Infrared Spectroscopy with Synchrotron Sources



Ferenc Borondics Mid-IR beamline Canadian Light Source

Cheiron 2011

SPring



Canadian Centre canadien Light de rayonnement Source synchrotron

Available online

http://midir.lightsource.ca/talks



Acknowledgements

Tim May





Brant Billinghurst

Luca Quaroni (SLS)



Outline

- IR spectroscopy basic theory
- IR instrumentation
- Some IR beamlines (CLS, ALS, NSLS, SRC...)
- Practical things
- Examples

Something to read...

SOFT X-RAYS AND EXTREME ULTRAVIOLET RADIATION

Principles and Applications



DAVID ATTWOOD

WILEY

FOURIER TRANSFORM INFRARED SPECTROMETRY

Second Edition

Peter R. Griffiths James A. de Haseth

Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications J. D. Winefordner, Series Editor

IR beamlines in the world



Source: http://infrared.als.lbl.gov



Sir William Herschel (1738-1822)





W. Herschel, Phil. Trans. R. Soc. London, Vol 90, 284-292, (1800)



With numbers...

Near-IR	12500 - 4000 cm ⁻¹	0.8 - 2.5 μm	1.55 - 0.5 eV
Mid-IR	4000 - 500 cm ⁻¹	2.5 - 20 μm	0.5 - 0.06 eV
Far-IR	500 - 5 cm ⁻¹	20 - 2000 µm	60 - 0.6 meV

What can we look at?

- Broad band electronic excitations
- Rotations
- Vibrations

Pro<u>cesses</u>



- Transmission
- Absorption
- Reflection

$$T = \frac{I}{I_0} = e^{-\varepsilon cl}$$

 $\begin{vmatrix} A = -logT = \varepsilon cl \\ R \end{vmatrix}$

An infrared spectrum





Energy

Basic optical functions

Goal: determine $\varepsilon(\omega)$, the dielectric function Information about the electronic structure

Measure: reflectivity, $r(\omega)$; transmittance, $T(\omega)$

 $\begin{aligned} & \textcircled{O} \quad \text{All of them are related} \\ & n = n' + (in'') = \frac{1+r}{1-r} = \frac{1+\sqrt{R}e^{i\Theta}}{1-\sqrt{R}e^{i\Theta}} \\ & R = \frac{(n'-1)^2 + n''^2}{(n'+1)^2 + n''^2} \\ & \epsilon_{rel} = \epsilon'_{rel} + (i\epsilon''_{rel}) = n^2 \end{aligned}$

Basic optical functions

Goal: determine $\varepsilon(\omega)$, the dielectric function Information about the electronic structure

Measure: reflectivity, $r(\omega)$; transmittance, $T(\omega)$

- All complex functions
- $\begin{aligned} & \textcircled{\odot} \quad \text{Kramers Kronig transformation} \\ & \Theta(\omega) = \frac{\omega}{\pi} \int_{0}^{\infty} \frac{\ln R(\xi) \ln R(\omega)}{\xi^2 \omega^2} d\xi \\ & \Theta(\omega) = -\frac{2\omega}{\pi} \int_{0}^{\infty} \frac{\ln T(\omega')}{\omega'^2 \omega^2} d\omega + 2\pi\omega d \end{aligned}$

Studies on low energy gaps

conduction band



Г-КК

General semiconductor

Graphene

Energy gaps of semiconductors

conduction band





Nanotubes

General semiconductor

Models to understand $\boldsymbol{\epsilon}$

Drude model

$$\epsilon_{rel} = \epsilon_{\infty} - \frac{\omega_{pl}^2}{\omega^2 + i\epsilon}$$





 $\omega_{pD} = \sqrt{\frac{n_e e^2}{m^* \varepsilon_0}}$

Models to understand ϵ



Vibrations

Harmonic oscillator Hooke's law F = ma $m\frac{d^2x}{dt} = -kx$

Potential energy $V = \frac{1}{2}kx^2$



Diatomic molecule, harmonic oscillator

BH 2400

2.04

CH 3000

2.55

OH 3600

$$x = r - r_{eq}$$
$$\mu = \frac{m_1 + m_2}{m_1 m_2}$$



$$-kx = F = \mu \ddot{x}$$
$$x(t) = X_0 sin(\omega t + \phi)$$

0

5

$$m_1$$
 m_2

OH 3600

3.44

FH 4000

3.98

NH 3400

3.04

OD 2600

$$-kx = -4\pi^{2}\nu^{2}x\mu$$

$$\tilde{\nu} = \frac{1}{2\pi d} \sqrt{\frac{kk}{\mu\nu}}$$

Diatomic molecule, ideal case (alone)



