# Far-IR/THz & High Spectral Resolution Spectroscopy Using Synchrotron Radiation

Dominique Appadoo Senior IR Beamline Scientist

# Australian Synchrotron



#### **Infrared beamlines worldwide**

	Number of beamlines	Purpose	Status
North America			
ALS Berkley	1	Microscopy and Far-IR	Operational
CAMD Baton Rouge	1	Місгоѕсору	Planned
CLS Saskatoon	2	1 Microscopy, 1 Far-IR	Operational
NSLS Brookhaven	6	3 Microscopy, 2 Far-IR, 1 THz	Operational
Surf III Gaithersburg	1	Місгоѕсору	Planned
SRC Madison	1	Microscopy	Operational
Asia and Australia			
Australian	1	Microscopy and Far-IR	Operational
Synchrotron			
INDUS I, India	1	Місгоѕсору	Planned
Helios II, Singapore	1	Microscopy and Far-IR	Operational
NSRRC, Taiwan	1	Microscopy	Operational
NSRL, Heife	1	Microscopy and Far-IR	Planned
BSRF, Beijing	1	Microscopy	Planned
Spring-8, Himeji	1	Microscopy and Far-IR	Operational
UVSOR, Okazaki	1	Far-IR	Operational
Europe			
ESRF, Grenoble	1	Місгоѕсору	Operational
Soleil, St. Aubin	2	1 Microscopy, 1 Far-IR	Commissioning
ELETTRA, Trieste	1	Microscopy and Far-IR	Operational
DAPHNE, Frascati	1	Far-IR	Operational
SLS, Villigen	1	Microscopy and Far-IR	Commissioning
ANKA, Karlsruhe	1	Microscopy and Far-IR	Operational
BESSY II, Berlin	1	Microscopy and Far-IR	Operational
DELTA, Dortmund	1	Місгозсору	Planned
MAX II, Lund	2	Microscopy and Far-IR	operational
DIAMOND, Didcot	1	Microscopy	Planned

#### **32 IR Beamlines**

# The far-IR/THz spectral region





λ = 1000 - 10 μm  $\overline{v} = 10 - 1000 cm^{-1}$  v = 0.3 - 30 THzE = 1 - 124 mEV

THz Energy Gap

# $Far-IR/THz \equiv XSX$

 $\rightarrow$  eXtremely Soft X-ray

- lack of adequate tunable lasers
- weakness of conventional thermal sources
- difficulties with far-IR detectors

wwww.lbl.gov/MicroWorlds/ALSTool/EMSpec/EMSpec2.html

**CHEIRON SCHOOL OCT 5, 2008** 

# **The Final Frontier**



- cw & pulsed THz lasers are now available

- Backward-wave oscillators
- Accelerator-based sources ...

# What kind of interactions take place in the far-IR?

#### van der Waals energies



#### H-bonding





phonon modes

- surface/adsorbate interactions
- biological processes
- chemical dynamics



rotation of smaller molecules

ro-vibration of larger molecules

# What can we learn from these interactions?

- How does energy flow within a molecule?
- What is the nature of the weak attractive forces that exist among atoms and molecules?
- How do metal atoms bond to other chemical groups?
- What are the structures of long carbon chain molecules?
- How do the optical properties of a material change under ultrahigh pressures?

# ... this is just the beginning!

# Overview

- I. IR Spectroscopy
- **II. Synchrotron IR Radiation**
- **III.** The IR Beamline at the Australian Synchrotron
- **IV. FT Spectroscopy**
- V. Applications of Far-IR & High Resolution Synchrotron Spectroscopy
- **VI. Coherent Synchrotron Radiation**

# **I. Introduction to IR spectroscopy**

# **Fingerprint spectral region**



Positions of Stretching Vibrations of Hydrogen iin the hatched ranges the boundaries are not well defined); Band intensity: s = strong, m = medium, w = weak, v = varying.



