Infrared Spectroscopy with Synchrotron Radiation

Mark Tobin
Australian Synchrotron

INTRODUCTION TO INFRARED SPECTROSCOPY

THE INFRARED BEAMLINES AT THE AUSTRALIAN SYNCHROTRON

APPLICATIONS OF SYNCHROTRON INFRARED SPECTROSCOPY

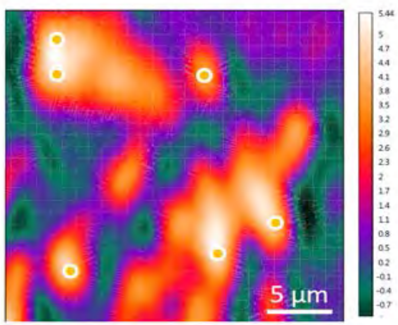
FUTURE DEVELOPMENTS

INTRODUCTION TO INFRARED SPECTROSCOPY

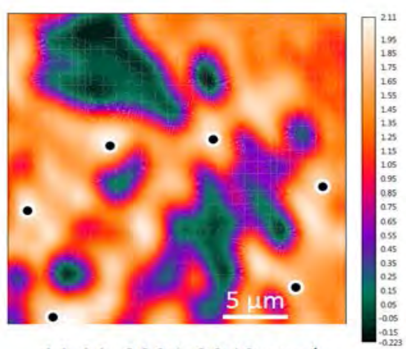
WHY INFRARED SPECTROSCOPY ?

Australian Government

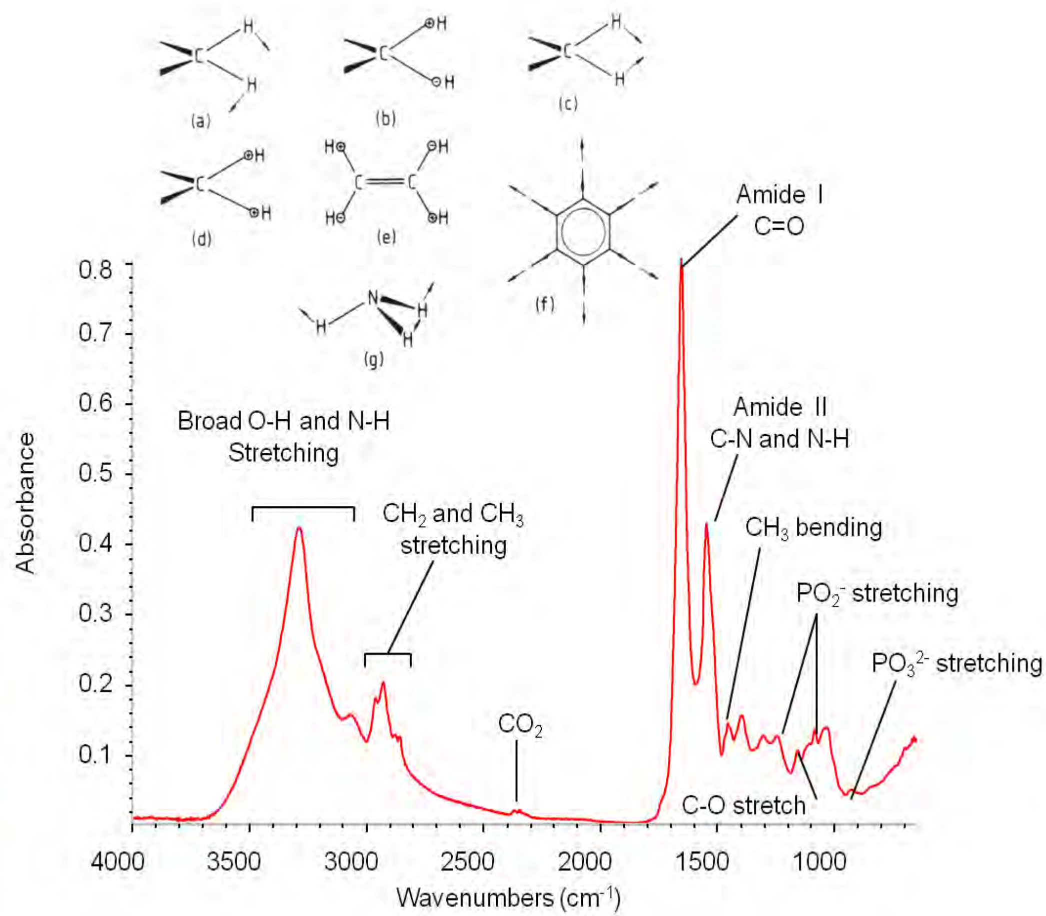
- Used for characterisation and identification of materials
- Peak shapes and positions are sensitive to molecular environment
- Applied to solids, liquids and gases
- Spectroscopic mapping and imaging
  - Visualise the distribution of chemical components
  - Maps/images are generated using unique spectral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



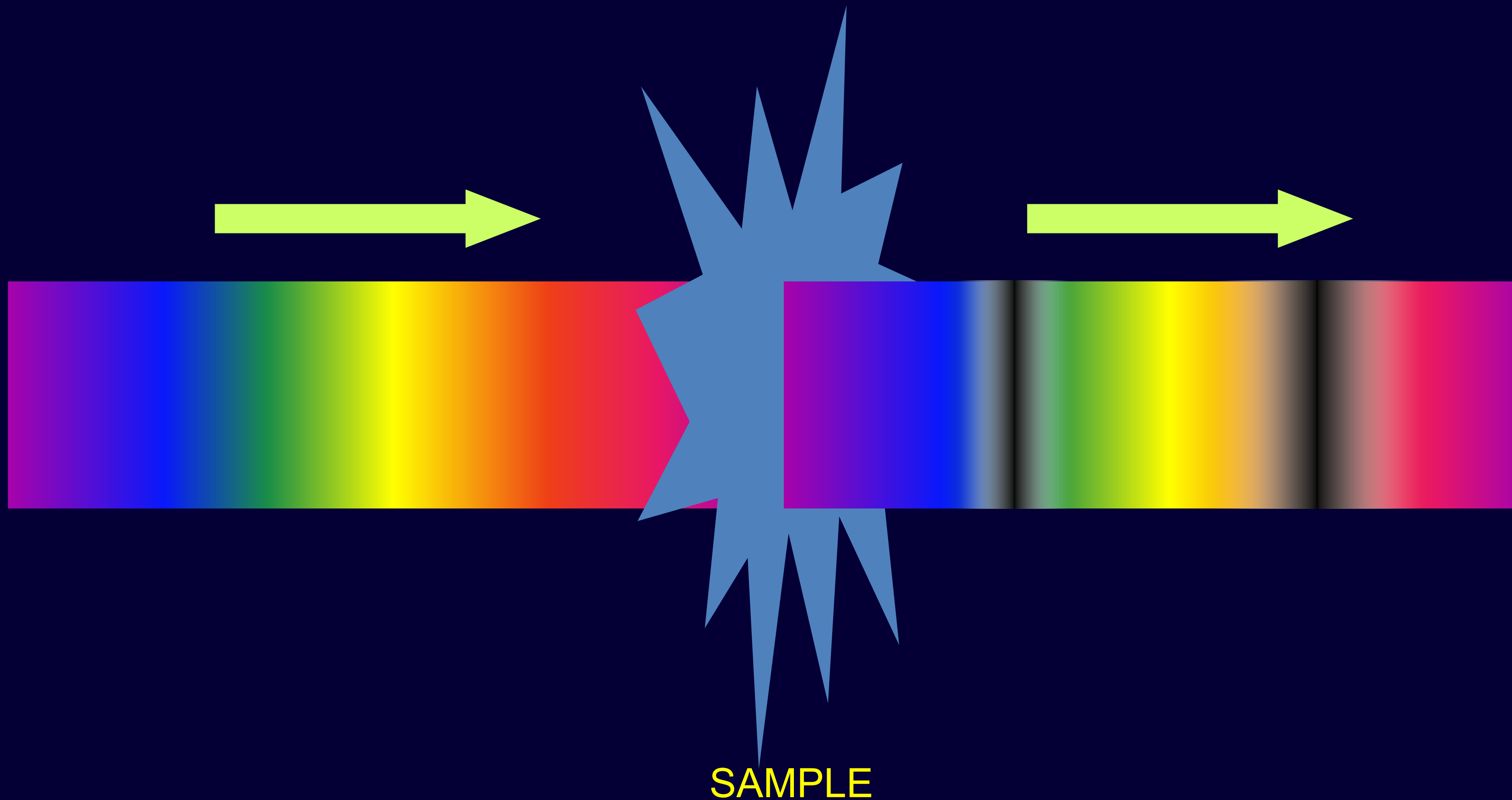
Protein: 1588-1704 cm⁻¹



Lipid: 2881-2946 cm⁻¹



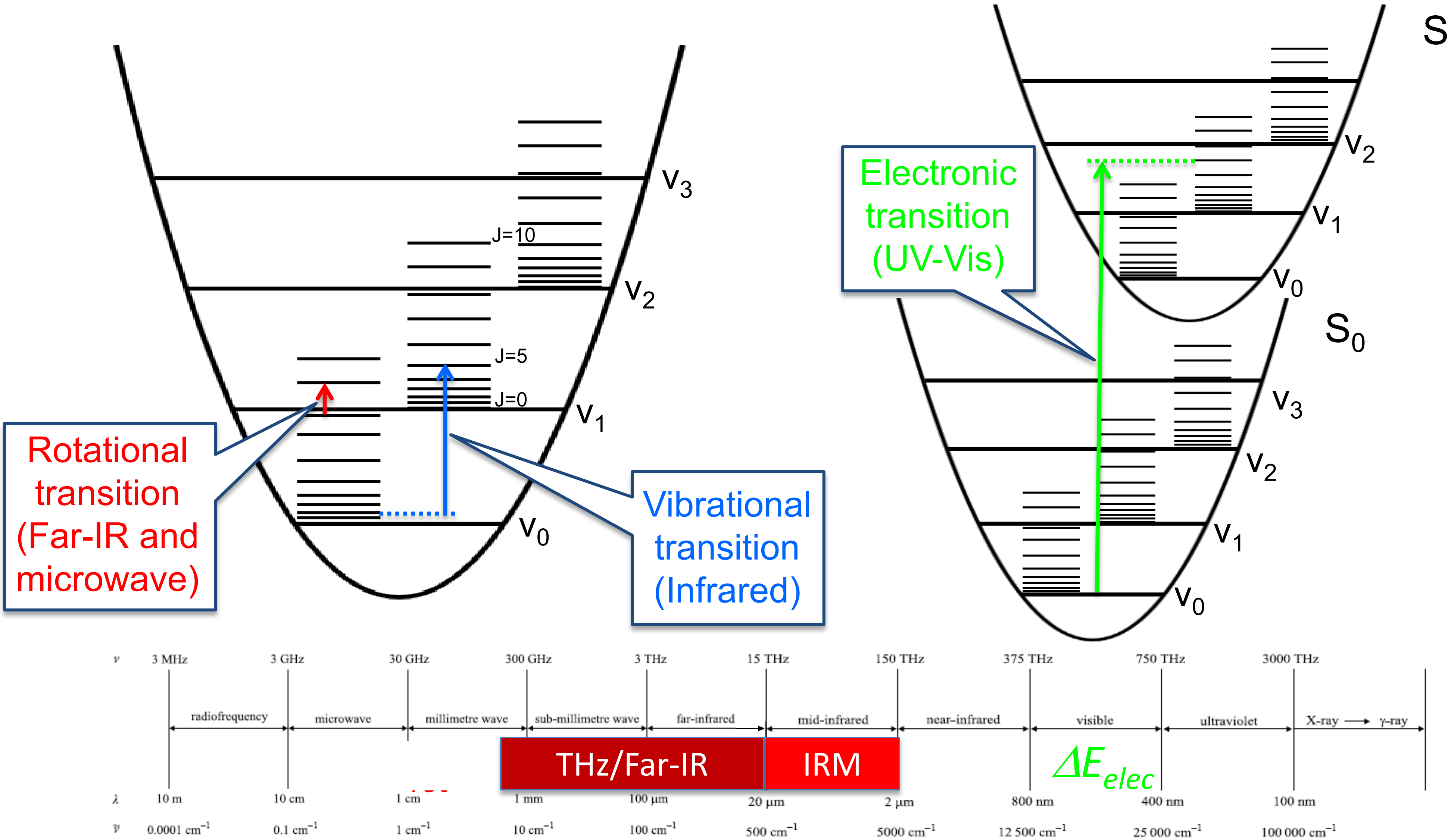
SPECTROSCOPY…

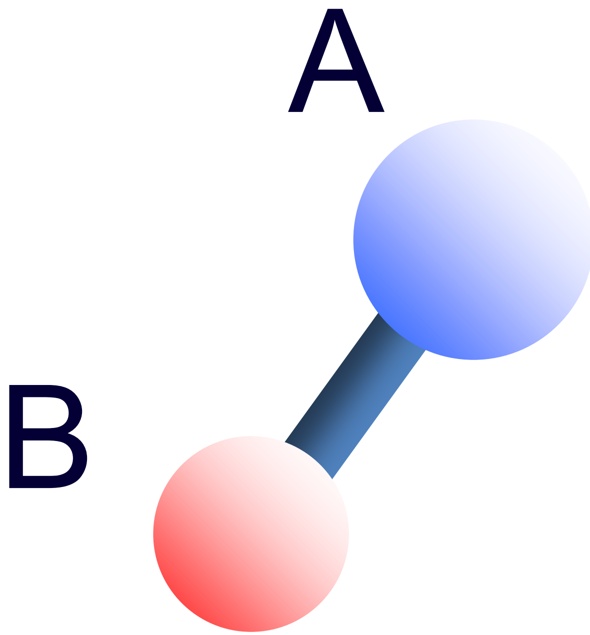


ROTATIONAL, VIBRATIONAL AND ELECTRONIC TRANSITIONS

Australian Government

ansto





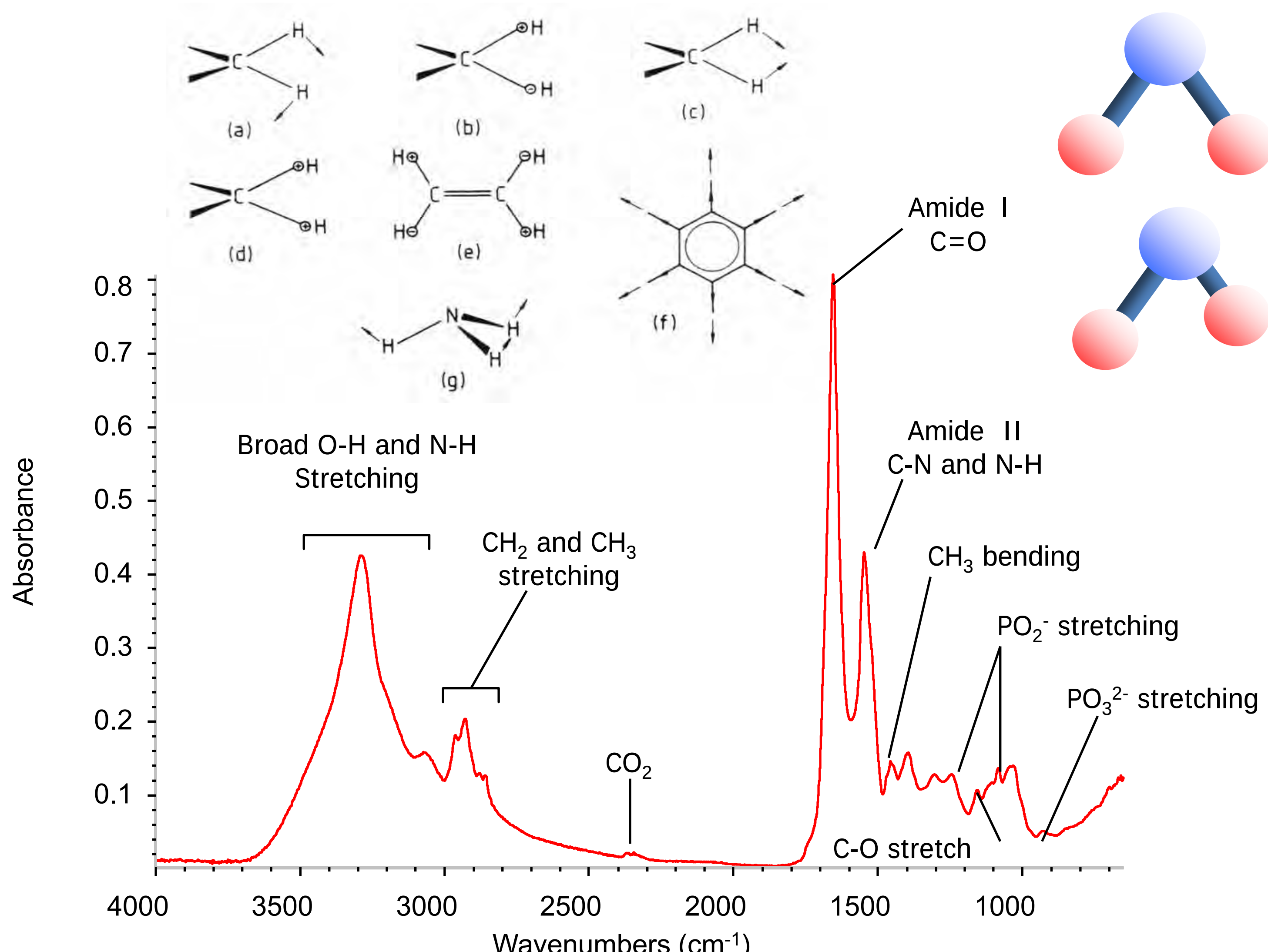
$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\mu = = \frac{m_A\, m_B}{m_A + m_B}$$