Diatomic molecule, realistic case (solution)



Diatomic molecule, realistic case (solution)



Molecular vibrations Quantized oscillator

Energy levels $E_{\nu} = \hbar \omega (\nu + \frac{1}{2})$



Anharmonicity

Diatomic molecule, anharmonic



Anharmonicity

Diatomic molecule, anharmonic



of molecular vibrations

3N-6 degrees of freedom $H_2O \rightarrow 3x3-6=3$ or 3N-5 for linear molecules $CO_2 \rightarrow 3x3-5=4$



More atoms

Polyatomic molecule, ideal case, harmonic



More atoms

Polyatomic molecule, real case, anharmonic



ocw.mit.edu – 5.61 – Physical Chemistry

Larger molecules?



Chromophores

Holt et al. Biochem J. 314, 1035-1039 (1996)



IR active vibrations

Selection Rules R:
$$\frac{\partial \mu}{\partial q} \neq 0$$
 Raman: $\frac{\partial \alpha}{\partial q} \neq 0$

Group theory



If there is an inversion symmetry IR≠Raman

Simplifying factors

- Chromophore groups
- Selection rules
- Symmetry



Characteristic frequencies



Influencing factors

Shifts



Rotations





 Δj =-1 Δj =0 Δj =+1

Rotational spectrum example Nitrous Oxide



Frequency / cm^{-1} Note: spectral range \rightarrow high resolution

Spectrometer designs

Dispersive



Slow, but simple Resolution, throughput, etc...


Spectrometer designs

Fourier Transform

Michaelson interferometer



FT spectroscopy advantages

- Connes advantage: internal calibration He/Ne
- Jacquinot advantage: interferometer is bright
- Fellgett advantage: all ${f v}$ in the same time
- No stray light

 Σ : FT is 2000x more sensitive than dispersive

A spectrometer layout



A – source

- B beamsplitter
- C sample
- D detector



Michaelson interferometer



Resolution

$$FT: f(\omega) = \int_{0}^{\infty} F(x)$$

$$f(\omega_i) = \sum_{i=0}^{\infty} F(x_i) \text{ discrete}$$

$$f(\omega_i) = \sum_{i=0}^{N} F(x_i) \text{ Resolution!}$$

Solutions: Zero filling – looks nicer, but useless Pathlength – real information

Size matters

Bruker Alpha

Bruker 125hr



A4 paper size



Moving mirror - meters

http://infrared.als.lbl.gov

Conventional Light Sources



www.brukeroptics.com/downloads.html

Detectors



Beamsplitters



IR Sources - a comparison -

Black body radiation GLOBAR – SiC rod, resistive heating





Using moving charges

Dipole radiation





http://ocw.mit.edu

 $\nu \ll c$

 $u \sim c$



 $\nu \sim c$



Synchrotron radiation

Insertion devices Radiation2D



Bending magnet radiation



Problem: source size, focusing

e⁻ beam

Bending magnet

Which one is better?





Globar

SR

Globar wins

 \odot



Total flux (CLS)

Synchrotron wins







Brightness (CLS)

High-resolution spectroscopy

Pathlength and resolution



Source size (pinhole)



http://www.newport.com/images/web600w-EN/images/2407.gif

SR advantage – low res?



35-350 cm⁻¹ | Resolution: 0.002 cm⁻¹ | <u>Aperture: 3.15 mm</u> | Velocity: 30 KHz / 5KHz

SR advantage



35-350 cm⁻¹ | Resolution: 0.00096 cm⁻¹ | Aperture: 2 mm | Velocity: <u>30 KHz / 5KHz</u>

SR advantage



SR advantage



500-1000 cm⁻¹ | Resolution: 0.001 cm⁻¹ | Aperture: 1.15 mm | Velocity: 40 KHz

Applications

High resolution FTIR on gases

Important for Astronomy
(interstellar gases, small molecules)

Atmospheric sciences

(ozone, pollution, radicals)

Basic physical chemistry

(molecular dynamics, radicals, etc...)

