makes the spectrometer insensitive to flux fluctuation for instance caused by mechanical vibrations. Detailed calculations using IR synchrotron radiation ($5.4\mathrm{x}10^{13}$ photons/s within 0.1% bandwidth at 10 µm wavelength) from the IRIS beamline [5] have shown that for a pixel size of 40 µm a signal-to-noise ratio of 1000 is achievable within 0.3 µs acquisition time. The detector element will even be saturated for acquisition times larger than 20 µs taking a reasonable detector full well capacity of $5\mathrm{x}10^{7}$ electrons into account. A parallel pixel read out with a master clock frequency of 20 MHz ensures a high data throughput via direct memory access. This allows to record time-resolved spectra over a broad time range from µs to s.

Acknowledgement

We acknowledge fundings from the European Research Grant (ERC) “TUDOR” and from the Strategy Investment Program of HZB.

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1530-1550

ELECTROCHEMICAL REACTION KINETICS FOLLOWED BY FTIR SPECTROMICROPSCOPY - APPROACHING THE DIFFRACTION LIMIT

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The combination of electrochemistry with spectroscopic techniques is a necessity for a full understanding of electrochemical kinetics. While electrochemistry provides control over reaction triggering and detecting currents, spectroscopy gives an insight into the details of chemical and structural changes otherwise invisible.

An inherent problem of such combination is the conflicting interest of observing fast reactions and the need for a reasonable spectral S/N ratio. The RC time constant of an electrochemical cell determines the speed a process can be controlled and studied. Decreasing the RC time constant is easily achievable by shrinking the electrode where the reaction of interest happens and ultramicroelectrodes (umes) are readily available to do so. However from the spectroscopist's point of view the larger an electrode the better, as it provides higher quality data. Ultimately – in a far-field setup – the diffraction limit determines the smallest applicable electrode size.

In this presentation we will report on using the Mid-IR spectromicroscopy beamline at the Canadian Light Source in combination with electrochemical cells utilizing umes. We will discuss instrumentation [1] and test experiments in rapid- [2] and Step/Scan modes [3] showing the potential of the technique with less then one microsecond time resolution and 10^{-14} molar sensitivity (in the case of ferrocyanide).

Acknowledgement

Research described in this paper was performed at the Mid-IR beamline of the Canadian Light Source, which is supported by the Natural Sciences and Engineering Research Council of Canada, the National Research Council Canada, the Canadian Institutes of Health Research, the Province of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan

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Posters

Poster - 1

THE SPECTROSCOPIC DETECTION OF EXOGENOUS MATERIALS IN THE LATENT FINGERPRINTS TREATED WITH POWDERS AND LIFTED WITH ADHESIVE TAPES

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Fingerprint evidence offers great value to criminal investigations since they are an internationally recognized and an established means of human identification. Recently, with advances in modern technology, scientists have started analyzing not only ridge patterns of the fingerprints but also substances which can be found within them.

The aim of this research was to determine whether Fourier Transform Infra-Red (FTIR) spectromicroscopy could be used to detect contamination in a fingerprint beneath a layer of powder typically used by police to enable visual detection of the latent fingerprints. The application of powders to fingerprints has already been recognized as an effective and reliable method for developing latent fingerprints.

Explosive materials (PETN, C-4, RDX, TNT) and non-controlled substances (caffeine, sugar, aspirin, paracetamol) were used to prepare contaminated fingerprints on various substrates. Freshly deposited fingermarks visualized with powders and lifted with adhesive tapes (provided by Singapore Police Force) were analysed under Hyperion 2000 IR microscope at ISMI beamline (Singapore Synchrotron Light Source).

Hence FTIR spectroscopy is a non-destructive technique and requires almost no sample preparation, the fingerprint undergone the analysis remains in pristine condition what could be useful for its further analysis including the identification of an individual.

All analysed substances could be successfully distinguished using their FTIR spectra in powdered and lifted fingerprints. This method potentially could have a significant impact on forensic science and could dramatically enhance the amount of information that can be obtained from the study of fingerprints treated with powders.

PROJECTS AT THE INFRARED MICROSPECTROCSOPY BEAMLINE (D7) AT THE MAX IV LABORATORY.

A. ENGDAHL

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A presentation of some of the recent projects at the infrared microspectroscopy beamline and some information about the new synchrotron radiation facility.

A new synchrotron radiation facility is being built up in Lund. The MAX IV facility which will have one 1.5 GeV and one 3.0 GeV ring. The facility is prepared with a future free electron laser in mind. The MAX IV facility will be inaugurated in June 2016.

Use of synchrotron-radiation-based FTIR imaging for characterizing changes in cell contents.

The FPA detector was controlled to switch on only 32×32 elements A series of 87 individual cells were analysed by use of 15× magnification forn a final image size of ~85×85 µm^2. Spectral images were obtained by co-addition of 128 scans at a spectral resolution of 8 cm^{-1}.

SR-FTIR imaging was used to distinguish between two cellular conditions.

Results from integration of absorption bands for the main molecular components of cells

	Amide I	*Amide II*	*Amide I/II*	*v(COCH)*
Control	2.28±0.22	1.16±0.18	1.97±0.27	0.02±0.01
Low-Glc	2.15±0.18	0.89±0.20	2.42±0.31	0.04±0.02

In collaboration with Cyril Petitbois, CNRS UMR 2048, University of Bordeaux.

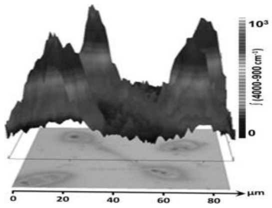

Fig. 1. FTIR image of cells cultures on Si_3N_4 substrate. FTIR image rendering shows absorption intensity for the full spectral region (4000–900 cm^{-1}).

Chemical imaging of urinary stones by far infrared microspectroscopy.

Infrared microspectroscopic imaging is used for the analysis cross-sectioned urinary stones. The identification of the constituent components of the stone enables to find out the underlying cause of the disease, prescribe treatment and prevent recurrences. The information about the morphology of the stone allows presuming the growth processes which are still unclear. The need to work in reflection mode with the IR microscope when imaging of the stones makes the analysis more complex. The reflection spectra contain Reststrahlen bands emanating from the anomalous dispersion of refractive index contributing to the contours of the spectral bands. Ideally, absorption spectral bands can be recreated from the Reststrahlen bands by applying standard Kramers-Kronig transform (KKT). However, in order to use the KKT, the recorded signal must be pure specular reflection signal. One way to diminish influence of the diffuse reflection is to increase the wavelength of the incident radiation. Under such experimental conditions the surface will be more “mirror like”.

In collaboration with Milda Pucetaite, Faculty of Physics, University of Vilnius

Molecular preservation of the pigment melanin in fossil melanosomes.

Using IR-microscopy at MAX-lab, among several other techniques, we show that melanonsomes in a 54 million years old fish eye contain high concentrations of melanin, having a molecular structure very similar to melanin found in modern melanosomes. The ir spectrum from the eye exhibits broad-band absorbance in the 900–1750 and 2700–3700 cm^{-1} regions, consistent with that of the melanin standard. The low-energy region is characteristically broad and featureless, and the vibrational modes are typically delocalized collective ring motions without any specific normal mode character.

In collaboration with Johan Lindgren, Geology department, Lund University.

Assessing the local distribution of the molecular composition of newly formed bone during fracture repair.

Fracture repair is a highly complex biological and mechanical process. Fracture healing is especially complicated in elderly patients with osteoporosis. The numbers of osteoporotic patients with complicated fractures are expected to increase with the increasing age of the population. In this study FTIR spectroscopy will be applied to quantify the composition and evaluate the bone quality in osteoporotic bone during bone fracture repair.

Hanna Isaksson, Solid Mechanics, Lund University

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SYNCHROTRON FAR INFRARED SPECTROSCOPY OF THE TWO LOWEST FUNDAMENTAL MODES OF 1,1 DIFLUOROETHANE

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The far-infrared (FIR) spectrum (50 – 600 cm^{-1}) of 1,1-difluoroethane was recorded using the high resolution infrared AILES beamline at the Soleil Synchrotron. A ro-vibrational assignment was performed on the lowest wavenumber, low intensity ν_{18} and ν_{17} modes, yielding band centres of 224.24190 (1) cm^{-1} and 384.25254 (1) cm^{-1} respectively. A total of 965 and 2031 FIR transitions were assigned to the ν_{18} and ν_{17} fundamentals respectively.

Previously measured pure rotational transitions from the upper states [1] were included into the respective fits to yield improved rotational and centrifugal distortion constants. The ν_{18}=2, ν_{18}=1 hot band was observed within the fundamental band, with 369 FIR transitions assigned and co-fitted with the fundamental to give an energy of 431.95640 (3) cm^{-1} for ν_{18}=2.

The *P* branch of ν_{18}=2 was observed and 432 transitions assigned and fitted to give an energy of 431.95286 (3) cm^{-1} for ν_{18}=2. The difference in energy is attributed to a torsional splitting of 0.00354 (4) cm^{-1} in the ν_{18}=2 state. Two how bands originating from the ν_{18}=1 and ν_{17}=1 states were observed within the ν_{17}=1 fundamental.

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ANALYSIS OF ULTRATHIN LAYERS ON SILICON WAFERS: SENSITIVITY BOOST BY WAFER ATR ACCESSORY

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In various fields of technology and research ultrathin layers on Silicon wafers have a major impact on surface passivation but can also serve additional important purposes. E.g. SiN passivation layers which protect most crystalline Si solar cells do also serve as antireflection coating. For electronic devices such as Si based integrated circuits in particular the isolation properties of ultrathin protection layers are of major interest and the development of so-called ultra-low k dielectric layers is pushed with increasing effort. But also in research e.g. concerning functional surfaces the investigation of ultrathin layers on Si such as SAMs (self-assembled monolayers) is an on-going topic of great interest.

The layer thickness for the above given examples typically ranges from the low (or even sub) nm to the intermediate nm scale. Although FTIR is well accepted and widely spread for the analysis of such layers, traditional approaches such as transmittance, reflectance or single bounce Ge ATR are limited in sensitivity by the small layer thickness. The alternative use of a multiple reflection Ge ATR is not practicable since the rigid sample does not allow for homogeneous contact pressure over a larger area. In general the classical ATR approach also implies the disadvantage that the investigated layer might be contaminated by contact with the ATR crystal or even be damaged by the necessarily applied mechanical pressure.

In order to overcome the aforesaid limitations of the classical ATR technique we developed a wafer ATR accessory in cooperation with the LETI/CEA research laboratories which strongly improves sensitivity for ultrathin layers on Si wafers.

The functional principle of the accessory is based on the so-called MIRS (Multiple Internal Reflection Spectroscopy) approach: the wafer ATR accessory couples the infrared light into the Si wafer under an angle fulfilling the conditions of total internal reflection in Si [1]. Consequently the Si wafer itself takes over the role of the ATR crystal and thus there is no need to apply mechanical pressure to the measured area or to contact it with an ATR crystal. The absorption signal of the ultrathin layer is amplified by the high number of internal reflections resulting in a strongly improved signal to noise ratio. Within this contribution we will show high quality spectra of various ultrathin layers from different fields measured with the first commercially available and easy to use accessory for this demanding type of application.

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FT-IR SPECTROSCOPY IN ULTRAHIGH VACUUM: SURFACE SCIENCE APPROACH FOR UNDERSTANDING REACTIONS ON CATALYTIC OXIDE POWDERS

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FTIR spectroscopy has been frequently used to characterize catalytic oxide surfaces, since it can be well combined to the density functional theory (DFT) calculations and has scarcely the limitations marking the other investigation methods used till now, such as scanning tunnelling microscopy and electron energy loss spectroscopy. To achieve the highest sensitivity of spectroscopy and to fulfill the standard handling conditions for single crystalline oxides FTIR spectrometer can be adapted to a UHV equipment.

The fundamental advantage of using FT-IR spectroscopy in vacuum is to avoid the absorption of atmospheric moisture and other gas species. Furthermore, the UHV-FTIR adaptation enables the closely combination of FT-IR technique with other UHV experimental methods.

A UHV-FTIRS apparatus dedicated to the spectroscopic characterization of oxides, single crystals as well as powders was developed [1]. It combines a Bruker VERTEX 80v vacuum FTIR spectrometer with a PREVAC UHV system.

Using this established equipment the amount of defects on rutile surface has been determined with the help of DFT calculations and the accordant catalytic activity of the oxide surface was deduced. For the first time IR data achieved for powder particles can be compared with single crystal reference system [2].

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EXPLORING POLARISATION IN THE THZ/FAR-IR REGION, AND SCATTERING EFFECTS IN PE PELLETS, USING A RADIALLY POLARISED SYNCHROTRON SOURCE

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Pressed PE pellets are commonly utilized as a technique for studying the far-IR spectra of samples [1]. An increase in intensity in THz region has been observed when a pressed pellet of pure MIPELONTM 13-1 PE is placed in the beam. Polarisation and scattering, as well as chemical composition, are good candidates to explain these effects.

There has been recent interest in the effects of focusing a radially polarised beam that may help to explain our observations. Radially polarised light may be focused below its diffraction limit, when that happens some of the electric field cancels out. [2] The PE pellets may be acting as a de-polariser, stopping some of the cancellation effects at long wavelengths.

Preliminary results show that the way the pellet is pressed determines whether or not the long wavelength shift is present or not. Heating the pellets removes any scattering effects from particle size.[3] The spectra of heated and pressed pellets is very similar to the spectra of the synchrotron with no sample present (see Figure 1).

PE with different particle sizes and different manufacturers will be investigated.

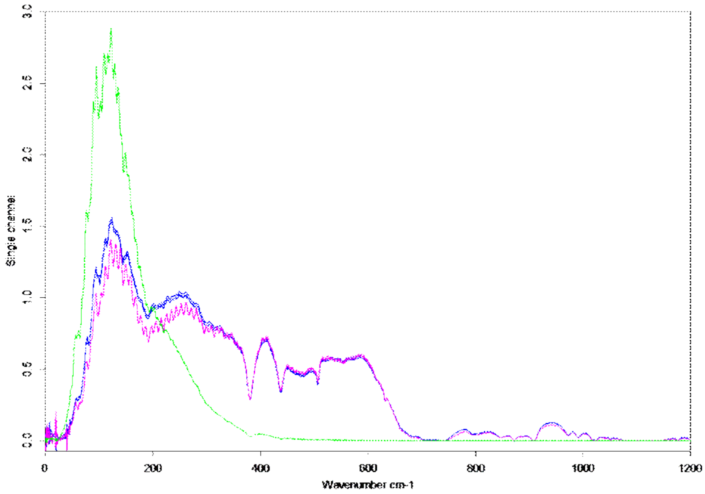

Figure 1. Spectra of MIPELON™ polyethelene, blue is spectral profile of the beam, pink is a heated and pressed sample and green is pressed only.

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MIR-FIR WIDE RANGE BEAMSPLITTER FOR AN FTIR SPECTROMETER

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The major optical components sources, beamsplitters and detectors define the measurement spectral ranges of FTIR spectrometers. Modern FTIR spectrometers used for demanding R&D applications provides software controlled switching of the source and detector positions. But automatic beamsplitter exchange is still challenging and requires robot like devices because typically up to four different types of beamsplitters are required to cover the full visible, near IR, mid IR and far IR/THz spectral ranges.

Especially for inorganic and organometallic chemistry as well as for geological, pharmaceutical and physical applications the extension of the mid IR towards the far IR spectral range below 400 cm^{-1} is for the research community of general interest. The lower boundary of the spectral range is very dependent upon the type of beamsplitter and typically limited to 350 cm^{-1} (based on a KBr substrate) or 200 cm^{-1} (based on CsI). To extend the spectral range further into the far IR and THz spectral ranges one or more additional far IR beamsplitters are required. Avoiding manual exchanges of beamsplitters Bruker introduced an automatic beamsplitter changer unit BMS-c for the VERTEX 80v high end research FTIR spectrometer in 2010 which works even under vacuum condition (Ref 1).

Recently we have introduced the world's first ultra-wide spectral range beamsplitter which covers in combination with a room temperature deuterated triglycine sulfate (DTGS) detector the complete mid and far infrared spectral range from 6000 cm^{-1} to 130 cm^{-1} within a single measurement in one step. In case the VERTEX 70 or its vacuum version VERTEX 70v is equipped on its second detector position with a far IR DTGS detector the same beamsplitter is used to extend the spectral range to 30 cm^{-1} and by selecting the externally adapted mercury arc lamp even the full far IR/THz spectral range down to 10 cm^{-1} is completely software controlled accessible.