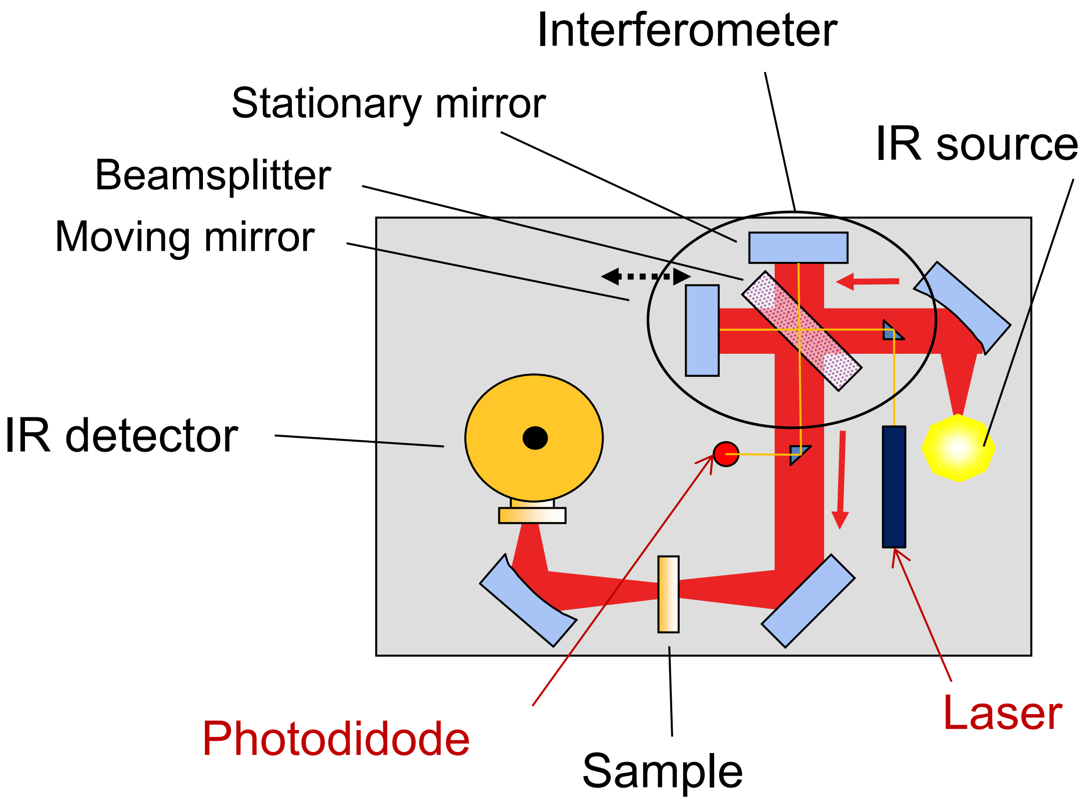
k = spring constant of bond

μ = reduced mass of the A-B system

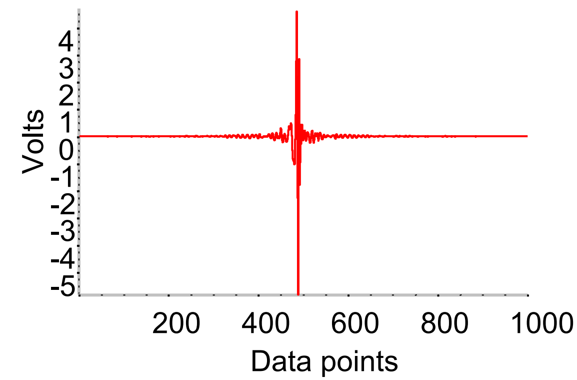
INFRARED SPECTROSCOPY

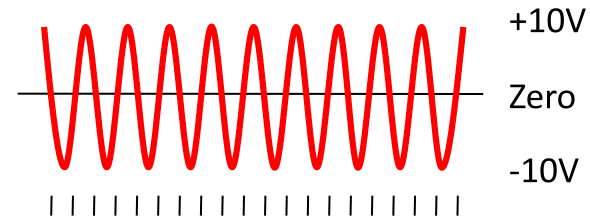


THE FTIR METHOD OF DATA COLLECTION…



IR detector signal



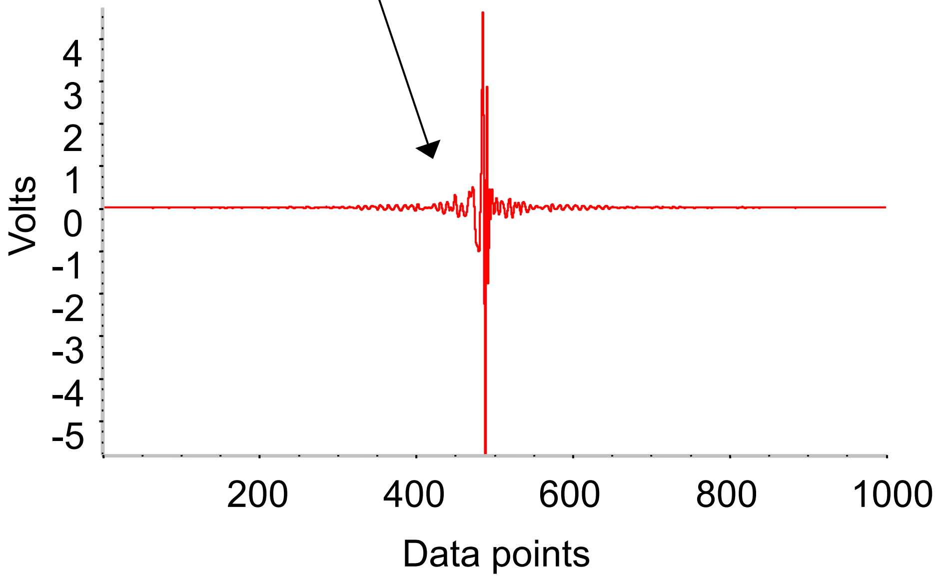


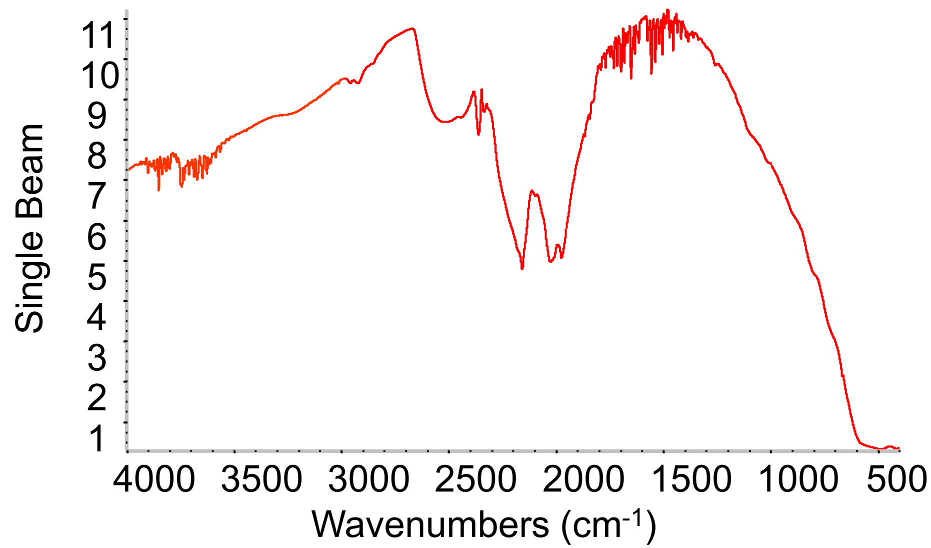
Laser signal

Fourier Transform Infrared is more common, but dispersive has applications, particularly for fast timing with intense beams

DATA OUTPUT FROM FTIR SYSTEM

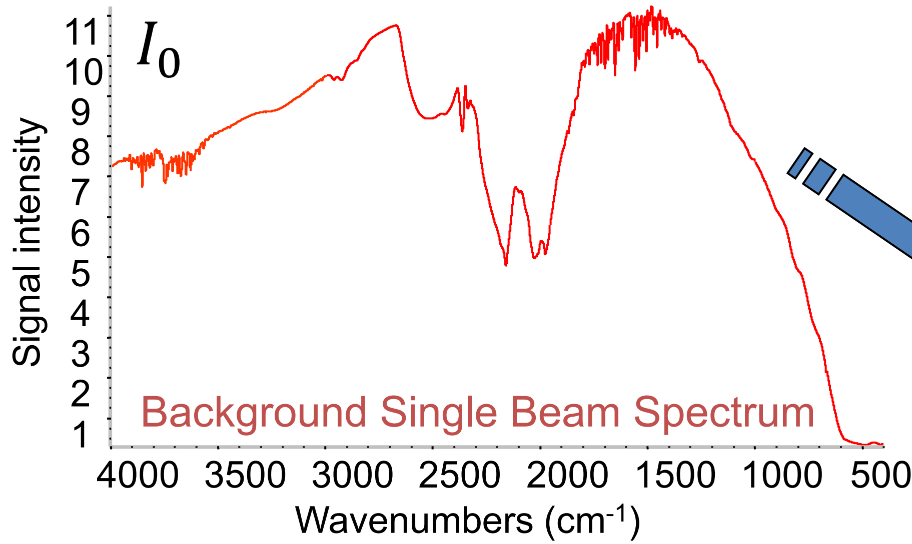
“Centre burst” at Zero Path Difference



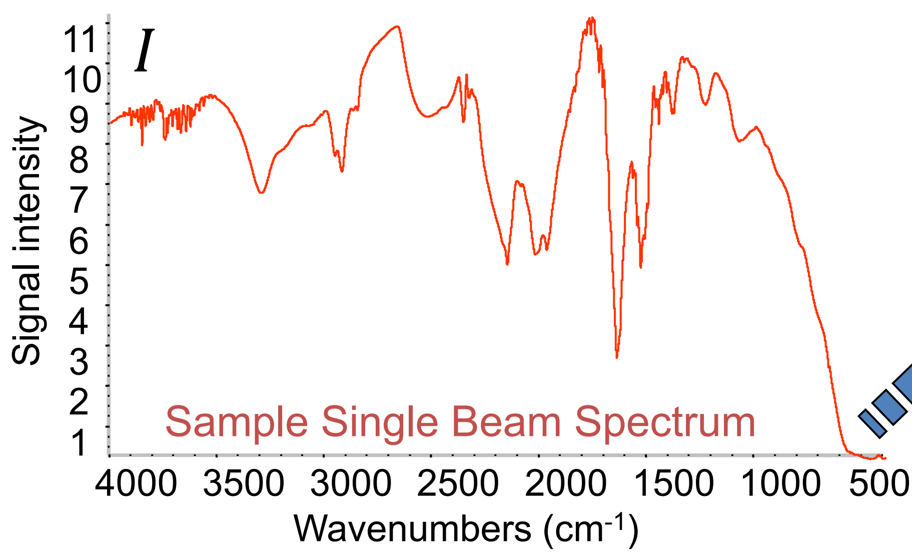


Interferogram → Fourier Transform → Single Beam Spectrum

DATA OUTPUT FROM FTIR SYSTEM

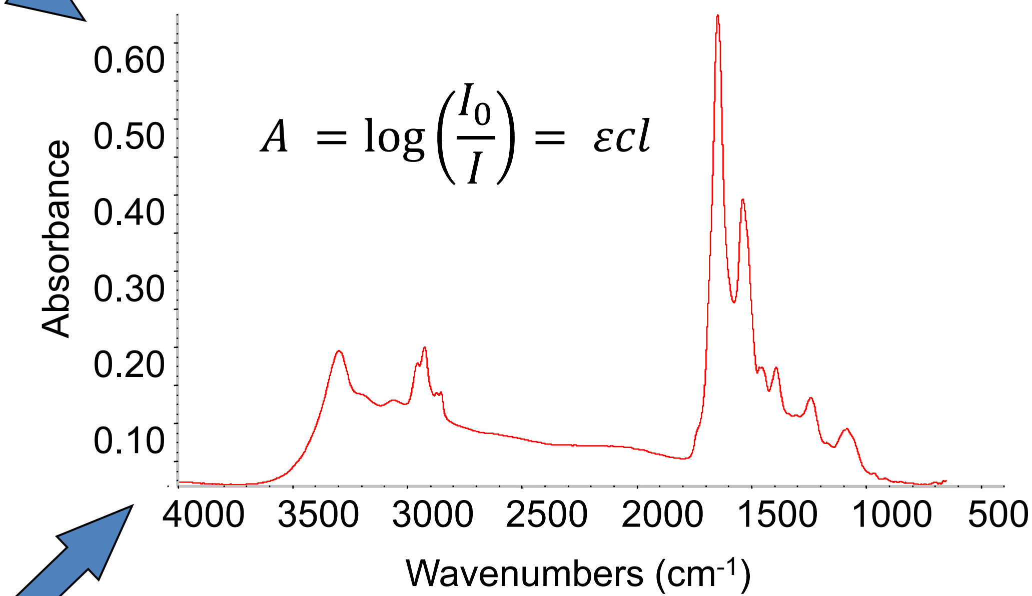


Background Single Beam Spectrum



Sample Single Beam Spectrum

Sample Absorbance Spectrum

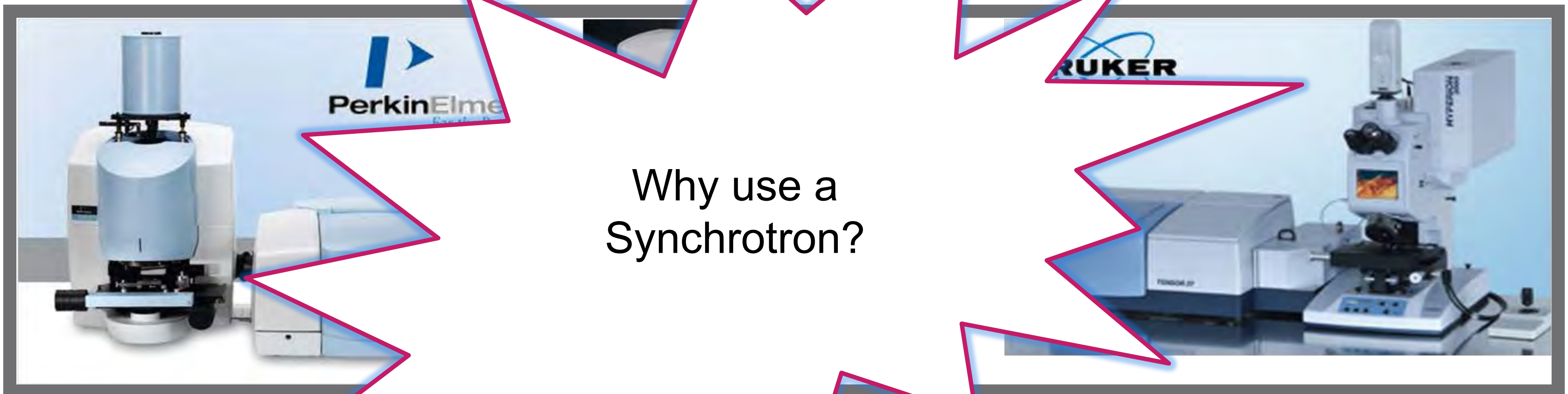


$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon c l$$

INFRARED MICROSPECTROSCOPY INSTRUMENTATION

Australian Government

ansto

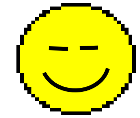


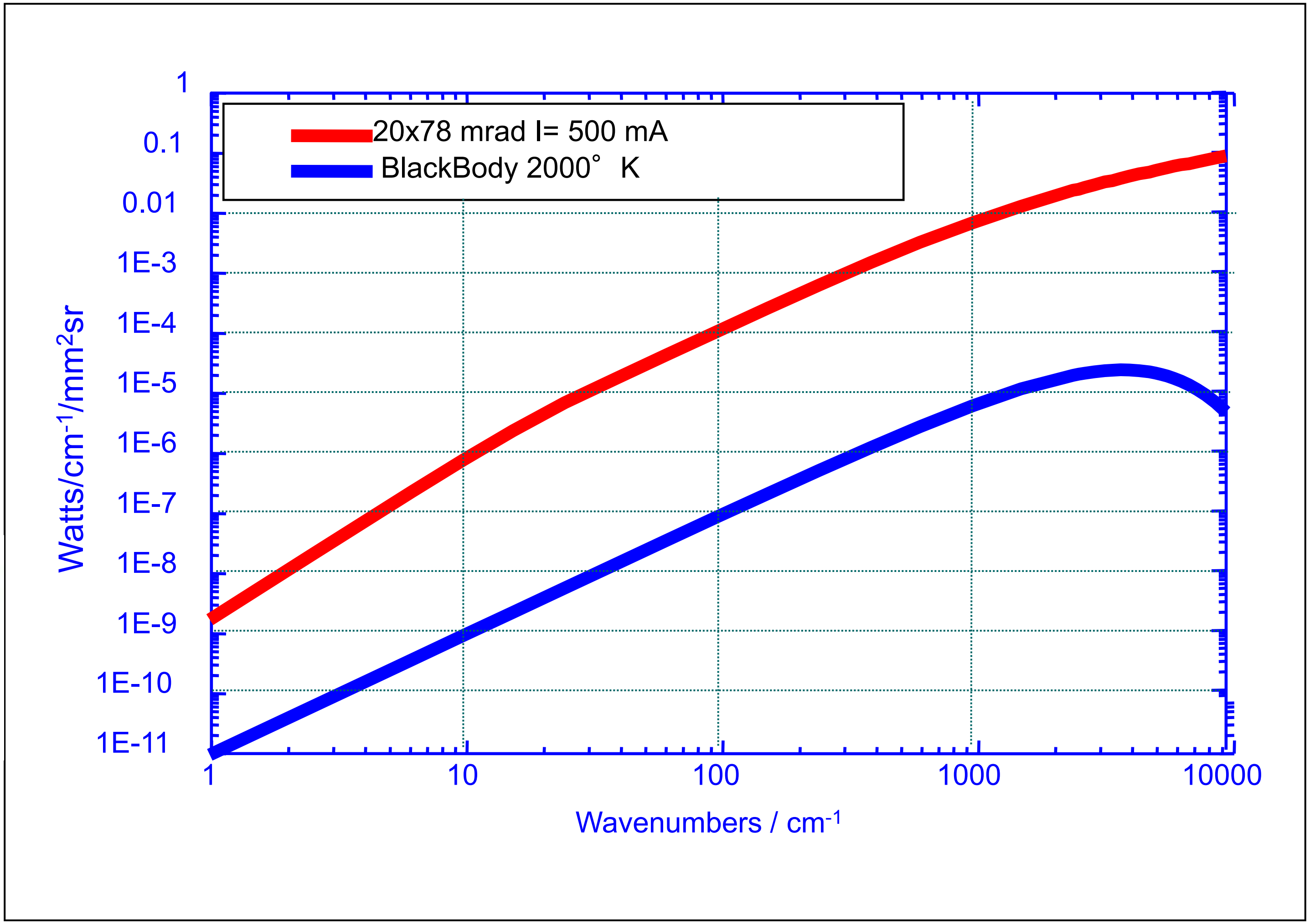
Why use a Synchrotron?

IT'S THE SYNCHROTRON BRIGHTNESS THAT COUNTS
IS THE SYNCHROTRON IR BEAM VERY INTENSE?

Australian Government

ansto



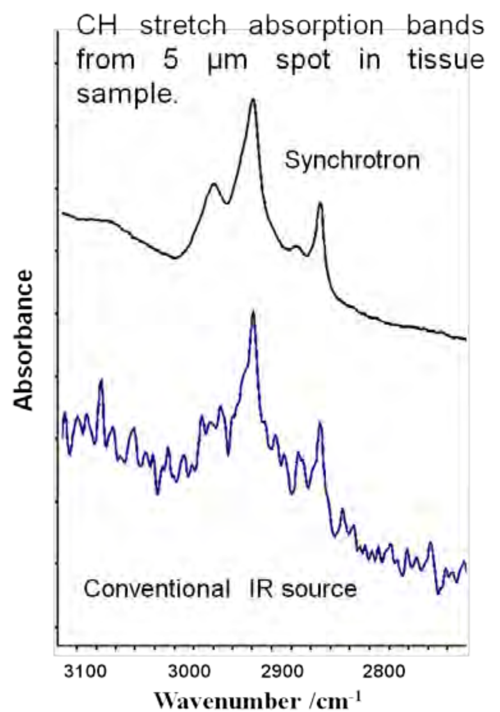


ADVANTAGES OF SYNCHROTRON FOR FTIR

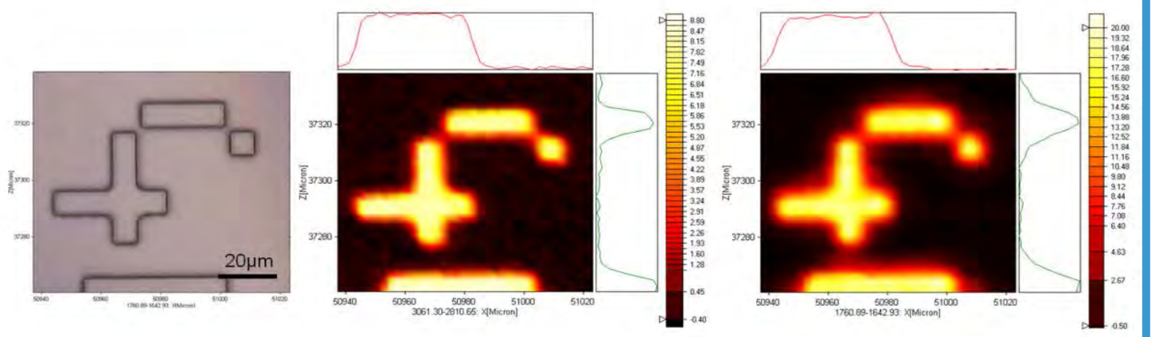
Australian Government

ansto

SIGNAL-TO-NOISE



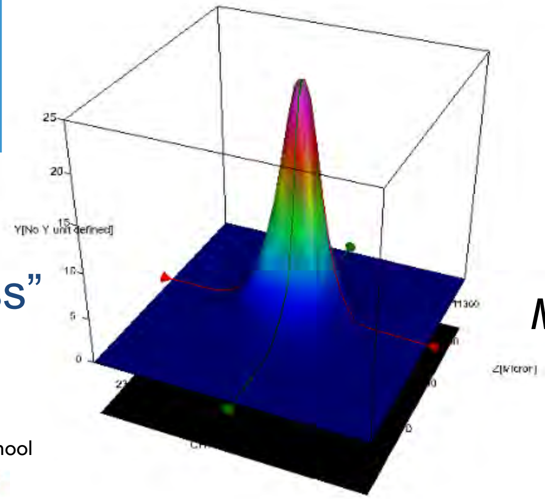
SPATIAL RESOLUTION



Polymer pattern on CaF_2 produced by photolithography

IR absorbance image At 2935 ±125 cm^{-1}

IR absorbance image At 1701 ± 59 cm^{-1}



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

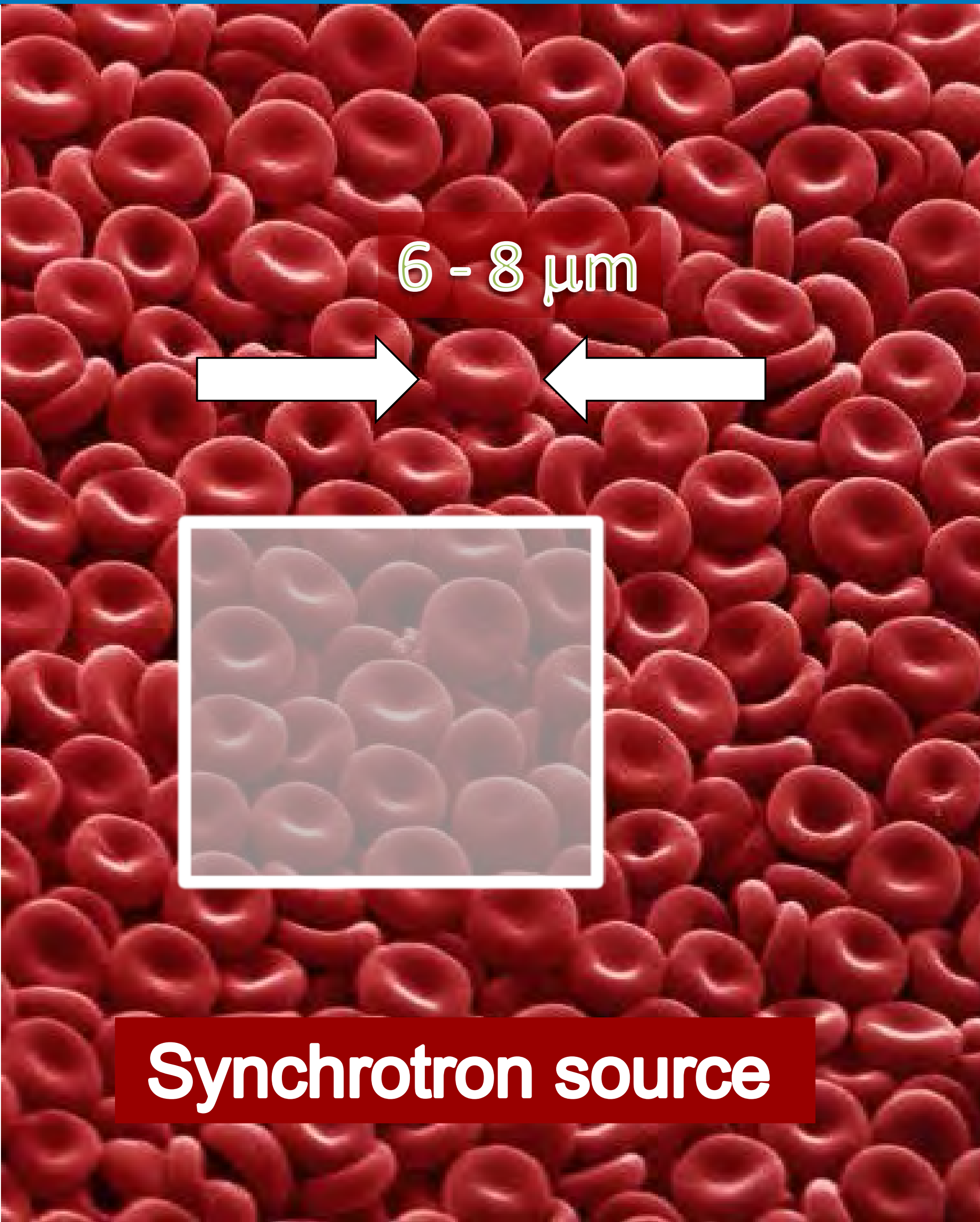
Mapped area = 40 x 40 microns.