Characteristic Absorptions in the Fingerprint Region (s = strong, m = medium, w = weak)

http://www.brukeroptics.com/downloads.html

IR spectroscopy of condensed samples: Vibrational Spectroscopy → spatial resolution



IR spectroscopy of gas-phase samples: Ro-Vibrational Spectroscopy → Spectral Resolution

**Diatomic molecules** 



#### Polyatomic molecules: linear 3N-5 modes non-linear 3N-6 modes



Potential energy curve of a diatomic molecule in its ground electronic state.

# Manifold of rotational states within each vibrational level







# **Diatomic** Model

 $\mathbf{E}(\mathbf{v},\mathbf{J}) = \mathbf{T}_{\mathbf{e}} + \mathbf{G}(\mathbf{v}) + \mathbf{F}_{\mathbf{v}}(\mathbf{J})$ 

#### where

 $G(\mathbf{v}) = \omega_{e}(\mathbf{v} + \frac{1}{2}) - \omega_{e}x_{e}(\mathbf{v} + \frac{1}{2})^{2} + \omega_{e}y_{e}(\mathbf{v} + \frac{1}{2})^{3} + \dots$  $F_{v}(\mathbf{J}) = B_{v}\mathbf{J}(\mathbf{J}+1) - D_{v}(\mathbf{J}(\mathbf{J}+1))^{2} + H_{v}(\mathbf{J}(\mathbf{J}+1))^{3} + \dots$ 

# where $B_v = B_e - \alpha_e (v + \frac{1}{2}) + \beta_e (v + \frac{1}{2})^2 + ...$ $B_e \alpha 1/\mu r_e^2$

 $\mathbf{D}_{\mathbf{e}} \thicksim \sum_{\mathbf{v}=\mathbf{0}} \Delta \mathbf{G}_{\mathbf{v}}$ 

 $\omega_{e}$  is the fundamental frequency ( $\alpha \mu^{-1/2}$ )  $r_{e}$  is the bond length  $D_{e}$  is the dissociation energy



# **Rotational, vibrational and electronic Transitions**



# IR emission spectrum of ZnD $(^{2}\Sigma)$



# Life can get complicated even for diatomics



#### **CHEIRON SCHOOL OCT 5, 2008**

# IR spectrum of MnH ( $^{7}\Sigma$ )



# Simply put, spectra for diatomic molecules can be complicated and congested!

- Heavy molecules: closely-spaced transitions, overlapping bands, and narrow linewidths
- Presence of naturally occurring isotopomers in measurable quantities
- High-spin electronic states due to open-shells: spinsplitting

... Need high spectral resolution!

**Polyatomics: Asymmetric Top Molecule** 

#### Normal modes of vibration of R152a

3N-6 modes where  $N=8 \equiv 18$  modes

#### **IR Spectrum of R152a at low resolution**

F

F

C

H

Н

H

Η



# Part of the IR spectrum of R152a



Low resolution EFC spectrum

**Asymmetric Rotor Model** 

 $\langle \mathbf{v}:\mathbf{J},\mathbf{K}|\mathbf{H}| \ \mathbf{v}:\mathbf{J},\mathbf{K}\rangle = \mathbf{v} + \mathbf{B}\mathbf{J}(\mathbf{J}+1) + (\mathbf{A} - \mathbf{B}) \ \mathbf{K}^2$ 

-  $\Delta_{JJ} [J(J+1)]^2$  -  $\Delta_{JK} J(J+1) K^2$  -  $\Delta_{KK} K^4$ 

 $+ \Phi_{JJJ} \ [J(J+1)]^3 + \Phi_{JJK} \ [J(J+1)]^2 \ K^2 + \Phi_{JKK} \ [J(J+1)] \ K^4 + \Phi_{KKK} \ K^6$ 

-  $\Lambda_{JJJJ} [J(J+1)]^4 - \Lambda_{JJJK} [J(J+1)]^3 K^2 - \Lambda_{JJKK} [J(J+1)]^2 K^4 - \Lambda_{JKKK} J(J+1) K^6 - \Lambda_{KKKK} K^8$  ....