With the poster we will present mid and far IR molecular vibrational spectra of samples from the area of inorganic chemistry and of pharmaceutical active agents and filler material using a single crystal diamond ATR accessory. The data will demonstrate the additional value and easy use of that new ultra-wide range beamsplitter option.

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THE EFFECT OF SPATIAL DISTRIBUTION OF NATURAL WAX ON THE SURFACE HYDROPHOBICITY AND SURFACE MORPHOLOGY IN HIGH AMYLOSE-GLYCEROL FILMS PRODUCED USING PEG-ISOCYANATE AS THE LINKER

D. MUSCAT[1], R. ADHIKARI[2], M. TOBIN[3], S. MCKNIGHT[1], L. WAKELING[1] AND B. ADHIKARI[1,4]

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[3]Australian Synchrotron, Clayton, 3168, Victoria, Australia.
[4]RMIT University, Melbourne, 3001, Victoria, Australia.

This study proposed a novel method in improving the surface hydrophobicity glycerol plasticized high amylose (HAG) films. We used polyethylene glycol isocyanate (PEG-iso) as a molecular crosslinker to link HAG and three natural wax (beeswax, candelilla wax and carnauba wax) to produce HAG+wax+PEG-iso films. This approach facilitates the anchoring of wax to the HAG by urethane linkage. The spatial distribution of wax and PEG-isocyanate across the films was quantified using Synchrotron-based Fourier transform infrared spectroscopy. The surface hydrophobicity and surface morphology of the films were determined using contact angle and Scanning Electron Microscopy measurements, respectively. The pattern of distribution of wax and the PEG-isocyanate especially on the film surface and the nature of crystalline patterns subsequently formed on the film surface (surface morphology) was found to be the key factor affecting the surface hydrophobicity in these films. The distribution of wax-rich domains either on the surface or in the middle of the films and the distribution of PEG-iso-rich domains in the middle of the films resulted into the highest hydrophobicity ($CA>90^o$) in these films. This pattern of distribution of wax and PEG-iso created a hierarchical pinnacle like structure of solidified wax structures. These structures were approximately 10 µm in diameter, were formed very close to each other and were adjoined with fine threads and formed a scaly (rough) film surface.

Acknowledgement
This work was undertaken on the infrared microspectroscopy beamline at the Australian Synchrotron, Clayton, Victoria, Australia. We thank our colleagues Dr Huihua Liu and Dr Amir Ghandi for their assistance with the film window preparation and data collection. This research was supported by Ballarat University led Collaborative Research Network (CRN).

UNDERSTANDING THE DISTRIBUTION OF NATURAL WAX IN STARCH-WAX FILMS USING SYNCHROTRON-BASED FTIR.

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High amylose starch-glycerol (HAG) films were produced incorporating beeswax, candelilla wax and carnauba wax in the presence and absence of Tween-80 in order to quantify the distribution of wax in the films during the film formation process. The distribution of these waxes within the film was quantified using Synchrotron based Fourier Transform Infrared Spectroscopy (S-FTIR) which provided 3D mapping along the thickness of the film. The incorporation of 5% and 10% wax in HAG films produced randomly distributed wax or wax-rich domains, respectively, within these films. Consequently, the addition of waxes to HAG increased the surface roughness and hydrophobicity of these films. The addition of Tween-80 caused variations in wax-rich bands within the films. The HAG+carnauba wax+Tween-80 films exhibited wax-rich domains at the surface of the films to produce rougher surface and higher CA values than the other films. The S-FTIR 3D images indicated that the distribution of wax in starch-wax films correlated with the roughness and hydrophobicity of the starch-wax films.

Acknowledgement

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DEVELOPMENT OF MID-INFRARED FREE ELECTRON LASER IN KYOTO UNIVERSITY

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A Mid-Infrared Free Electron Laser (MIR-FEL) named as Kyoto University FEL (KU-FEL) has been developed for energy related sciences in Institute of Advanced Energy, Kyoto University. The KU-FEL is an oscillator type FEL based on linear accelerator. The main feature of KU-FEL is utilization of the thermionic RF gun as its electron beam source as same as Mark-III FEL in Stanford University [1] and FEL-TUS in Tokyo University of Science [2]. The construction of KU-FEL facility was started in 1998. The first lasing at 12 µm was achieved in March 2008 [3] and the first power saturation at 13 µm was achieved in May 2008 [4]. Then the tunable range of the FEL wavelength was limited to 10-13 µm because of small FEL gain and short electron beam macro-pulse duration.

After the first lasing, some efforts have already been carried out to extend the tunable range of KU-FEL. In 2012, we replaced old undulator with new one which has higher K-value and larger number of periods and had been used for ERL-FEL in JAEA [5]. At the same time, the optical cavity mirrors have also been replaced with newly designed ones. The major difference of new and old cavity mirrors were the sizes of out-coupling hole which is arranged on the upstream mirror and used for extracting laser light from the optical cavity. The hole size of new one is 1 mm and that of old one is 2 mm in diameter. This modification reduces the optical loss in short wavelength region and contributes to extend the tunable range of KU-FEL to shorter wavelength. Currently, the tunable range is 5-22 µ m. The available pulse energy over the tunable range is plotted in Fig. 1. The maximum macro-pulse energy of 30 mJ can be generated at the wavelength of 9 µm. However, the pulse energy at the longer wavelength than 15 µm is smaller than 5 mJ. The reason why the macro-pulse energy decrease so much in the wavelength region is under investigation. The typical spectral bandwidth, macro-pulse duration and micro-pulse duration of KU-FEL are around 3%, 1-2 µs and around 1 ps in FWHM, respectively.

Recently, six electron beam position monitors (BPMs) have been installed. By using those BPMs, a feedback control of electron beam energy and position has been developed. Thanks to the feedback control, the FEL power stability is improved to be 15% in FWHM. In addition, the wavelength stability was measured as 1.3% (root mean square) [6]. We are still making efforts to improve the power and wavelength stability.

Several internal and external users have used KU-FEL for their research since 2009. Present status of KU-FEL and some results of user experiments will be reported in this presentation.

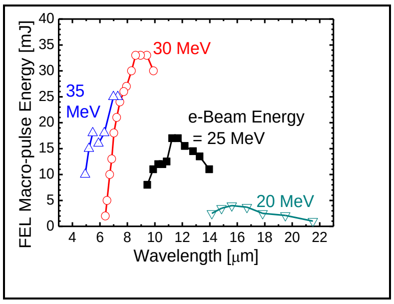

Fig. 1. The available pulse energy of KU-FEL in its tunable range (5-22 □m).

Acknowledgement

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A NOVEL TECHNIQUE FOR A COHERENT CHERENKOV RADIATION BASED ON VELOCITY MATCHING BY BUNCH TILTING

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We propose a novel method of accelerator based radiation source for a coherent Cherenkov radiation (CCR) based on velocity matching between electron bunch from accelerator and THz or IR radiation by tilting the electron bunch. Accelerator based THz sources were developed in the various methods. A monochromatic THz radiation was generated by CCR using a hollow cylindrical dielectric-lined waveguide.[1][2] Another method, which utilized a periodic electron bunch distribution, generated narrow-band THz radiation by a coherent transition radiation (CTR).[3] On the other hand, ultrafast laser based source was also developed. Recently, the tilted-pump-pulse-front scheme demonstrated a 1MV/cm amplitude THz pulse generation by the LiNO3 crystal.[4] This scheme was proposed by Hebling in 2002[5], which can be applied for an accelerator based source by means of the rf electron bunch deflector.

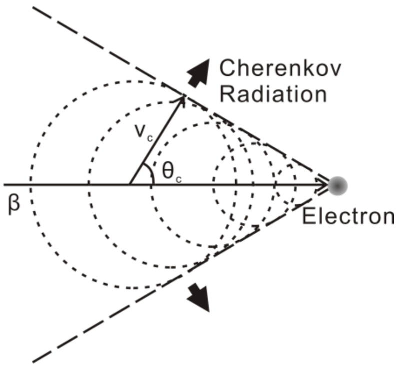

Fig. 1. Schematic of Cherenkov radiation generated from a relativistic electron.

The schematic of Cherenkov radiation is shown in Fig. 1. The Cherenkov radiation propagates along a cone with an angle θ_c, which is determined by electron beam velocity β and refractive index n of the target material. This phenomenon makes it difficult to collect the radiation coherently for the application uses.

Thus we propose a new scheme for coherently collect a CCR by tilted electron bunch. Fig. 2 shows the schematic of this technique. The relativistic electron bunch is swept by the rf deflector cavity in order to achieve the tilt. The rf deflector cavity is widely used for measuring a longitudinal bunch distributions. [6] The tilted bunch is tuned the angle and transverse divergence by the quadrupole magnets. The Cherenkov radiator has a correct angle, which corresponds with a CR propagation angle of θ_c. The advantage of this novel technique is that the radiation created at different times coherently overlap with each other increasing a conversion efficiency. A further advantage of this technique is non-necessity of the bunch compression for the coherent radiation. The longitudinal duration of this tilted bunch is determined by the transverse focusing of electron bunch before the rf deflector cavity.

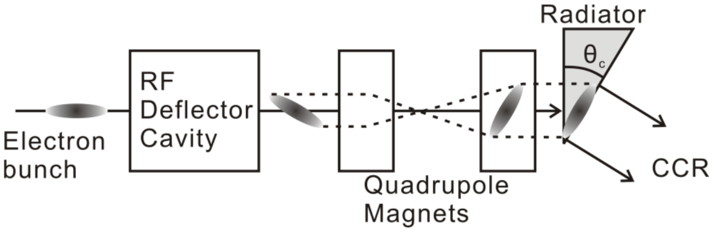

Fig. 2. Schematic drawing of a tilted electron bunch CCR source.

In this method, it is clear that the pico-second bunch can produce CCR up to THz region. The detail of this novel method, calculated result of CCR, and future prospective will be presented at the conference.

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SR-FTIR MICROSPECTROSCOPY INVESTIGATIONS INTO THE INTRACELLULAR CHANGES INDUCED IN COLON CANCER CELLS FOLLOWING TREATMENT WITH BISMUTH COMPLEXES DERIVED FROM NON-STEROIDAL ANTI-INFLAMMATORY DRUGS

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Non-steroidal anti-inflammatory drugs (NSAIDs) have shown potential for use in preventative colon cancer therapies; however, serious gastrointestinal side effects such as gastric ulceration limit their use [1]. Bismuth drugs are primarily used in the treatment of gastritis and stomach ulceration. In addition, bismuth is used in combination therapies (with antibiotics) to specifically combat *Helicobacter pylori* [2]. Bismuth NSAIDs (BiNSAIDs) were synthesised under the premise that the combination of bismuth and NSAIDs incorporated within one drug may provide a safer alternative drug for anti-cancer therapy with reduced gastrointestinal side effects [3]. The present study evaluated three BiNSAIDs, with the general formula $[Bi(L)_3]_n$, where L = diflunisal (difl), mefenamic acid (mef) or tolfenamic acid (tolf). Synchrotron radiation Fourier transform infrared (SR-FTIR) microspectroscopy was performed on single HCT-8 human ileocecal colon cancer cells (n > 100) in order to elucidate any differences in the biochemical responses following treatment (24 h) with the aforementioned BiNSAIDs, in comparison to their respective free NSAIDs. The HCT-8 cells were treated with equimolar doses of NSAID, which were known to cause a biological response without inducing high rates of cell death (*i.e.* the approximate IC_{50} of the BiNSAIDs).

The 'dispersion artefact' or resonant Mie scattering (RMieS), which is observed as a sharp decrease in intensity on the high wavenumber side of the Amide I band (~1655 cm^{-1}), was exhibited by the spectra collected in this study. In order to minimise the effects of RMieS, thus improving the reliability of biochemical interpretation, the RMieS Extended Multiplicative Signal Correction (EMSC) algorithm [4] was applied to the spectra (100 iterations). The chemometric technique, Principal Component Analysis (PCA), was used for multivariate reduction in order to assess the biochemical differences between cell subpopulations. The results of the spectral analyses will be presented with a focus on the potential biomolecular changes that occur and how these correlate with the primary mechanism of action of the NSAIDs, specifically the inhibition of the membrane-bound cyclooxygenase (COX) enzymes.

Acknowledgement

CTD and ELH acknowledge travel funding provided by the Australian Synchrotron. ELH and CTD acknowledge P. Bassan and P. Gardner for provision of the RMieS algorithm and correction guide. CTD acknowledges UOW small grant scheme for financial support of this project.

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PRESSURE-INDUCED PHASE TRANSITIONS IN $CuF_2(H_2O)_2$(3-CHLOROPYRIDINE) AS REVEALED BY INFRARED AND RAMAN SPECTROSCOPIES

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Multifunctional materials exhibit a rich interplay between charge, spin, and lattice degrees of freedom that lead to complex phase diagrams and highly tuneable properties. Molecular solids provide particularly useful insights into these interactions owing to their low energy scales and experimentally realizable transitions under various external stimuli. $CuF_2(H_2O)_2$(3-Clpyd), where (3-Clpyd) is 3-chloropyridine, attracted our attention due to its unusual trigonal bipyrimidal copper environment, extensive two dimensional hydrogen bonding network, and a pressure-induced magnetoelastic transition at 0.8 GPa that drives the system from an antiferromagnetic to ferromagnetic state at low temperature. We combined diamond anvil cell techniques, synchrotron-based infrared spectroscopy, and complimentary density functional theory based calculations to investigate the mechanism of the pressure-induced magnetoelastic phase transition. While pressure drives a number of local lattice distortions, those associated with the 3-Clpyd ring are most important at 0.8 GPa. Our spectra reveal a low-frequency ring-related mode that disappears and three sets of higher frequency ring-related doublets that collapse into singlets through the magnetic crossover. These changes suggest a pressure-induced increase in crystal symmetry brought about by the tilting of the 3-Clpyd rings in the direction of the chlorine. This tilting brings the chlorine center closer to the H_2O ligands, a process that is evidenced in our spectra as hardening of the H-O-H bending mode as the chlorine interacts with the hydrogens and dampens the bending motion, and the softening of the O-H stretching modes. The increased electrostatic interaction may establish additional hydrogen bonding linkages in the *c* direction that can act as superexchange pathways between copper centers. Development of this new exchange pathway combined with the buckled *ab* plane hydrogen bonding exchange pathway yields a three dimensional superexchange network between copper centers that may facilitate the antiferromagnetic to ferromagnetic crossover. Analysis of the local lattice distortions also allows us to identify two additional structural phase transitions at 4 and 6 GPa. These findings are important for understanding magnetoelastic coupling in molecule-based materials and other multifunctional materials (like oxides) where the energy scales are higher and are not easily realized.

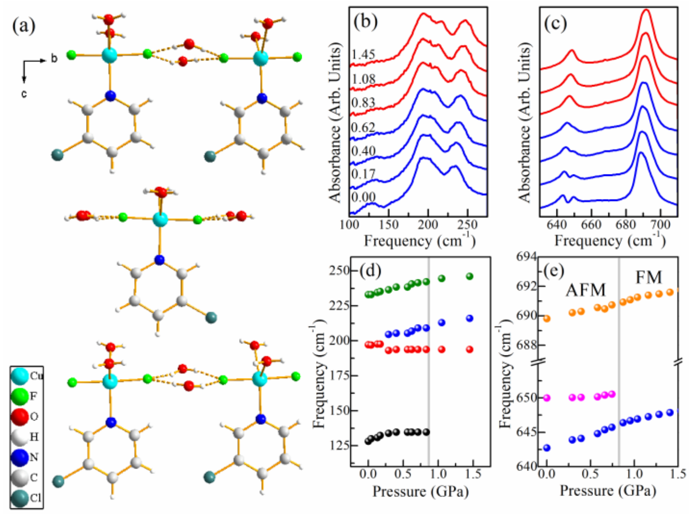

Figure 1. (a) Crystal structure of $CuF_2(H_2O)_2$(3-Clpyd) showing the interlayer hydrogen bonding along the b direction between fluorine and hydrogen atoms. As the chlorine is forced closer to the H_2O ligands, hydrogen bonding could be established between layers creating three dimensional superexchange pathways. (b, c) Infrared spectra as a function of pressure between 0 and 1.5 GPa. (d, e) Frequency of selected modes vs. pressure through the 0.8 GPa magnetoelastic transition. The vertical gray line indicates the antiferromagnetic → ferromagnetic crossover, and the infrared and Raman spectra reveal the local lattice distortions that trigger this crossover.