Profile of "High Brightness" Beam on sample

AN IDEA OF THE SIZE OF THE IR BEAM…

Australian Government

ansto



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)

Australian Government

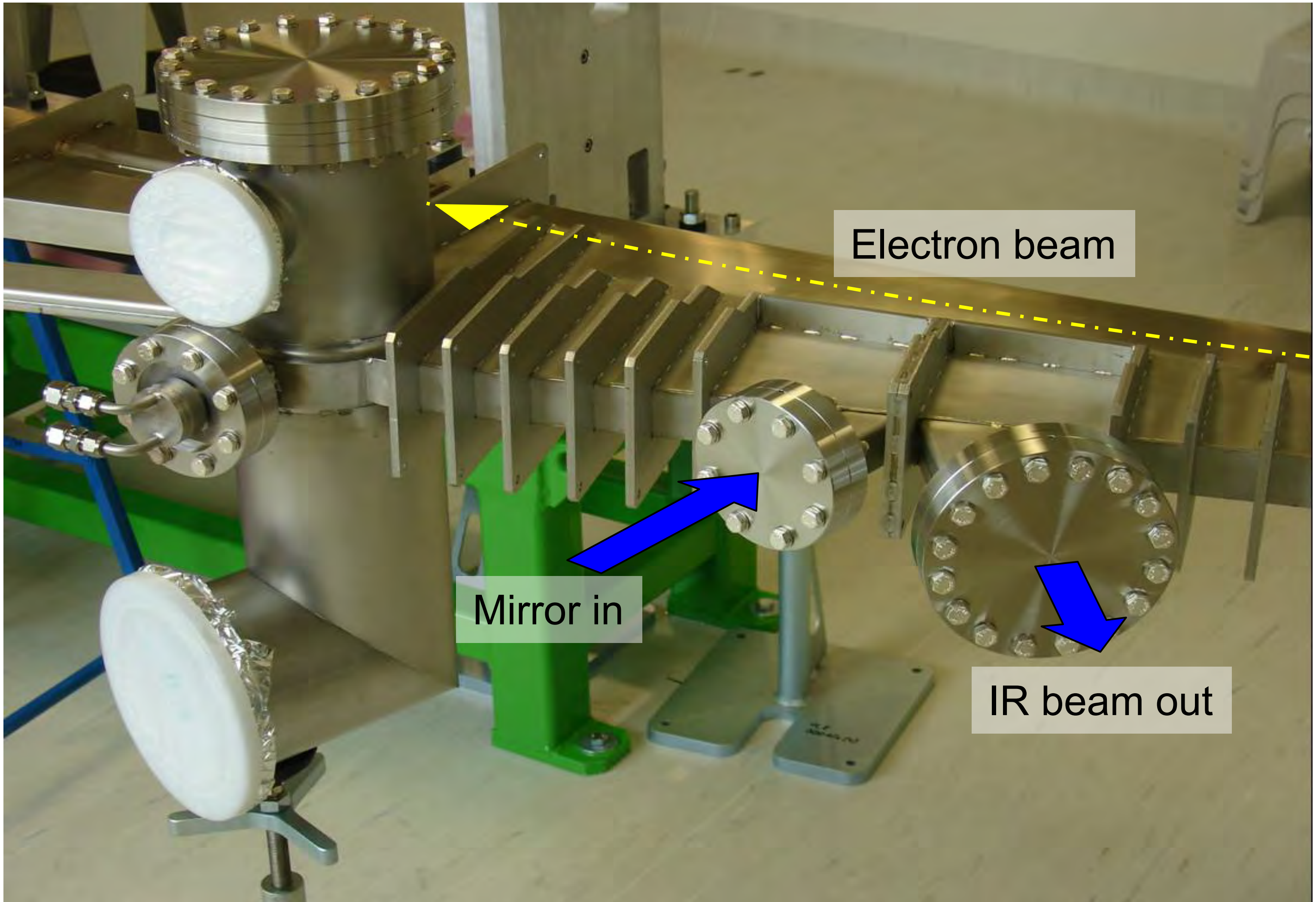
THE INFRARED BEAMLINES AT THE AUSTRALIAN SYNCHROTRON

Australian Synchrotron

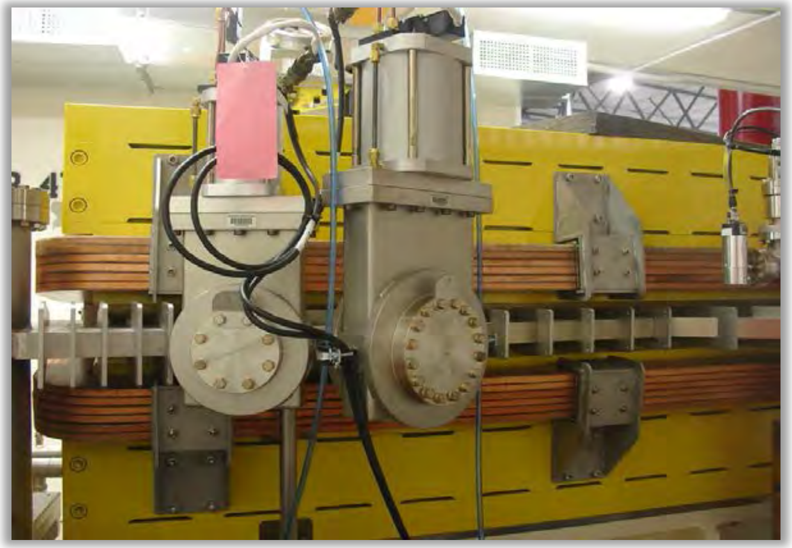
ADAPTED INFRARED DIPOLE CHAMBER AT AUSTRALIAN SYNCHROTRON

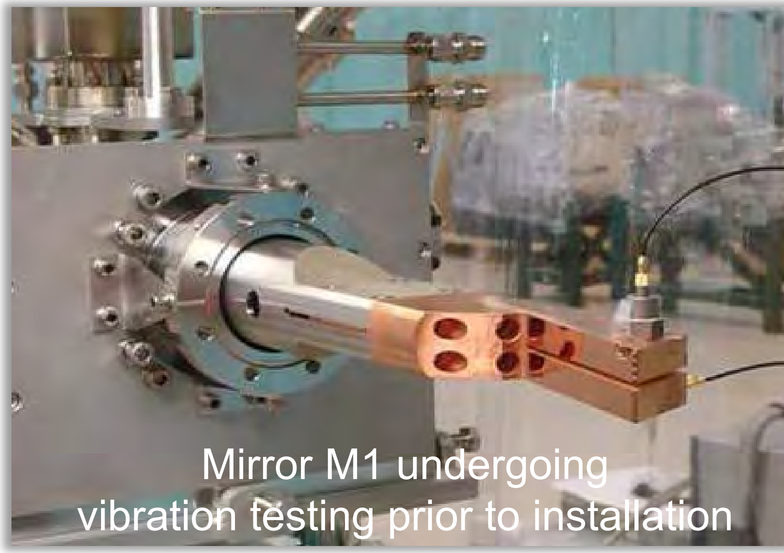
Australian Government

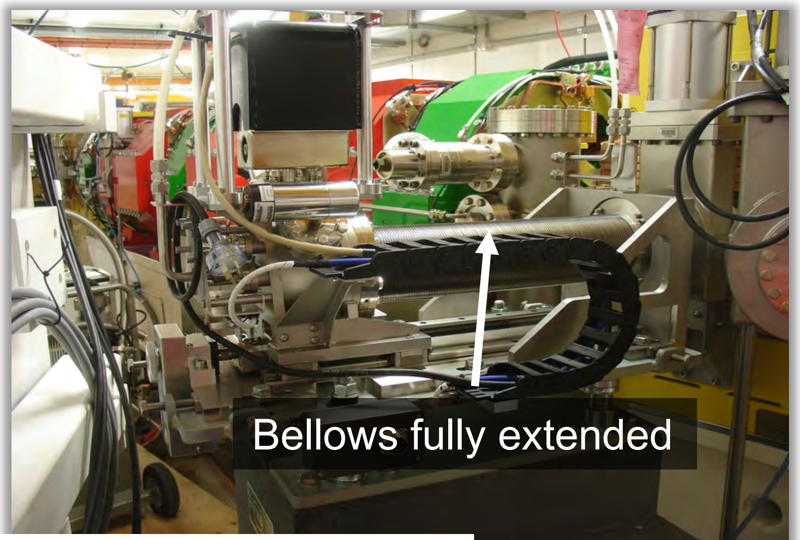
ansto

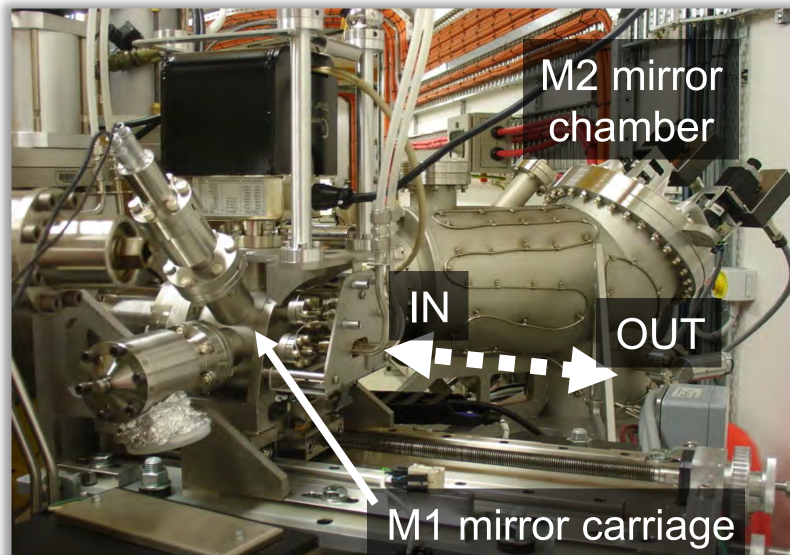


DIPOLE CHAMBER IN STORAGE RING AND MIRROR M1 INSERTION





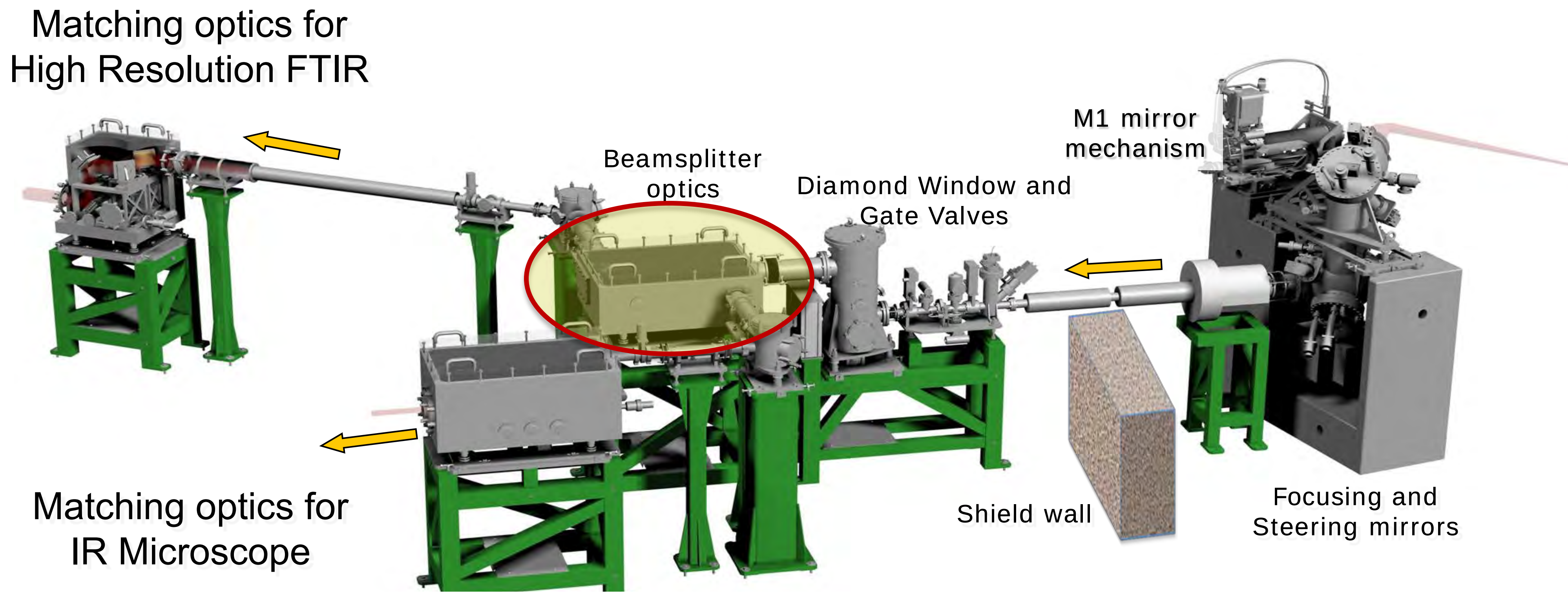




SYNCHROTORN BEAM SEPARATED TO TWO INFRARED BEAMLINES

Australian Government

ansto



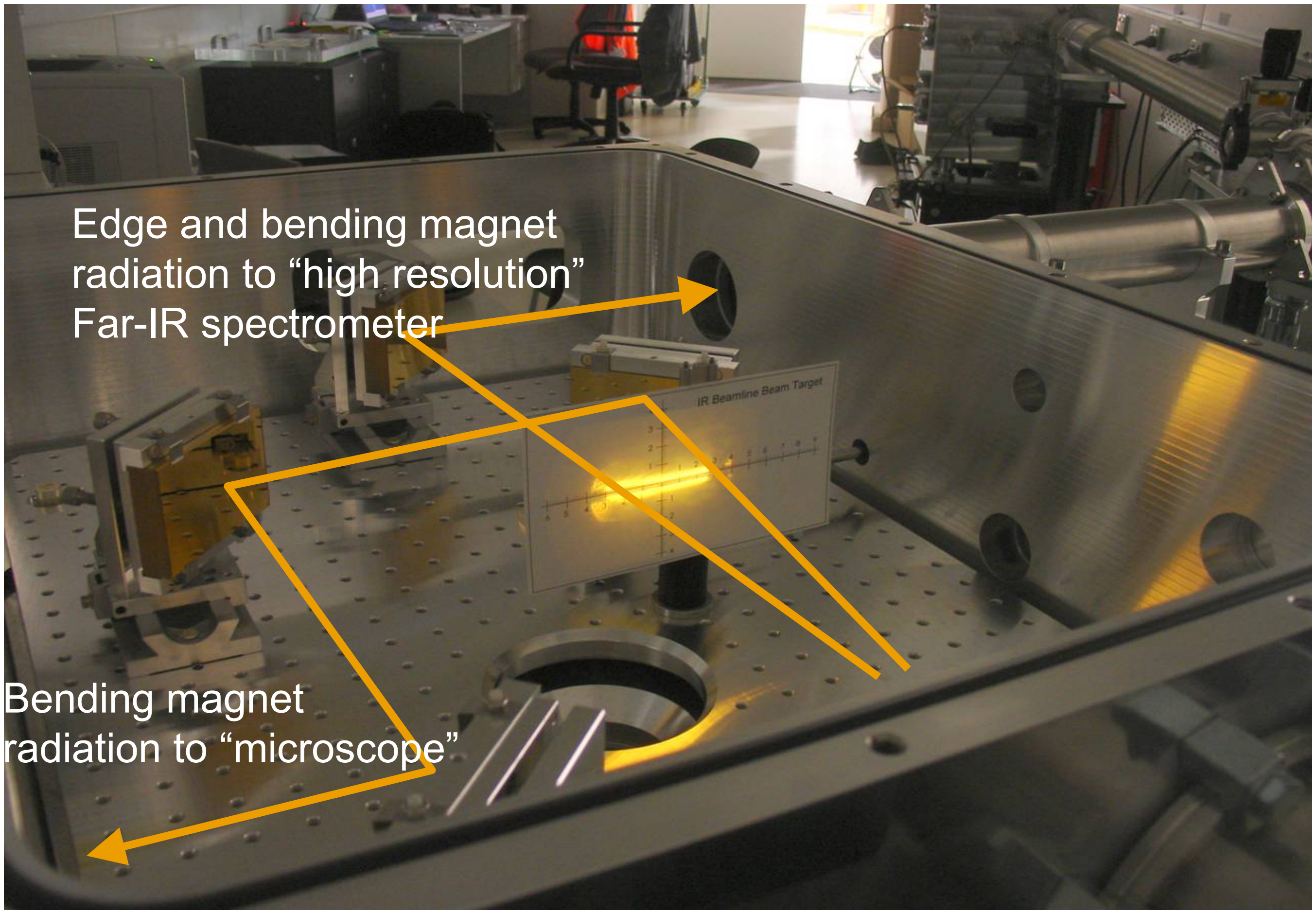
Infrared beamline showing (from right) synchrotron beam entering front end optics (M1, M2, M3, M3a), diamond exit window, beamsplitter optics vessel and matching optics boxes for the two endstation instruments.

SYNCHROTORN BEAM SEPARATED TO TWO INFRARED BEAMLINES

Australian Government

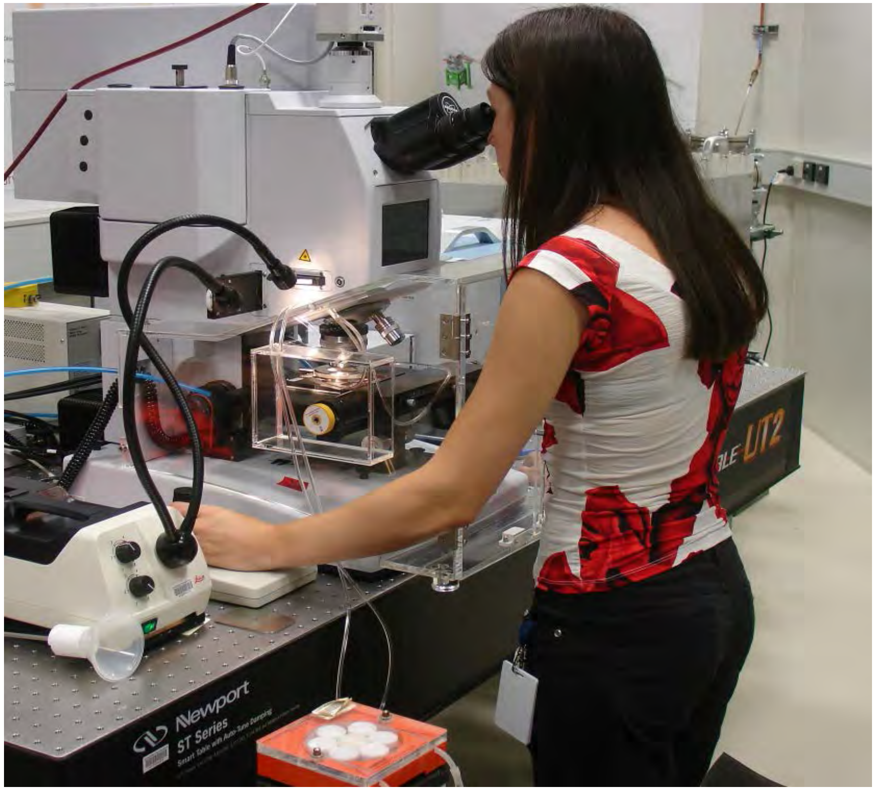
ansto

Visible light in the beamsplitter chamber at the Australian Synchrotron Infrared Beamline



