Infrared Spectroscopy with Synchrotron Radiation

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INTRODUCTION TO INFRARED SPECTROSCOPY

THE INFRARED BEAMLINES AT THE AUSTRALIAN SYNCHROTRON

APPLICATIONS OF SYNCHROTRON INFRARED SPECTROSCOPY

FUTURE DEVELOPMENTS
INTRODUCTION TO INFRARED SPECTROSCOPY
WHY INFRARED SPECTROSCOPY?

- Used for characterisation and identification of materials
- Peak shapes and positions are sensitive to molecular environment
- Applied to solids, liquids and gases
- Spectroscopic mapping and imaging
  - Visualise the distribution of chemical components
  - Maps/images are generated using unique spectral features
- Non-destructive

Protein: 1588-1704 cm\(^{-1}\)
Lipid: 2881-2946 cm\(^{-1}\)
SAMPLE
Rotational transition (Far-IR and microwave)

Vibrational transition (Infrared)

Electronic transition (UV-Vis)
FREQUENCY OF BOND VIBRATIONS

\[ \nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \]

\[ \mu = \frac{m_A m_B}{m_A + m_B} \]

\( k \) = spring constant of bond

\( \mu \) = reduced mass of the A-B system
INFRARED SPECTROSCOPY

Absorbance vs. Wavenumbers (cm\(^{-1}\))

- **PO\(_3^2\)^- stretching**
- **C-O stretch**
- **CO\(_2\)**
- **CH\(_2\) and CH\(_3\) stretching**
- **C-N and N-H**
- **CH\(_3\) bending**
- **Amide I**
  - C=O
- **Amide II**
  - C-N and N-H
- **Broad O-H and N-H**
  - Stretching
Fourier Transform Infrared is more common, but dispersive has applications, particularly for fast timing with intense beams.
"Centre burst" at Zero Path Difference

Interferogram → Fourier Transform → Single Beam Spectrum

DATA OUTPUT FROM FTIR SYSTEM

Volts
-5 -4 -3 -2 -1 0 1 2 3 4

Data points
200 400 600 800 1000

Wavenumbers (cm⁻¹)
4000 3500 3000 2500 2000 1500 1000 500

Interferogram

Fourier Transform

Single Beam Spectrum

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Sample Absorbance Spectrum

\[ A = \log \left( \frac{I_0}{I} \right) = \varepsilon cl \]
Why use a Synchrotron?
IT'S THE SYNCHROTRON BRIGHTNESS THAT COUNTS

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ADVANTAGES OF SYNCHROTRON FOR FTIR

**SIGNAL-TO-NOISE**

- CH stretch absorption bands from 5 μm spot in tissue sample.
- Synchrotron

**SPATIAL RESOLUTION**

- Fast data acquisition
- Superior signal to noise
- Diffraction limited lateral resolution

Profile of “High Brightness” Beam on sample

Mapped area = 40 x 40 microns.
Single malaria infected cells at different stages of the intra-erythrocytic life cycle

Grant Webster, Don McNaughton, Bayden Wood (Monash University), Torsten Frosch (University Jena)
THE INFRARED BEAMLINES AT THE AUSTRALIAN SYNCHROTRON
ADAPTED INFRARED DIPOLE CHAMBER AT AUSTRALIAN SYNCHROTRON

Electron beam

Mirror in

IR beam out
Mirror M1 undergoing vibration testing prior to installation

Bellows fully extended

M1 mirror carriage

M2 mirror chamber
Matching optics for High Resolution FTIR

Matching optics for IR Microscope

Infrared beamline showing (from right) synchrotron beam entering front end optics (M1, M2, M3, M3a), diamond exit window, beamsplitter optics vessel and matching optics boxes for the two endstation instruments.
Visible light in the beamsplitter chamber at the Australian Synchrotron Infrared Beamline

Edge and bending magnet radiation to “high resolution” Far-IR spectrometer

Bending magnet radiation to “microscope”
INFRARED BEAMLINES AT THE AUSTRALIAN SYNCHROTRON

- Bruker HYPERION microscope
- Resolution down to a few microns

- Bruker Far Infrared Spectrometer
- For studying atmospheric reactions
- For Far-IR and “Terahertz” studies
- Low T capability “unique”
INFRARED DETECTORS
SOME CURRENTLY AVAILABLE IR DETECTORS

Narrow-Band MCT
D* $4 \times 10^{10}$
Cut-off 750 cm$^{-1}$

Mid-Band MCT
D* $2.5 \times 10^{10}$
Cut-off 600 cm$^{-1}$

Wide-Band MCT
D* $5 \times 10^{9}$
Cut-off 420 cm$^{-1}$

Background limited performance

Silicon Bolometer – Far-IR and THz
INFRARED MICROSCOPIC SPECTROSCOPY
Collimated synchrotron beam is coupled to a Bruker V80v FTIR spectrometer and Hyperion IR microscope.