Sample preparation



Multi-pass cells



Gas cells





- 30 cm White Cell
- Ambient Temperature
- Paths up to 12 m

- 2 m White Cell
- Coolable (down to -80 °C)
- Paths up to 80 m

Gas cells (discharge)



1 m White Cell
Adjustable Power
4 m Path

The CLS high resolution IR BL



Bruker IFS 125 HR Maximum Resolution: 0.00096 cm⁻¹ ~0.1 μeV

Beamsplitter	Spectral Range
Mylar 6 µm	30-630 cm ⁻¹
Mylar 75 µm	12-35 cm ⁻¹
Ge/KBr	400-4800 cm ⁻¹
CaF ₂	1850-20000 cm ⁻¹
Detectors	
MCT N	600-10000 cm ⁻¹
МСТ В	450-10000 cm ⁻¹
DTGS	100-3000 cm ⁻¹
DTGS PE	15-700 cm ⁻¹
Si Bolometer	10-370 cm ⁻¹
Ge:Cu	300-1850 cm ⁻¹
Internal Sources	
Globar	10 – 13000 cm ⁻¹
Hg – Lamp	10 – 1000 cm ⁻¹
Tungsten Lamp	1000-25000 cm ⁻¹

More information

The CLS Far IR website: http://goo.gl/idUP

Brant Billinghurst







- microspectroscopy or spectromicroscopy -

Theoretical optical resolution Rayleigh's Resolution Limit $d = \lambda/2NA$

(Diffraction Limit)

Intensity Distribution at the Focal Point



 $NA = nsin(\theta)$

 \boldsymbol{P} θ

General Layout



The Schwarzschild objective






Globar

SR

Why use a synchrotron?





Globar Light Spot in Plane of Confocal Aperture Synchrotron Light Spot in Plane of Confocal Aperture

Beam spot in the CLS



Beam spot in the CLS



Globar vs. Synchrotron



Globar vs. synchrotron 2x2 μm pinhole 5x5 μm pinhole

$3x3 \ \mu m$ pinhole

10x10 µm pinhole



Globar vs. synchrotron

6x6 μm aperture (single cell)



Spatial resolution



Spatial resolution...



Diffraction limited resolution can be achieved only by SR

...diffraction limited



Infrared beamlines - some examples -

Canadian Light Source Mid-IR



SHADOW Beam shapes on mirror surfaces for 25 micron wavelength. M1

synchrotron

Canadian Light Source Mid-IR



Advanced Light Source, BI 5.4



~10 m

+ Beamline 1.4

NSLS VUV-IR ring

- U2A Geophysics, materials at extreme pressures and microspectroscopy
- **U2B** Mid-IR microspectroscopy
- **U4IR** Instrumentation development
- **U10A** Far-IR microspectroscopy
- **U10B** Mid-IR microspectroscopy
- **U12IR** Far-IR, THz and millimeter wave spectroscopy. Materials physics

Shutting down soon because of NSLS II

IRENI beamline, SRC



IRENI beamline, SRC



Focal Plane Array



Thermal source ATR linear array (1.56 μm) Point mapping (10 μm)

74× FPA (0.54 μm)

Multi-beam synchr. source 74× FPA (0.54 μm)

Nasse et al., Nature Methods 2011, DOI:10.1038/nmeth.1585

SPring-8, BL43B

Three IR endstations





- spectromicroscopy
- magneto-optical spectroscopy
- high-pressure studies
- near field microscopy

- samples and measurement techniques -

Sample forms



Multi-pass cells



Sample forms

Liquids







Transmission

Reflection

Reflection-absorption Transflecion

Self supporting Lying on substrate Suspended in carrier KBr Nujol

Reflection setups

Regular Convenient

Sample Substrate

Very thin samples Grazing angle incidence

Special microscope objectives Increases optical pathlength Monolayers Sub-monolayers

Sample Substrate



Reflection setups

We are happy



Not so lucky



DRIFTS Diffuse reflection Integrating sphere



Application:PowdersCatalysis!!!