Australian Synchrotron

INFRARED BEAMLINES AT THE AUSTRALIAN SYNCHROTRON

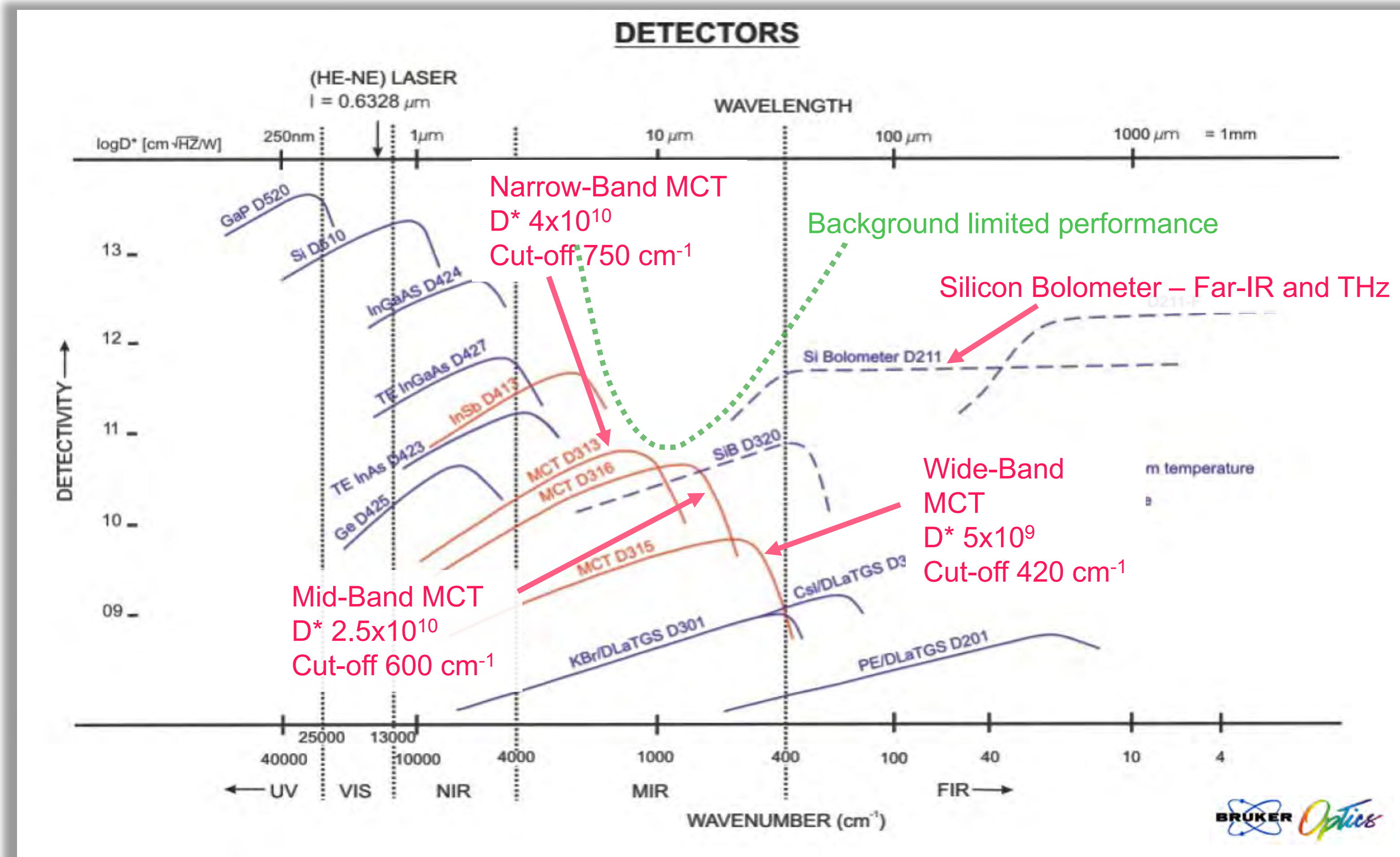


- Bruker HYPERION microscope
- Resolution down to a few microns

- 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

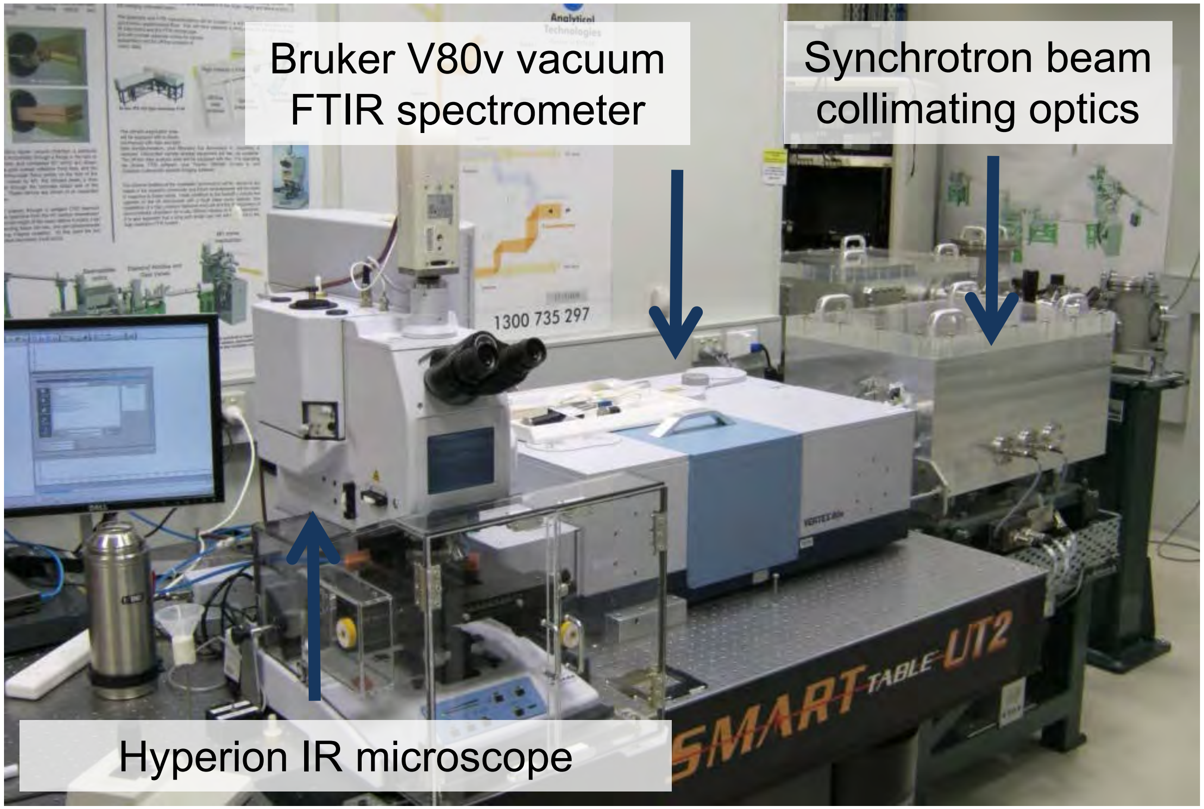
Australian Government

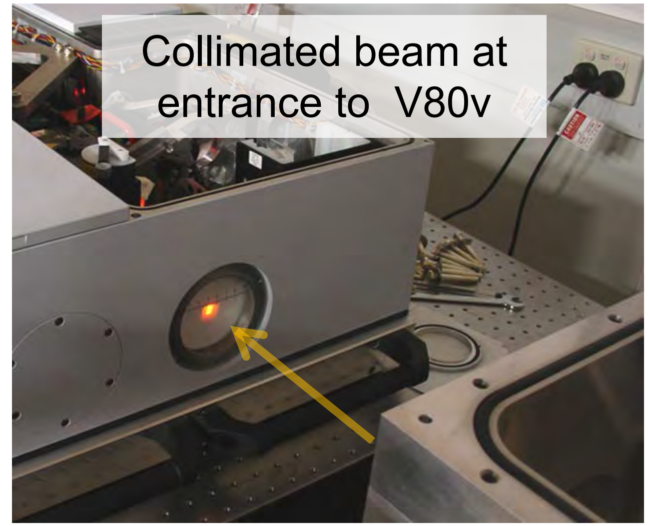


Australian Government

INFRARED MICROSPECTROSCOPY

Collimated synchrotron beam is coupled to a Bruker V80v FTIR spectrometer and Hyperion IR microscope

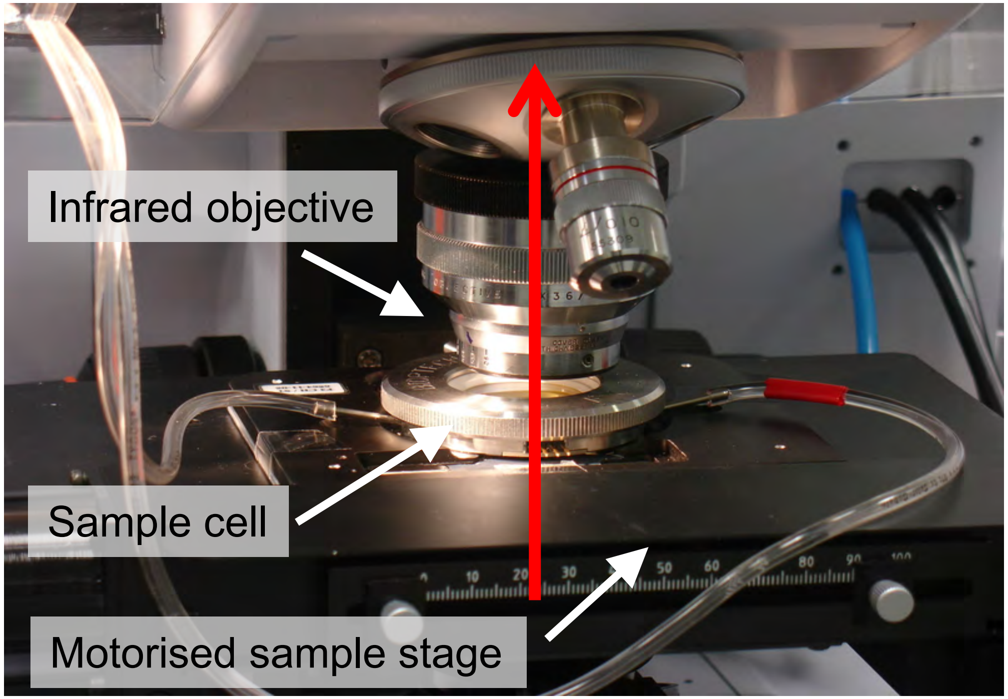


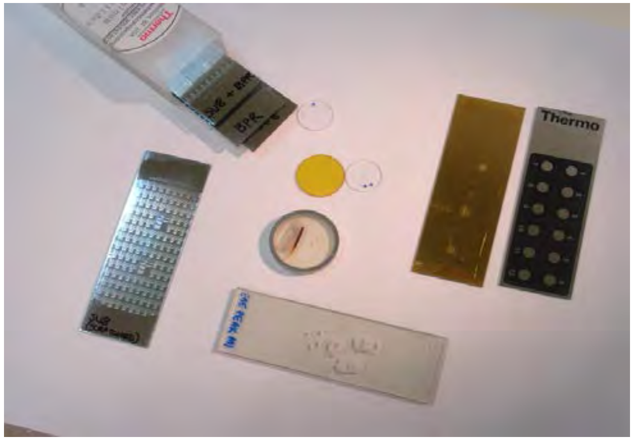


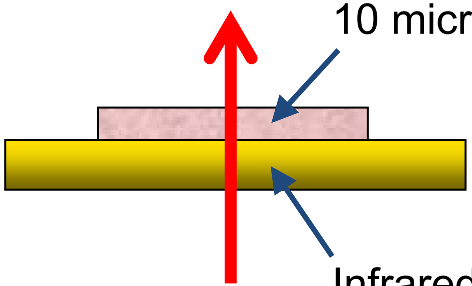
Standard operation

- 4 cm^{-1} resolution
- Narrowband 50 µm MCT detector
- Range = 750-3850 cm^{-1}

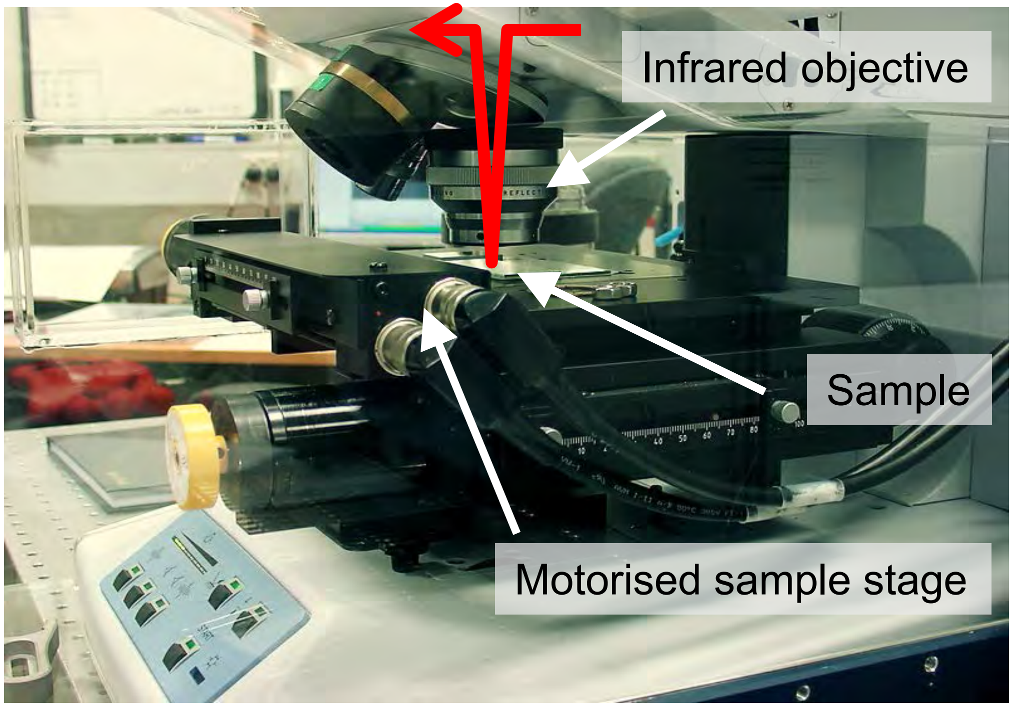
SAMPLING MODES - TRANSMISSION

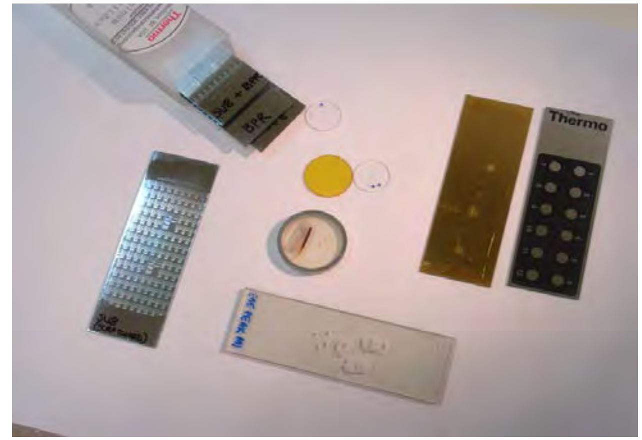


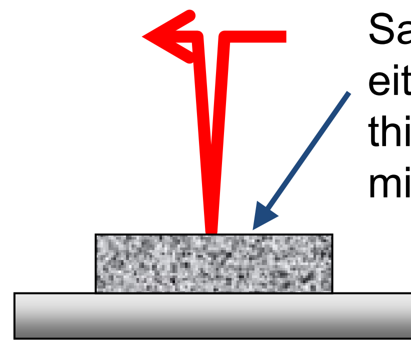




SAMPLING MODES - REFLECTANCE







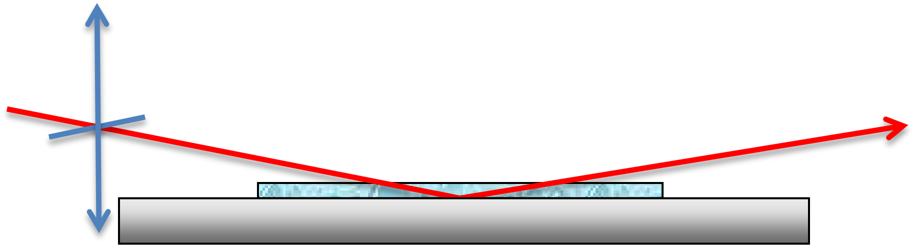
Sample must be either polished, or thin and placed on a mirror substrate

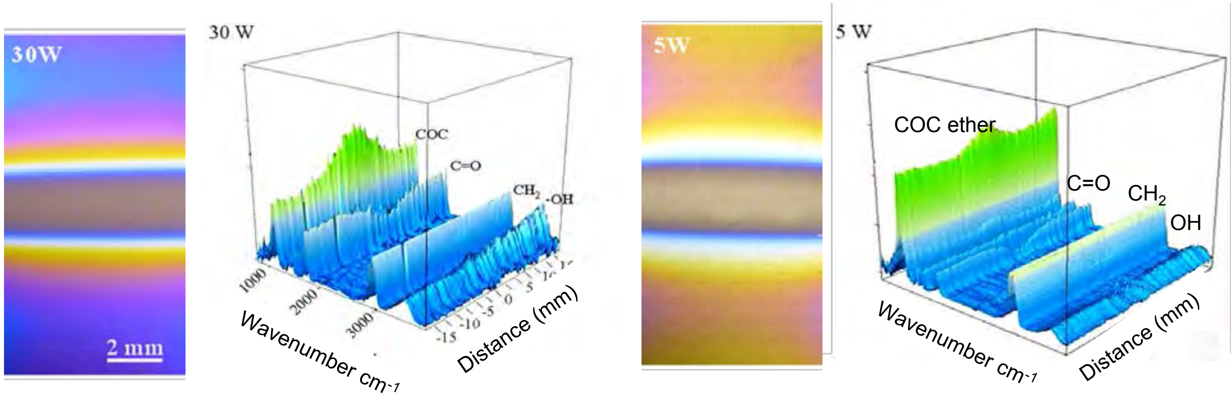
Sample

Substrate

SAMPLING MODES – GRAZING INCIDENCE

p polarised light





Thin layers of sample down to monolayers on reflective metallic surfaces (e.g. gold, steel, ITO glass)

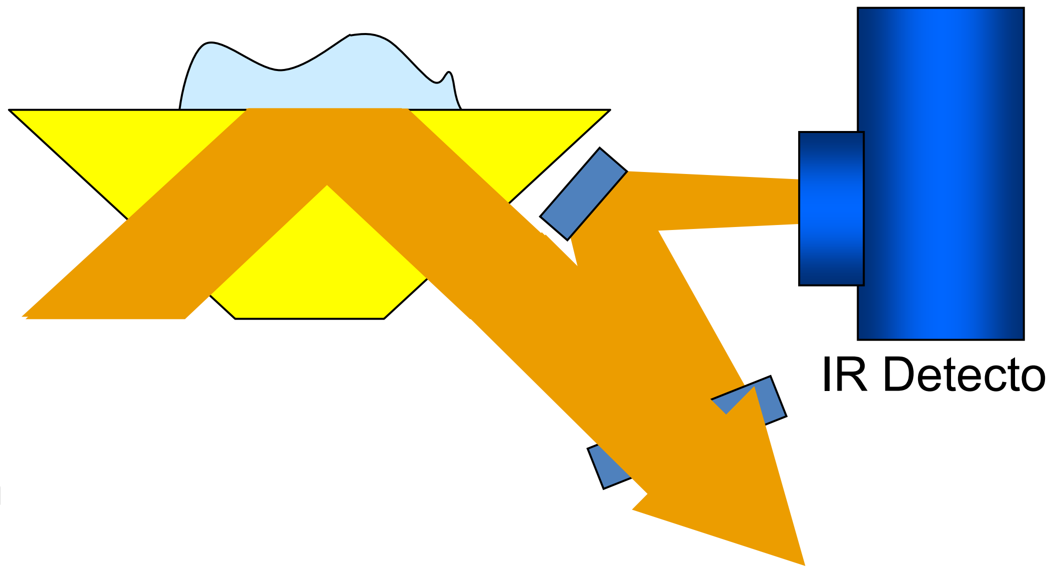
e.g. Protein resistant plasma polymer thin films. Mapping the compositional chance along a plasma gradient.