 $\langle v:J,K|H| v:J,K \pm 2 \rangle = [\frac{1}{B} - \delta_J J(J+1) - \delta_K \{(K \pm 2)^2 + K^2\}$ 

 $+ \phi_{JJ} \left[ J(J+1) \right]^2 + 1/2 \phi_{JK} \left[ J(J+1) \right] \left\{ (K \pm 2)^2 + K^2 \right\} + 1/2 \phi_{KK} \left\{ (K \pm 2)^4 + K^4 \right\}$ 

-  $\lambda_{JJJ} [J(J+1)]^3 - \lambda_{JJK} [J(J+1)]^2 \{(K \pm 2)^2 + K^2\} - \lambda_{JKK} [J(J+1)] \{(K \pm 2)^4 + K^4\}$ 

-  $\lambda_{KKK} \{ (K \pm 2)^6 + K^6 \} \dots \} F_{\pm} (J,K) F_{\pm} (J,K \pm 1)$ 

```
where F_{\pm}(J,K) = \{ J(J+1) - K(K \pm 1) \}^{1/2}
\overline{B} = 1/2 (B-C)
```



wavenumbers / cmcHEIRON SCHOOL OCT 5, 2008

# **Spectroscopic issues to contend with**

- Overlapping & Hot bands
- Coupling of vibrational modes: Coriolis and Fermi resonnances
- Closely spaced lines & Narrow linewidths as the MW increases
- Isotope splitting
- Hyperfine structure

.... Clearly we need **high spectral** resolution in order to resolve these narrow spectral lines!

How high a resolution is required?

**Observed Linewidth:**  $\Delta v_{Obs} \sim \sqrt{\Delta v_{Dop}^2 + \Delta v_{col}^2 + \Delta v_{ILW}^2}$ 

Different factors contribute to the width of an observed transition

Doppler width,  $\Delta v_{\rm D} = 2 v \sqrt{2 \ln 2k/c^2} \sqrt{T/M} \sim 7.16\text{E-7} v \sqrt{T/M}$ Pressure broadening,  $\Delta v_{\rm col} = 16 p r^2 / \sqrt{\pi M k T} \sim 3\text{E-4 cm}^{-1} / \text{Torr}$ 

Instrument linewidth  $\equiv \Delta v_{ILW}$  dictated by apodisation function

**Therefore, the observed linewidth can be minimised by reducing the Temperature and Pressure!** 

# **Spectroscopic issues to contend with**

- Small quantity of sample to minimize Pressure broadening effects or hard to synthesize
- Isotopologues with low natural abundance
- Weak absorbers

.... Need bright source!

# **II. SYNCHROTRON INFRARED LIGHT**

#### Infrared mission from a synchrotron bending magnet

#### **Edge Radiation and Bending Magnet Radiation**



# Port 02B1-1 @ CLS: Far-IR



It's thetsynchrotrophorightness/thansounts\_\_



# SR Advantages over thermal sources

- Brightness: better S/N
- Small source: better throughput with small samples
- Highly collimated: higher resolution achievable
- Polarized: ellispsometry
- Pulsed: pump & probe experiments

# **Far-IR SR wavelength limits**

• Height of dipole chamber:

$$\lambda_o = 2h\sqrt{h/R}$$

where *h* is the height of the dipole chamber and *R* the radius of the bend magnet

• Extraction aperture:

 $\lambda_c = R(\Theta_{Nat}/1.66188)^3$ 

where  $\Theta_{Nat}$  represents the vertical angle in radians

# **EXTRACTION OF SYNCHROTRON IR RADIATION**

#### 2. Mirror M1 inserted into dipole "crotch" from above or below



#### 2. Mirror M1 inserted into dipole "crotch" from above or below

e.g. Soleil, ESRF...







#### M1 Mirror with thermocouple wires



Top view of mirror insertion port
## 3. Mirror inserted into dipole chamber from side

#### e.g. Australian Synchrotron





### Which brings us to...

## III. The Australian SYNCHROTRON INFRARED BEAMLINE

#### Adapted Infrared Dipole Chamber at Australian Synchrotron





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.