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Poster - 14

UNDERSTANDING CHEMICAL CHANGES IN POLY (AMIDE) THIN-FILM COMPOSITE SIMULATED BY PLASMA AND DIVERSE ENVIRONMENTS, WITH SYNCHROTRON IR

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Poly (amide) thin-film composite membranes are a common technology for desalination, water recycling and foods processing. However their current surface chemistries are prone to attach from oxidants (e.g. chlorine) or chemicals used for membrane cleaning (e.g. nitric acid). Plasma modification of poly (amide) membranes has been studied to improve chemical resistance in application, but little is understood about the altered poly (amide) chemistry supporting this observed improvements [1]. In this work, the poly (amide) surface has been modified by plasma, then exposed to various environmental chemicals. The influence of both the plasma and chemical exposure has been analysed by synchrotron ATR–MIR (Attenuated Total Reflectance - Microscopic Infra-Red). Two types of plasma were applied, gas plasma and plasma polymerisation using maleic anhydride as the monomer [2]. Gas plasma was found to alter the poly (amide) functional groups with consistent decrease in absorbance with increasing time of plasma exposure on the treated membrane surface (Figure 1). Meanwhile plasma polymerisation was found to add carboxylic groups to the surface with peak enhancement in the vicinity of frequency 1735 cm^{-1}.

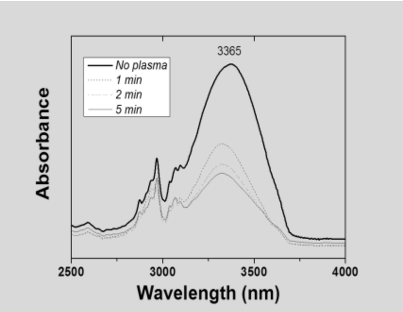

Fig.1. ATR-IR spectra for BW30 membrane modified by plasma obtained by Bruker Optics.

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Poster - 15

EVALUATION OF SPATIAL AND TEMPORAL INFORMATION FROM INFRA-RED SPECTRAL DATA SETS BY USING R ENVIRONMENT FOR STATISTICAL ANALYSIS

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Infra-red spectral datasets nowadays often include additional variables like spatial coordinates of points where spectra were collected (in case of imaging techniques) or time when particular data entry was recorded (in case of time trial experiments). Taking into account that these data sets could be considerably large in size there is a need for the tools for semi-automatic data evaluation and information extraction. Open-source R environment [1,2] with its flexibility and growing potential fits nicely to these requirements. There are a few of packages [3,4] available in R for processing hyper-spectral data. In this contribution examples of practical implementation of methods available in R for real-life spatial and temporal spectroscopic data problems will be presented.

Acknowledgement

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SELF-ORGANIZING MAPS, K-MEANS, MODEL-BASED CLUSTERING AND OTHERS... - COMPARISON OF VARIOUS ALGORITHMS FOR CLASSIFICATION AND CLUSTERING OF INFRA-RED SPECTRA

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Researchers in many fields including infra-red spectroscopy are able to collect and analyse data sets of increasingly size and dimensionality. Exploratory analysis has become more difficult due to this fact. There is a real need for methods that provide meaningful mappings those dimensions into two or three most important factors. There are many approaches to complete this task; one of the most frequently used is principal component analysis (PCA) [1]. However in its pure form it does not incorporate information on how objects should be compared. One of the alternative solution is model-based clustering [2] that assumes that groups within data set are multivariate normally distributed. Another approach represents technique called self-organizing maps (SOM) [3-5]. In this contribution we discuss and compare performance in terms of sensitivity, specificity and computational speed of various statistical algorithms for classification and clustering of infra-red spectral data.

Acknowledgement

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USING NEAR-FIELD AFMIR-PTIR MICROSCOPY TO EXPLORE THE BACTERICIDAL ACTIVITY OF BISMUTH AGAINST *HELICOBACTER PYLORI*.

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Helicobacter pylori is a pathogenic bacterium that invades the mucus lining of the stomach. It is estimated that at least half the world's population are infected with *H. pylori* and without treatment, infection is present in its host for life [1,2]. Long-term infection is associated with both peptic ulceration; more than 90% of duodenal ulcers are related to *H. pylori* infections; and gastric cancer [1,3]. Gastric cancer is responsible for over 700,000 deaths per year and is the second most prevalent cancer in the world [4]. Current methods of treatment include the administration of proton pump inhibitors combined with antibiotics [5]. These treatments are however declining in efficiency, as resistance rates to the commonly used antibiotics are increasing worldwide; in some countries to as high as 60-70% [5]. The addition of bismuth (Bi) compounds such as Bi subsalicylate or colloidal Bi citrate, are also common practise but the exact antimicrobial role that Bi plays in this regime is poorly understood. Critically there is no evidence of the bacteria displaying resistance towards Bi [6]. Despite this, little is known about the bioactivity of Bi or even the overall chemistry of Bi compounds, particularly when compared to related metals and their complexes.

This project aims to use the AFMIR-PTIR beamline at CLIO Free Electron Laser (FEL) to gain a better insight into the antimicrobial activity of Bi against the pathogenic bacteria *H. pylori*. This near-field AFM-based method can measure FTIR chemical maps at submicron spatial resolutions (to approximately 100 nm), across a range of wavelengths extending into the far IR (80-3000 cm^{-1} [7]). It is thus ideal for studying small samples such as bacteria and for identifying the presence of metals such as Bi within treated samples.

Bi compounds have been shown to be ingested by *H. pylori*, believed via certain iron-transport pathways [8], and are suspected to demonstrate toxicity by their strong interaction with sulphur-based proteins *in vivo* e.g. cysteine [9]. By identifying Bi-*X* bonds within the treated samples, their positions will highlight structural changes to the administered complex upon ingestion. Bi-*X* bonds appear between 200-600 cm^{-1} depending on the structure of the Bi complex [10]. Far IR microspectroscopy studies of treated *H. pylori* could therefore provide evidence for the bioactive mode of Bi binding, allowing the *in vivo* structure of bioactive Bi to be better elucidated. Results will be presented.

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SCHOTTKY DIODE DETECTORS FOR MONITORING COHERENT THz SYNCHROTRON PULSES

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Extremely high brilliance promotes coherent synchrotron radiation (CSR) in the terahertz frequency range to a powerful tool for spectroscopy [1]. On the other hand, in the low-α operation mode subpicosecond THz pulses enable relaxation and correlation studies of low-energy excitation in solids by means of the pump-probe [2] or photoresponse [3] technique. Another possible application is the diagnostics of the electron-beam relying on the fact that the emission spectrum of THz CSR depends on the shape of the electron bunch from which the radiation is emitted [4]. THz CSR pulses are emitted by single electron bunches in a stable mode at constant intensity but of less power or in a bursting mode at higher intensity. Intensity typically available below the bursting threshold is barely sufficient for pump-probe experiments. On the other hand, bursting mode inherently contains instabilities which produce intensity fluctuations and time jitter. These instabilities jointly with the CSR pulse duration and implemented THz detectors will limit the time resolution in pump-probe experiments.

Among available direct THz detectors only superconducting microbolometers and Schottky diodes are potentially capable to resolve in time single CSR pulses. Detection of CSR pulses with the time resolution better than 20 ps has been recently demonstrated with YBCO detector [5]. However, its a few picoseconds fast vortex-assisted photoresponse in the sub-THz range [3] turns to be predominantly bolometric and slow at far-infrared waves. We have recently shown that the high responsivity of a quasioptically coupled zero-bias Schottky diode detector spans over the whole CSR frequency range [6] where the response time of the diode should not vary.

Here we present recent photoresponse measurements, which were performed with CSR and a quasioptical zero-bias Schottky diode detector, which was produced at ACST GmbH. The kern part of the detector is a THz Monolithically Integrated Circuit (MIC) including the diode, which was integrated with a planar log-spiral antenna on a transferrable membrane-substrate. THz-MIC was brought onto the rear flat side of an elliptical silicon lens. Depending on the particular application the detector was backed either with a dc or microwave amplifier. The non-saturated diode signal surpasses the noise level of modern sampling oscilloscopes. Hence, the response to CSR pulsed could be analysed with the time resolution up to a few picoseconds. Figure 1 shows the response of the detector to a single CSR pulse shorter than 6 ps. The rise-time of the transient is approximately 15 ps that corresponds to the 20-GHz bandwidth of interconnecting cables. Non-saturated responsivity of the detector, that is the amplitude of the voltage transient referred to the total CSR pulse energy in the detector quasioptical mode, was approximately 1.5 mv/fJ. The dynamic range of the detector spans almost two and a half orders of magnitude from 8 fJ to 1 pJ. At the same time, the intrinsic jitter of the detector was less than 2 ps thus not affecting the effective time resolution.

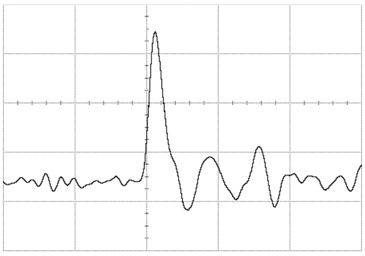

Fig. 1. Response of our Schottky diode detector to 6-ps CSR pulse. Horizontal span is 500 ps. The full width at half maximum of the main peak is less than 20 ps.

Finally, using slow, averaged over many bunches response of the Shottky diode we measured a convolution of the CSR spectrum and the spectral sensitivity of the detector with a Martin-Pupplet interferometer. In the range up to 1.5 THz the measured spectrum coincided with the FTS CSR spectrum that was obtained with a slow Golay Cell detector.

Acknowledgement

We thank Dr. V. Judin from the Karlsruhe Institute of Technology (ANKA), Dr. K. Holldack from the Helmholtz-Zentrum Berlin, BESSY II; and Dr. G. Wüstefeld with M. Ries both from the Helmholtz-Zentrum Berlin, Institut für Beschleunigerphysik for their help with the measurements. Federal Ministry of Economics and Technology partly supported this work in the framework of ZIM Programme.

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NOVEL AUSTRALIAN PROTISTS AS ALTERNATIVE OMEGA-3 POLYUNSATURATED FATTY ACID (PUFA) RESOURCES TO FISH OILS ANALYSED IN VIVO BY SYNCHROTRON FTIR MICROSPECTROSCOPY

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In recent years, omega-3 (n-3) polyunsaturated fatty acids (PUFAs), particularly the n-3 docosahexaenoic acid (DHA; 22:6n-3) and eicosapentaenoic acid (EPA; 20:5n-3), have become increasingly popular in the nutraceutical arena due to their important roles in brain function and prevention of cardiovascular diseases as well as maintaining good health. This has led to a rapid increase in PUFA consumption, based primarily on fish oils. Other potential alternative resources not relying on fish stocks have been the subject of active research.[1-4] The superior characteristics of high photon flux and diffraction limited resolution achieved in the synchrotron infrared radiation allows studies of individual live cells. In this study, we developed a method based on synchrotron FTIR (S-FTIR) spectroscopy and multivariate data analysis for characterization and classification of cellular constituents and lipid compositions in *live* thraustochytrids – marine fungoid protists that possess a strong potential for large-scale PUFA production.[2]

The technique together with multivariate data analysis approach including principal component analysis (PCA), unsupervised hierarchical cluster analysis (UHCA) and partial least squares discriminant analysis (PLS-DA), was shown to be a powerful taxonomic classification tool leading to good discrimination of our newly isolated thraustochytrium strain[4] collected locally from Queenscliff (Victoria, Australia) from a strain collected from the New Zealand coast (No. 7) and two commercial strains obtained from the ATCC culture collection (i.e. *Thraustochytrium* sp. ATCC® PRA-296™ and *Schizochytrium* sp. S31 ATCC® 20888™).

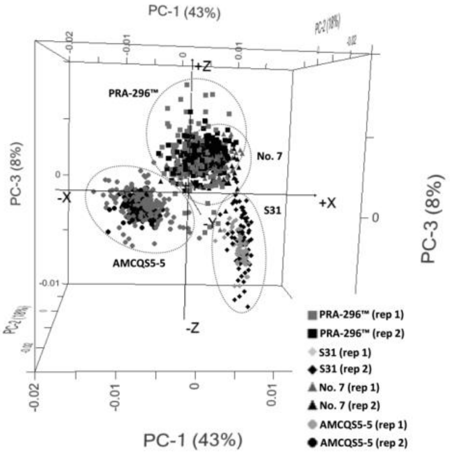

Fig. 1. Distinct clustering by PCA of the newly isolated Australian thraustochytrid (AMCQS5-5) in comparison to other commercial ATCC strains (i.e. PRA-296™, S31 and No. 7).

The results emphasized the superiority of the S-FTIR technique over conventional laboratory-based FTIR methods for obtaining information about biomolecules in the *in vivo* state from measurements of fully hydrated single *live* cells without perturbation of the cells through any sample preparation. The insights gained about cellular composition should lead to a deeper understanding of lipid and carotenoid production in these marine microbes as well as accelerating screening methods for new strains suitable for industrial production of valuable PUFAs for food and nutraceutical purposes.

Acknowledgement

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NON-DESTRUCTIVE ELEMENTAL IMAGING STUDIES OF 16TH-17TH CENTURY MAJOLICA TILES FROM ANTWERP (BELGIUM) USING SYNCHROTRON AND LABORATORY BASED MICRO-XRF TECHNIQUES

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As a complementary technique to synchrotron based infrared techniques, scanning X-ray fluorescence (XRF) microanalysis using highly focused synchrotron radiation or laboratory X-rays is a well-established non-destructive method to provide two- or three-dimensional information on the elemental distributions in the probed sample volume down to trace level detection limits. The method is based on the use of an X-ray micro/nanobeam to perform 2D/3D raster scans on the investigated samples, typically collecting the XRF point spectra using single-element energy-dispersive detectors.

During the last two decades there has been a considerable effort to move from compact single element X-ray detectors to spatially resolving area detectors. Most of these detection systems can measure spatial information, i.e. the intensity at a pixel, only. The advantage of the presented X-ray CCD camera prototype (IFG Color X-ray Camera, Institute for Scientific Instruments GmbH, Berlin, Germany) lies in its ability to record spatially and spectrally resolved images simultaneously by measuring the position of single photons and their energy in the energy range of 3-40 keV [1,2]. The combination offers new applications in X-ray microanalysis, especially with respect to 2D/3D elemental imaging, including X-ray fluorescence microtomography.

The new detection system will likely represent a new stage of development in 2D/3D elemental imaging with a broad range of applications in life and environmental science, geo-, cosmochemistry and archaeology. Experiments using the IFG Color X-ray Camera prototype at synchrotron radiation sources (BESSY-II BAM-line and PETRA-III Beamline P06) demonstrated that trace element detection limits can be achieved in imaging mode for transition metals using either pinhole or fiber optics coupled with the camera even in case of biological samples.

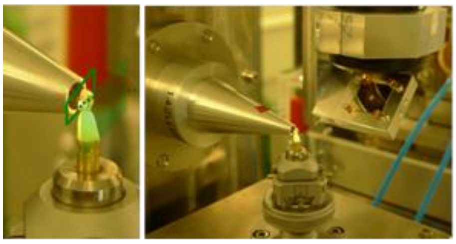

Fig. 1. Experimental setup at PETRA-III beamline P06, showing the investigated sample mounted in front of the energy-dispersive CCD detector.

Applications of the novel full-field X-ray fluorescence (XRF) imaging approach using the above mentioned unique two-dimensional energy-dispersive detection system will be presented for the non-destructive elemental microanalysis of 16th - 17th Century Majolica tiles from Antwerp (Belgium). The full-field elemental imaging results will be compared to conventional scanning type of elemental imaging methods using both laboratory and SR-sources.

From the beginning of the 16th until the end of the 17th century, Antwerp was an important majolica production center, together with the production of the *façon de Venise* glass. Hence, it is not surprising that the Antwerp majolica was the subject of several (art)historical and archaeometric studies. Our studies represent the analysis of 30 representative majolica tiles, which were selected from the vast amount of excavated majolica artifacts found in Antwerp. The manufacturing period of the tiles cover a period of approximately 100 years (~1550-1650) with fragments originating from local archaeological production centers in Antwerp. These representative tiles are named after the streets were they found: Aalmoezenierstraat (2), Schoyestraat (8), Steenhouwersvest (13) and Sint-Jansvliet (7). The chemical composition of the body and the glaze provide valuable information concerning (1) the technology used in a specific period, (2) technological changes over a longer period, and (3) production defects caused by the used materials.

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INVESTIGATION OF 19TH CENTURY PORCELAIN CARDS USING COMBINED MICRO-SPECTROSCOPIC TECHNIQUES

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In the 19th century, porcelain cards were very often used in the Flemish region (Belgium) as a medium to advertise, to invite, or in general, to inform people on special and specific social events, or on private business activities (see Fig.1). The production of these cards was done by a lithographic procedure, but because this manufacturing process has not been described in literature, the details on the actual production of the porcelain card can be considered as being lost.

