

Infrared Spectroscopy with Synchrotron Sources

September 30, 2013
Cheiron 2013 School
SPring-8
Hyogo, Japan

Ferenc Borondics
Mid-IR beamline
Canadian Light Source
Saskatoon, Canada SK



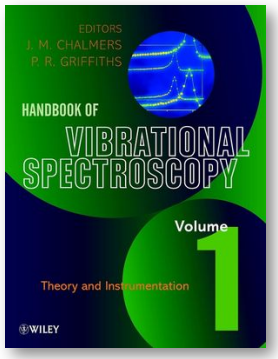


Cheiron 2013

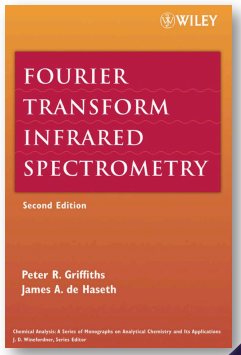
Outline

- IR spectroscopy – basic theory
- IR instrumentation
- Some IR beamlines (CLS, ALS, NSLS, SRC…)
- Exotic techniques – recent developments
- Practical things
- Examples

Something to read…



Five volumes

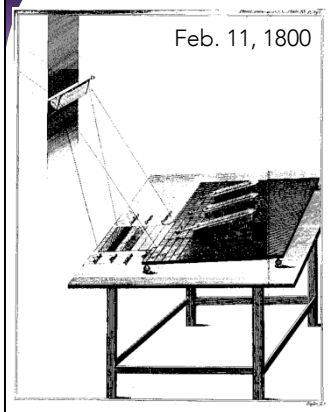


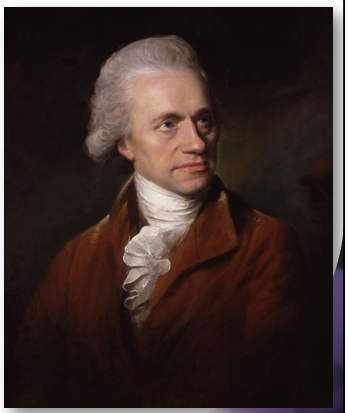
IR beamlines around the world



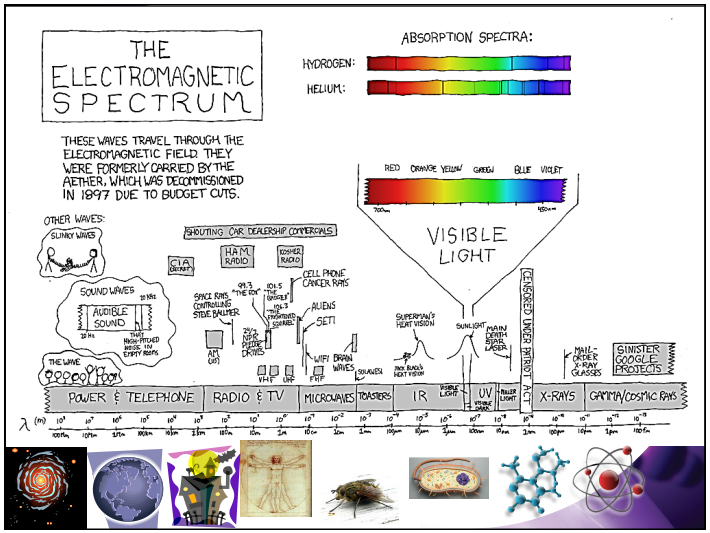
Source: http://infrared.als.lbl.gov

Sir William Herschel (1738-1822)





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



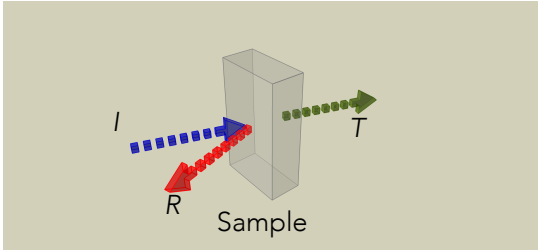
With numbers…

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?

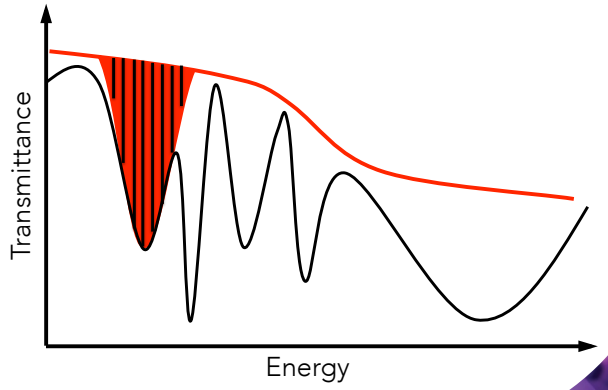
- Broad band electronic excitations
- Rotations
- Vibrations