**Far-IR & High-Res Beamline** 

**Microscope beamline** 

## SR beamsplitter vacuum chamber

#### Visible light in the beamsplitter vessel at the Australian Synchrotron Infrared beamline





## IR beam profile – comparison with SRW



## **INFRARED BEAMLINE INSTRUMENTATION**

Infrared Beamline at the Australian Synchrotron Microscope Branch

Confocal point scanning Street Current technology

Transmission Trans-Reflection Grazing Incidence Angle Attenuated Total Reflectance

Bruker V80v with Hyperion 3000 microscope

 $50{\times}50~\mu m^2$  Narrow-Band MCT  $250{\times}250~\mu m^2$  Wide- Band MCT Option for bolometer



**Microscope Branch** 

### Focal Plane Array - next technology

#### 64x64 photovoltaic MCT Focal Plane Array



### **Infrared Beamline at the Australian Synchrotron High Resolution branch**



OPD: 942 cm  $\rightarrow$  resolution  $\geq$  0.00096 cm<sup>-1</sup> (0.1  $\mu$ eV) Optics: f/6.5

#### **Bruker IFS 125HR FTIR Spectrometer**

#### **Beamsplitters**

- Multi/Mylar
- Ge/KBr
- $30 630 \& 12 35 \text{ cm}^{-1}$ 450 – 4 800 cm<sup>-1</sup>

#### **IR Detectors**

- Si bolometer 10 370 cm<sup>-1</sup>
- Si:B bolometer 300 1850 cm<sup>-1</sup>
- DTGS
  - $100 3000 \text{ cm}^{-1}$ 700 – 5 000 cm<sup>-1</sup>
- MCT<sub>N</sub> • MCT<sub>M</sub>

600 – 5 000 cm<sup>-1</sup>

#### Sources

- Synchrotron mw vis
- Hg-Arc lamp 5 1 000 cm<sup>-1</sup>
- Globar 10 13 000 cm<sup>-1</sup>
- Tunsten lamp 1 000 25 000 cm<sup>-1</sup> **Optical Filters**
- series of narrow band pass IR filters Apertures
- 0.5 <u>- 12.5 mm</u> <u>CHEIRON SCHOOL OCT 5, 2008</u>



Recall ....

## **Observed Linewidth:** $\Delta v_{Obs} \sim \sqrt{\Delta v_{Dop}^2 + \Delta v_{col}^2 + \Delta v_{ILW}^2}$

# Therefore, the observed linewidth can be minimised by reducing the Pressure and Temperature!

**50 cm Multipass gas cell for high resolution spectroscopy of room temperature samples** Small quantity of sample to minimize Pressure broadening effects



Recall that Absorbance  $\alpha$  *scl* where *c* is the concentration and *l* the interaction path.

#### MCT detector

## Australian Synchrotron

**Enclosive Flow Cooling** multipass cell for gas-phase studies at cryogenic temperatures.



N<sub>2</sub>O mid-IR spectrum (0.002 cm<sup>-1</sup>)



## **More Scientific Apparatus**

#### **Grazing Incidence Angle Cell**



**Diamond Anvil Cell** 



**Supersonic Jet Expansion chamber** 

## IR Cryostat for matrix isolation studies Low freq. vibrations of biological samples



#### Down to 10 K!

**Minimise H<sub>2</sub>O interference Increase Absorption coefficient for a range of substances** CHEIRON SCHOOL OCT 5, 2008

## Assessing beamline performance

## **Performance of the microscope beamline**

#### Synchrotron infrared beam focused on sample



Beamline 11 at SRS - unapertured beam profile at sample stage. Area mapped =  $30x30 \ \mu m$ . Beam halfwidth =  $8x8 \ \mu m$ .

#### Advantage of using a synchrotron seen in spectra...



Absorbance spectra of tissue sample recorded at 10  $\mu$ m spatial resolution under identical collection conditions using a Globar<sup>TM</sup> infrared source and synchrotron radiation.