- **Standard operation**
  - 4 cm\(^{-1}\) resolution
  - Narrowband 50 µm MCT detector
  - Range = 750-3850 cm\(^{-1}\)
Most samples must be 10 microns or thinner.

**Infrared transmitting Window, e.g. CaF$_2$, BaF$_2$ or ZnSe**

**Sample Cell**

**Motorised sample stage**

**Infrared objective**
Sample must be either polished, or thin and placed on a mirror substrate.
Thin layers of sample down to monolayers on reflective metallic surfaces (e.g. gold, steel, ITO glass)

e.g. Protein resistant plasma polymer thin films. Mapping the compositional change along a plasma gradient.

Donna Menzies, Thomas Gengenbach, Celesta Fong, John Forsythe, Ben Muir – CSIRO / Monash
\[ d = \frac{\lambda}{2\pi n_1 \left[ \sin^2 \theta - \left( \frac{n_2}{n_1} \right)^2 \right]^{1/2}} \]

For \( \lambda = 6 \, \mu m \), \( d = 0.9 \, \mu m \)

\( \theta = 45^\circ \)

ZnSe prism

Sample refractive index = 1.35

Chan, K.L.A., Kazarian, S.G., FTIR imaging for high-throughput analysis of pharmaceutical formulations

Multilayer paint fragment from exterior of Provincial Hotel, Fitzroy
Sample was not suitable for thin sectioning.

Bruker ATR 20x objective
Ge crystal, 100 or 250 micron tip
variable pressure selection.

CN absorption probably
indicating Prussian Blue

R. Sloggett et al.
Vibrational Spectroscopy 53 (2010)
Why “single contact”?

Visible image of a paint cross section recorded after standard “mapping” ATR measurements (left), showing indentation marks from the ATR crystal (arrowed)

- Macro ATR device from Bruker
- ATR crystal is only applied once prior to mapping or imaging of areas up to 600 x 600 µm
- Sample is mapped while in contact with crystal
- Allows ATR mapping of brittle and soft samples with spatial resolution down to 1 µm
- Operates with dedicated high NA 20x objective
ENHANCED SPATIAL RESOLUTION WITH TOTAL INTERNAL REFLECTION

Airy disk radius is given by
$$r = \frac{1.22 \lambda}{2NA}$$

Numerical aperture
$$NA = n(\sin \theta)$$

At $\lambda = 6 \mu m$
For $NA$ (air) = 0.65
$$r = 5.6 \mu m$$

At $\lambda = 6 \mu m$
For $NA$ (ZnSe) = 1.56
$$r = 2.3 \mu m$$

At $\lambda = 6 \mu m$
For $NA$ (Ge) = 2.6
$$r = 1.6 \mu m$$
EXAMPLES FROM
IR MICROSCOPY BEAMLINE
• Software used to mark positions for analysis
• Spectral library used to assist identification
Note strong $\nu\text{C}=\text{O}$

In some polymers can be used to study oxidation in failure analysis

- Software used to mark positions for analysis
- Spectral library used to assist identification
Advantageous properties of Cicada wings
• Superhydrophobic
• Self cleaning
• Antireflective
• Antibacterial

Industrial application: manufacture of synthetic materials that mimic those properties

Elena Ivanova group, Swinburne University

Infrared images of protein and wax were collected, at the Australian Synchrotron, then at IRENI beamline SRC Madison, Wisconsin.

The observed “patterned” distribution of wax may account for the wings self-cleaning properties.

RGB images
Yellow = wax
Blue = protein

CHEMICAL COMPONENT MIGRATION IN AUTOMOTIVE PAINT

- Investigation of interlayer component migration:
  - Cross-linking additive-melamine
- From a forensic science viewpoint, the outcomes are significant as the relative abundance of melamine and pigments in the clear coat will vary greatly depending upon the region of the layer analysed.
- Need to develop methods to eliminate the diffusion of melamine and other components within layers

M. Maric, W. van Bronswijk, S. Lewis (Curtin University)
K. Pitts (ChemCentre) D. Martin (Australian Synchrotron)
Principal Component Analysis (PCA) revealed a correlation between the chemical composition of the clear coat and the vehicle origin.

PCA scores plot

PCA-3 shows separation between the Ford and General motors Holden vehicles.

ATR FTIR on ~40 microns thick clear coat layer
1. Polyacrylonitrile fibre

2. Carbon fibre

3. Woven carbon fibre

4. Carbon fibre reinforced product

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Macro ATR cantilever arms:
1. As supplied with 1mm diam.
   Facet germanium ATR crystal.
2. In-house modification to accept
   250 µm and 100 µm crystals from
   Micro ATR objective.
PAN fibres mapped with Hybrid Macro ATR. Low resolution and high resolution maps. Maps are integral of nitrile peak around 2240 cm$^{-1}$. High resolution step size is 500 nm.
Biopolymer gels have many applications including medical implant coating, contact lenses, drug delivery and scaffolds for tissue engineering.

Hydration and behaviour under “stress” of multilayers are important in overall performance.