Processes



- Transmission $T(\tilde{\nu}) = \frac{I(\tilde{\nu})}{I_0(\tilde{\nu})} = exp[-\alpha(\tilde{\nu})l]$
- Absorption $A(\tilde{\nu}) = -logT(\tilde{\nu}) = \alpha(\tilde{\nu})l$
- Reflection $R(\tilde{\nu}) = \frac{R_{sample}(\tilde{\nu})}{R_{ref}(\tilde{\nu})}$

An infrared spectrum



Basic optical functions

Goal: determine ε(ω), the dielectric function
Information about the electronic structure
Measure: reflectivity, r(ω); transmittance, T(ω)

☺ All of them are related

$$n = n' + in'' = \frac{1+r}{1-r} = \frac{1+\sqrt{R}e^{i\Theta}}{1-\sqrt{R}e^{i\Theta}}$$

$$R = \frac{(n'-1)^2 + n''^2}{(n'+1)^2 + n''^2}$$

$$\varepsilon_{rel} = \varepsilon'_{rel} + i\varepsilon''_{rel} = n^2$$

Basic optical functions

Goal: determine ε(ω), the dielectric function
Information about the electronic structure
Measure: reflectivity, r(ω); transmittance, T(ω)

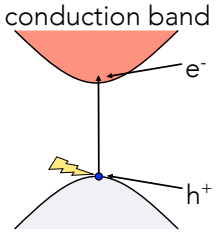
☹ All complex functions

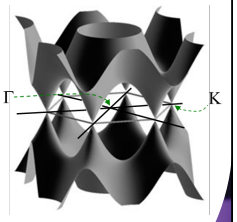
☺ Kramers Kronig transformation

$$\Theta(\omega) = \frac{\omega}{\pi}\int_0^{\infty} \frac{lnR(\xi) - lnR(\omega)}{\xi^2 - \omega^2} d\xi$$

$$\Theta(\omega) = -\frac{2\omega}{\pi}\int_0^{\infty} \frac{lnT(\omega')}{\omega'^2 - \omega^2} d\omega + 2\pi\omega d$$

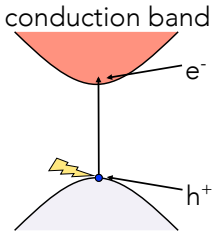
Studies on low energy gaps



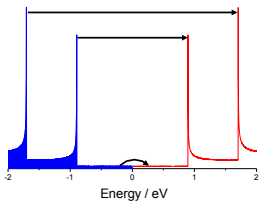


Graphene

Energy gaps of semiconductors



valence band
General
semiconductor

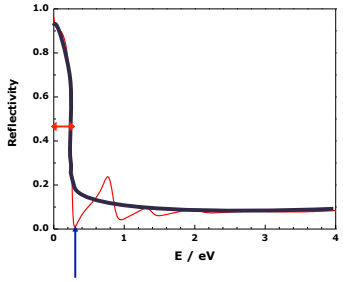


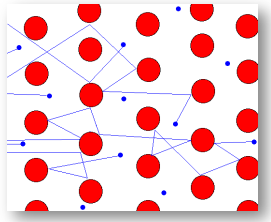
Nanotubes

Models to understand ε

Drude model

$$\varepsilon_{rel} = \varepsilon_{inf} - \frac{\omega_{pD}^2}{\omega^2 + i\gamma_D\omega}$$



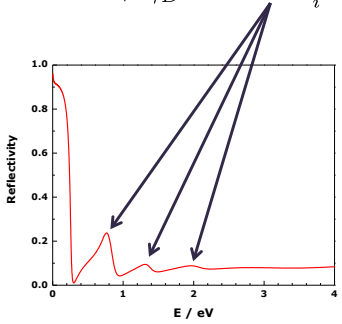


$$\omega_{pD} = \sqrt{\frac{n_e e^2}{m^* \varepsilon_0}}$$

Models to understand ε

Drude – Lorentz model

$$\varepsilon_{rel} = \varepsilon_\infty - \frac{\omega_{pD}^2}{\omega^2 + i\gamma_D\omega} + \sum \frac{\omega_{pi}^2}{\omega_i^2 - \omega + i\gamma_D\omega}$$

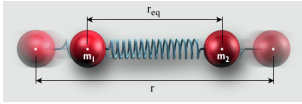


Molecular vibrations

Diatomic molecule, harmonic oscillator

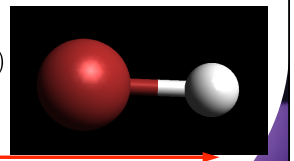
$$x = r - r_{eq}$$

$$\mu = \frac{m_1 + m_2}{m_1 m_2}$$



$$-kx = F = \mu\ddot{x}$$

$$x(t) = X_0 sin(\omega t + \phi)$$



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

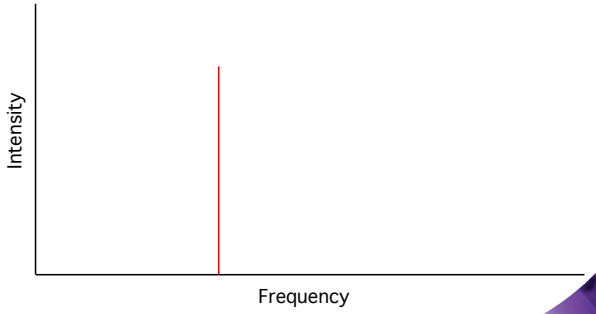
$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