There seems to be some common belief amongst collectors and curators that the front of the cardboard is covered with a thin layer of lead white ($2PbCO_3.Pb(OH)_2$) mixed with kaolin ($Al_2Si_2O_5(OH)_4$). This mixture was pressed on the cardboard to give it a high-gloss finish, having the look of porcelain, so probably explaining the name of the cards.

Figure 1. An example of a 19th century porcelain card from Ghent, Belgium.

As a complementary approach to synchrotron based infrared methods, we used a combination of Raman-spectroscopy, scanning and full-field micro X-ray fluorescence (XRF) techniques using synchrotron radiation or laboratory X-rays to provide two-dimensional elemental/molecular information in the probed sample volume. The laboratory measurements were performed using a laboratory EDAX Eagle III micro-XRF spectrometer and a Bruker Optics 'Senterra' Raman spectrometer. The EDAX Eagle III spectrometer is based on polycapillary optics, while the Raman spectrometer is equipped with 532 (Nd:YAG) and 785 nm (diode) laser sources. Complementary full-field micro-XRF synchrotron measurements were performed at BAM-line of BESSY-2 (Berlin, Germany). Both Raman and XRF allow the investigation of samples on the microscopic level in a non-destructive manner which is essential in cultural heritage projects. Moreover, the combination of Raman and XRF measurements offers a more easy interpretation of the spectroscopic data-sets by complementing molecular information with element specific information and vice versa.

In this work the combination of the micro-XRF technique and the micro-Raman method is explored in order to characterize selected porcelain cards. Next to the initial goal of identifying the materials being used in a porcelain card, special attention has been paid to data evaluation strategies using the resulting fused data set made from the data of the different techniques, and to see what effect this 'data fusion' has on the interpretation compared to the conclusions that are based on only one type of spectroscopic data (i.e. only the XRF data set, or only the Raman data set). Next to the use of Raman and scanning micro-XRF spectroscopy, the potential of a novel full-field XRF micro-imaging method is also explored for the analysis of these valuable objects of art.

LATEST DEVELOPMENTS AT THE THz/FAR-IR BEAMLINE AT THE AUSTRALIAN SYNCHROTRON

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The Far-IR/THz beamline at the Australian Synchrotron is coupled to a 9-chamber Bruker IFS125HR FT spectrometer equipped with a variety of optical components which can cover the spectral range from 10 to 5000 cm^{-1}; this instrument can offer an optimum unapodized resolution of ≥ 0.00064 cm^{-1}. Experiments from a variety of fields such as atmospheric and astrophysical science, geology, electrochemistry, nano-materials as well as biology have been successfully conducted at the beamline.

There is a range of instruments to accommodate the diverse requirements of the User community. For the gas-phase, we have two room-temperature gas cells with multiple-pass optics, one of which can be coupled to a furnace to study reactive species; there is also a multiple-pass gas cell which can be cooled to liquid nitrogen or helium temperatures in order to study aerosols and cold gases. We also have two cryostats (a liquid and a closed-loop pulse tube), and a grazing incidence angle and a near-normal reflection accessory as well as a motorized polariser to study condensed phase systems, thin films and surface interactions.

The synchrotron infrared light offers a S/N advantage over conventional thermal sources, and this advantage varies to a great degree upon the spectral range and the resolution required by the experiment. In this paper, the capabilities of the Far-IR beamline at the Australian Synchrotron will be presented as well as some applications undertaken at the beamline, and future developments such as laser & high-pressure studies.

FLUTE: A VERSATILE LINAC-BASED SOURCE OF ULTRA-SHORT FAR-INFRARED/THzPULSES

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The Karlsruhe Institute of Technology (KIT), in collaboration with DESY and PSI, is currently designing and constructing a new ultra-short far-infrared/THz pulse source and accelerator test facility [1]. This source, named FLUTE (*Ferninfrarot Linac- Und Test-Experiment*—far infrared linac- and test-experiment), is based on a 41 MeV linear electron accelerator and designed to cover a large charge range from a few pC to 3 nC. The main components of the machine are the photo-injector gun using picosecond UV laser pulses to generate electron bunches from a cathode, a linac accelerating the bunches to 41 MeV, a magnetic D-shaped chicane to compress the bunches longitudinally, the THz radiation generation/extraction, and finally an electron dump [1]. FLUTE will have a total length of around 15 m and operate at a repetition rate of 10 Hz. It will be optimized to achieve ultra-short electron bunches with a root-mean-square length down to a few femtoseconds. We will use coherent synchrotron, edge, and transition radiation (CSR, CER, and CTR) to generate very short and intense electro-magnetic pulses in the far-infrared/THz regime (see Fig. 1).

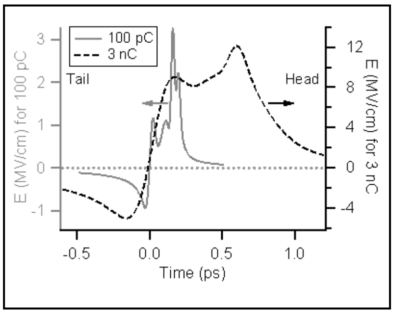

Fig. 1. Simulated electric field pulse. The pulse is assumed to be focused to a disc with 1 mm radius at a distance of 1 m from the source.

This type of short and intense electro-magnetic pulses can be used for various experiments ranging from 2D spectroscopy, studying the influence of THz radiation on biomedical samples like stem cells to pump-probe setups of new materials. Furthermore, FLUTE will be an accelerator physics test facility to develop and test new instrumentation and diagnostics needed for such short electron bunches. It will allow studying bunch compression schemes and comparing the experimental results to various simulation tools, as well as studying the complex non-linear dynamics due to coherent synchrotron bunch-radiation self-interactions, space charge effects and instabilities. This knowledge is the basis for future compact, broadband accelerator-based THz user-facilities.

Acknowledgement

We thank our colleagues from DESY, Germany, particularly R. Assmann, M. Felber, K. Floettmann, M. Hoffmann, and H. Schlarb, as well as from PSI, Switzerland, notably H.-H. Braun, R. Ganter, and L. Stingelin for their indispensable support. Furthermore, we acknowledge H. Wiedemann for his suggestions and ideas, and also the staff at KIT involved in this project, especially the technicians at ANKA.

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Poster - 24

THE AUSTRALIAN SYNCHROTRON: DEVELOPING SOURCES OF INTENSE IR SYNCHROTRON RADIATION

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The Australian Synchrotron is a 3 GeV third generation Light Source and hosts two IR beamlines, utilising the IR spectrum of the synchrotron radiation for spectroscopy and microscopy. To extend the capability of the beamlines in the Far-IR spectrum a special mode of operation has been developed. This mode of operation takes advantage of the property of temporal coherence of the emission of synchrotron radiation to increase the photon flux of millimeter waves (10 to 20 cm^{-1}) by two to four orders of magnitude (Coherent Synchrotron Radiation, CSR). Investigations are underway to increase the spectral range to 40 cm^{-1} and improve the stability of the source intensity.

In addition to expanding the capability of the existing light source, a conceptual design for an IR Free Electron Laser (FEL) at the Australian Synchrotron has been completed. The source of the FEL will be an RF photocathode, creating pulses of electrons with a width of 200 fs and a charge of 200 pC per pulse. The pulse repetition frequency in the current design is 500 MHz for a period of 2 μs (macro pulse length) and a repetition rate of 5 Hz (of the macro pulse). The generation of synchrotron radiation will come from two sources, dipole magnets and an in-vacuum undulator (IVU).

The dipoles will be a source of coherent synchrotron radiation (CSR) with a total flux that is a factor 100 greater than the flux in the existing light source (at 200 mA) for bandwidths up to 60 cm^{-1} (170 μm; 1.8 THz). The IVU, with mirrors at each end to produce an optical cavity, will produce synchrotron radiation covering a range from 40 cm^{-1}(250 μm; 1.2 THz) to 3333 cm^{-1} (3 μm; 100 THz).

The results of the work on the existing light source and the details of the conceptual design of an IR FEL will be outlined in this report.

PERFORMANCE OF AN OPTICAL STABILIZATION SYSTEM AT NSLS BEAMLINE U12IR

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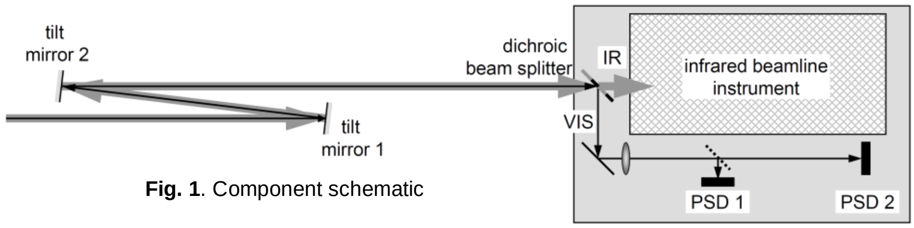

Fig. 1. Component schematic

At many synchrotron facilities, the signal detected in the infrared spectrometer is less than ideal due to the relative movement of the optical components and the electron beam in the accelerator itself. This can be especially problematic for facilities that are not operating in "top up" mode where the large variation in beam current and the associated heating of mechanical components can vary by factors of 3 or more. The result is an effective source whose position appears to shift in time and also "wobbles" due to additional motion from mechanical vibrations and electrical systems. Both of these introduce noise and error that limit the spectroscopic performance.

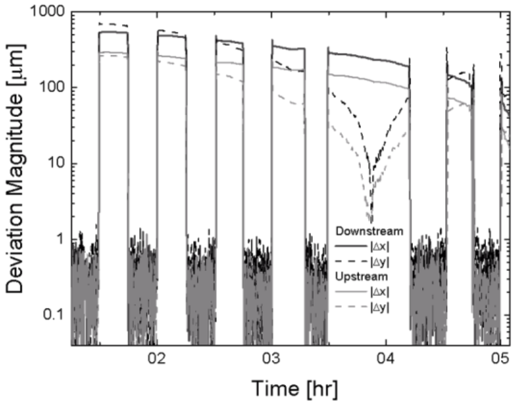

Fig. 2. Beam position deviation for two sets of x & y coordinates with feedback switched between ON & OFF over a 4 hour period.

To manage these issues, several facilities with infrared programs [1,2,3] have implemented optical feedback systems that actively monitor the beam position and constantly correct it using a pair of dynamic steering mirrors. A typical system has 2 dichroic beamsplitters, a pair of position sensing detectors (PSDs), readout electronics, and piezo-controlled mirrors in flexure-type mounts with driving electronics. One limitation has been the availability of inexpensive components that can be easily integrated into a practical system at reasonable cost. Another limitation is the constraint associated with inserting the feedback system's components within the optical layout of an existing beamline.

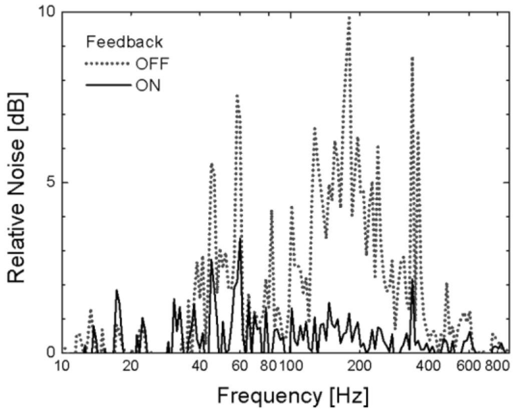

Fig. 3. Detected noise spectrum over the 10 Hz to 800 Hz frequency range comparing feedback OFF (dotted curve) and feedback ON (solid curve).

In the past few years, commercial components have become available at acceptable cost, giving us the opportunity to investigate a system to stabilize the existing NSLS U12IR beamline that operates for far- and mid-infrared microspectroscopy. Our setup (see fig. 1) has some unique aspects, among them: 1) a *single* dichroic beamsplitter, for separating the beams for infrared (for spectroscopy) and visible light (for position sensing), situated just upstream of the instrument endstation and 2) the piezo-driven flexure mirror mounts in a separate upstream optical chamber. Results indicate that a system, using entirely off-the-shelf (and LabView^{TM} compatible) components, provides useful performance benefits at a total component cost below US$12,000. For example, without the stabilization system, beam drift of ~100 µm or more is held to an accuracy better than 1 µm at the PSDs. By keeping the beam centered on the microspectrometer's apertures, noise is reduced up to a factor of 10.

Acknowledgement

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INITIAL DESIGN OF THE NSLS-II INFRARED BEAMLINE FOR CONDENSED MATTER AND MATERIALS PHYSICS (FIS/MET)

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The NSLS-II synchrotron light source at Brookhaven National Laboratory is scheduled to begin operations in the summer of 2014. Our goal is to have two infrared beamlines constructed within the first years of operation, with one serving initially both the condensed matter physics and high-pressure materials science communities. The relevant measurement and science programs include far-infrared magnetospectroscopy and ellipsometry of complex oxides (superconductors, multiferroics), novel materials such as graphene, heavy fermion systems and dilute magnetic semiconductors, as well as the vibrational & electronic response of Earth and planetary materials from near-surface conditions to those of the deepest interiors (extreme pressures and temperatures). A key spectral range for studying some of these materials is $\lambda > 1$ mm (frequencies < 10 cm^{-1}).

A unique feature of the NSLS-II storage ring is the large bending radius of the dipole magnets. For infrared, the result is a smaller angle of emission and larger effective source size (see Fig. 1) by a factor of 2.35 compared to the existing NSLS VUV/IR ring. When the source size exceeds the interior vacuum chamber dimensions, emission is affected. Thus, to have proper performance at long wavelengths, the NSLS-II dipole vacuum chamber must have a large interior diameter as well as provide adequate angular extraction. The gap between pole faces for a standard NSLS-II dipole bending magnet allows for a vacuum chamber interior height of about 2.5 cm. This would normally restrict the vertical angular collection to less than 20 milliradians and truncate the source at frequencies below 20 cm^{-1}. The resulting performance is shown in Fig. 1 (solid gray curve in right panel). From this we see that the standard gap dipole will provide excellent performance in the mid-infrared for techniques such as microspectroscopy, but is not ideal in the very far-infrared.

To achieve high performance in the far-infrared, the NSLS-II design includes 3 pairs of large gap (90 mm between pole faces) dipole bending magnets specifically for extracting long wavelengths. We anticipate a dipole vacuum chamber having interior height of 7.5 cm and total angular collection approaching 50 milliradians. As a result, the NSLS-II long-wavelength flux will be among the world leaders and very similar to the existing U4IR and U12IR beamlines at the NSLS. Of course the NSLS-II facility has been designed for very high beam stability that should provide major performance benefits over the existing NSLS VUV/IR ring.

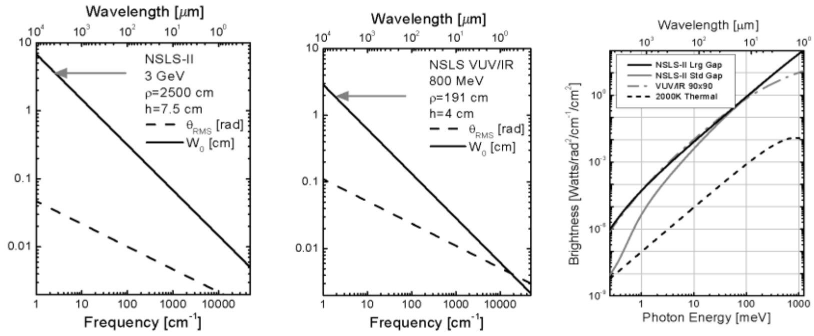

Fig. 1. *Left & middle panels:* Approximate RMS source size (waist, in cm) and emission angle (in radians) for NSLS and NSLS-II. Gray arrows indicate the start of cutoff effects where the beam waist equals the vacuum chamber half-height. *Right panel:* Calculated brightness for NSLS and NSLS-II assuming standard and large-gap dipole chambers.

We are presently developing the detailed dipole chamber and optical extraction system design for bringing the infrared out to the experimental floor, as well as the beamline instrument layout for ellipsometry and samples under extreme conditions (pressure, temperature and magnetic field).

Acknowledgement

Supported by the U.S. Dep't of Energy under contract DE-AC02-98CH10886 at Brookhaven National Laboratory and by COMPRES, the Consortium for Materials Properties Research in Earth Sciences under NSF Cooperative Agreement EAR 06-49658.