Donna Menzies, Thomas Gengenbach, Celesta Fong, John Forsythe, Ben Muir – CSIRO / Monash
Langmuir 26 **(17) 13987–13994 (2010).**

ATTENUATED TOTAL REFLECTANCE

$$d = \lambda / (2\pi\, n_1[\sin^2\theta - (n_2/n_1)^2]^{1/2})$$

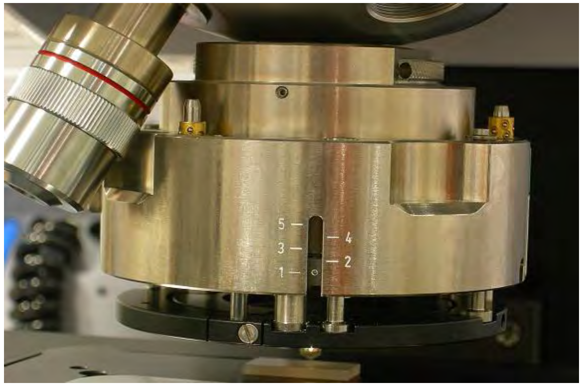
IR transmitting prism

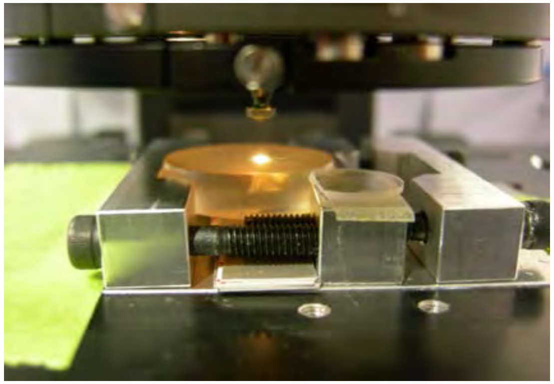


For λ = 6 µm   *d* = 0.9 µm
θ = 45°
ZnSe prism
Sample refractive index = 1.35

Chan,K.L.A., Kazarian,S.G.,
FTIR imaging for high-throughput analysis of pharmaceutical formulations
Journal of Computational Chemistry, 2005, Vol: 7, Pages: 185 - 189

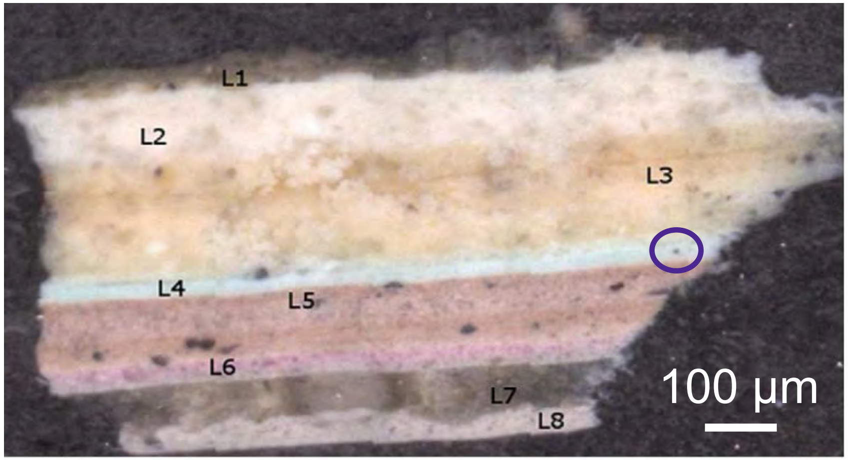
SAMPLING MODES – MICRO ATR



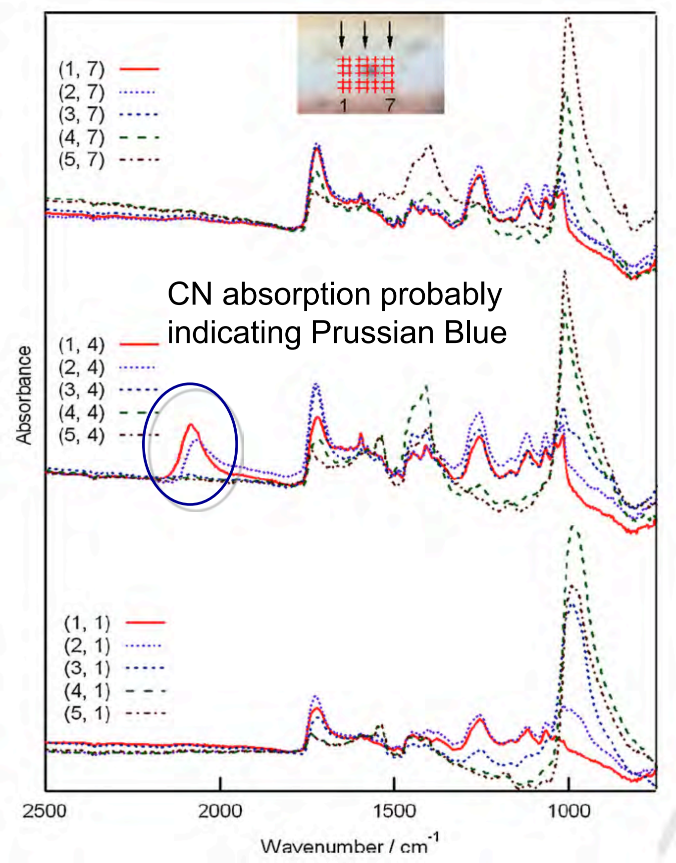


Bruker ATR 20x objective

Ge crystal, 100 or 250 micron tip variable pressure selection.



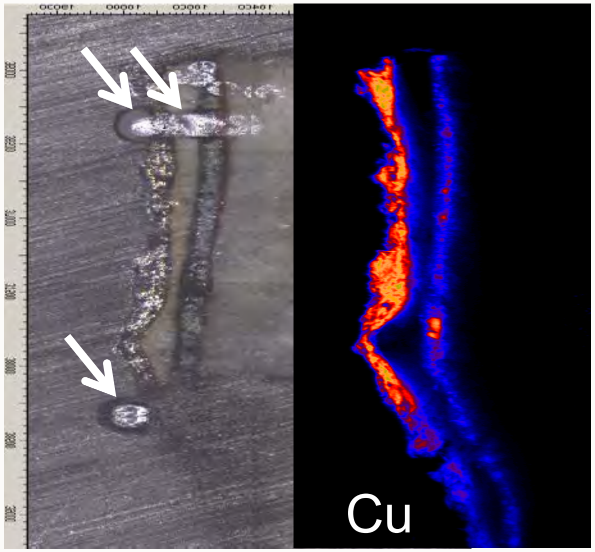
Multilayer paint fragment from exterior of Provincial Hotel, Fitzroy
Sample was not suitable for thin sectioning.



R. Sloggett et al.
Vibrational Spectroscopy 53 (2010)

SAMPLING MODES – MACRO ATR

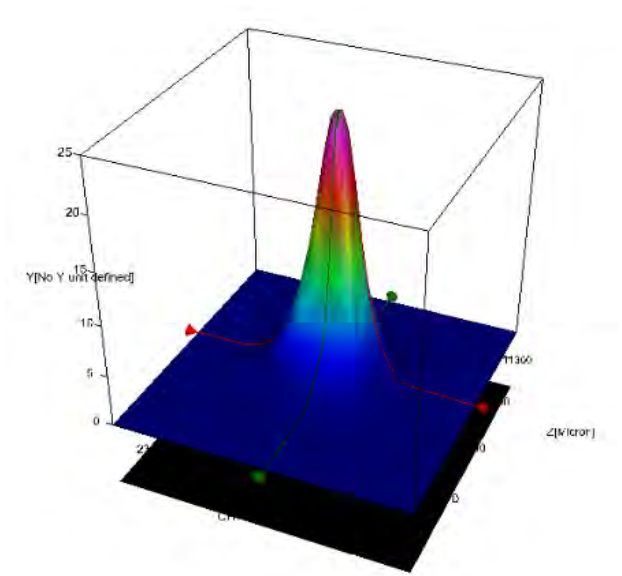
Why "single contact"?



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

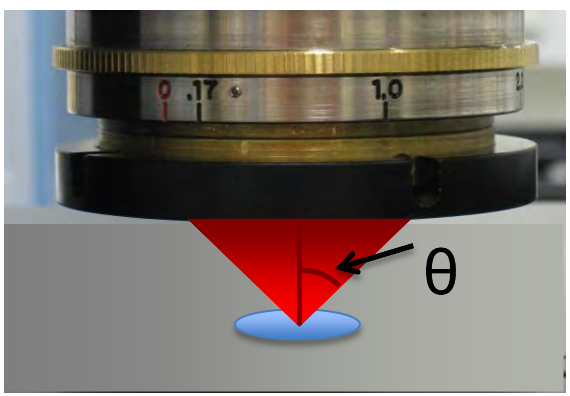


Airy disk radius is given by

$$r = 1.22\,\lambda\ /\ 2NA$$

Numerical aperture

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



At λ = 6 μm
For NA (air) = 0.65
r = 5.6 μm

At λ = 6 μm
For NA (ZnSe) = 1.56
r = 2.3 μm

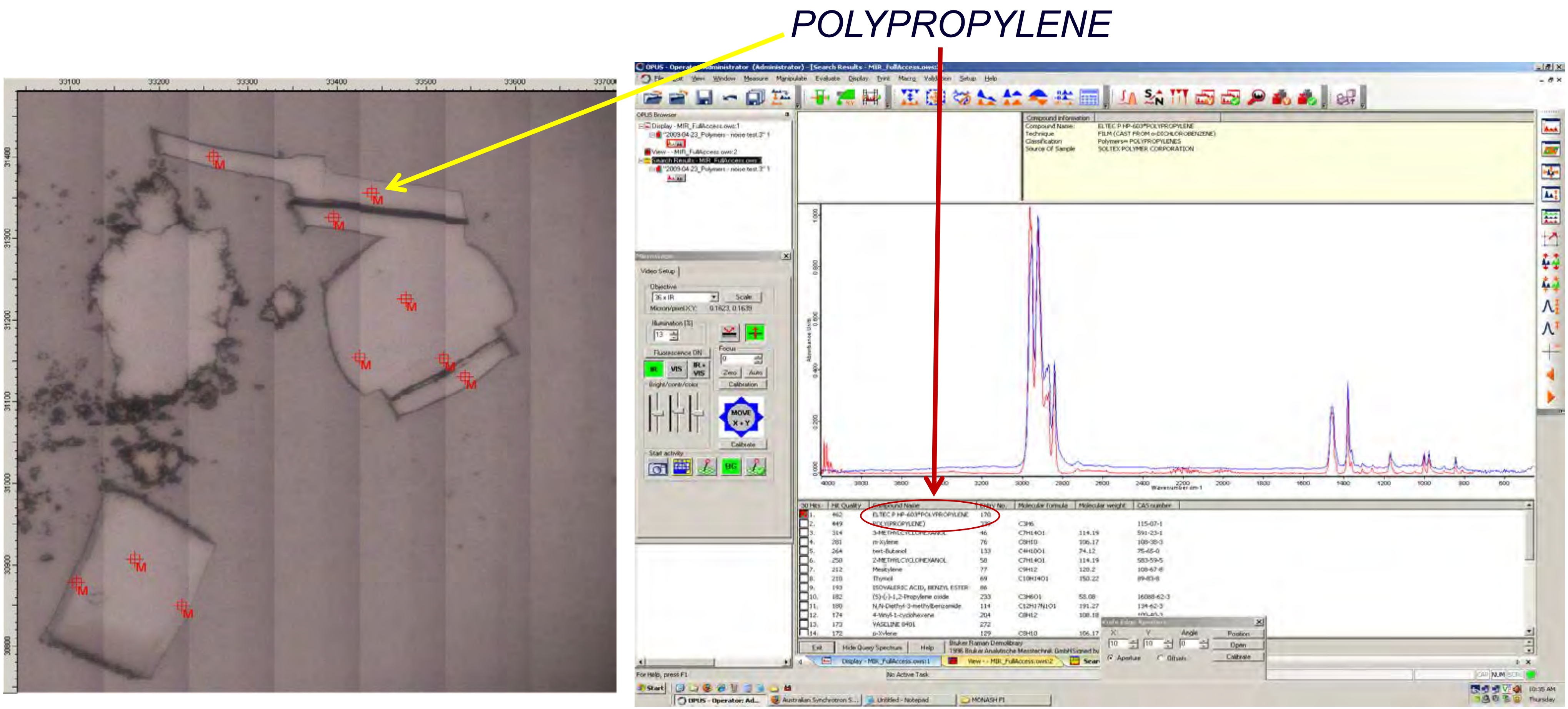
At λ = 6 μm
For NA (Ge) = 2.6
r = 1.6 μm

EXAMPLES FROM IR MICROSPECTROSCOPY BEAMLINE

BASIC APPLICATION
MATERIALS IDENTIFICATION

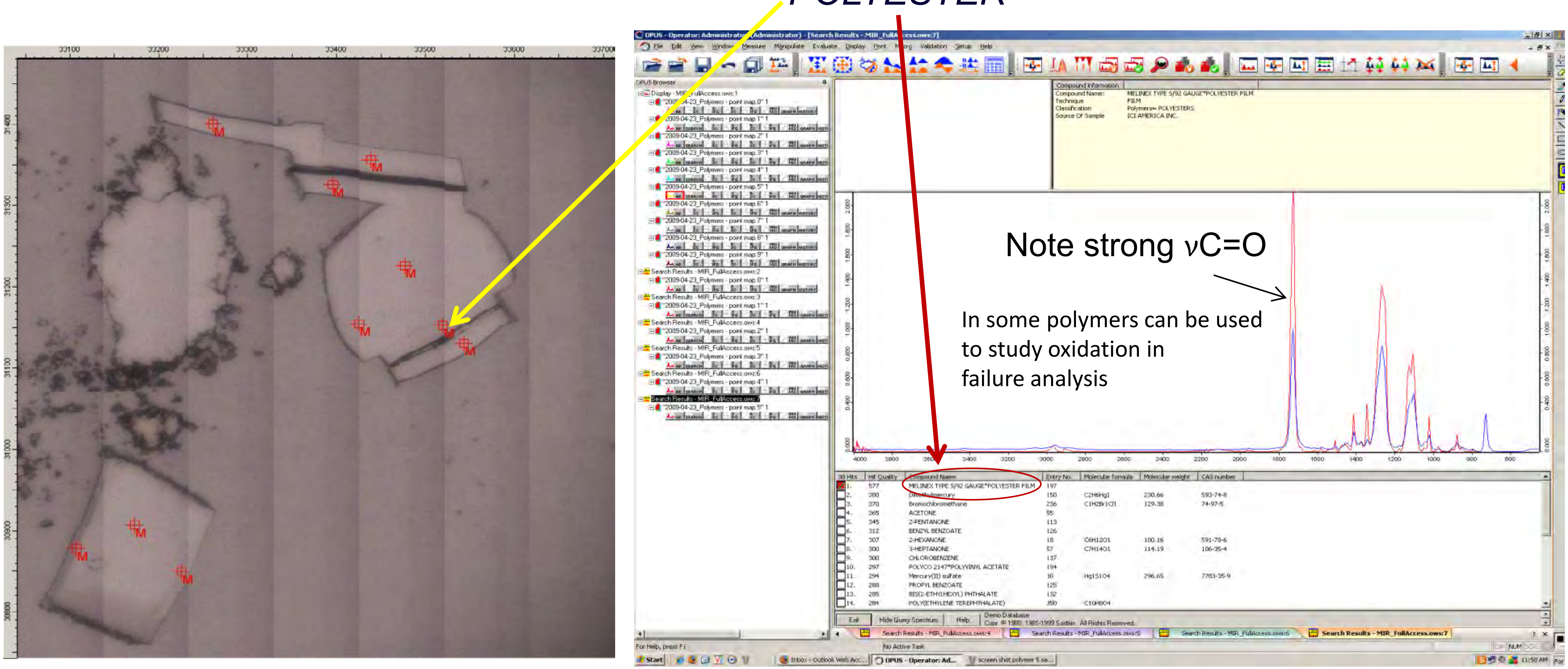
Australian Government

ansto



- Software used to mark positions for analysis
- Spectral library used to assist identification

BASIC APPLICATION
MATERIALS IDENTIFICATION



- Software used to mark positions for analysis
- Spectral library used to assist identification

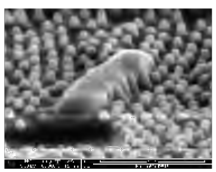
SURFACE COATING OF CICADA WING USING TWO SYNCHROTRONS

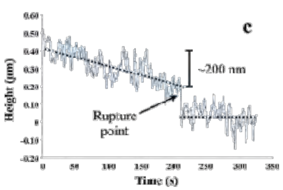
Australian Government | ansto

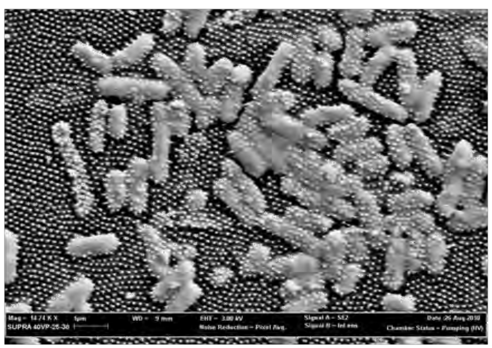
Advantageous properties of Cicada wings

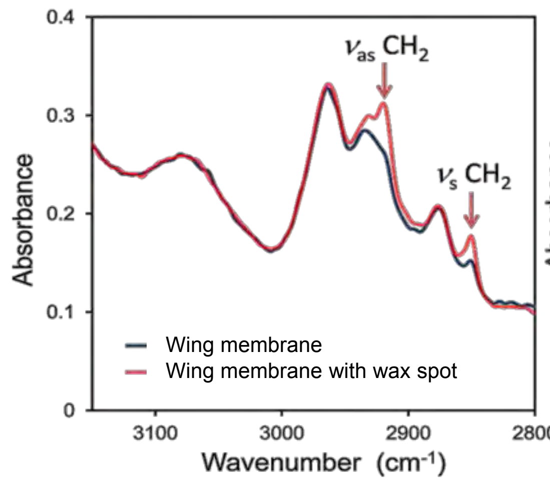
- Superhydrophobic
- Self cleaning
- Antireflective
- Antibacterial

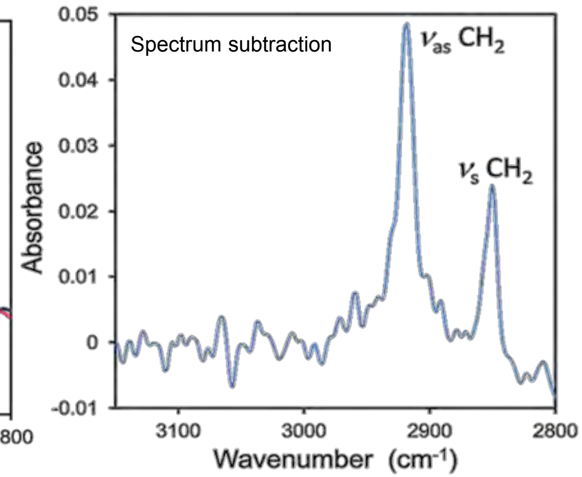
Industrial application: manufacture of synthetic materials that mimic those properties











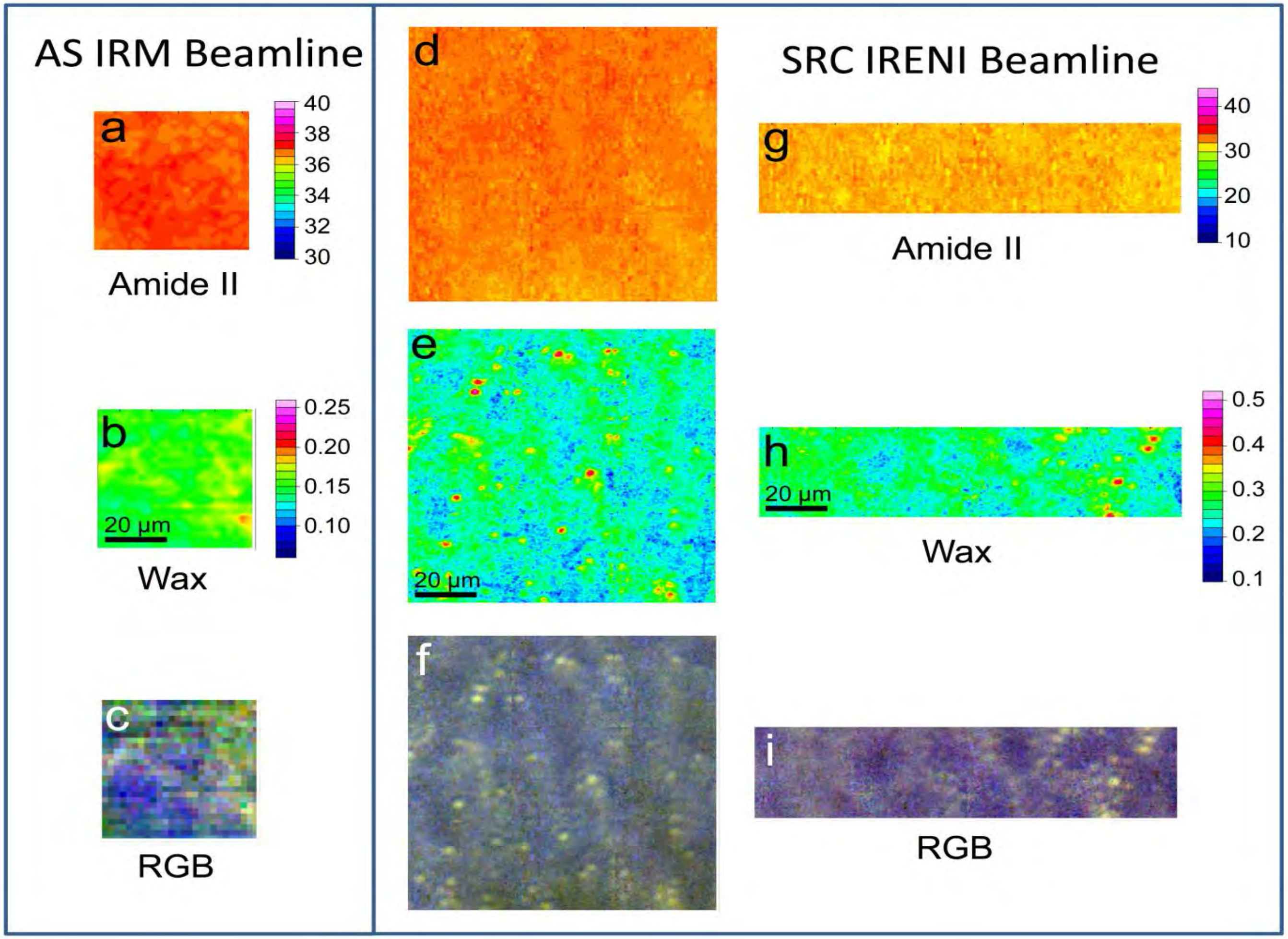
Elena Ivanova group, Swinburne University

Tobin M.J., Puskar L. et. al.
J. Synchrotron Rad. (2013). 20, 482-489

SWINBURNE UNIVERSITY OF TECHNOLOGY | Australian Synchrotron

SURFACE COATING OF CICADA WING USING TWO SYNCHROTRONS

Australian Government | ansto



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

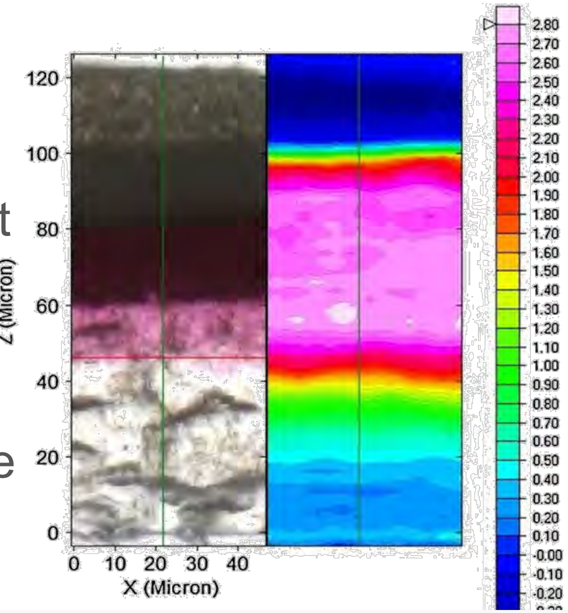
Tobin M.J., Puskar L. et. al.
J. Synchrotron Rad. (2013). 20, 482-489

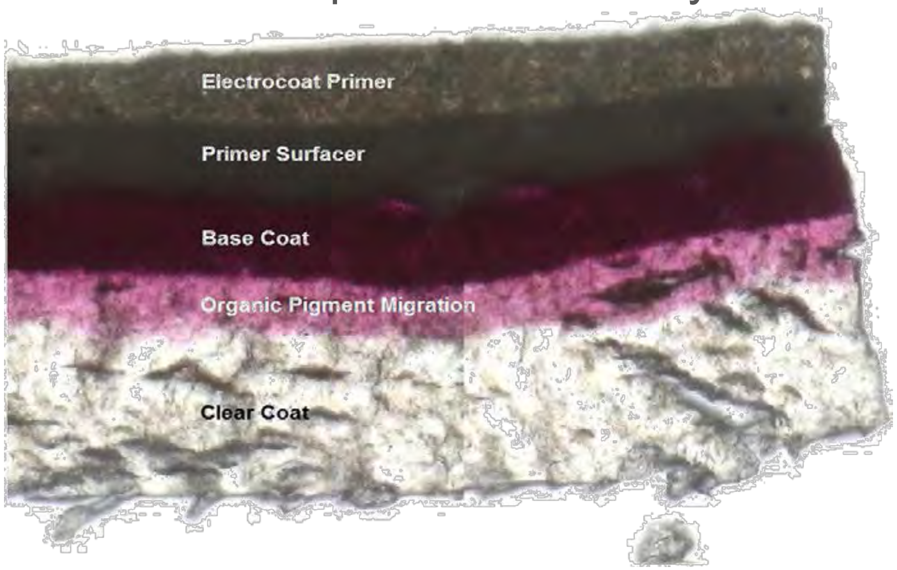
CHEMICAL COMPONENT MIGRATION IN AUTOMOTIVE PAINT

Australian Government

ansto

- 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)
Langmuir 26 (17) 13987–13994 (2010).