BH	CH	NH	OH	FH
2400	3000	3400	3600	4000
2.04	2.55	3.04	3.44	3.98

OH 3600 OD 2600

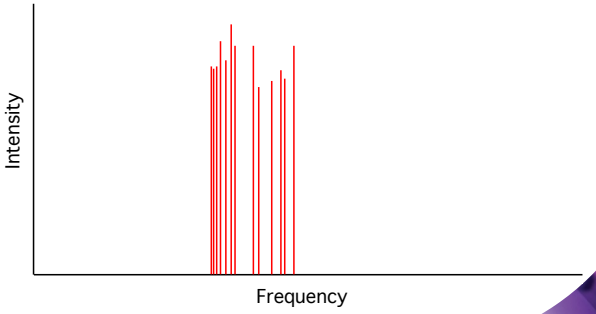
Molecular vibrations

Diatomic molecule, ideal case (alone)



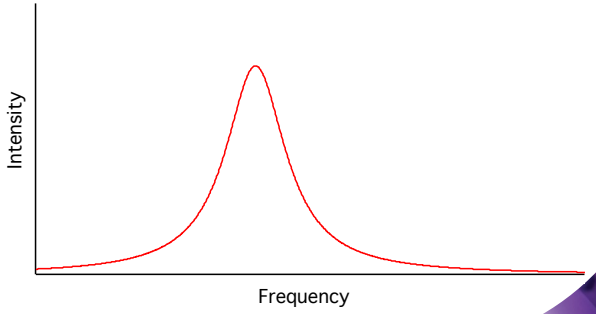
Molecular vibrations

Diatomic molecule, realistic case (solution)



Molecular vibrations

Diatomic molecule, realistic case (solution)