Poster - 27

MIRAS: THE INFRARED MICROSPECTROSCOPY BEAMLINE PROJECT AT THE SPANISH SYNCHROTRON, ALBA

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The MIRAS Project [1] to design and build an up-to-date infrared microspectroscopy beamline at ALBA Synchrotron Light Facility was launched in 2009, with the aim to provide experimental options in both the far-IR and mid-IR regions and with the capacity to address the present and future requirements of the scientific community, not only in Spain but also in Europe as a whole. After unanimous approval by the SAC in 2009 as the first Phase II beamline and the subsequent formal approval for funding in 2010, project funding was frozen as a result of the economic situation in Spain. However, encouraged by the Spanish user community [2], and through close collaboration between scientists and engineers from ALBA, SOLEIL and the CSIC, the project is once more gaining momentum. The objective of this communication is to provide a progress report and update on the characteristics of the proposed beamline.

ALBA is a 3rd generation 3 GeV synchrotron light source, with a storage ring circumference of 268.8 m, a very small emittance of 4.6 nm rad and a projected maximum intensity of 250 mA, designed to be used in "top-up" mode. At present ALBA has 7 beamlines, and can house up to 31 ports (16 bending and 15 insertion devices). More information on ALBA can be found here [3].

For the MIRAS Beamline the IR radiation will be extracted from a bending Magnet (BM04). A modified dipole vessel enabling collection angles of 43 (H) x 25.17 (V) mrad has been designed, manufactured and delivered to ALBA. The design employs a horizontal IR beam extraction geometry, similar to that successfully implemented at Australian Synchrotron [4]. Radiation is collected by means of a laterally inserted slotted mirror that allows the hard x-rays to pass through and directs the IR beam through an optical transfer train, with an approx. 1:1 symmetrical imaging scheme, to the experimental area. At present this optical design is in the process of refinement using SRW, Ray and Spotx codes, and the projected performance will be compared to that of other IR beamlines. The mirror mounts and adjustment mechanisms are carefully designed to fulfil requirements for increased vibration stability, and a novel mechanism for reproducible insertion and extraction of the first mirror is under consideration.

Fig. 1. Aerial view of ALBA Synchrotron

In the first instance, it is projected that a confocal point scanning microscope system with a high sensitivity HgCdTe detector coupled to a commercial FTIR instrument will be commissioned to provide diffraction-limited mapping capabilities, with a spot size at the microscope focus in the 2 – 10 µm diameter range. However, the collimated beam will be divided in the experimental area to eventually deliver light to two end-stations.

The MIRAS beamline is of high priority in the ALBA Strategic Plan [5]. With adequate funding, the forecast is that construction will begin during 2014 and light for users may be available before 2017. Our team is working hard to make this projection a reality.

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Poster - 28

COHERENT TERAHERTZ EMISSION AT THE ADVANCED LIGHT SOURCE

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Coherent terahertz (THz) radiation can be produced in a synchrotron storage ring by modulating the electron beam profile with femtosecond laser pulses[1,2], or by reducing the electron bunch length to nearly or shorter than the emitted wavelengths[3,4]. The generation of coherent THz radiation using the femtosecond laser slicing method has been successfully demonstrated at the Advanced Light Source (ALS)[1], but these measurements were limited by the beamline vertical acceptance angle, dispersion in the storage ring, and beamline instrumentation. These limitations have been resolved with the construction of the new Beamline 5.4. This beamline utilizes an infrared port on the storage ring that allows collection of larger vertical and horizontal acceptance angles, and is located immediately downstream from the wiggler insertion device used for femtosecond laser slicing. Beamline 5.4 is able to use this coherent radiation as an input to a Bruker IFS125HR high resolution vacuum FTIR spectrometer. Modulation of the electron bunch via the laser pulse creates clear changes in the THz radiation, allowing tunable spectral shapes and powers in the THz region. We present intensity and spectral measurements of coherent radiation (see an example in Fig. 1) over a variety of slicing laser pulse settings.

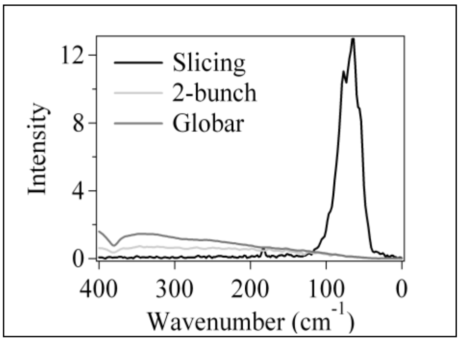

Fig. 1. Spectral measurement of coherent THz radiation from femtosecond laser sliced bunches at BL 5.4 compared to the normal non-coherent emission of the storage ring (2-bunch) and a globar thermal IR source.

Prior to 2013, the triple-bend achromat lattice of the ALS did not allow for very low momentum compaction factors, meaning the electron bunch length was too long to emit high-power full-bunch coherent terahertz radiation[5]. In early 2013 the ALS completed the installation of a family of sextapole magnets to replace corrector magnets which enables the ALS to tune to low-alpha modes on a periodic basis. Here, we also report on our initial observations with low-alpha coherent THz emission with the new ALS lattice as measured with the new beamline and IFS125HR spectrometer.

Acknowledgement

The new beamline is supported by the Office of Science, Office of Biological and Environmental Research, of the U.S. Department of Energy. The Bruker IFS125HR spectrometer was provided by Stony Brook University. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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Poster - 29

SIMULATIONS OF IR/THZ PULSE DYNAMICS

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The evaluation of spatial intensity distributions of synchrotron radiation is one capability of our new code, as already described in another contribution to this meeting [1]. In addition to that we can also simulate dynamic features such as the polarity and the temporal length of the coherent IR/THz pulses emitted from short electron bunches. This work is motivated by recent developments in fast IR/THz detectors with picosecond time resolution [2]. We therefore have devised an algorithm for numerical investigation of the dynamic features for a longitudinal charge distribution with emphasis on the low frequency range from 0.3 THz to 300 THz.

In a first step, the time dependent electric field is calculated for a given electron trajectory. This is done using the representation of the electric field of a single charge in vacuum as a combination of a velocity dependent and an acceleration dependent term. In a second step, we extract the desired low frequency part with a Fourier filter algorithm specifically developed for this purpose.

We will present the status of development as well as preliminary results on the IR/THz pulse dynamics performed with our new code.

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DEVELOPMENT OF THE HIGH-POWER THZ TIME-DOMAIN SPECTROSCOPY ON THE BASIS OF AN S-BAND COMPACT ELECTRON LINAC

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The high-power terahertz time-domain spectroscopy (THz-TDS) has been developed on the basis of an S-band compact electron linac at AIST [1-3], Japan. Such high-power THz-TDS system is strongly expected for inspection of dangerous materials in the homeland security field [4]. The high-power THz radiations are generated in two methods with the high-brightness ultra-short electron bunch. One is THz coherent synchrotron radiation (THz-CSR) for THz imaging applications. The other is THz coherent transition radiation (THz-CTR) for THz spectroscopy applications. In the preliminary experiment to obtain the characteristics of THz-CTR, it was observed that the focused THz-CTR had the donut profile in the transverse field due to its initial radial polarization. It was considered to be z-polarization at the focus point. In case of the THz-TDS experiment, THz-CTR was controlled to linearly polarization with the polarizer and focused to an electro optical (EO) crystal to obtain a THz temporal waveform using EO sampling method.

The THz-CTR-TDS is based on the EO sampling methods with the pump-probe technique. The THz spectrum is obtained by Fourier transform of the measured temporal THz waveform. Figure 1 shows the schematic diagram of the THz-CTR-TDS system with EO sampling method. When the THz pulse passes through the EO crystal, the birefringence is occurred in the crystal by the THz electric fields. The polarization of the co-propagative probe laser is changed by the birefringence [5]. The intensity difference between the p- and s-polarization of the probe laser has been measured with a photo detector. The difference corresponds to the intensity of THz electric field. The THz temporal waveform is obtained with the pump-probe technique using optical time delay stage and the THz spectrum is calculated by Fourier transform.

In the preliminary experiment, THz-CTR is controlled to horizontal polarization and focused to the (1, 0, 0) oriented ZnTe crystal as an EO crystal. The measured frequency range and signal intensity depend on the thickness [6]. It is realized to make a temporal overlap in the EO crystal between the probe laser and optical transition radiation (instead of THz-CTR) with a same optical photo-detector.

The high-power THz wave has been generated using coherent transition radiation (CTR) with polarization control for THz time domain spectroscopy (THz-TDS) with the S-band compact linac at AIST. The THz-CTR-TDS System has been constructed with EO sampling method. As a result, the THz temporal waveform has been successfully measured with this system. In the next step, we will performed the single-shot measurement with a chirped probe laser in order to improve the stability of this system and to extend the measured spectral range. In this workshop, we will describe details of system and results of the THz-CTR-TDS experiments.

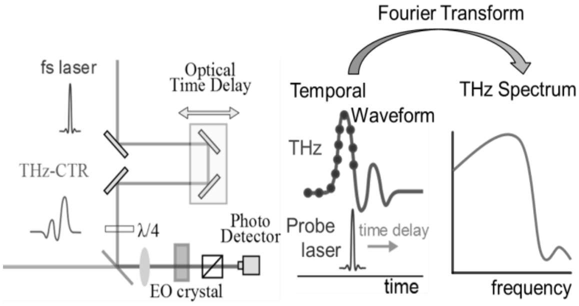

Fig. 1. Schematic diagram of THz-CTR-TDS system with EO sampling method.

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INFRARED NANO-IMAGING WITH SCANNING NEAR-FIELD OPTICAL MICROSCOPY

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Presented by H. Bechtel

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The properties of many soft matter systems, biological functional units, and nano-crystalline materials emerge from mesoscopic structures and associated phenomena with characteristic length scales ranging from sub-micron dimensions down to a few nm. In order to effectively study these materials with optical spectroscopic techniques therefore requires a means to directly resolve nanometer length scales well beyond the conventional diffraction limit. Scattering-type scanning near-field optical microscopy (s-SNOM) directly enables all-optical sub-diffraction limit imaging over a broad wavelength range from the UV into the IR by taking advantage of the evanescent fields spatially confined to the apex of an ultrasharp scanning probe tip [1]. In its IR s-SNOM implementation [2] the resulting vibrational nano-imaging and -spectroscopy is compatible with a wide range of broad- and narrow-band infrared light sources [3], including synchrotron radiation [4], and can provide structural and morphological information [5,6] as well as chemical identification [7] with high sensitivity.

Here we demonstrate the application of IR s-SNOM to biological, crystalline, and two-dimensional electron systems, using both monochromatic and broadband illumination sources. In particular we focus on native lipid bilayers of Halobacterium Salinarum (purple membrane) containing the transmembrane protein bacteriorhodopsin (bR). Together with a tuneable mid-IR quantum cascade laser (QCL), we show that s-SNOM imaging under resonant excitation of the Amide I vibrational resonance can provide a nanometer resolved map of bR concentration with sensitivity on the single bR level [8]. We additionally use s-SNOM to probe the thermal near-field of both molecular and crystalline systems, providing a direct means to measure the electromagnetic local density of states and its dependence on surface polariton modes. This thermal near-field further provides a broadband source for imaging while eliminating the need for external illumination optics [9].

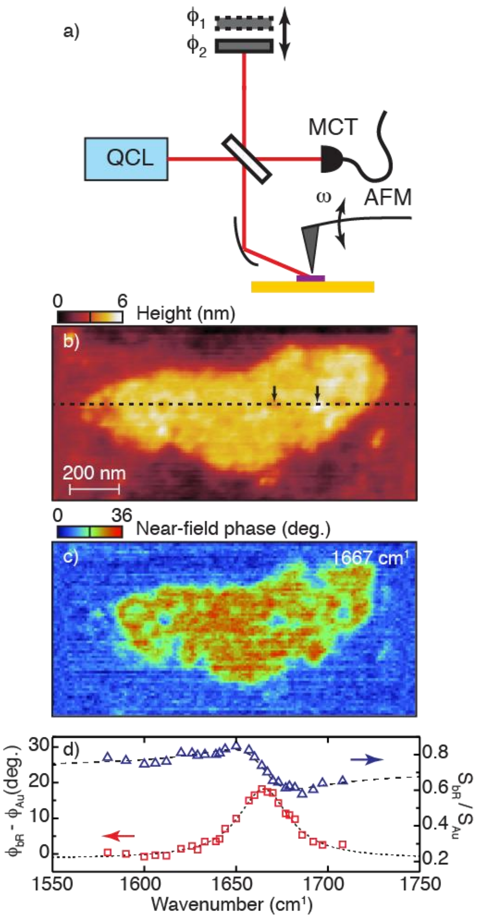

Fig. 1. a) Schematic of the s-SNOM setup. b) Tapping mode AFM topography and c) simultaneous *s*-SNOM near-field phase image of a purple membrane patch. The near-field phase provides a direct measure of the membrane protein concentration with single protein sensitivity. d) Near-field spectrum taken from the membrane patch clearly identifying the Amide I mode.

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MODELLING INFRARED BEAM LINES WITH SHADOW AND ZEMAX

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Ray-tracing software is an important tool to design and develop infrared beam lines. It provides for physical layout coordinates, beam shape and size in chambers and at mirrors, foci locations, and performance estimates. Of the available software that is suitable for reflective optics, a combination of SHADOW [1] and ZEMAX [2] in particular are discussed. These packages are commonly used for synchrotron and FEL beam line designs [3,4,5]. As no commercial software we have seen provides for a synchrotron bend magnet as a light source there is a need to either approximate one or import an accurate model's rays. Programs like the Synchrotron Radiation Workshop [6] and others provide modelling various types of synchrotron sources – bend magnets and insertion devices – to propagate wave fronts along a system of ideal optics. Arrays of amplitude and phase are employed but rays as such are not available. Using SHADOW to generate the source rays from its accurate modelling provides realistic ray distributions. The optic path can be traced from this source to a final image. The traced system information gives the optic component's placement in the lab frame. These source rays and coordinates can be used in ZEMAX to position optics and launch the rays to simulate the actual system. A conversion of the synchrotron source generated in SHADOW that ZEMAX can use is discussed. An example of its use in adding active optics on the CLS Far Infrared beam line is shown. Using the wave propagation capability of ZEMAX is a future goal, as turning the beam at each reflection in the "Non-sequential" mode breaks the rotational symmetry it requires.

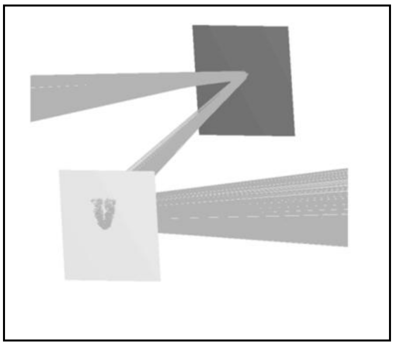

Fig. 1. Bend magnet ray pattern at 10 micron wavelength traced upon mirrors along IR beam line layout.

Acknowledgement

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BIOMEDICAL IMAGING BY INFRARED NANOSCOPY (NANO-FTIR)

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We apply nano-FTIR, a fascinating new imaging technique combining Fourier Transform Infrared Spectroscopy (FTIR) and scanning type optical microscopy (sSNOM), to study bio-medical hard matter at impressive lateral resolution of λ/1000.

Spectroscopic methods with high spatial resolution are crucial to understand the physical and chemical properties of nanoscale heterogeneous materials. A widely common used tool is FTIR spectroscopy, which use fingerprint absorbance spectra in the 5-20 µm mid-infrared region to identify and quantify material compositions. The strength of this method relays on the already established spectral databases which allow a rapid molecular identification, however a huge drawback is the spatial resolution of FTIR microscopes which are limited by diffraction to about one wavelength on the order of micrometers. Nano-FTIR is a fascinating new imaging and spectroscopy method [1,2], allowing nanoscale chemical identification and mapping of heterogeneous material. Selecting the high-resolution monochromatic mode we were enabled to map individual lacunae (bone cells) and canaliculus of standard polished human bone sections (Fig 1.) [3].

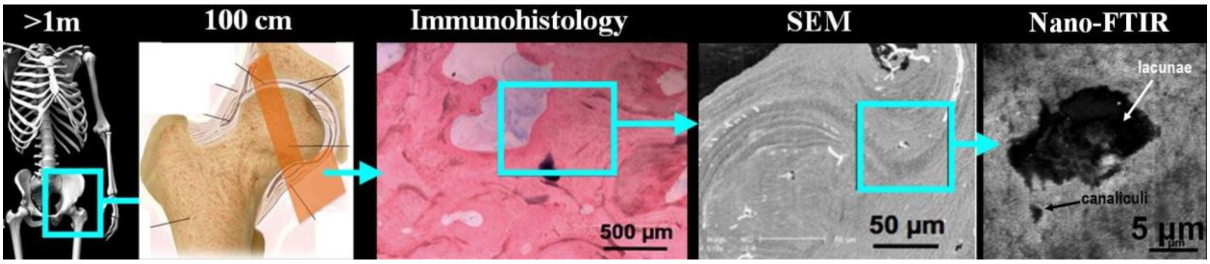

Fig. 1. Bone specimen imaged at increasing magnifications, each rectangle designating the zoom area of the following image, using light microscopy of stained section, scanning electron microscopy, and nano-FTIR imaging.