**CHEIRON SCHOOL OCT 5, 2008** 

#### Testing the IR Beamline Performance with Custom Resolution targets



Y[No Y-unit defined]

## WAVELENGTH DEPENDENCE OF MICROSCOPE SPATIAL RESOLUTION DEMONSTRATED AT INFRARED BEAMLINE



Polymer pattern on CaF<sub>2</sub> produced by photolithography

IR absorbance image At 2935 ±125 cm<sup>-1</sup> CH band region

IR absorbance image At 1701 ±59 cm<sup>-1</sup> C=O band region

## **Performance of the far-IR beamline**





10<sup>-13</sup> × Photons/s/0.1%BW

Spectrum of Pyrrole at 0.001 cm<sup>-1</sup> resolution



## IV. Introduction to Fourier transform Infrared spectroscopy

## Fourier transform spectroscopy





 $\mathbf{Res} = \mathbf{0.9} / \mathbf{OPD}$ 

### OPD = SCL/2

#### **CHEIRON SCHOOL OCT 5, 2008**

Many frequencies are present in the infrared beam

– Position of "zero path difference" CHEIRON SCHOOL OCT 5, 2008

## Summing of all frequencies for each position of the mirror



Position of "zero path difference"

## **Data output from FTIR system**





## **Pros and Cons of Fourier transform spectrometry**

## **Advantages over grating spectrometers**

- Felgett or Multiplex
- Jacquinot or throughput: apertures instead of slits
- High wavenumber accuracy: sampling  $\lambda_{HeNe}/2$
- High resolving power:  $\sim 10^6$
- Fast

## Disadvantages

- Complex system (but can be used as a black box by Users)
- Expensive ....
- Can take a lot of room!



## V. APPLICATIONS OF SYNCHROTRON INFRARED LIGHT

## **Applications of synchrotron IR radiation with a microscope**

## **ATR objective**

2790-2989 cm<sup>-1</sup>

837-1165 cm<sup>-1</sup>

Cross sections of agricultural soils: analysis of distribution and forms of carbon functional groups



19<sup>th</sup> century parchment sample



#### Forensic examination of paper documents



10 microns aperture, 5 microns steps

Peter Fisher, Matt Kitching (DPI Victoria) / Simon Lewis, Bill van Bronswijk (Curtin University) Kenneth Paul Kirkbride, Vincent Otieno-Alego (AFP) / Alana Treasure, @uterr@sections.com/sec



## **Grazing angle objective**







Plasma polimerisation technique used to produce high throughput gradient PEG (poly (ethylene glycol) based films on a nanometer scale.

Systematically varied chemistry by altering the plasma processing conditions.

Study the mechanism of protein repellant properties of PEG coatings.

Donna Menzies, Thomas Gengenbach, Celesta Fong, John Forsythe, Ban Muir ON SCHOOL OCT 5, 2008

## SINGLE CELL WORK

#### Live Human Mesenchymal Stem Cells





#### **Fixed mouse Oocyte Cell**

#### Live Leukaemia Cells





#### **Fixed Malaria infected RBCs**



**CHEIRON SCHOOL OCT 5, 2008**
# Response of single living phytoplankton cells to changes in the environment

#### Lipid concentration FTIR maps





Freshwater alga Micrasterias hardyi.

#### Phil Heraud, Sally Cane, Anthony Eden, Don McNaughton, Baydeo Mooashs University

## Applications of synchrotron IR radiation with a High-Resolution FT spectrometer

**Molecular species of Astrophysical interest** 

prototype system for torsional motion
Intramolecular Vib<sup>1</sup> Redistribution
Earth and Jovian atmospheres
Pluto: clues to evolution early solar system

Australian Synchrotron

## **Molecular species of Astrophysical interest**

Telescope missions in the submillimeter region for the study of star formation

- Herschel Space Observatory (2008, 3-4 years)
- Stratospheric Observatory for Infrared Astronomy: SOFIA (2010, 20 years)
- Atacama Large Millimeter Array: ALMA (2011, decades)

Astrophysical weed-molecules & their isotopologues

-Class I: CH<sub>3</sub>OH, HCOOCH<sub>3</sub>, CH<sub>3</sub>OCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>CN