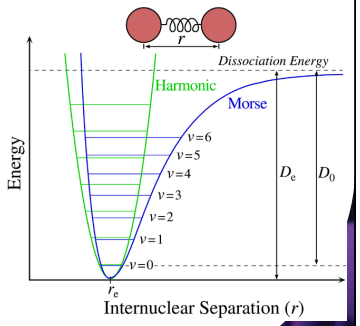


Molecular vibrations

Quantized oscillator

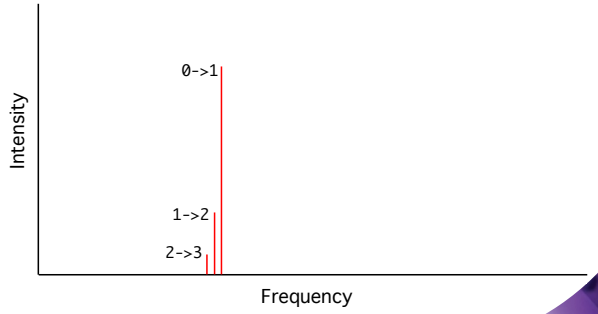
Energy levels

$$E_\nu = \hbar\omega_0\left(\nu + \frac{1}{2}\right)$$



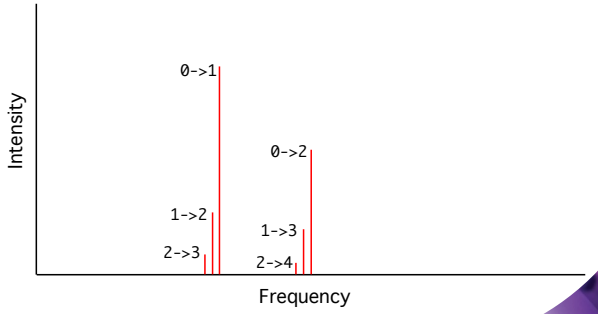
Anharmonicity

Diatomic molecule, anharmonic



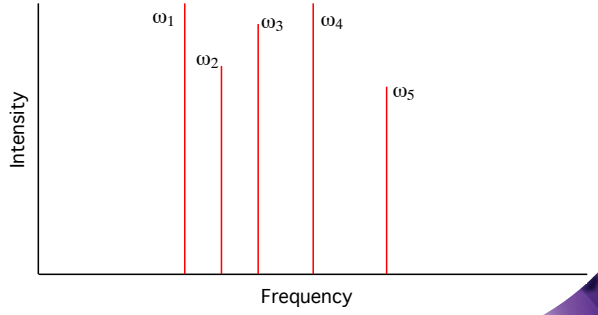
Anharmonicity

Diatomic molecule, anharmonic



More atoms

Polyatomic molecule, ideal case, harmonic



of molecular vibrations

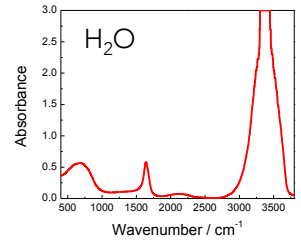
3N-6 degrees of freedom

or

3N-5 for linear molecules

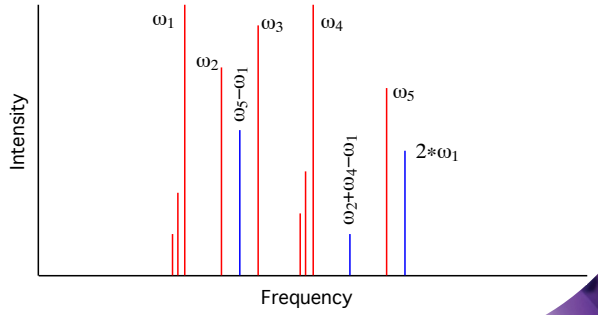
H_2O → 3x3-6=3

CO_2 → 3x3-5=4

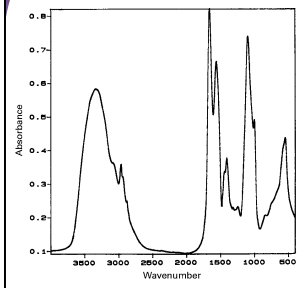


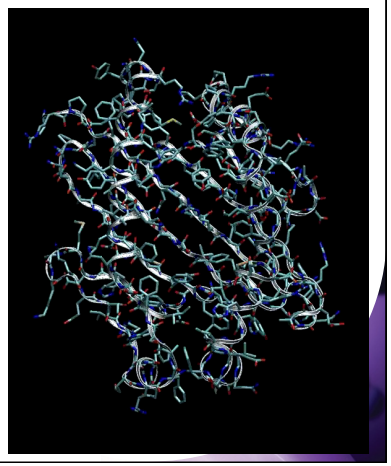
More atoms

Polyatomic molecule, real case, **an**harmonic



Larger molecules?





Chromophores

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

IR active vibrations

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

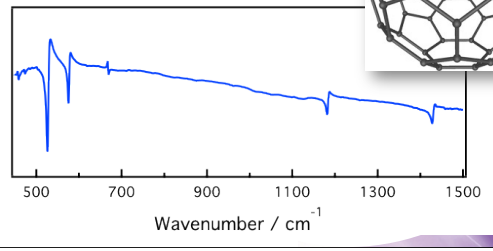
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z, xy
B_1	1	-1	1	-1	x, R_y, xz
B_2	1	-1	-1	1	y, R_x, yz