Furthermore, we apply this powerful new method to map the local distribution of bone-matrix and PMMA embedded material of human tooth section. In accordance with far-field FTIR measurements (Fig. 2 lower panel) we were able to highlight either mineral vibration using 1020 cm^{-1} radiation or PMMA by tuning the illumination light-source to 1150 cm^{-1}. Our studies show clear label-free chemical recognition at impressive lateral resolution. In contrast to common used electron microscopy techniques we use low energy photons offering a non-destructive method, which works under ambient conditions and requires low level of sample preparation. Giving that a huge application potential is foreseen in biology and medicine.

Once the technique is established and basic chemical/structural contrasts are optimized, infrared nanoscopy should have a high potential for bone research and possibly even clinical diagnosis.

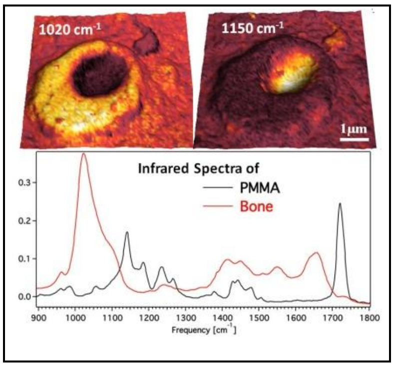

Fig. 2. Upper panel: nano-FTIR mineral and PMMA mapping of human dentin. Lower panel: FTIR spectra of bone-matrix and PMMA.

Acknowledgement

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Poster - 34

FAR-INFRARED SPECTROSCOPY OF BIOCHAR

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Biochars are carbon rich materials formed by heating various types of organic matter (green waste, plant offcuts etc.) in a low oxygen environment, locking the carbon compounds into the material [1, 2]. Studies of Amazonian soils called terra preta have shown that the existence of these materials in soil can help to improve soil fertility [3]. Therefore, the manufacture of these materials serves a dual purpose of carbon sequestrations and soil enrichment.

The constituent aromatic molecules in biochar are complex and diverse and it is still largely unknown what constituents are responsible for improving soil quality. Furthermore, not all forms of biochar are effective fertilisers. It is important to determine what makes Amazonian terra preta so effective by comparing it with various forms of artificial biochars. An understanding of the important constituents in terra preta, will allow better artificial biochars to be tailored to specific crop applications. Identifying molecular signatures using far-infrared spectroscopy to locate characteristic vibrational modes presents an ideal method for characterising the different types of biochar. The high concentrations of aromatic carbons in biochars, which are active in the infrared region, means that this technique should be very effective.

Infrared spectroscopy of such materials is limited when using conventional radiation sources. The high absorption and low transmission of these materials necessitates the use of samples prepared with low concentrations. Therefore, the already weak vibrational modes become difficult to locate in the transmission spectra. Figure 1 shows the infrared spectra of two different forms of biochar. As can be seen from the figure, the absorption lines presented by these materials are weak and broad due to the low concentration of the material. The use of accelerator-based sources provides a solution to this problem. The high luminosity of synchrotron radiation, for example, allows the use of highly concentrated samples. The weak vibrational modes should then provide a stronger signature against the background and be much easier to identify. The higher signal available when using accelerator sources also allows for rapid spectrum scans at high resolutions. Performing higher resolution spectroscopy can reveal more information about the finer structure in the absorption peaks which might have overlapped or smeared out at low resolution. This then provides more information for effective characterisation of the biochar materials.

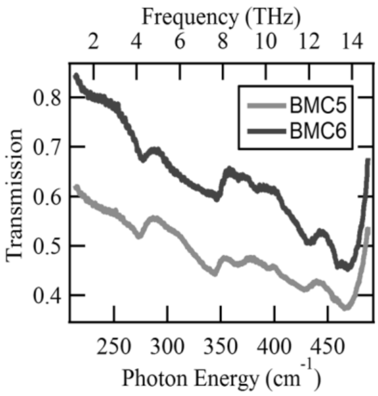

Fig. 1. Transmission spectra of two biochar samples (BMC5 and BMC6). Spectra were taken using globar source. Absorption features appear weak due to low concentration of sample.

Acknowledgement

We acknowledge the Australian Research Council.

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DEVELOPMENT OF COHERENT THz BEAMLINE OF COMPACT ENERGY RECOVERY LINAC AT KEK

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In order to demonstrate required accelerator technologies in the 3 GeV energy recovery linac light source at KEK Japan [1], the compact energy recovery linac (cERL) accelerator shown in Fig. 1 is starting the commissioning of an injector part from April 2013. Along with the operation, the quantum beam obtained from cERL is providing to user experiments. In 2014-15, the construction of beamlines for advanced researches using X- and γ-rays and terahertz (THz) beam will be started. Due to an inverse Compton scattering (ICS) of laser pulses on relativistic electron bunches in a ring of the cERL, ultra-short X-ray is produced. The 100 fs X-ray beam from cERL, which is generated by the ICS using high-power and ultra-short laser pulses, is significantly benefit for researches in the field of ultrafast science. On the other hand, high-flux x and γ-rays, which is generated by the ICS using an optical build-up cavity and high-frequency laser pulses, is an ideal light source for X-ray imaging and nuclear resonance fluorescence. Furthermore, the coherent synchrotron radiation (CSR) from electronic bunch in cERL can be used as a novel light source for researches of physical properties, because it has high intensity in the THz region [2]. In addition to the hard X-ray beamline, the THz beamline is also constructed. In this paper, we will present the outline of the design of the THz beamline, expected performance, and designed applications.

Fig. 1. Overview of compact energy recovery linac accelerator at KEK.

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MAPPING INTERFACES ACROSS POROUS METAL - ION EXCHANGE REINFORCED HYBRID MEMBRANES BY FTIR SPECTROSCOPY AT THE AUSTRALIAN SYNCHROTRON

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Porous metal frameworks exhibit superior catalytic, electric and thermo-mechanical properties highly promising for storage and separation applications. Porous metal frameworks may therefore be complementary to current ceramic or polymeric materials and tackle issues in water treatment, industrial waste purification or specific catalytic degradation of contaminants [1]. Our project aims at developing novel metal reinforced ion exchange membranes for water desalination by electro-dialysis. These hybrids composite membranes are composed of a surface functionalized porous metal framework filled with an ion exchange resin. It is crucial, in order to understand the diffusion mechanisms across these membranes, to investigate the nature and role of interfaces across the material [2].

Here, we present our latest results on the characterization of the novel ion exchange metal membranes. Porous stainless steel fibre meshes were first plasma surface treated in order to enhance the amount of surface oxides and increase their hydrophilicity. Then, the metal meshes were functionalized through a simple, but yet efficient, sol-gel reaction with various silanes (fluoro, amino and alkoxy terminated). Cation exchange resin was prepared by mixing cation exchange powder and a binding polymer, and then it was wet-cast across the functional stainless steel frameworks to form a new class of highly promising dense and electrically conductive ion exchange membranes. To introduce anion-exchange groups, a polymer film was cast across the metal meshes following by a chemical treatment.

Highly polished cross sections of the composite membranes embedded into Polyfast resin revealed interfaces between metallic frameworks and composite polymer. The morphology of the interface was investigated with SEM followed by SAXS and FTIR microscopy at the Australian Synchrotron. FTIR mapping was done using the Attenuated Total Reflectance (ATR) mode on the polished cross-sections. The chemical groups investigated the nature of the interface between the metal fibres composing the metal framework and the ion exchange resin.

The performance of the novel hybrid membranes is discussed and correlated to the investigated materials properties.

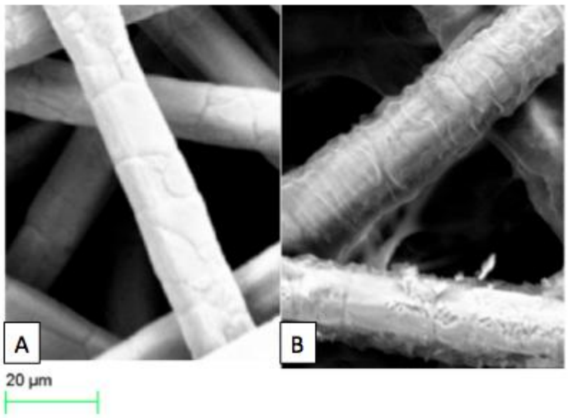

Fig. 1. SEM Images A: un-coated stainless steel fiber; B: silane-coated stainless steel fiber.

Acknowledgement

We acknowledge the Australian Synchrotron through the beamtimes M6414 and M6410. We also thank the Cooperative Research Network (CRN) 2012/2 project and Prof. Hodgson for supporting this work. The authors also thank Dr. Lili Puskar, Mark Tobin (FTIR beamline), Stephen Mudie and Nigel Kirby (SAXS/WAXS) for advice and fruitful discussions.

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PROPERTY OF LINEARLY POLARIZED COHERENT TRANSITION RADIATION EMITTED FROM WIRE-GRID RADIATORS

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For the spectroscopic purpose, various types of coherent radiation emitted from a relativistic electron beam have attracted a considerable attention as a new and powerful light source in the THz-wave region. Coherent transition radiation (CTR) is one of such a light source. Whereas synchrotron radiation has linear polarization along an electron orbit, the electric vector of transition radiation (TR) emitted from a metallic screen is axially symmetric with respect to the trajectory of an electron beam. Therefore, CTR is usually utilized as a non-polarized light source in the spectroscopic application. However, circularly polarized light has been useful in the circular dichroism spectroscopy. Shibata *et al.* has developed a technique of generation of circularly polarized THz-wave radiation with the phase difference between the forward TR and the backward TR [1]. However, it was difficult to control the polarization degree because the geometrical arrangement was important in order to generate both the linearly polarized the forward and the backward TR. In this paper the property of the linearly polarized CTR with wire-grid radiators has been experimentally investigated in order to develop a new technique of generation of circular polarized THz radiation.

The experiment was performed at the coherent radiation beamline [2] at the 40-MeV L-band linear accelerator of the Research Reactor Institute, Kyoto University. The schematic layout of the experiment is shown in Fig. 1. As a forward radiator (FR in Fig. 1) of forward CTR and the backward one (BR), wire-grid polarizers 10 µm thick with 25 µm spacing were used. The CTR was detected by a liquid-helium-cooled Si bolometer.

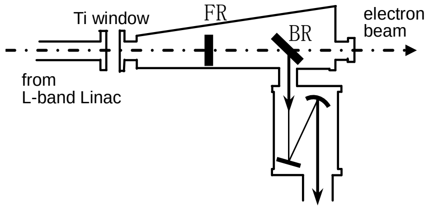

Fig. 1. The arrangement of the experiment.

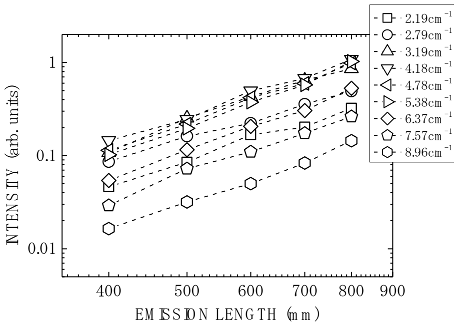

Fig. 2. The relation between the observed intensity and the emission length. the direction of both grids of FR and BR was vertical.

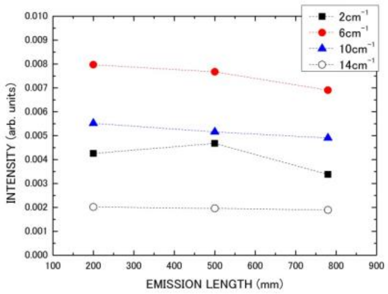

Fig. 3. The emission length dependence. The direction of grid of FR was horizontal and that of BR was vertical.

The distance between the forward and backward radiators is usually called the emission length. Figure 2 shows the dependence of intensity on the emission length at some wavelengths on a logarithmic scale. In this measurement the direction of both grids of FR and BR was vertical. When the emission length is far shorter than the formation length, the intensity of CTR from metallic foils is proportional to the square of the emission length [3]. The formation length in the millimeter-wave region is longer than 15 m for the 40-MeV electron beam. Each plots in fig. 2 was fitted by the equation of $y=x^a$ in order to confirm the quadratic dependence in fig. 2. The results were a=2.6 for the shorter wavelengths and a=3.0 for the longer wavelengths. These are larger than the expected value of 2. The reason of this discrepancy is not clear at present. Figure 3 shows the dependence of intensity on the emission length on a linear scale in the case where the direction of grid of the first polarizer (FR) was horizontal and that of the second one (BR) was vertical. The observed intensity was almost constant regardless of the variation of the emission length. It became clear that the CTR with horizontal polarization emitted from the FR was not reflected to the detector by the BR and the observed intensity depended on the distance between the forward Ti window and the BR.

Acknowledgement

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Poster - 38

SYNCHROTRON FTIR SPECTRA OF PROTEINS ON CARDIOVASCULAR DEVICES

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With economic development and the associated decline in communicable diseases globally, cardiovascular disease is now the leading cause of death worldwide and is expected to remain so well into the 21st century. A disproportionate 40% of total deaths in Australia arise from cardiovascular disease alone, with many patients dying suddenly while waiting for suitable medical intervention. The treatment costs are greater than for any other disease and consume more than 11% of the Australian annual healthcare budget. If loss of productivity and quality of life are included, the costs are higher still. Despite this, effective and biocompatible synthetic materials for cardiovascular repair are currently lacking, creating a scientific imperative to develop improved materials. However, currently used materials fail to establish a luminal coating of endothelial cells, remain thrombogenic and generate an unfavourable immune response that leads to chronic inflammation. Polymers used for grafts have mismatched compliance, resulting in anastomotic intimal hyperplasia and leading to graft occlusion. The key question to resolve is the “foreign body response” of the host. The foreign body response results from the host organism’s identification of the implanted material as foreign. When attempts to break down and eliminate the material fail, a thick layer of fibrous scar tissue is formed around the implant in an attempt to isolate it from the rest of the organism. The thickness of this fibrous tissue layer depends on the extent to which the implanted material is recognised as an irritant. A thick layer of scar tissue may limit the effectiveness of the device, requiring its removal. The foreign body response can be decreased or even eliminated with a protein coating that can be that does not appear foreign to the immune system of organism as a host layer. This is why the attachment of protein in its natural conformation on the device surface is of interest for the development of biocompatible materials for use in implantable biomedical devices.

We improve the protein attachment on medical polymers with plasma methods [1-2]. The modification of the polymers by plasma methods changes significantly its chemical nature and accordingly the wettability. The modified polymer is activated with embedded radicals that attach the protein molecules through covalent bonds formed due to radical reactions on the modified polymer surface with proton-donor groups of the protein molecule. Since the forces of interaction of the protein molecule with the surface are strongly influenced by wettability and surface charge, changes in the protein attached amount and protein conformation can be expected to occur as these properties vary. The medical device surface has to be covered completely and uniformly with a dense protein layer in its bioactive conformation to prevent immune cells from recognising the device as a “foreign body”.

We have analysed changes in the amount, conformation and activity of the attached protein on flat polymer surfaces by FTIR ATR, XPS, ellipsometry, QCM, AFM, SPR and a number of other methods [1-6]. However, actual medical devices have complicated shapes that make it difficult or impossible to use these methods of analysis. For real medical devices, we used the Australian Synchrotron infrared facility. The protein attached on complex shape surfaces has been studied with IR-microscopy. A beam spot of 20 µm diameter corresponding to the size of cells was used for uniformity analysis of the protein coverage. The conformation of the protein was studied with component analysis of the Amide I line and with direct observation of interchain vibrations in far-IR spectra.

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FAR-INFRARED STUDIES ON NAFION AND PERFLUOROIMIDE ACID (PFIA) AND THEIR ALKALI SALTS

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Heightened interest in Nafion [1-3] (registered trademark of DuPont for its perfluorosulfonated acid products) and PFIA [4] stem from their use as the proton exchange membranes (PEM) in fuel cells and, more recently, also as a highly-efficient water purification membrane [5]. The molecular structure of the Dupont Nafion polymer consists of a Teflon (PTFE) backbone with perfluorinated pendant chains that terminate with sulfonate groups (SO_3-M^+) where M^+=H^+ in the acid form or M^+=Li^+, Na^+, K^+, Rb^+, Cs^+ in its alkali salt form. Likewise, the 3M perfluoroimide acid (PFIA) polymer consists of a Teflon backbone and pendant chains terminated with sulfonate groups. However, the 3M-PFIA polymer offers an additional exchangeable -H in the form of a sulfonyl imide group along the pendant chain prior to the terminal sulfonate group.