### Far-IR spectroscopy of aromatic cycles containing heteroatoms

Dennis Tokaryk (U. of New Brunswick) & Jen van Winjgaarden (U. of Manitoba)



#### These heterocycles and their derivatives are:

- building blocks of organic chemistry

  -pharmaceuticals, agrochemicals, dyes

  constituents of biologically active molecule such as heme and chlorophyll
- byproducts of combustion processes
- candidates for interstellar detection
- solvents/additives in industrial processes
  naturally found in wood, petroleum



### Samples of Environmental interest

Spotted Tiger Muscovite – self supported crystal: Mylar multilayer beamsplitter, Si Bolometer



Strong positive pleochroism at 146 cm<sup>-1</sup> – implies out-of-plane mode Slight negative at 167,189, 264 cm<sup>-1</sup> – implies in-plane mode No change at 110 cm<sup>-1</sup> – expected if interlayer cation 'rattle'

To better understand the dynamics of cation exchange reactions of important minerals, commonly used as environmental barriers to contaminated wastes such as radionuclides



## VI. COHERENT SYNCHROTRON RADIATION

## **Incoherent Synchrotron** < 100 cm<sup>-1</sup>

#### Bolometer / 6µm Mylar



# Coherent Synchrotron Radiation $P_{SR} \alpha N + N^2 e^{-(\omega \sigma_z/c)^2}$



**CHEIRON SCHOOL OCT 5, 2008** 

**CSR** at the CLS



## Australian Synchrotron N<sub>2</sub>O THz absorption spectrum



### Summary

- Synchrotrons provide intense beams at long wavelengths into the Far-IR
- IR spectroscopy is used to provide information on the chemical composition of materials based on the vibration of the bonds present.
- Synchrotron IR allows these measurements to be made rapidly at a few microns dimension (micoscope), or at low concentration (and high SPECTRAL resolution).
- Synchrotron IR has applications in a diverse range of research areas.
- Future developments in the field will allow imaging below the diffraction limit and the use of intense Far-IR and Terahertz beams CHEIRON SCHOOL OCT 5, 2008

#### Acknowledgements

- Dudley Creagh Canberra University
- Don McNaughton Monash Univerrsity
- Phil Heraud Monash Immunology and Stem Cell Laboratories
- Bayden Wood Monash University
- Liz Carter University of Sydney
- Peter Lay University of Sydney
- Mark Hackett University of Sydney
- Sally Caine Monash Immunology and Stem Cell Laboratories
- Vivienne Juan Monash Immunology and Stem Cell Laboratories
- Alice Brandli Monash University
- Cassie Jean Monash University
- Alana Treasure University of Canberra
- Bill van Bronswijk Curtin University
- Evan Robertson Monash University
- Ljiljana Puskar Monash University
- Tarekegn Chimdi Monash University
- Paul Dumas Soleil
- Mike Martin ALS
- Ulli Schade BESSY II
- David Moss ANKA
- Yves-Laurant Mathis ANKA
- Jonathan McKinlay Australian Synchrotron
- Nati Salvado University of Barcelona
- Azzedine Hammiche University of Lancaster
- John Prag Manchester Museum
- FMB Berlin
- Biolab/Bruker Instruments

Thanks...

Dominique Appadoo Australian Synchrotron 800 Blackburn Road Clayton 3168 VIC AUSTRALIA

Tel: (03) 8540 4127 Email: dominique.appadoo@synchrotron.vic.gov.au

## Infrared Spectroscopy

Energy range 0.001 eV to 1 eV (10 cm<sup>-1</sup> to 10,000 cm<sup>-1</sup>) **Property accessible** molecular vibrations & rotations Measurements vibrational & rotational spectra Information molecular structure, chemical analysis

**Synchrotron Benefits** signal to noise, spatial resolution (down to the diffraction limit)

**AS Contact Scientists** 

Dr Mark Tobin, 613 8540 4172 Dr Dominique Appadoo, +613 8540 4127 Dr Lillijana Puskar, 613 8540 4185