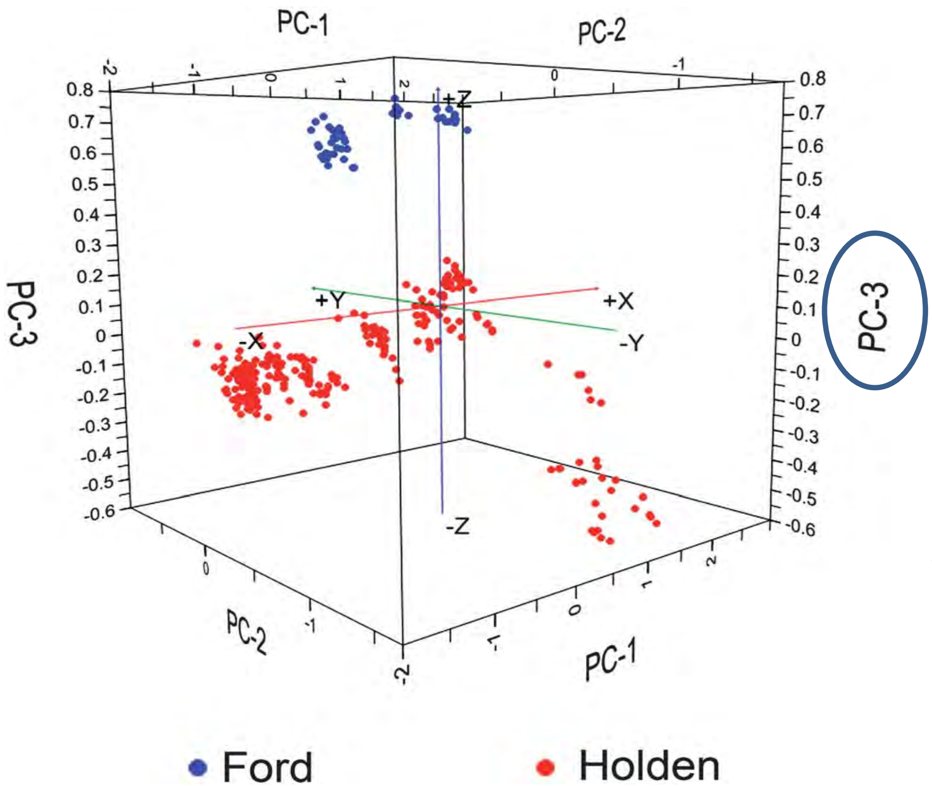
RAPID CHARACTERISATION AND CLASSIFICATION OF AUTOMOTIVE CLEAR COATS

Australian Government

ansto

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 .

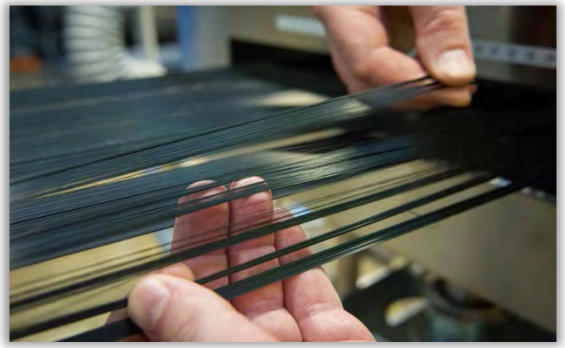
ATR FTIR on ~40 microns thick clear coat layer

Mark Maric, Wilhelm van Bronswijk,
Simon W. Lewis and Kari Pitts,
Analytical Methods, 2012,4, 2687-2693

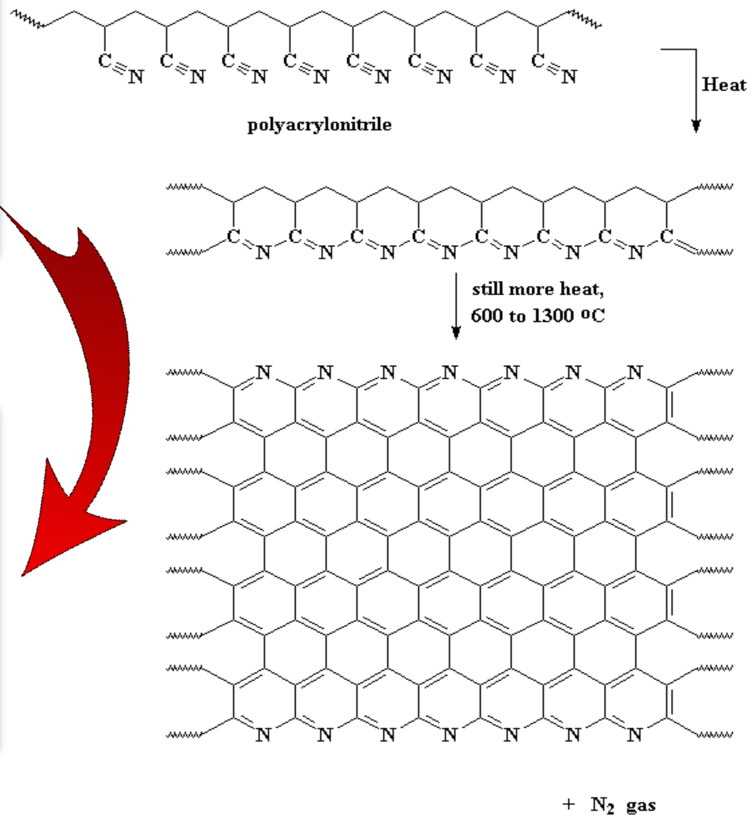
Australian Synchrotron

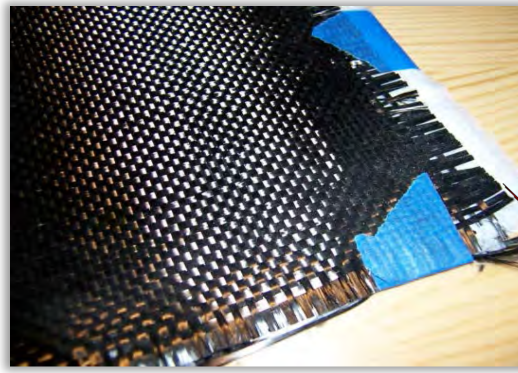
OPTIMISING THE PROCESS OF CARBON FIBRE PRODUCTION

1. Polyacrylonitrile fibre



2. Carbon fibre

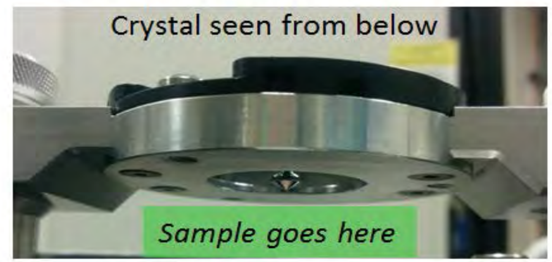


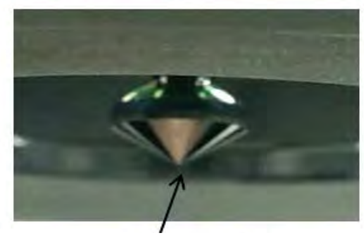


3. Woven carbon fibre

4. Carbon fibre reinforced product

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.

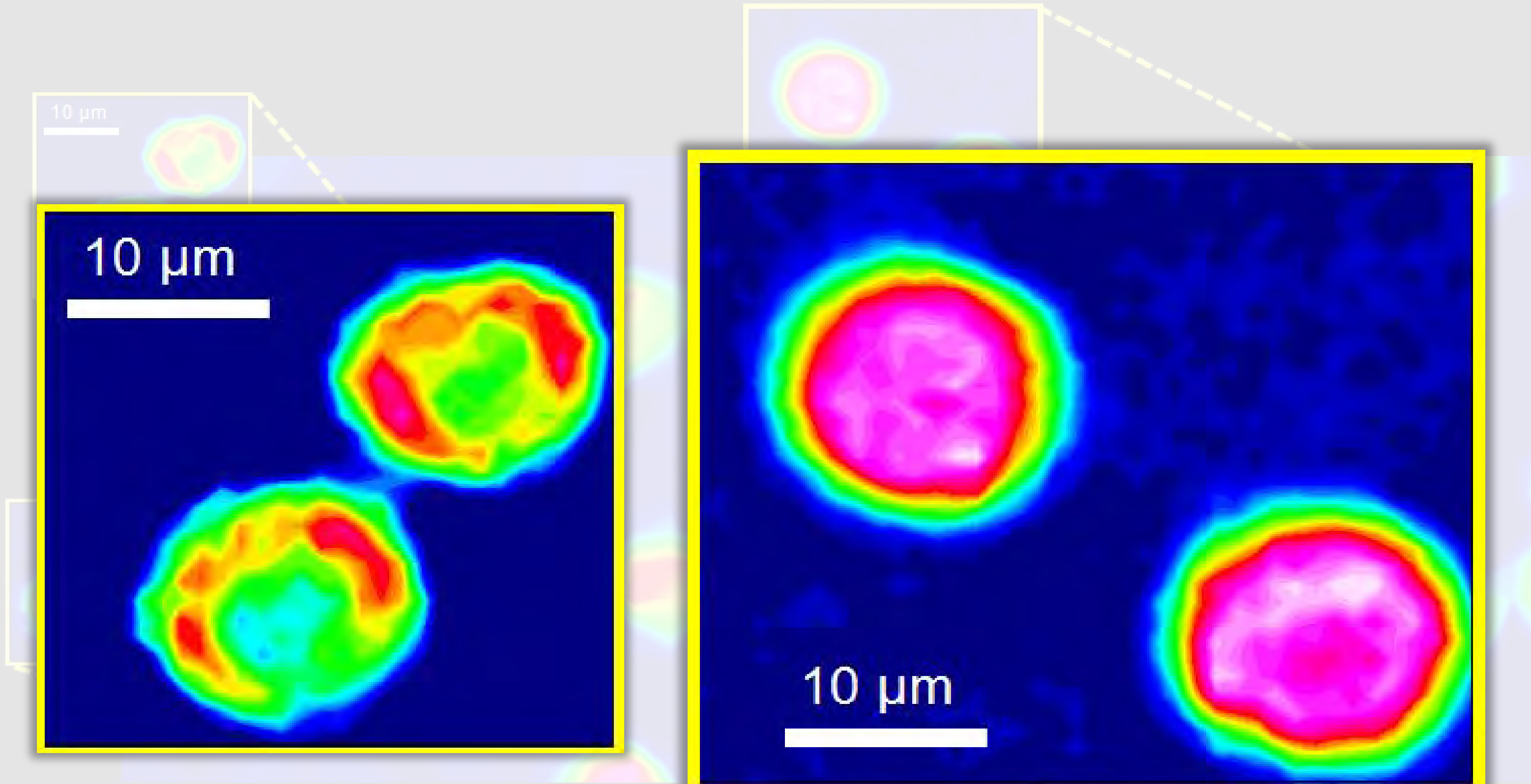




250 µm or 100 µm ATR tip

OPTIMISING THE PROCESS OF CARBON FIBRE PRODUCTION

Australian Government | ansto

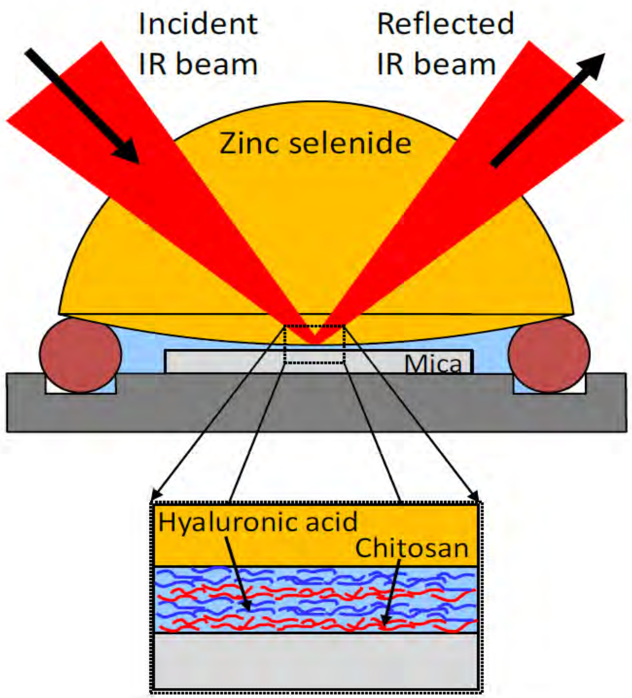


PAN fibres mapped with Hybrid Macro ATR. Low resolution and high resolution maps. Maps are integral of nitrile peak around 2240 cm^{-1}
High resolution step size is 500 nm

PERFORMANCE UNDER PRESSURE OF BIOPOLYMER GELS

Australian Government

ansto



- 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

Australian Synchrotron
Turning bright ideas into brilliant outcomes

University of South Australia

CUSTOM "SINGLE CONTACT" ATR

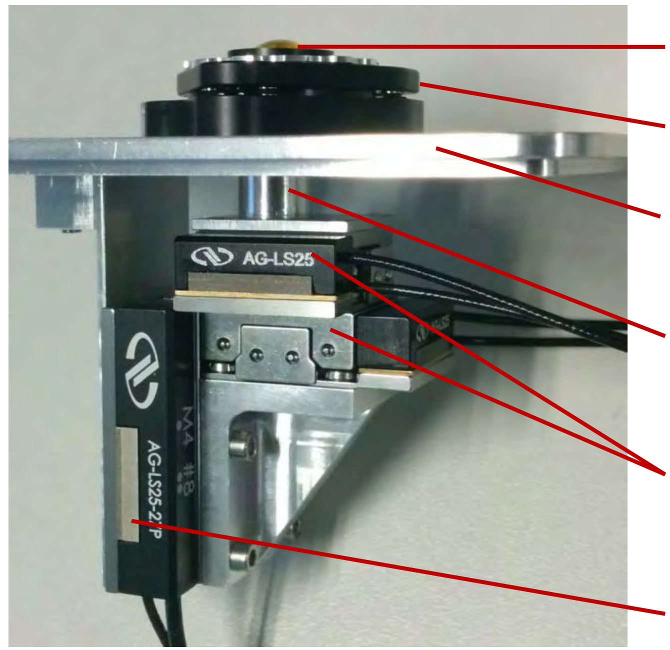
Australian Government

ansto

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)

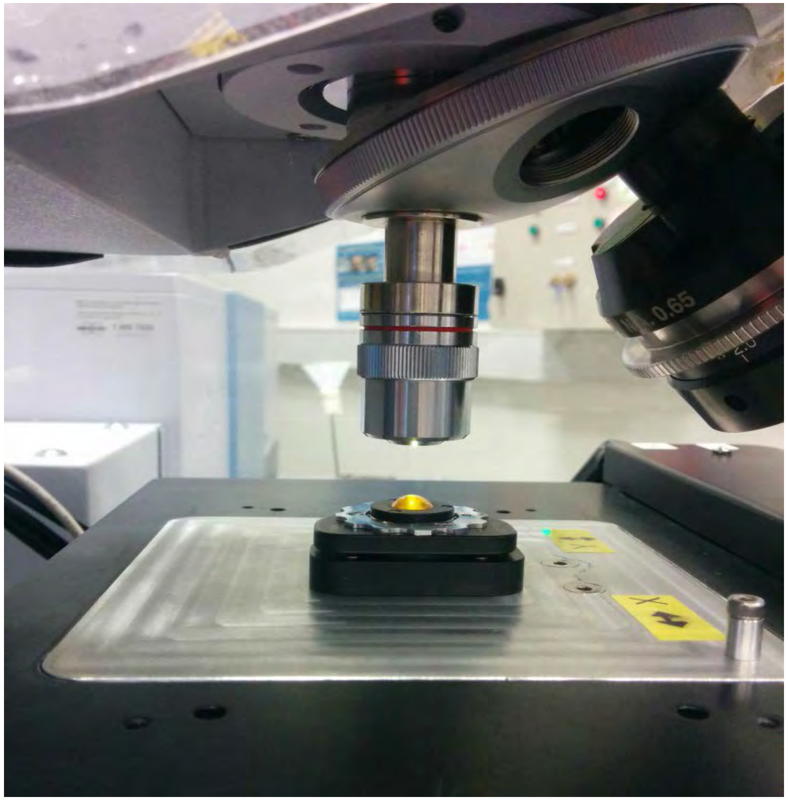


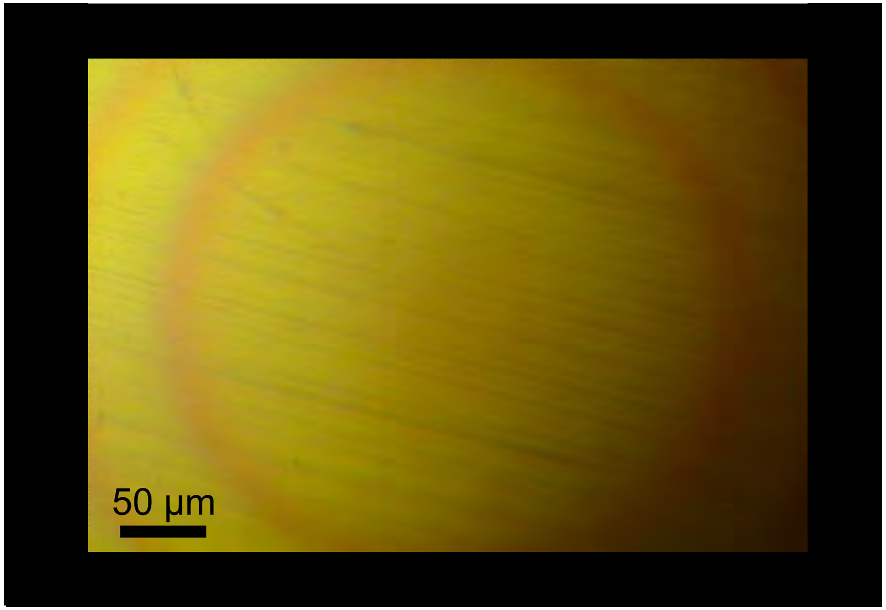
Custom ZnSe and germanium ATR crystals

Australian Synchrotron
Turning bright ideas into brilliant outcomes

University of South Australia

PERFORMANCE OF POLY STYRENE SULFONATE / POLY ALLYLAMINE HYDROCHLORIDE MULTILAYER





- 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

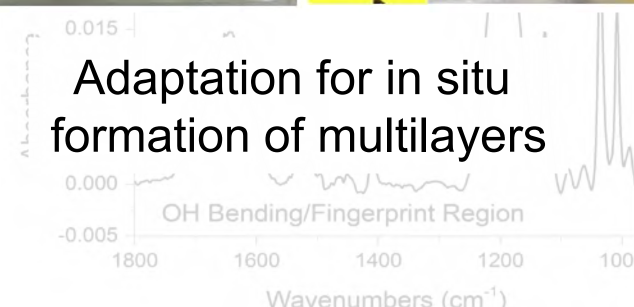
Australian Government

ansto

PERFORMANCE OF POLY STYRENE SULFONATE / POLY ALLYLAMINE HYDROCHLORIDE MULTILAYER

Adaptation for in situ formation of multilayers

ATR contact is just visible in 32x objective overview



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

Australian Synchrotron
Turning bright ideas into brilliant outcomes

University of South Australia

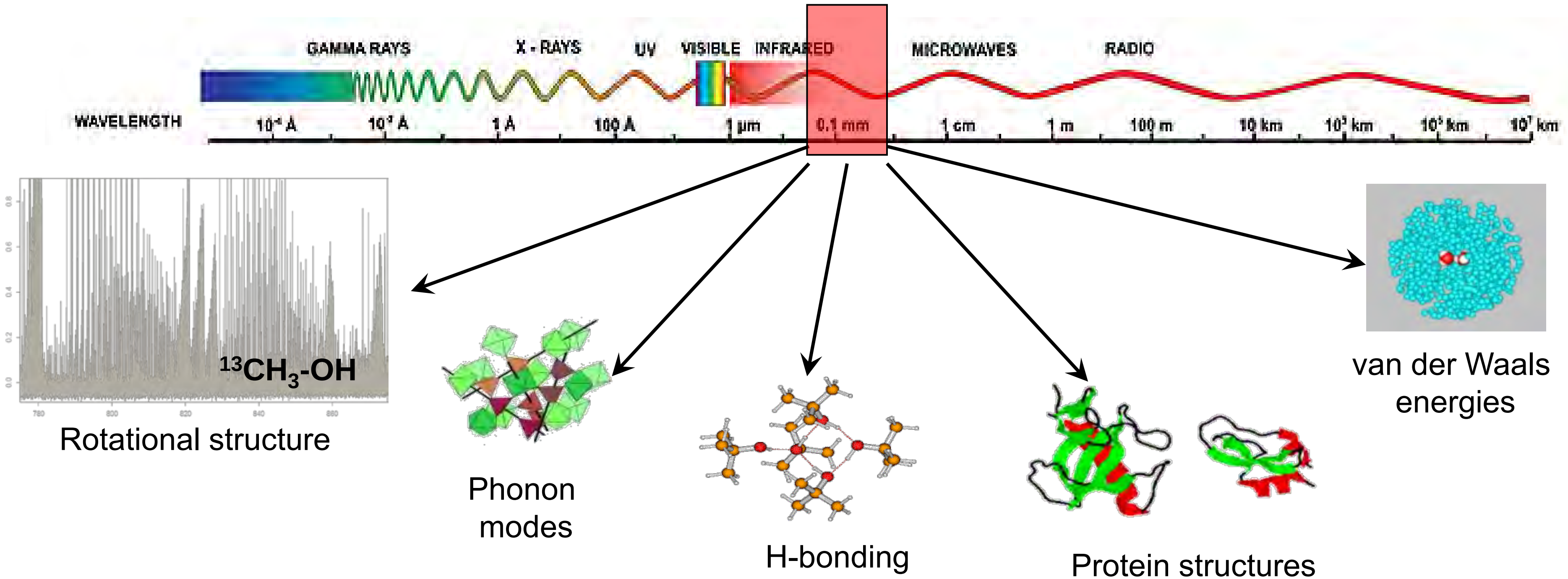
D.A. Beattie, A. Beaussart, A. Mierczynska-Vasilev, S.L. Harmer, B. Thierry, L. Puskar and M. Tobin, ***Langmuir, 28, 1683-1688, (2012)***
T.T.M. Ho, K.E. Bremmell, M. Krasowska, S.V. MacWilliams, C. Richard, D.N. Stringer, and D.A. Beattie. ***Langmuir, 31, 11249-11259. (2015)***