Experiment required study of hydrated multilayers under conditions of applied pressure.
In-house device developed for specific experiment with University of South Australia has proved ideal for a wide range of softer materials.

7mm radius ZnSe ATR crystal

Underside of ATR crystal showing 1mm contact facet (arrow)

ATR element
Magnetic mount
Microscope stage insert
Sample support post
X and Y sample stages
Closed loop Z-axis piezo

Custom ZnSe and germanium ATR crystals
• Piezo stage allows precise control of sample-prism approach
• Reproducible centering of ATR contact
• Approach shown at 50 nm steps
PERFORMANCE UNDER PRESSURE OF BIOPOLYMER GELS

PERFORMANCE OF POLY STYRENE SULFONATE / POLY ALLYLAMINE HYDROCHLORIDE MULTILAYER

ATR contact is just visible in 32x objective overview

Adaptation for in situ formation of multilayers

10 bilayer poly styrene sulfonate/poly allylamine hydrochloride on gold, in contact with ZnSe hemisphere


THz / FAR-INFRARED BEAMLINE
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THz / FAR-INFRARED BEAMLINE

GAS PHASE experiments
- Atmospheric & astrophysical sciences

CONDENSED PHASE experiments
- Geology & mineralogy studies
- Nanoparticle studies
- Biology & biomedical studies
- Thin layer & monolayers
Bruker IFS 125HR High Resolution FTIR Spectrometer

OPD: 942 cm
Resolution ≥ 0.00096 cm⁻¹ (0.1 meV)
Optics: f/6.5
PORTION OF THE FAR-IR SPECTRUM OF FORMAMIDE AT 0.00096 CM\(^{-1}\) RESOLUTION

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EXAMPLES FROM
THz/Far-IR BEAMLINE
CF$_3$I High Resolution Spectrum

CF$_3$I is an potential alternative to Halon 1301 (CBrF$_3$) as a gaseous fire suppressant. Breaks down more readily in contact with water. Important to understand chemistry at upper atmosphere conditions.

D. Appadoo, D. Martin and R. Plathe – International Science Linkage with Soleil Far-IR beamline. AS team able to access extra long path length gas cell at Soleil. Soleil Far-IR team able to access low temperature gas cell at AS.
ENCLOSIVE FLOW COOLING MULTIPASS CELL FOR GAS-PHASE STUDIES AT CRYOGENIC TEMPERATURES.
Comprehensive Vibrational Spectroscopic Investigation of trans,trans,trans-[Pt(N₃)₂(OH)₂(py)₂], a Pt(IV) Diazido Anticancer Prodrug Candidate


Future technique: Laser photolysis
Far-infrared spectra (absorbance) of Ac-β³[LIA], Ac-β³[ALI] and Ac-β³[IAL].

L → Leucine, I → Isoleucine, A → Alanine

far-infrared spectroscopy was used to characterize the fibrils in terms of the effect of geometric factors and second order interactions on molecular vibrations

Rania S. Seoudi, Annette Dowd, Mark Del Borgo, Ketav Kulkarni, Patrick Perlmutter, Marie-Isabel Aguilar, Adam Mechler, Pure and Applied Chemistry, 2015, 87, 1021–1028
FUTURE SYNCHROTRON FTIR DEVELOPMENTS
IR superfocused by IR antenna (AFM tip)
Signal demodulated using Lock in. Use higher harmonics
Detection of the amplitude and the phase spectra of the backscattered light
Synchrotron provides broader spectral range than is available from lasers

H.A. Bechtel E.A. Muller R.L. Olmon M.C. Martin and M.B. Raschke
PNAS (2014) vol. 111 7191–7196
Use of Focal Plane Array (FPA) imaging detector for data acquisition coupled to high magnification optics.
1st experiments expected during the 2016-2 cycle; available to users 2016-3

Simulation of astrophysical ice surfaces by vapour deposition of molecular component onto a reflective substrate or optical window cooled to 10 K.

- Infrared signatures for qualitative ice composition analysis.
- Integrated absorption bands for quantitative analysis (using thin-film A-values)
- THz region for ice morphology analysis; lattice bands, low-frequency vibration modes.
- Coupled onto Nd-YAG photolysis system to generate and trap reactive intermediates or can be used for direct surface irradiation.
ACKNOWLEDGMENTS

- David Beattie, Marta Krasowska, Jessie Webber and Natalie Benbow – University of South Australia
- Elena Ivanova, Hayden Webb and Song Ha Nguyen – Swinburne University
- Gregory Watson – University of the Sunshine Coast
- Nishar Hameed – Swinburne University and Srinivas Nunna – Deakin University
- Ljiljana Puskar – Methods for Material Development, HZB, Berlin
- Courtney Ennis, Rebecca Auchettl – La Trobe University
- Alan Easdon – Australian Synchrotron

Beamline Staff

- Pimm Vongsvivut
- Danielle Martin
- Katie Sizeland
- Keith Bambery
- Dom Appadoo
- Ruth Plathe

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Thank you

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