In this study we investigated the cation-motion vibration in Nafion and PFIA. Thin films of Nafion and PFIA were measured below 300 cm^{-1} in transmission geometry by means of Fourier Transform infrared (FTIR) spectroscopy. Special care was taken to remove interference fringes caused by the coherent superposition of light from the two film surfaces. The interference effect can lead to an erroneous quantitative analysis of the chemical study especially in the far infrared, since the fringe features can be in amplitude and spectral width very similar to the absorption band under investigation.

Pronounced spectral bands that correlate systematically with the corresponding cation mass in the terahertz or far-infrared regime are observed in the corrected spectra. We calculated from the band position the effective force constant for the forces acting between the sulfonate site and the cations. The present results for Nafion and PFIA and their alkali salts may encourage further development of more accurate force field calculations as well as more accurate molecular dynamics and quantum mechanical calculations.

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MULTI-ANALYTICAL STUDY OF DECAYED GILDED DECORATIONS IN THE ALHAMBRA MONUMENTAL ENSEMBLE

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Golden decorations in the Alhambra complex are poorly studied. Previous works have been restricted to a very limited amount of fragments of carpentry [1] and plasterwork [2] from different buildings of the complex. In this work, we conducted a study of the decayed gilding decorations of the Hall of the Kings. The integration of different analytical techniques allows an extensive characterization of these decorations as well as the identification of several gilding technologies. Hence, our results provide us a comprehensive perspective of the evolution of gilding throughout the history of the Alhambra.

The basic knowledge of the composition and structure of the metal layers was achieved by means of SEM-EDX. Thus, two main different gilding techniques have been established, the original one that consisted on a thin gold leaf (1-2 µm) and redecorations with a laminated structure formed by a gold leaf over a thicker tin foil (10-15 µm). FTIR microspectroscopy with synchrotron radiation allowed the identification of the organic adhesive used to fix the metals. The gold leaf was applied directly over the finishing layer of the plasterwork employing a proteinaceous glue while in the case of the laminated structures either glue or a natural resin were found. Calcium oxalates and tin (II) oxide are the main decay products found in the gildings and were detected by using Raman micro-spectroscopy. In addition, in one of the seven vaults of the Hall, two examples of false gilding have been encountered. One was based on a tin foil tinted to look like gold by means of a varnish (composed of a drying oil and a natural resin) and the second was made up with a tin-copper alloy (bronze) that appears severely degraded to copper oxalate and SnO.

Acknowledgement

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SR-FTIR MICROSPECTROSCOPY INVESTIGATIONS INTO THE IN VITRO ACTIVITY OF THE PHOTOACTIVE CHROMIUM DNA INTERCALATOR, $[Cr(TMP)_2(DPPZ)]^{3+}$, IN A549 HUMAN LUNG CANCER CELLS

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To date studies have shown that $[Cr(diimine)_2(diimine')]^{3+}$ complexes intercalate with B-DNA and are capable of causing DNA strand scission following exposure to UV irradiation [1]. This study has investigated the cytotoxicity, cellular uptake and intracellular interactions of $[Cr(TMP)_2(DPPZ)]^{3+}$ (TMP = 3,4,7,8-tetramethyl-1,10-phenanthroline, DPPZ = dipyrido[3,2-a:2',3'-c]phenazine) (Figure 1), in the human lung cancer cells (A549) in order to assess its potential as a photoactive anti-cancer agent. The cytotoxicity of $[Cr(TMP)_2(DPPZ)]^{3+}$ was evaluated using the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. Cells treated with $[Cr(TMP)_2(DPPZ)]^{3+}$ (4 h) displayed significantly increased cytotoxicity following the UV irradiation of the cells (350 nm, 10 min) whereby the IC_{50} was 750 ± 150 µM for non-irradiated cells versus 8.5 ± 0.7 µM for irradiated cells. Graphite furnace atomic absorption spectroscopy (GFAAS) studies showed that the cellular chromium content of $[Cr(TMP)_2(DPPZ)]^{3+}$-treated cells (4 h) was not significant compared to the control cells, demonstrating that only small intracellular concentrations of the complex are required to induce cytotoxic and photoactive effects.

Synchrotron radiation Fourier transform infrared (SR-FTIR) microspectroscopy was employed to determine whether spectral changes indicative of DNA strand scission could be detected in single A549 cells after treatment with $[Cr(TMP)_2(DPPZ)]^{3+}$ (4 h, 50 µM) followed by irradiation (10 or 30 min). In comparison to the control cells (0, 10 and 30 min irradiation), a significant increase in the intensity of the symmetric phosphate band, ($\nu_s(PO_2^-)$) at ~ 1080 cm^{-1} was observed in the spectra of irradiated $[Cr(TMP)_2(DPPZ)]^{3+}$-treated cells (4 h, 10 or 30 min irradiation). The intensity of the phosphate bands is normally quite low due to the tightly packed nature of DNA in chromatin [2]. The chemometric technique, principal component analysis (PCA), was used for multivariate reduction in order to assess the biochemical differences between cell subpopulations. PCA of the phosphate region (1350-1000 cm^{-1}) showed some separation of the irradiated $Cr(TMP)_2(DPPZ)]^{3+}$-treated cells (4 h, 10 or 30 min irradiation) from the control cells (0, 10 and 30 min irradiation) and non-irradiated $Cr(TMP)_2(DPPZ)]^{3+}$-treated cells (4 h).

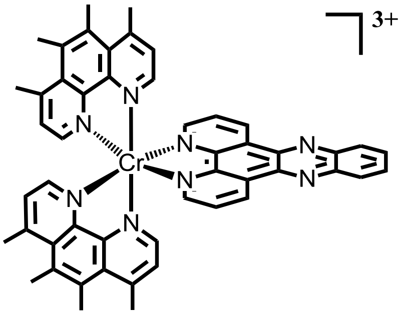

Fig. 1. Structure of $[Cr(TMP)_2(DPPZ)]^{3+}$.

The 'dispersion artefact' or resonant Mie scattering (RMieS), which is observed as a sharp decrease in intensity on the high wavenumber side of the Amide I band (~1655 cm^{-1}) was exhibited by the single cell spectra collected in this study, thus the reliability of biochemical interpretation may be significantly reduced without compensation for this effect. In order to minimise the effects of Mie scattering, the RMieS Extended Multiplicative Signal Correction (EMSC) algorithm [3] was applied to the spectra (30 or 100 iterations). Importantly, the increased intensity in the $\nu_s(PO_2^-)$ band remained observable following RMieS correction of the spectra confirming that the increased intensity of the $\nu_s(PO_2^-)$ band was not merely an artefact caused by RMieS. These results suggest that $[Cr(TMP)_2(DPPZ)]^{3+}$ may interact with DNA intracellularly to cause DNA single-strand breaks when irradiated with UV light.

Acknowledgement

ELH and CTD thank Noel Kane-Macguire (Furman University, USA) for providing $[Cr(TMP)_2(DPPZ)]^{3+}$ for this study, and also acknowledge Paul Bassan and Peter Gardner for provision of the RMieS algorithm and correction guide and Geraud Sansom (University of Wollongong) for performing RMieS correction of the spectra. ELH and CTD acknowledge the Australian Synchrotron for providing travel funding.

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MEASUREMENT OF RADIALLY POLARIZED TERAHERTZ RADIATION USING A TERAHERTZ CAMERA

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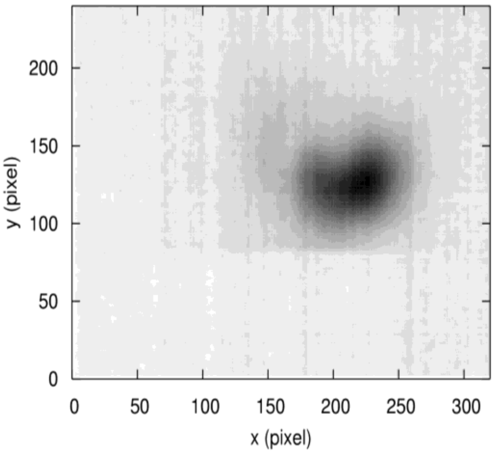

Fig. 1. Profile of the coherent transition radiation measured with a terahertz camera.

Coherent terahertz (THz) radiation sources have been developed using an ultra-short pulsed electron beam generated by an S-band compact electron linac at National Institute of Advanced Industrial Science and Technology (AIST) [1-4]. Compared to conventional laser-based terahertz radiation sources, the electron linac-based terahertz radiation sources are expected to be generated high peak power radiation. The designed terahertz radiation pulses have a high peak power of more than 1 kW in the frequency range of 0.1 to 2 THz. The S-band compact electron linac consists of an injector, a linear accelerator, and an achromatic arc section. The injector consists of a Cs_2Te laser photocathode RF gun with an S-band 1.6 cell cavity and a solenoid magnet for emittance compensation. The linear accelerator has two 1.5-m-long S-band accelerating tubes which have a π/2 mode standing wave structure. A high quality electron beam is emitted via the photoelectric effect by injecting the laser into the photocathode. The charge, bunch length, and accelerated energy of the electron beam generated from the injector are 1 nC/bunch, 3ps (rms), and 4 MeV, respectively. The electron beam can be accelerated up to approximately 42 MeV with the S-band accelerating tubes. The electron beam then passes through the achromatic arc section and was compressed to less than 1 ps (rms).

Coherent synchrotron radiation (CSR) in the terahertz frequency range is generated from the ultra-short pulsed electron beam when it passes through a 90-degree bending magnet. We have developed a scanning transmission imaging system using the CSR [3-4]. The imaging system was consisted of a schottky diode rf detector and a X-Y motorized stage. A sensitive area of the typical rf detector is 2 mm^2. Typical scanning time for the transmission imaging was 17 min/cm^2. We have also developed the coherent transition radiation (CTR) in the terahertz frequency range having a small source size. CTR is generated from an alumina fluorescent plate when the tight focused electron beam passes through it. Polarization of the CTR is radial polarization. The profile of CTR was measured as a ring with the rf detector due to its polarization dependence.

To shorten the time for the imaging and measure the profile of the CTR correctly, we have developed a terahertz imaging system using a terahertz camera. The terahertz camera (NEC, IRV-T0831) contains an uncooled microbolometer focal plane array which has nearly flat spectral response over a frequency range of 1.5 to 100 THz, and operated at 30 Hz frame rate [5]. The pixel number and pixel pitch of the terahertz camera are 320 x 240 pixels and 23.5 μm. The profile of the CTR measured with the terahertz camera in real time is shown in Fig. 1. The repetition rate of the electron beam was 25 Hz. The CTR was injected into the camera using a parabolic mirror and two lenses. We have successfully measured the profile of the CTR. In this workshop, we will present a polarization analysis of the radially polarized CTR using the terahertz camera.

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FROM PORCELAIN TO PIMPLES: A STUDY OF SYNCHROTRON-SOURCED INFRARED SPECTROSCOPY FOR UNDERSTANDING THE LOCALISED AGGREGATION OF ZINC SOAPS IN A PAINTING BY SIR FREDERICK LEIGHTON

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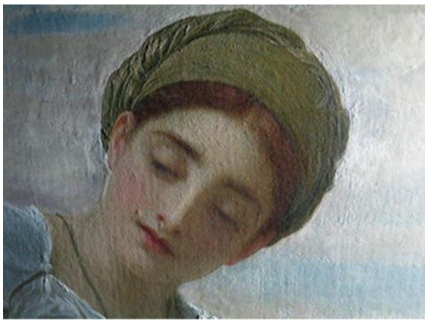

Fig. 1. Detail in raking light of painting by Frederic Leighton *Winding the skein*, 1878. Collection: Art Gallery of New South Wales.

A recent conservation treatment of Frederick Leighton's painting *Winding the Skein*, 1878 (oil on canvas, 100.3 x 161.3 cm) revealed that the smooth porcelain-like surface of the painting has been disrupted by a profusion of tiny lumps (Fig. 1.). Microscopic cross-sections of samples taken from these areas showed that the lumps were originating from swellings in the zinc oxide and chalk-based ground preparation. They were concentrated in discrete and defined areas of the composition, primarily the figures. Other regions such as the sea and sky were apparently unaffected. Fourier Transform Infrared (FTIR) analysis characterised the white, waxy contents of the eruptions as soaps by the absorption peaks in the carboxylate region 1500 to 1650 cm^{-1} wavenumbers.

There is an emerging body of evidence linking soaps formed by reaction of zinc oxide with fatty acids from oil-binding medium, to lumps and surface disruption of paintings[1]. The precise factors influencing this process are unclear and are the subject of ongoing research[2]. The study of Leighton's painting offers a unique opportunity to enhance our understanding of the specific mechanisms of zinc soap aggregation in oil paintings through comparison of areas of paint in which agglomerates have formed against those without apparent disturbance.

Samples from affected and unaffected areas of the composition were compared in cross-section using synchrotron FTIR microspectroscopy (SR-µFTIR). The technique enabled comparison of chemical detail of the samples in particular the carboxylate phases present in the paint samples, interpreted in conjuction with elemental maps acquired using scanning electron microspcopy with energy dispersive x-ray analysis. Samples were prepared for the microscope transmission measurements by setting in polyester resin and cutting 10 micron thin-sections. These were placed on a diamond cell and measured in adjacent 5 micron sample sized areas at 5 micron steps to build FTIR spectral maps covering the full area of the sample.

SR-µFTIR maps of the large soap aggregate taken from the figure of the woman demonstrate peak absorption intensity over wavenumber range 1540-1570 cm^{-1} with spectra containing strong carboxylate doublets at 1549/1530 and 1409/1398 cm^{-1}, characteristic of zinc oleate/linoleate[3]. Basic zinc carbonate is also indicated within aggregates.

In a sample from an apparently unaffected area, small zinc soap aggregates can be seen in the SR- µFTIR map when integrated on the zinc oleate peaks. These have however remained within the ground in a more distributed form. The exact catalyst for the transformation of the zinc oleate soaps into large moveable agglomerates in the figure areas of the painting is still under investigation, involving correlation of analytical data with the artist's own record of his materials and techniques and with the painting itself.

Acknowledgement

The conservation treatment and research of the painting *Winding the skein* by Frederick Leighton was funded by the Friends of Conservation, Art Gallery of New South Wales

Australian Synchrotron

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THE INFRARED BEAMLINE BL43IR AT SPRING-8: CURRENT STATUS AND RECENT STUDIES

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The infrared beamline BL43IR at SPring-8 has been in operation since 2000. The high brilliance property of infrared synchrotron radiation is utilized by a microspectroscopy measurement at BL43IR [1]. In this contribution, we describe the current status of BL43IR and recent studies. Futhermore, we will discuss a future prospect of the beamline.

BL43IR has three microspectroscopy stations, i.e., the microscopes are a high spatial resolution microscope, a long working distance microscope and a magneto-optical microscope. In addition, in order to overcome the diffraction limit, we are developing a near-field spectroscopy apparatus. Fig. 1 shows end stations at BL43IR.

At BL43IR, various fields of studies have been conducted. Physics researches have been the most productive. The representative activities are, for example, high pressure experiments of strongly correlated electron system [2], microspectroscopy studies of molecular organic conductors [3] and microspectroscopy experiments under multi-extreme conditions [4]. Recently, studies in other fields than physics are increasing, and we introduce some of them. A research to verify the effect of a hair treatment agent was done as an industrial use. In this study, a mapping image of a sliced hair was measured to identify the penetration of the functional components of the treatment agent into the hair [5]. One of the archaeological studies related to the identification of a kind of excavated textile fibers. The identification of a kind of bast fibers was sometimes difficult, because their infrared spectra resembled each other. New procedure was discussed to identify the bast fibers by analyzing the polarization angle dependence of spectral pattern [6]. One of a polymer science studies was conducted to investigate a wetting behaviour of a polyelectrolyte brush surface. By infrared microspectroscopy, the presence of the water was confirmed even outside the water droplet, and the wetting mechanism was discussed [7].

In SPring-8, various research fields in wide photon energy range have been covered at the many beamlines. We are currently trying to promote utilizations of the multiple synchrotron beamlines, in order to encourage more use of BL43IR.