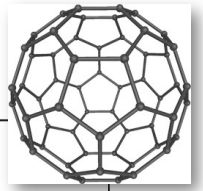
Example: H_2O

If there is an inversion symmetry IR≠Raman

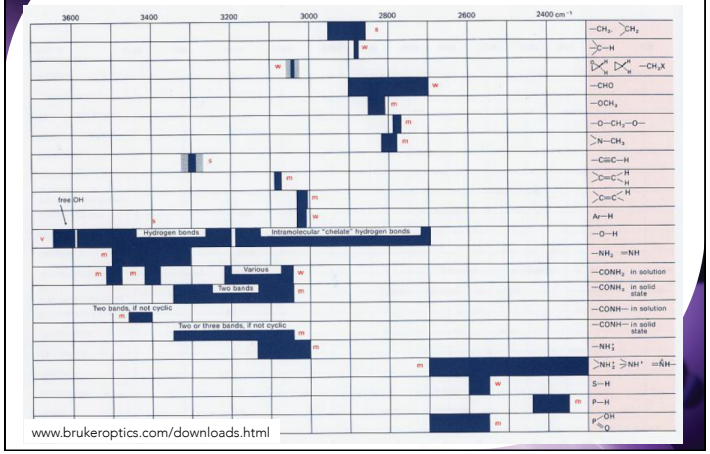
Simplifying factors

- Chromophore groups
- Selection rules
- Symmetry



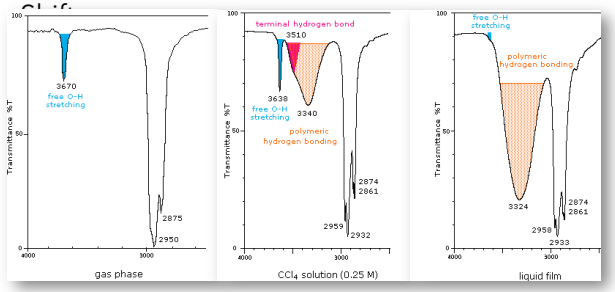


Characteristic frequencies

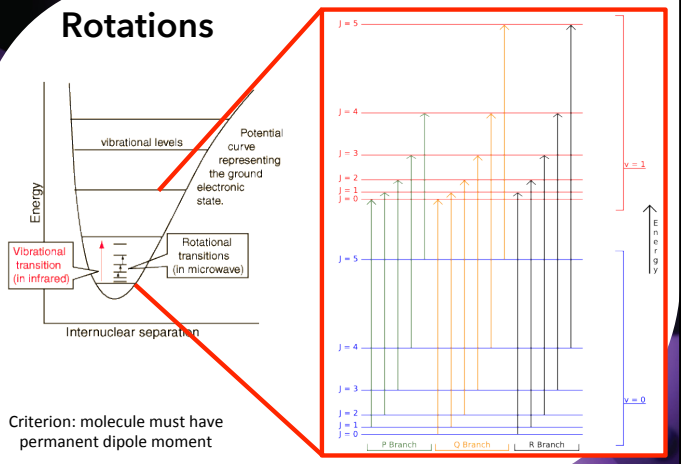


www.brukeroptics.com/downloads.html

Influencing factors



Rotations

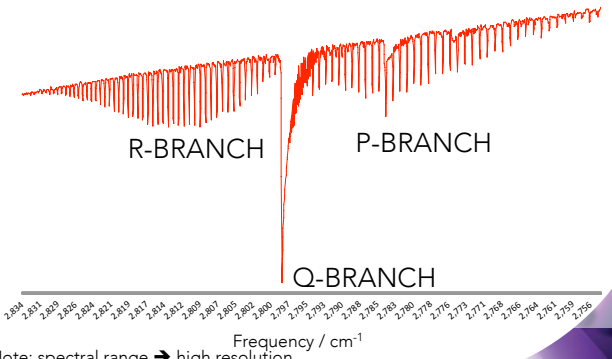


Criterion: molecule must have permanent dipole moment

$\Delta j=-1 \quad \Delta j=0 \quad \Delta j=+1$

Rotational spectrum example

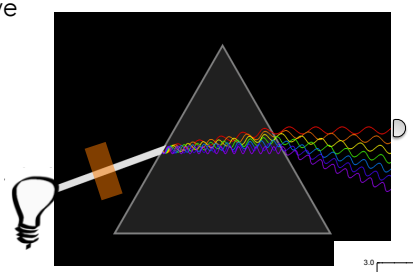
Nitrous Oxide

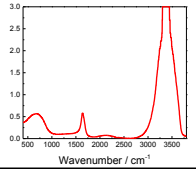


Note: spectral range ➔ high resolution

Spectrometer designs

Dispersive

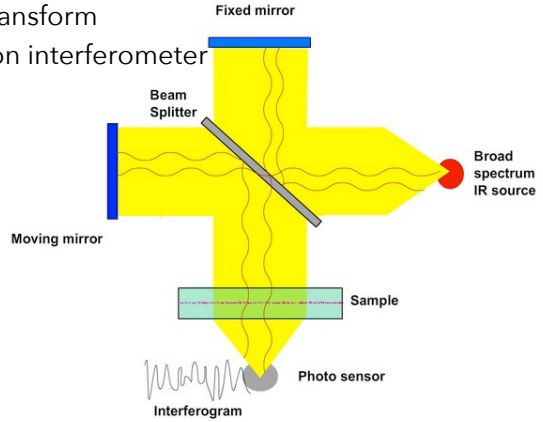




Slow, but simple
Resolution, throughput, etc…

Spectrometer designs

Fourier Transform
Michaelson interferometer

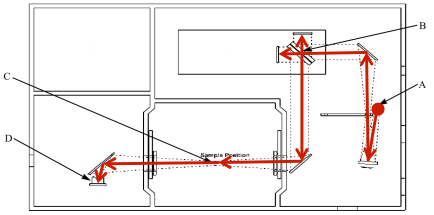


FT spectroscopy advantages

- Connes advantage: internal calibration He/Ne
- Jacquinot advantage: interferometer is bright
- Fellgett advantage: all **n** in the same time
- No stray light

∑: FT is 2000x more sensitive than dispersive

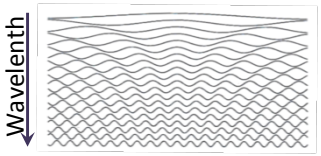
A spectrometer layout



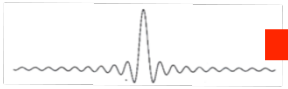
A – source
B – beamsplitter
C – sample
D - detector

FT-IR

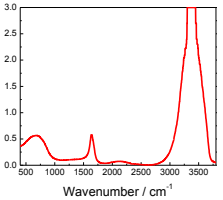
Michaelson interferometer



$$I(x,\tilde{\nu}) = I_0(\tilde{\nu})cos(2\pi\tilde{\nu}x)$$



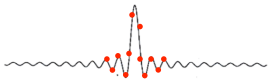
FT



$$I(x) = \int_0^{\infty} I(x,\tilde{\nu})d\tilde{\nu} \qquad I(\tilde{\nu}) = \int_{-\infty}^{+\infty} I(x)cos(2\pi\tilde{\nu})dx$$