Reflection setups Total internal reflection

n_2 n_1 θ_2 θ_1

$$\Theta_c = \sin^{-1}\left(\frac{n_1}{n_2}\right)$$
$$E_T = E_0 e^{-z/d_p}$$
$$d_p = \frac{\lambda}{\sqrt{1-2\lambda^2}}$$

$$= \overline{2\pi n_1 \sqrt{\sin^2\theta - n_{21}^2}}$$





Reflection setups

Attenuated total internal reflection



Single reflection Surface sensitive Microscopy $d = \frac{\lambda}{2NA}$ $NA = nsin(\theta)$

Reflection setups

Attenuated total internal reflection



Possible problems

Samples are not ideal...thickness/roughness



Life gets very complicated

Samples are not ideal...



$$\begin{aligned} & \text{Mie Scattering} \\ Q &= 2 - \frac{4}{p} \sin p + \frac{4}{p^2} (1 - \cos p) \\ & p &= 4\pi a \frac{n - 1}{\lambda} \\ & a : r_{sphere} \\ & n &= \frac{n_{inside}}{n} \end{aligned}$$

 $n_{outside}$

Mohlenhoff et al., Biophysical Journal 88, 3635-3640, (2005)

Samples are not ideal...scattering.





FIGURE 5 IR spectrum of oral mucosa cell (*bottom*), and scattering spectrum for a dielectric sphere with $a = 4.2 \ \mu m$ (*top*).

Mohlenhoff et al., Biophysical Journal 88, 3635-3640, (2005)

Artifacts? – solutions...

- Second derivatives
- EMSC (extended multiplicative scattering correction)
- Mie Scattering corr., Resonant Mie Scattering corr.

- How to differentiate spectra? Cytospe
- Statistical analysis
 - Cluster analysis
 - Principal Component Analysis
 - Partial Least Squares regression
- Cytospec R, Matlab, Eigenvetcor The Unscrambler

Artifacts? – RMieSc

Samples are not ideal... resonant scattering.

Amide I – 1641 cm⁻¹ β -sheet, random

Amide I – 1650 cm⁻¹ random, turns

Amide I – 1654 cm⁻¹ α -helix

Bassan et al., The Analyst 135, 268-277, (2010)



Artifacts? – RMieSc...

Samples are not ideal...resonant scattering.



Artifacts? – RMieSc...

Samples are not ideal...resonant scattering.



Bassan et al., Analyst 135, 268-277 (2010)



Does the synchrotron light heat the sample?



Synchrotron source: Measured 1 mW focused onto ~10 X 10 μm^2

DPPC = dipalmitoylphosphatidylcholine, a phospholipid bilayer

Undergoes a gel to liquid-crystalline phase transition at T= 316 K



Important: No Evidence for Cytotoxic Effects on Living Cells

M.C. Martin et al., Applied Spectroscopy 55, 111 (2001)
SR IR spectroscopy - applications -

The Burgess Research Group

Kinetics: problem RC time constant of the electrode solution: decrease size

Small electrode size \sim 10 μm







Rosendahl SM; Borondics F; May T; Pedersen T; Burgess I, Anal. Chem. 83 (10), 3632-3639, 2011.





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Rosendahl SM; Borondics F; May T; Pedersen T; Burgess I, Anal. Chem. 83 (10), 3632-3639, 2011.



Two-dimensional atomic crystals

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Exfoliation (Scotch tape-ing)

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Exfoliated superconductors

L.J. Sandilands et al., PRB 82, 064503 (2010)



Bi₂Sr₂Ca_{1-x}Dy_xCu₂O_{8+δ} x=0.3,0.4



http://www.physics.utoronto.ca/~kburch/



Biology





de ravonnement

Spectromicroscopy in Rod Cells





Measurement of molecular orientation in a subcellular compartment by synchrotron infrared spectromicroscopy

Quaroni et al., ChemPhysChem 9 (10) 1380-1382, 2008

Results – polarization studies



The measurement confirmed previous results obtained by crystallography on model systems.



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Others

Chemical Imaging

Biology, medicine, etc.

...Materials Science



of pixels: 128*128 = **16384**

Something to remember

Synchrotron = high brightness

Diffraction limited resolution Small samples!

High spectral resolution

Data processing...another story



Resources

- CLS Mid-IR webpage http://midir.lightsource.ca
- ALS Infrared beamlines http://infrared.als.lbl.gov
- William Reusch: Virtual Textbook of Organic Chemistry http://goo.gl/NEUW
- David Attwood SR course (EE290f) at UC Berkeley (http://www.youtube.com/watch?v=1WWnxA6odso)
- Wolfram Demonstrations Project (<u>http://demonstrations.wolfram.com</u>)
- Synchrotron Simulator
 T. Shintake, Nuclear Instruments and Methods in Physics, 507 (1-2), 89-92 (2003) (http://www-xfel.spring8.or.jp/dlmonitor.html)

Contact

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