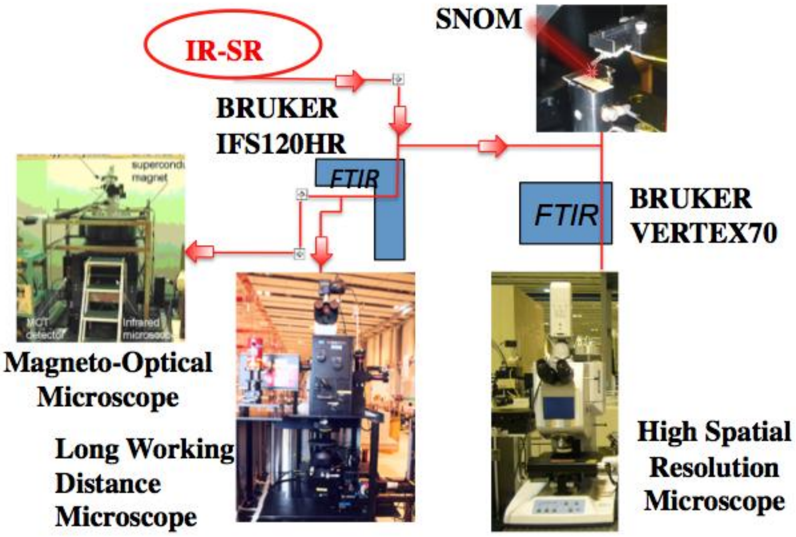

Fig. 1. End stations at BL43IR, SPring-8.

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SYNCHROTRON MICRO FTIR COMPARISON OF THE EFFECTS OF SLOW AND RAPID FERMENTATION METHODS ON THE PROTEIN STRUCTURE OF BREAD

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Since the early 1960s fundamental changes have been made to the method by which commercially produced bread dough is prepared for baking. These changes followed research by the British Baking Industries Research Association aimed at enabling lower protein UK-grown wheat to be used in the making of bread products, and in reducing the time and cost of bread production. The process developed involves the use of rapid dough mixing, high yeast levels, and the addition of vegetable fat, and of various enzymes and flour "improvers". This so called "Chorleywood" Bread Process now accounts for the production of 80% of bread in the UK, Australia and New Zealand. Prior to this, most leavened bread was prepared by the slow fermentation of dough by yeast and bacteria naturally present in the flour, a method more commonly referred to as the "sourdough" method.

Recent research has shown significant degradation processes of immunogenic gluten epitopes by sourdough bacterial and yeast proteases, which do not occur during rapid yeast-only fermentation, [1] as well as reduced glycaemic responses to the intake of sourdough fermented breads, when compared with breads rapidly fermented by baker's yeast alone.[2] High consumption of food producing a high glycaemic response may contribute to the development of insulin resistance and the incidence of type 2 diabetes, [3] and the potential health impacts of rapidly fermented bread doughs are now coming to light, with the change in the nature of bread over the last 50 years being implicated as one potential factor in the increased occurrence of gluten intolerance and type 2 diabetes.

Research to date into the differences between sourdough and yeast fermented breads has focused on either the analysis of blood constituents after bread consumption, or the bulk chemical analysis of breads. At the Australian Synchrotron IRM beamline we have undertaken infrared micro imaging of baked bread dough prepared using slow sourdough fermentation and using rapid fermentation with baker’s yeast. FTIR microspectroscopy is shown to clearly identify the spatially separated protein and starch components of the baked bread, at a spatial resolution of a few microns. Preliminary analysis of our data shows detectable differences, at the micron scale, of the protein structure within the crumb of the bread. These structural variations within the bread structure may account for some of the dietary factors observed by others, such gluten immunogenic responses, and glycaemic response.

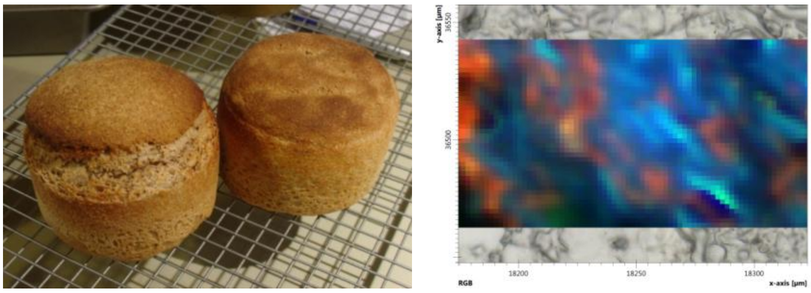

Fig 1. Sourdough (left) and yeast (right) fermented breads immediately after baking are shown in photograph to the left. The infrared RGB map to the right shows the clear separation of protein (red) and carbohydrate (blue) components within the baked dough. (IR Map = 150 x 80 microns)

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HIGH-SPATIAL-RESOLUTION MAPPING OF SUPERHYDROPHOBIC CICADA WING SURFACE CHEMISTRY USING INFRARED MICROSPECTROSCOPY AND INFRARED IMAGING AT TWO SYNCHROTRON BEAMLINES

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The wings of some insects, such as cicadae, have been reported to possess a number of interesting and unusual qualities such as superhydrophobicity, anisotropic wetting and antibacterial properties. Here, the chemical composition of the wings of the Clanger cicada (*Psaltoda claripennis*) were characterized using infrared (IR) microspectroscopy. In addition, the data generated from two separate synchrotron IR facilities, the Australian Synchrotron Infrared Microspectroscopy beamline (AS-IRM) and the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison, IRENI beamline, were analysed and compared. Characteristic peaks in the IR spectra of the wings were assigned primarily to aliphatic hydrocarbon and amide functionalities, which were considered to be an indication of the presence of waxy and proteinaceous components, respectively, in good agreement with the literature. Chemical distribution maps showed that, while the protein component was homogeneously distributed, a significant degree of heterogeneity was observed in the distribution of the waxy component, which may contribute to the self-cleaning and aerodynamic properties of the cicada wing. When comparing the data generated from the two beamlines, it was determined that the SRC IRENI beamline was capable of producing higher-spatial-resolution distribution images in a shorter time than was achievable at the AS-IRM beamline, but that spectral noise levels per pixel were considerably lower on the AS-IRM beamline, resulting in more favourable data where the detection of weak absorbances is required. The data generated by the two complementary synchrotron IR methods on the chemical composition of cicada wings will be immensely useful in understanding their unusual properties with a view to reproducing their characteristics in, for example, industry applications.

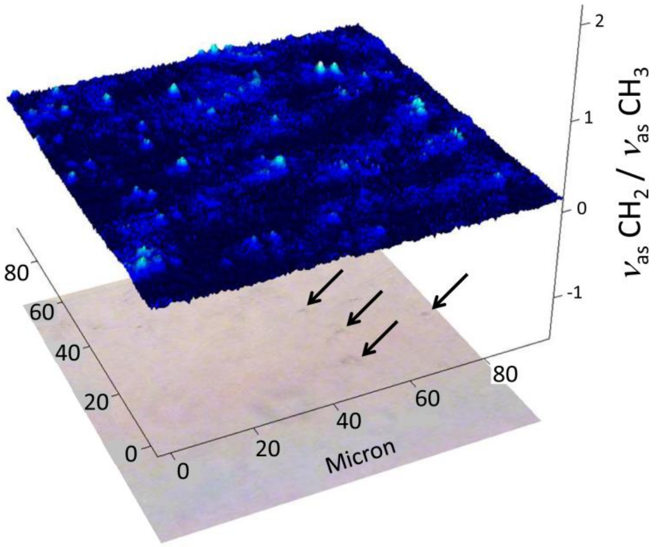

Fig. 1. Pattern of wax distribution on the surface of the wing of the cicada *Psaltoda claripennis*.

CHARACTERIZATION OF THZ RADIATION GENERATED BY ULTRA-SHORT BUNCH FROM ECC-RF-GUN

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Ultra-short bunch which is shorter than 1ps is essential for generating coherent THz light. 1ps (0.3mm) is equivalent to the wavelength of 1THz light. When the bunch length is shorter than this, the radiation is enhanced and the power would be proportional to the square of the number of electrons. That means an ultra-short bunch with high charge would be a great tool for an intense THz light source. In general, such an ultra-short bunch is available using a number of buncher systems, but in that case the whole system gets large. It is the best if such an electron bunch is generated by only an electron gun.

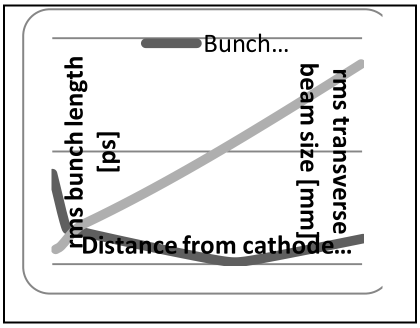

Fig. 1. Bunch length and beam size as a function of distance from cathode.

Energy Chirping Cell attached rf gun (ECC rf gun) is a photocathode rf gun specialized for ultra-short bunch generation. This ECC rf gun has been made with the collaboration of High Energy Accelerator Research Organization (KEK) [1] [2]. Although the bunch length could be controlled by the laser pulse width, the bunch length ends up being bigger than 1ps due to the severe space charge effect when using a femto-second laser and a normal 1.6 cell cavity. Concerning this phenomenon, ECC is attached right after the 1.6 cell so that the electron bunch would be compressed after the electron bunch is accelerated around 5MeV. The roll of ECC is to chirp the energy with the linear part of the rf electric field. The electron bunch would be compressed by velocity difference as it drifts. The velocity difference is large enough in the energy region of around 5MeV. This bunching process is called the velocity bunching [3].

Simulation results of PARMELA and GPT show that the ECC rf gun can accelerate an 100pC bunch with the bunch length less than 100fsec. The simulation result of bunch compression is shown in figure 1. It shows that the electron bunch is compressed down to 86fsec at the distance of 2.4m away from the cathode.

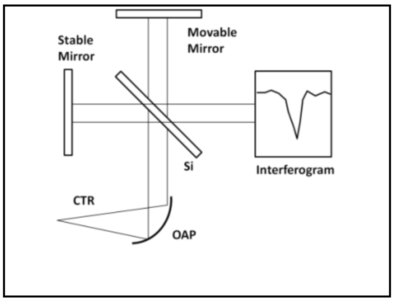

Fig. 2. Schematic of Michelson interferometer.

We have generated THz light by coherent transition radiation (CTR) and coherent synchrotron radiation (CSR) using the ultra-short electron bunch from the ECC rf gun. By measuring the frequency of CTR or CSR, we can estimate the bunch length. We have used Schottky barrier diodes in order to detect the THz radiation. We have successfully measured the 0.2THz radiation by CSR. By the detection of 0.2THz radiation and the calculation of CSR spectrum, we can say that the bunch length is surely shorter than 1ps and could be less than 500fsec [4]. For measuring the bunch length more precisely, we are now constructing a Michelson interferometer. The schematic of the Michelson interferometer is shown in figure 2. The CTR is reflected by an off-axis parabolic mirror into a parallel light. A thin silicon plate would be used as a beam splitter. The alignment of the components is done using a He-Ne laser, and we were able to measure the interference fringes. At this workshop, we will report the performance of the ECC rf gun, the results of interferometer experiments, and some future plans.

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CURRENT SCIENTIFIC RESEARCH AT NSRL INFRARED BEAMLINE

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The infrared beamline and station at NSRL was reconstructed in 2009. During the last 3-4 years, new experimental methods such as diffraction limited microspectroscopy and imaging, variable temperature reflection spectroscopy and in-situ technique were developed and provided powerful ability for the users from many research fields. Here, current scientific research at infrared beamline which covers materials science, polymer science, physics, biomedicine and chemistry are introduced.

1. Microspectroscopy and imaging

(a)The mechanical property of silkworm fibers is closely related to their structure. Thanks to high brightness synchrotron infrared source, we can monitor both protein secondary structures (conformations) and their orientations in single silk fibers. The changes of orientation and content of different secondary structures in single silk fibers can help us to understand further the relationship between structure and properties. These observations provide an explanation for the supercontraction behavior of certain animal silks and are likely to facilitate understanding and optimization of postdrawing used in the conjunction with the wet-spinning of silk fibers from regenerated silk fibroin solutions[1].

(b) By developing in-situ infrared microspectroscopic imaging methods, we studied the conformational order in the growing process of a single spherulite, and the deformation behavior of a single spherulite under tensile force. The results provide very valuable information to understand the relationship between microstructure and macroscopic physical properties of polymers[2]. In addition, we used infrared imaging to study the phase behavior of silk protein-based polymer blends [3].

2. Infrared spectroscopy

Dielectric constant is closely related to infrared phonon mode. The understanding of the relationship between dielectric constant and infrared phonon mode is very important for developing dielectric materials such as microswave dielectric ceramic and High-k gate dielectric. By far infrared spectroscopy, we studied the dependences of infrared phonon modes on doping and temperature for BiVO4 type scheelite monoclinic solid solution and $AMoO_4$–TiO_2. The results show that they are good candidates for microwave electronic device applications[4]. We also studied the structure, infrared phonon mode and dielectric constant of $La_2Hf_2O_7$ and $La_xHf_{(1-x)}Oy$ thin films. The physical origin of the static dielectric constant and its relationship with lattice dynamics of these materials were revealed[5].

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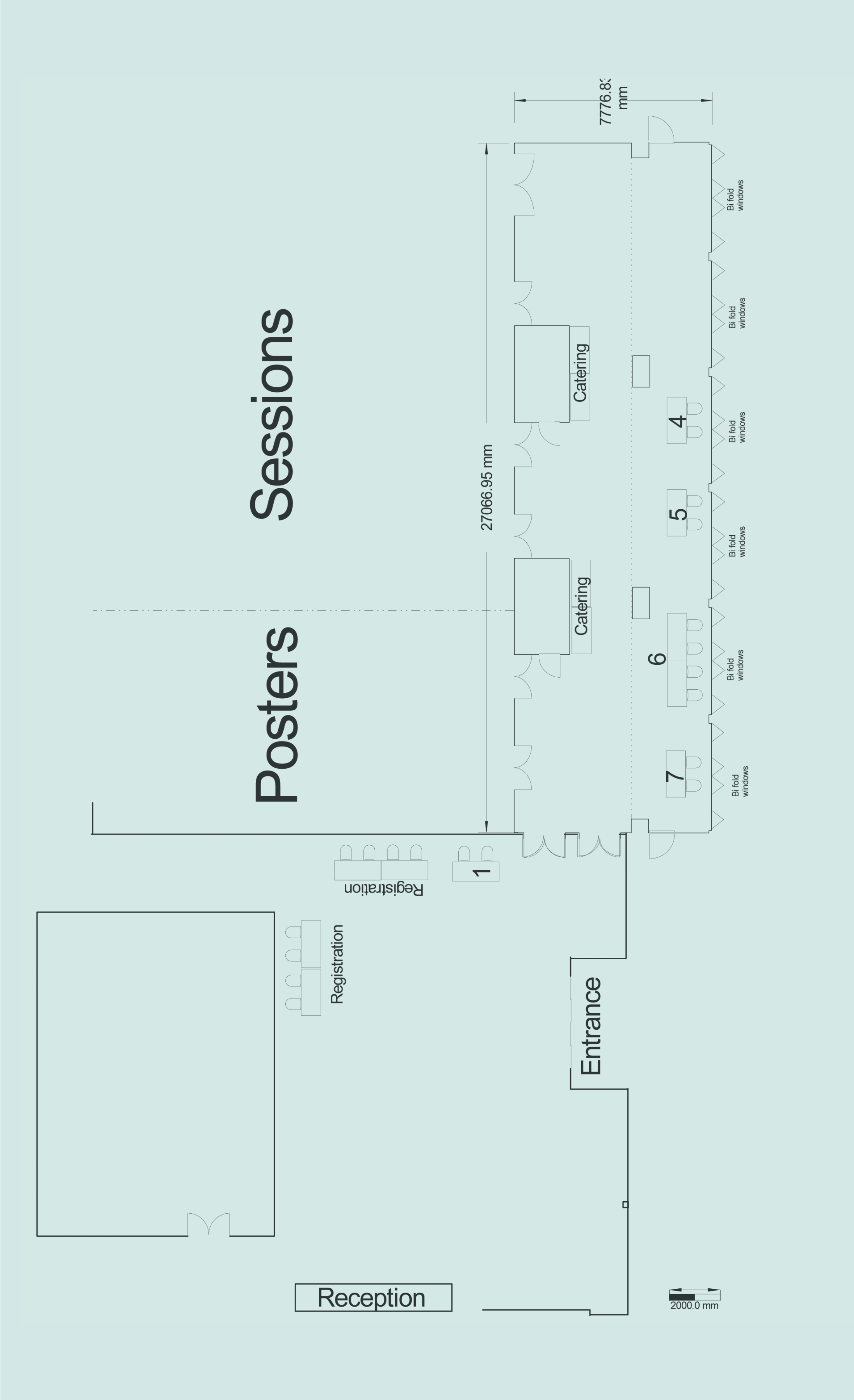

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