Resolution

FT: $f(\omega) = \int_0^{\infty} F(x)$



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

Nyquist: $\omega_{max} = \frac{1}{2\Delta x}$

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



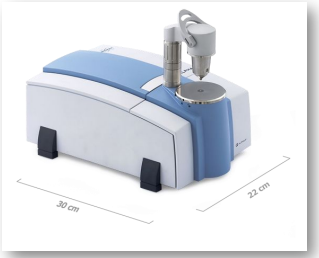
Solutions:

Zero filling – looks nicer, but useless

Pathlength – real information

Size matters

Bruker Alpha



A4 paper size

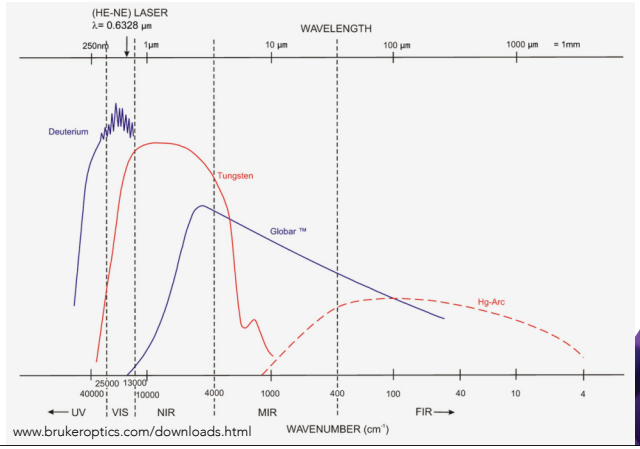
Bruker 125hr



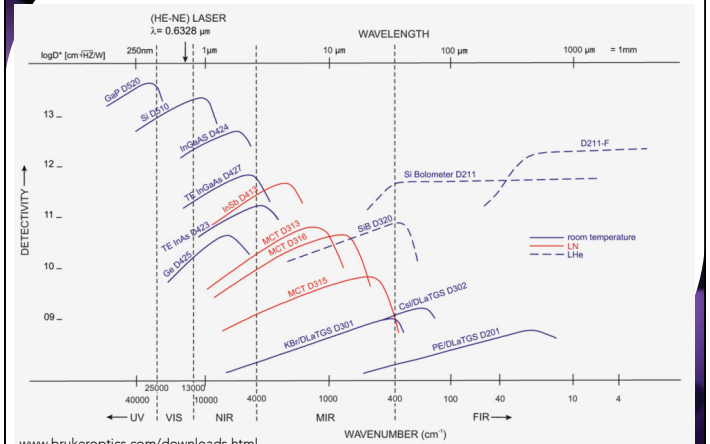
Moving mirror - meters

http://infrared.als.lbl.gov

Conventional Light Sources

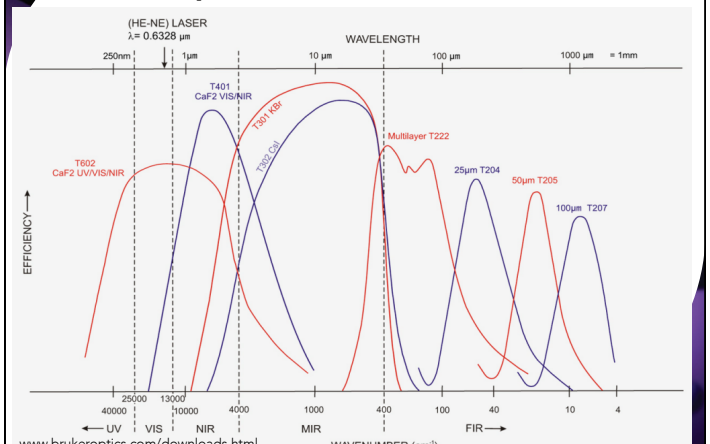


Detectors



www.brukeroptics.com/downloads.html

Beamsplitters



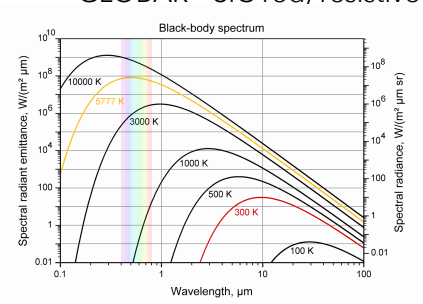
www.brukeroptics.com/downloads.html

IR Sources
- a comparison -

Producing IR light

Black body radiation

GLOBAR – SiC rod, resistive heating

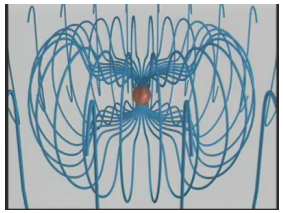


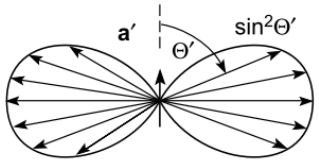


Producing IR light