THz / FAR-INFRARED BEAMLINE

THz / FAR-INFRARED BEAMLINE

Australian Government

ansto



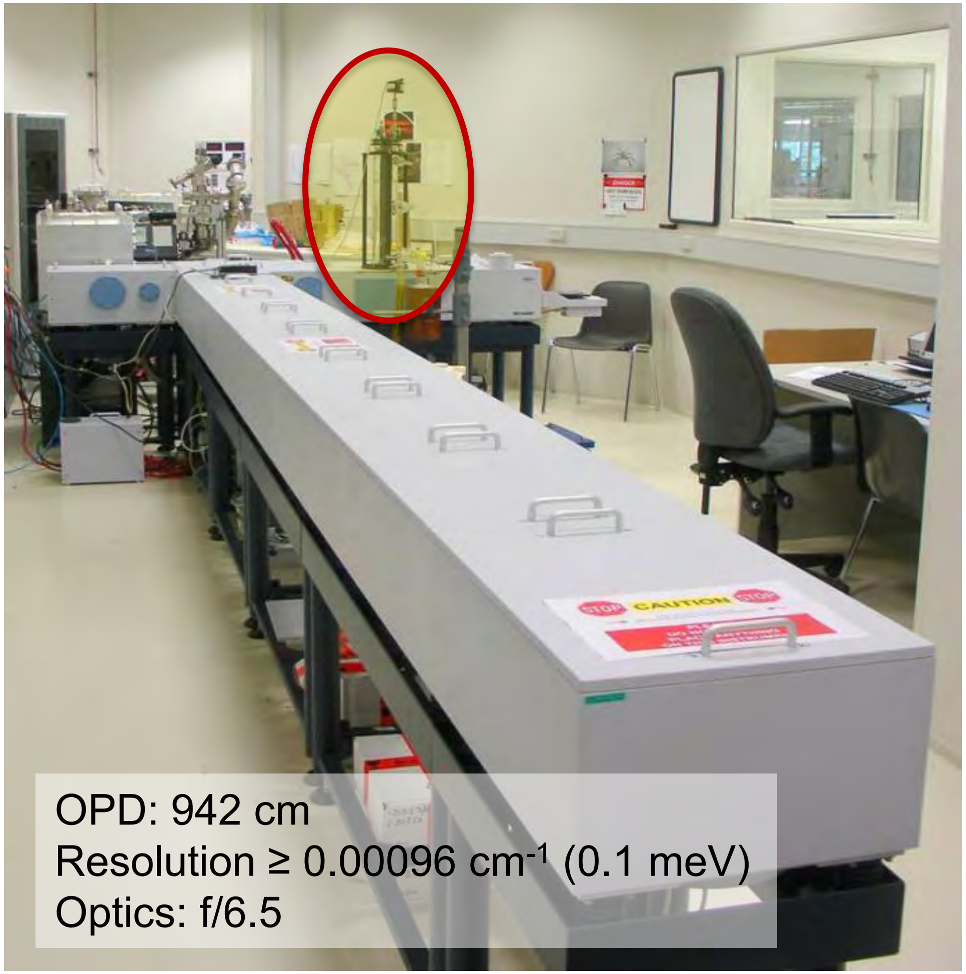
GAS PHASE experiments

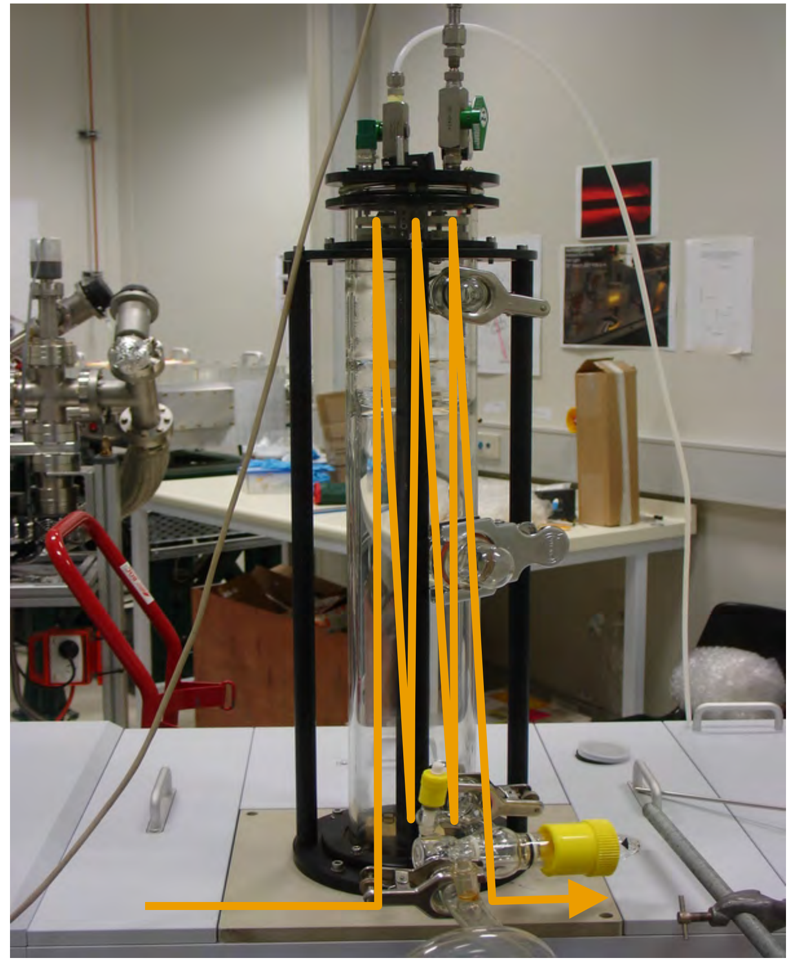
- Atmospheric & astrophysical sciences

CONDENSED PHASE experiments

- Geology & mineralogy studies
- Nanoparticle studies
- Biology & biomedical studies
- Thin layer & monolayers

Bruker IFS 125HR High Resolution FTIR Spectrometer

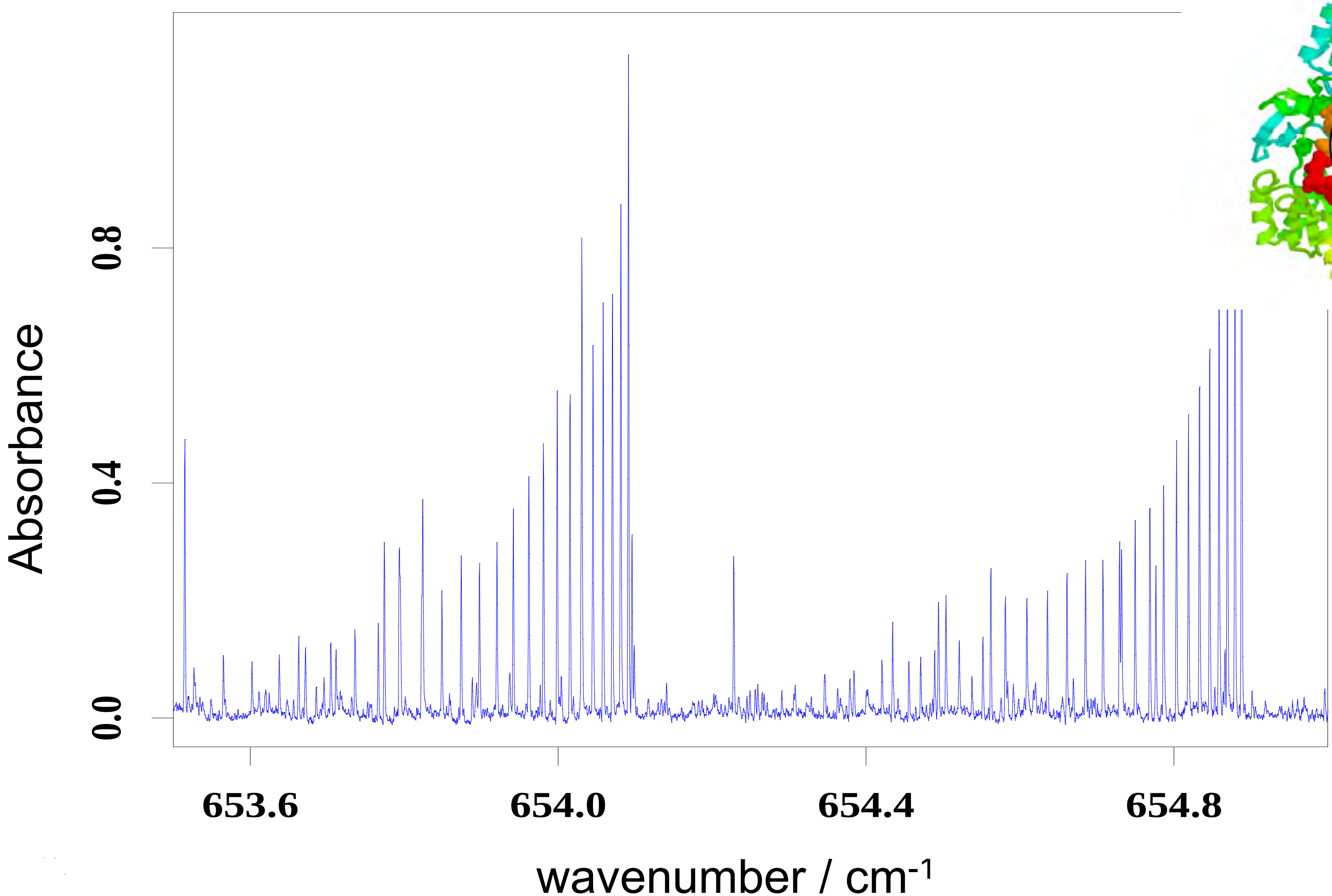


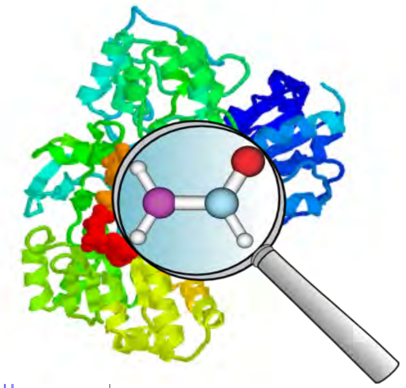


PORTION OF THE FAR-IR SPECTRUM OF FORMAMIDE AT 0.00096 CM-1 RESOLUTION

Australian Government

ansto



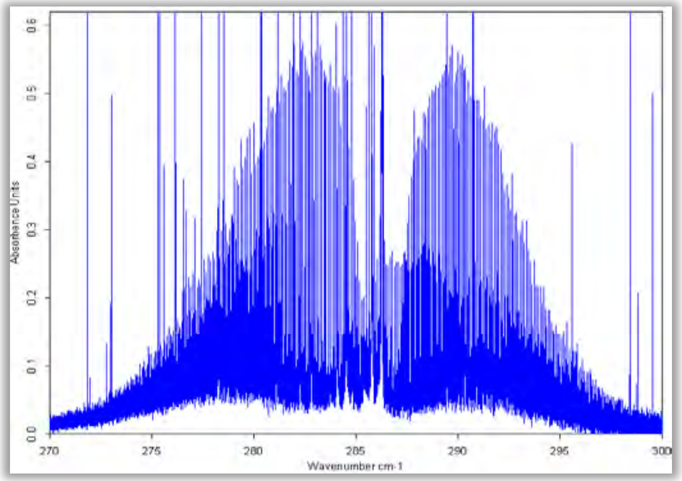


EXAMPLES FROM THz/Far-IR BEAMLINE

STUDY OF GASES AND AEROSOLS OF ENVIRONMENTAL/ATMOSPHERIC IMPORTANCE

Australian Government

ansto



CF_3I High Resolution Spectrum

Multipass room temp cell at Soleil
Optical Path Length ~ 152 m

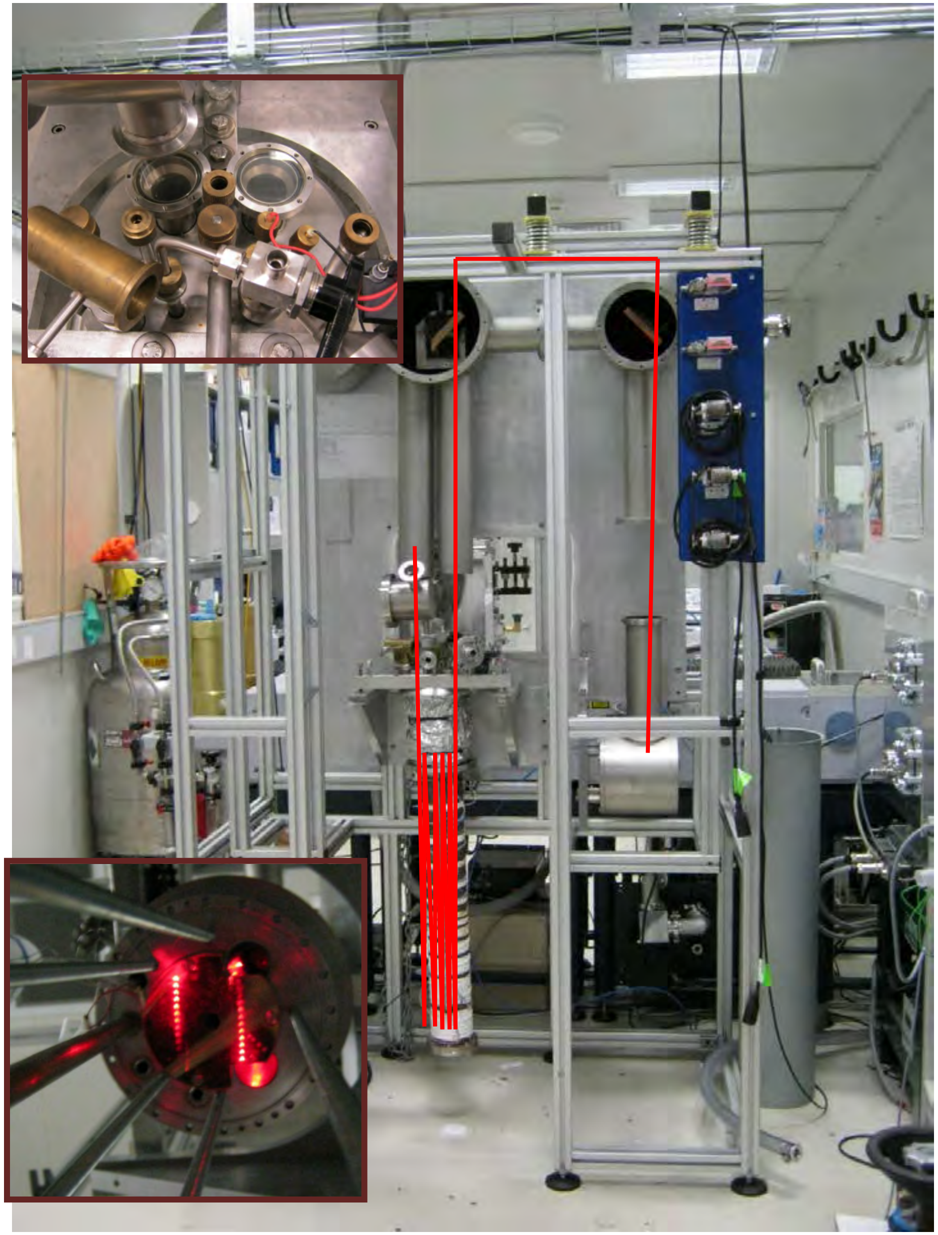
CF_3I is an potential alternative to Halon 1301 ($CBrF_3$) as a gaseous fire suppressant. Breaks down more readily in contact with water. Important to understand chemistry at upper atmosphere conditions

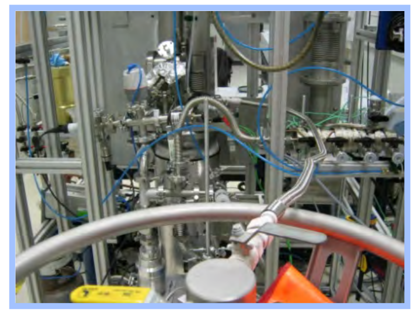
D. Appadoo, D. Martin and R. Plathe – International Science Linkage with Soleil Far-IR beamline. AS team able to access extra long path length gas cell at Soleil. Soleil Far-IR team able to access low temperature gas cell at AS.

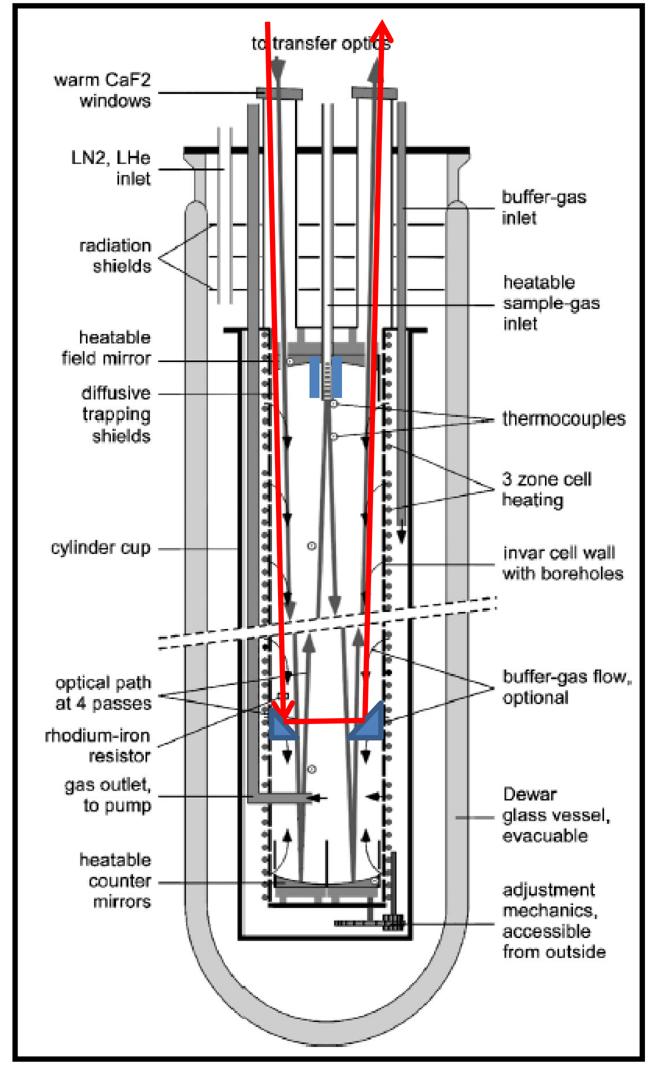
ENCLOSIVE FLOW COOLING MULTIPASS CELL FOR GAS-PHASE STUDIES AT CRYOGENIC TEMPERATURES.