Using moving charges

Dipole radiation



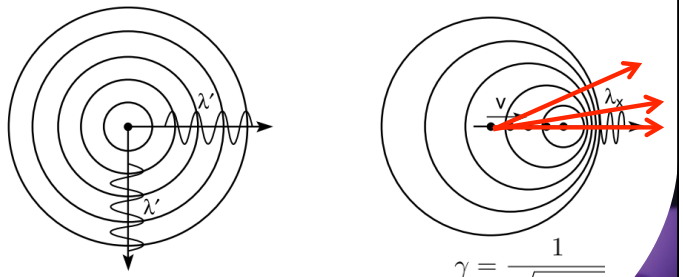


http://ocw.mit.edu

Producing IR light

$\nu \ll c$

$\nu \sim c$



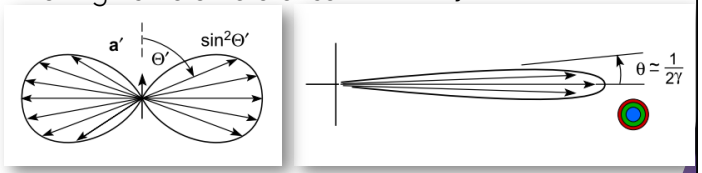
$$\lambda' = \lambda'\gamma(1 - \frac{\nu}{c}cos\theta)$$

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

Producing IR light

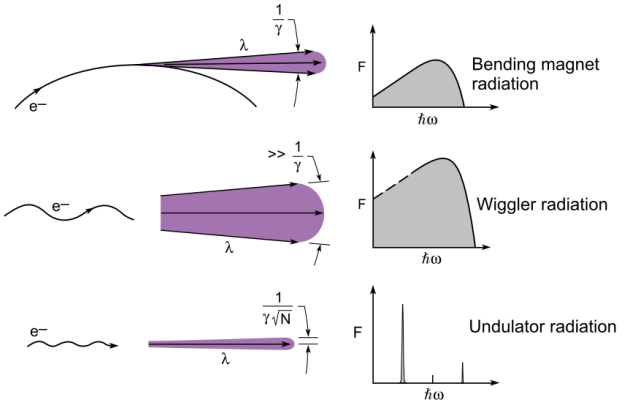
Moving frame of reference

Laboratory frame of reference



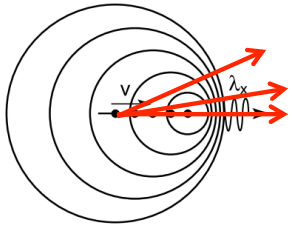
Synchrotron radiation

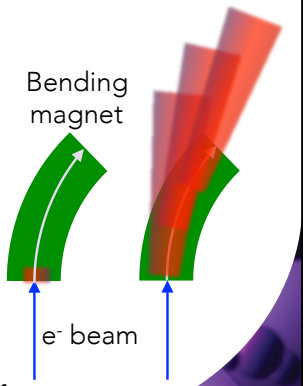
Insertion devices



Producing IR light

Bending magnet radiation

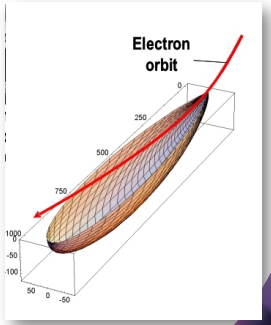




Problem: source size, focusing

Which one is better?

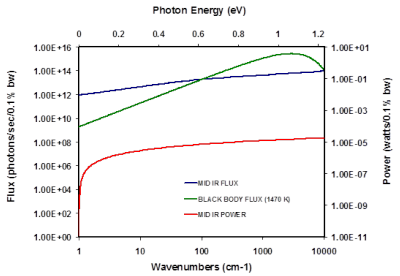




Globar SR

Globar wins

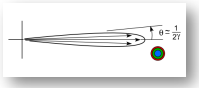


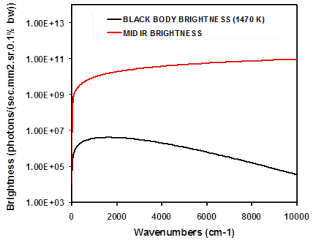


Total flux (CLS)

Synchrotron wins







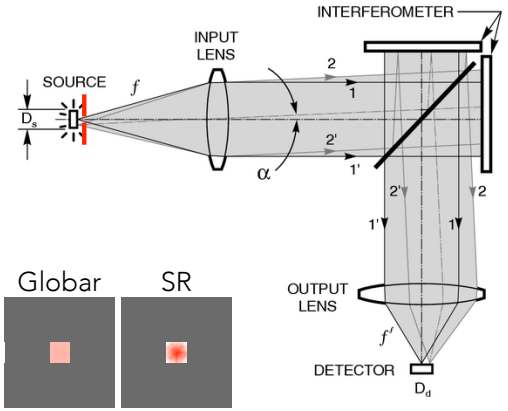
Brightness (CLS)