Australian Government

ansto





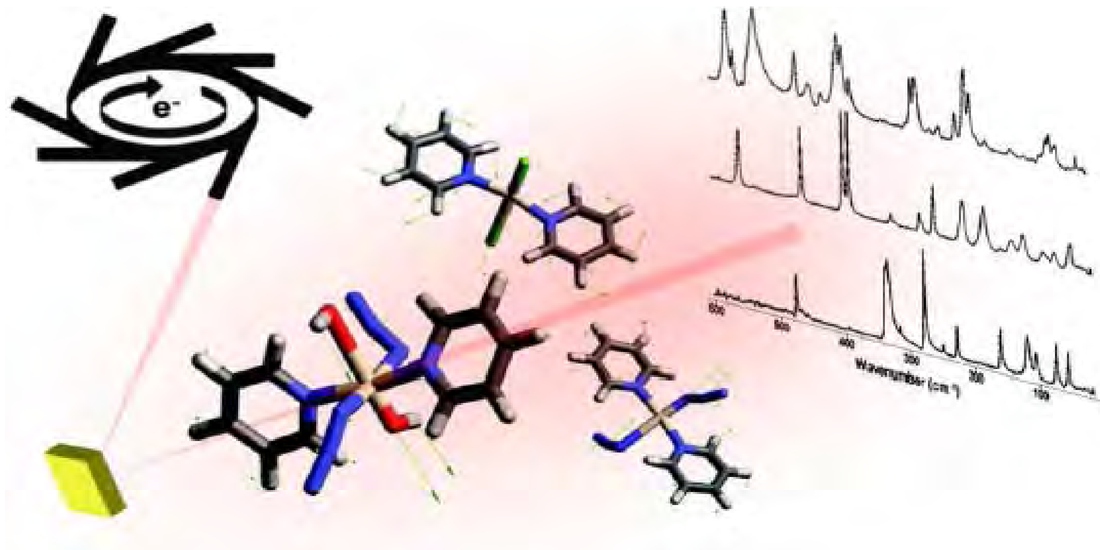


Comprehensive Vibrational Spectroscopic Investigation of trans,trans,trans-$[Pt(N_3)_2(OH)_2(py)_2]$, a Pt(IV) Diazido Anticancer Prodrug Candidate

Australian Government

ansto

Robbin R. Vernooij, Tanmaya Joshi, Evyenia Shaili, Manja Kubeil, Dominique R. T. Appadoo, Ekaterina I. Izgorodina, Bim Graham, Peter J. Sadler, Bayden R. Wood, and Leone Spiccia



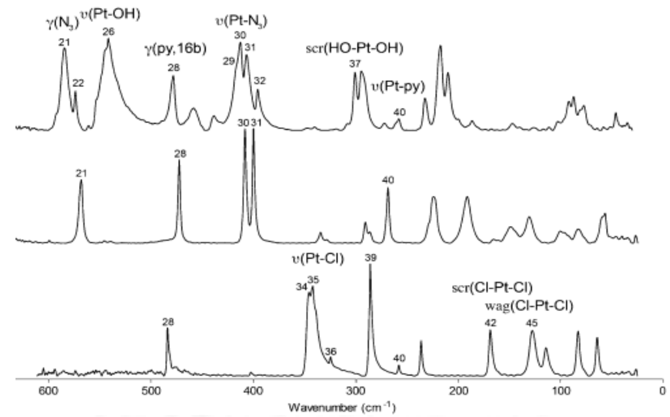


Figure 6. SR-FIR spectra of solid C1, C2, and C3 measured at 77 K.

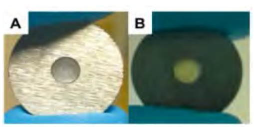
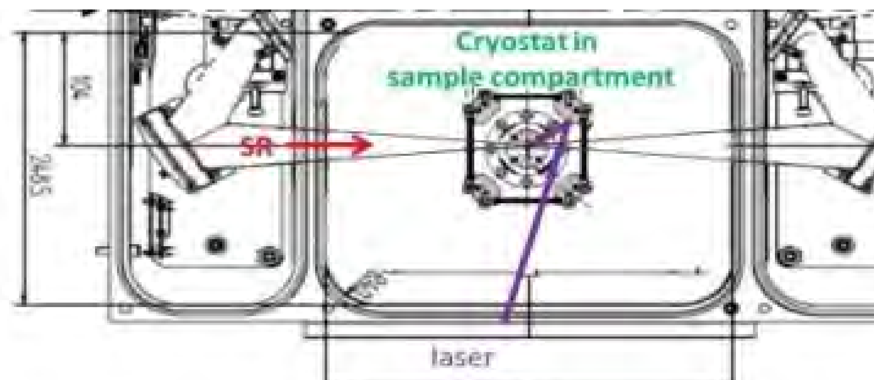


Figure 8. SR-FIR sample holders; (A) paraffin blank; (B) paraffin holding C1 (1 mg).



Future technique: Laser photolysis

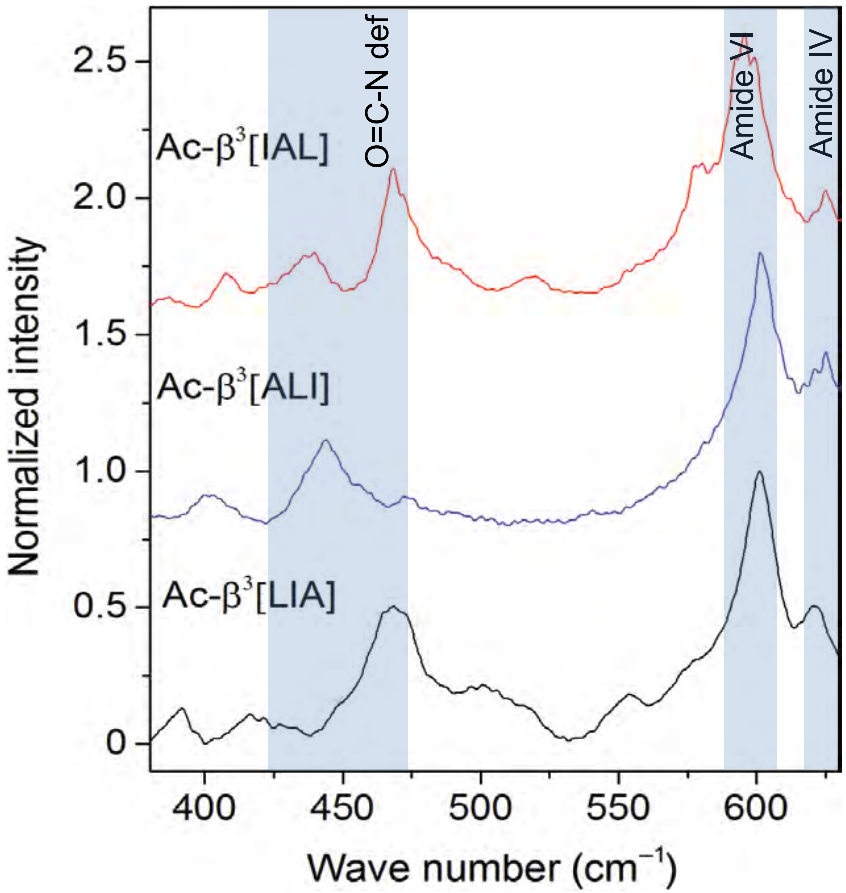
Study of amino-acids sequence in N-acetylated tri-β^3-peptides

Australian Government

ansto

Far-infrared spectra (absorbance) of Ac-β^3[LIA], Ac-β^3[ALI] and Ac-β^3[IAL].
L→ Leucine, I → Isoleucine, A → Alanine

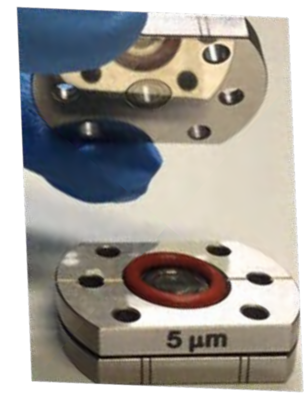
Rania S. Seoudi, Annette Dowd, Mark Del Borgo, Ketav Kulkarni, Patrick Perlmutter, Marie-Isabel Aguilar, Adam Mechler , Pure and ***Applied Chemistry, 2015, 87, 1021–1028***



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

PolyEthylene Liquid Cell

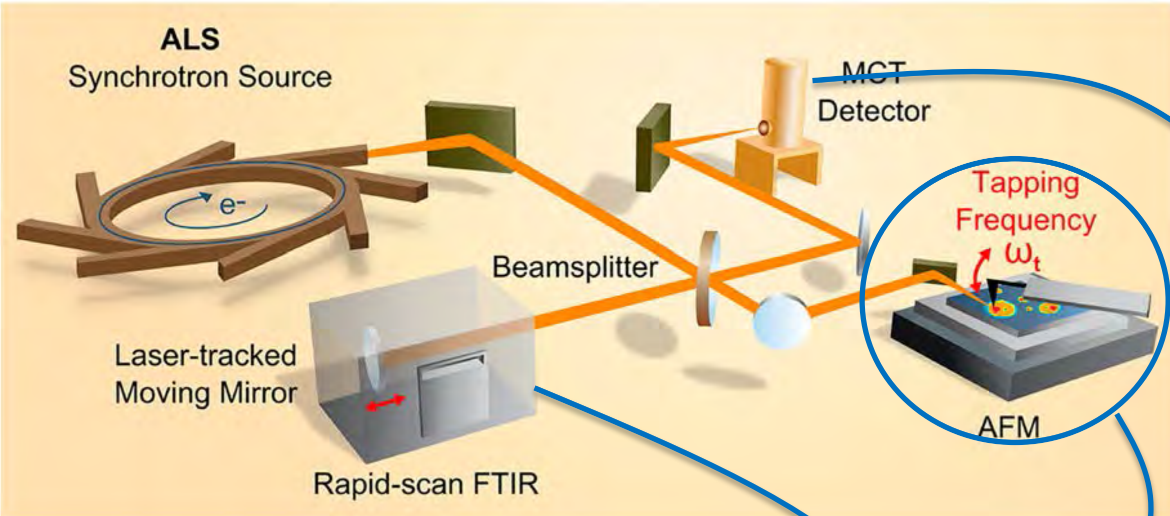
→



Diamond Liquid Cell

FUTURE SYNCHROTRON FTIR DEVELOPMENTS

AFM-BASED NANO FTIR



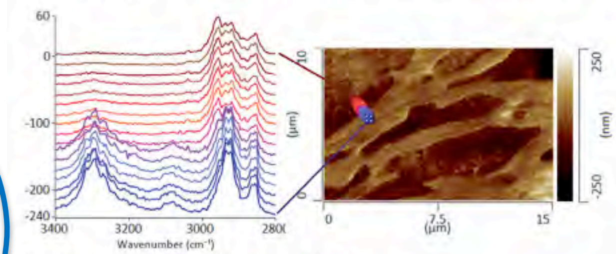
- IR superfocused by IR antenna (AFM tip)
- Signal demodulated using Lock in. Use higher harmonics
- Detection of the amplitude and the phase spectra of the backscattered light
- Synchrotron provides broader spectral range than is available from lasers

H.A. Bechtel E.A. Muller R.L. Olmon M.C. Martin and M.B. Raschke
PNAS (2014) vol. 111 7191–7196

Lock-in

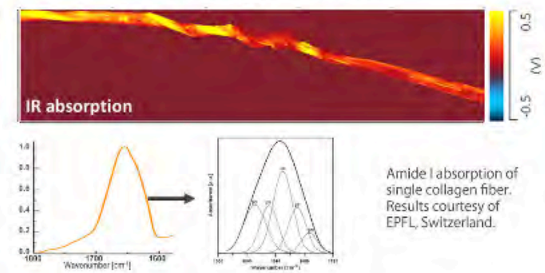
Computer

Polymer interface chemistry



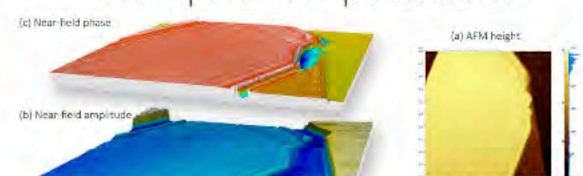
AFM-IR spectra (left) and morphology (right) of a polymer blend across a rubber/nylon interface.

Protein secondary structure single fibril



Amide I absorption of single collagen fiber. Results courtesy of EPFL, Switzerland.

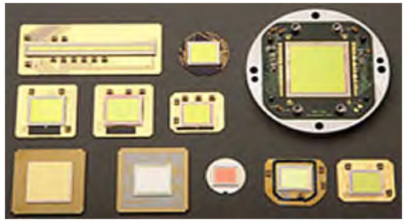
hBN phonon-polaritons

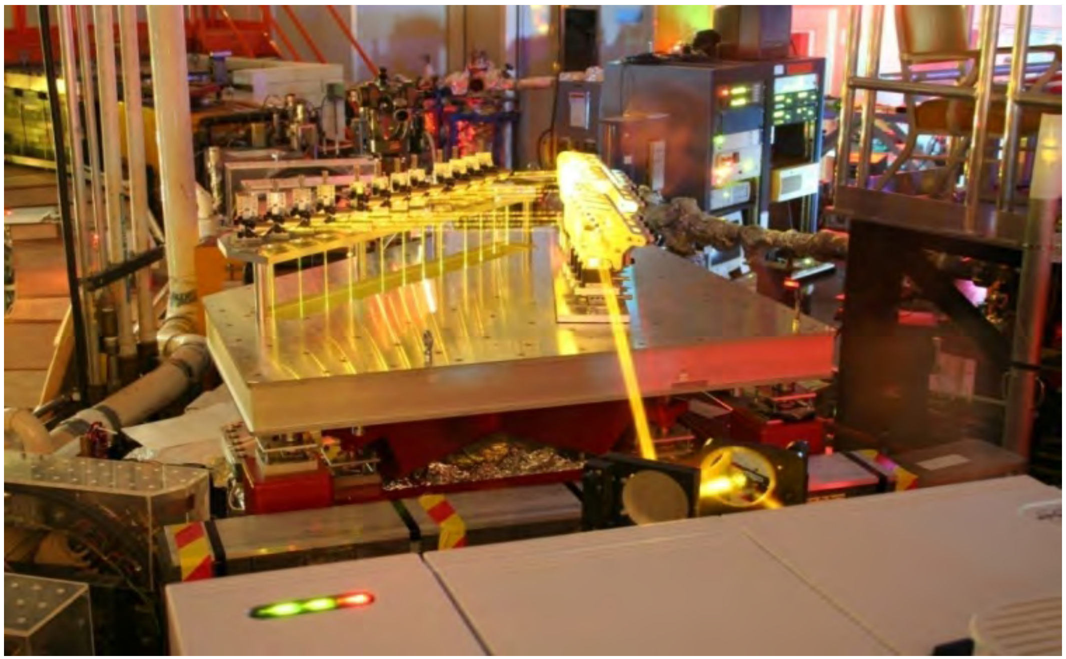


Nano imaging of surface phonon polaritons (SPhP) on hexagonal boron nitride (hBN). (a) AFM height image shows homogeneous hBN surface with different layers on Si substrate; (b) s-SNOM amplitude shows strong interference fringes due to propagating SPhP along the surface on hBN; (c) s-SNOM phase shows a difference phase with layer thickness. From the image b and c, we can also see the wavelength of the SPhP changes with the number of layers.

FULL-FIELD IR IMAGING

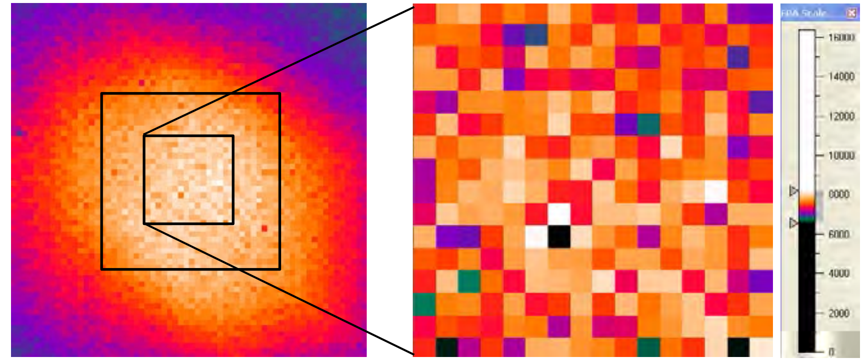
Use of Focal Plane Array (FPA) imaging detector for data acquisition coupled to high magnification optics





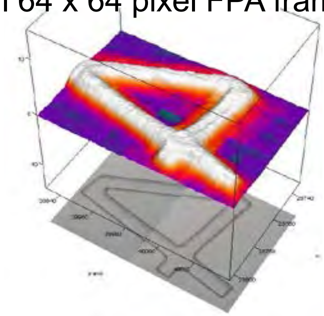
IRENI BEAMLINE – SRC WISCONSIN

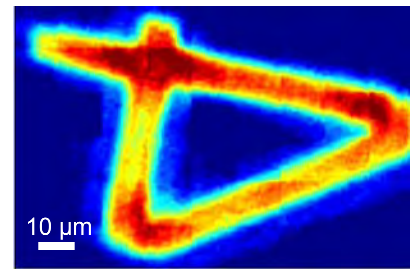
50 mrad four-beam illumination of FPA



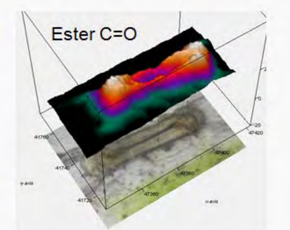
Four overlapping beams on full 64 x 64 pixel FPA frame

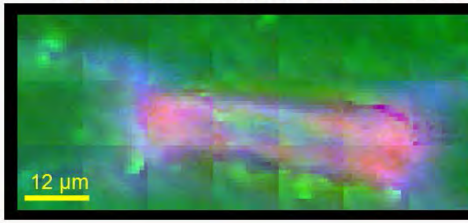
Illumination of 16 x 16 pixels





Sample courtesy of Prof. Enzo Lombi, University of South Australia





RGB composite FTIR image of three absorption peaks

CH_2 stretch

C=O of protein

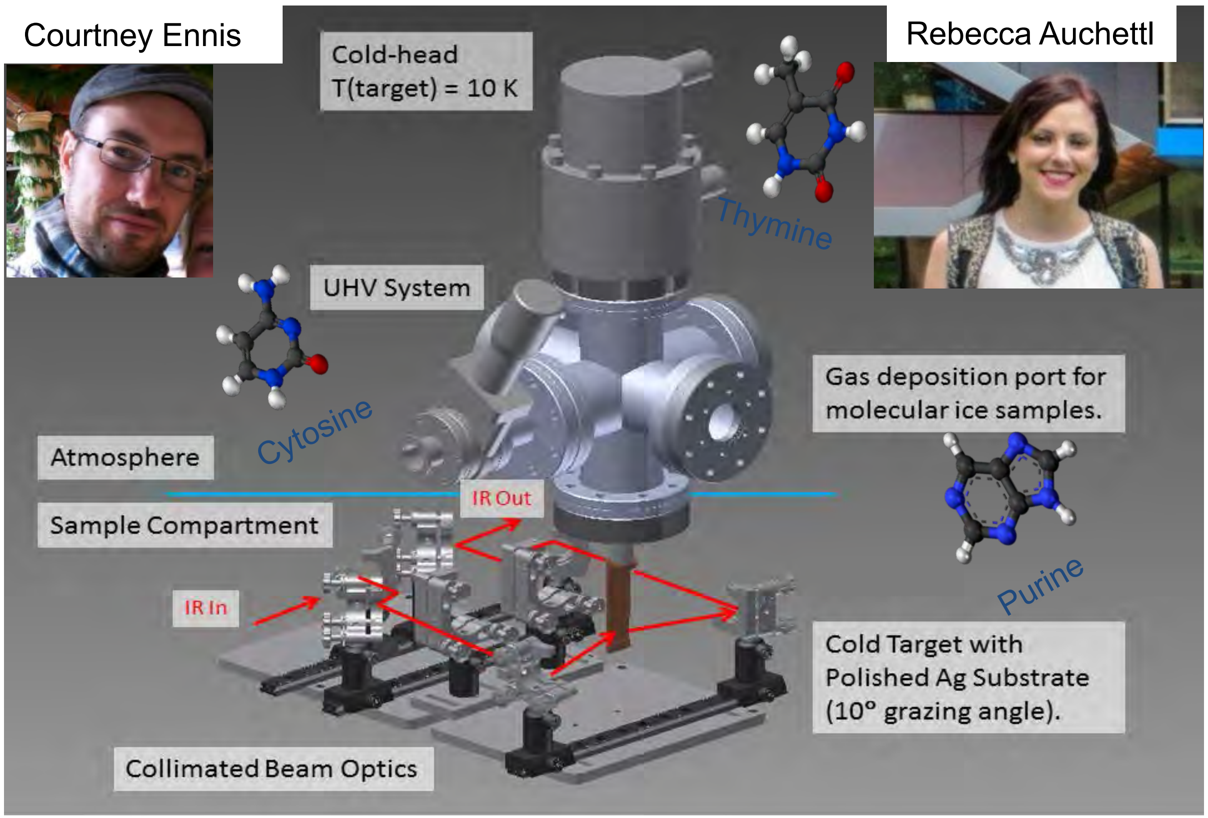
Ester C=O of lipid, or lignin

LOW-TEMPERATURE GRAZING REFLECTION & MATRIX ISOLATION

Australian Government

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

mark.tobin@synchrotron.org.au

Australian Government

Thank you

Mark Tobin
Mark.Tobin@synchrotron.org.au
www.synchrotron.org.au
(03) 8540 4172