High-resolution spectroscopy

Pathlength and resolution

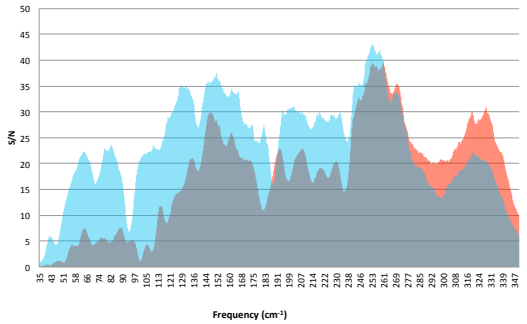


Source size (pinhole)



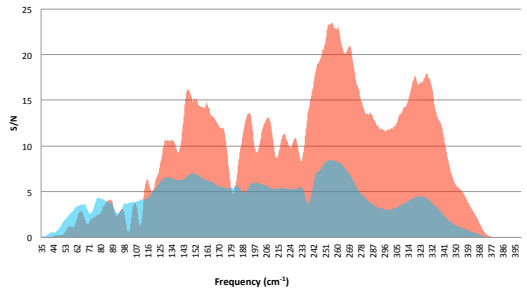
http://www.newport.com/images/web600w-EN/images/2407.gif

SR advantage – "low" res…



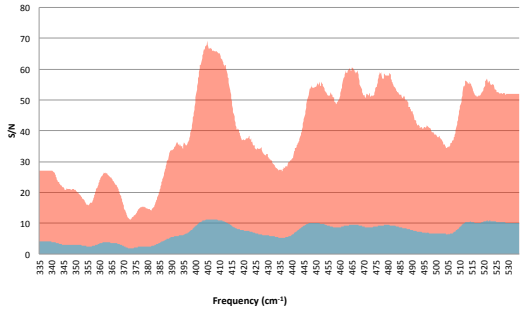
35-350 cm^{-1} | Resolution: 0.002 cm^{-1} | Aperture: 3.15 mm | Velocity: 30 KHz / 5KHz

SR advantage



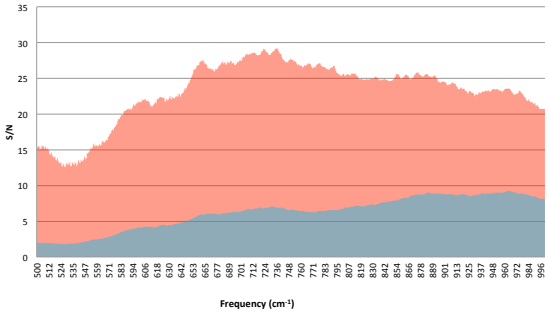
35-350 cm^{-1} | Resolution: 0.00096 cm^{-1} | Aperture: 2 mm | Velocity: 30 KHz / 5KHz

SR advantage



335-535 cm^{-1} | Resolution: 0.001 cm^{-1} | Aperture: 1.5 mm | Velocity: 40 KHz

SR advantage



500-1000 cm^{-1} | Resolution: 0.001 cm^{-1} | Aperture: 1.15 mm | Velocity: 40 KHz

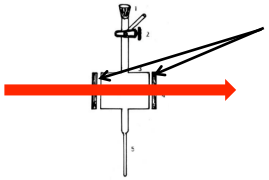
Applications

High resolution FTIR on gases

- Important for Astronomy
  (interstellar gases, small molecules)
- Atmospheric sciences
  (ozone, pollution, radicals)
- Basic physical chemistry
  (molecular dynamics, radicals, etc…)

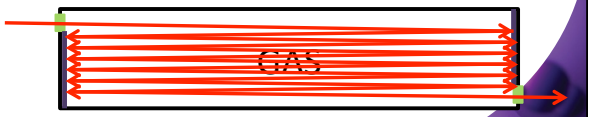
Sample preparation

Gases



IR transparent windows

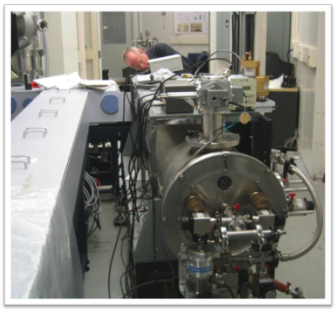
Multi-pass cells



Gas cells

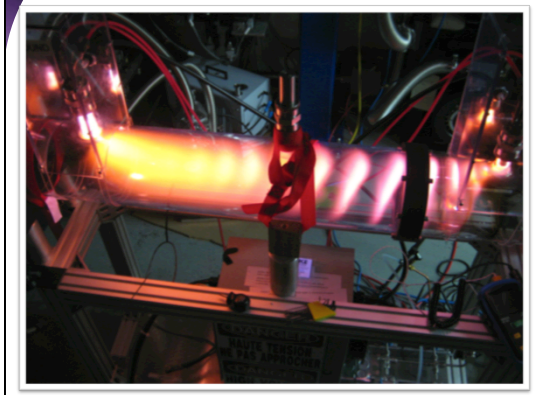


- 30 cm White Cell
- Ambient Temperature
- Paths up to 12 m



- 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}
~1.2x10^{-7} eV

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}
MCT B	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 

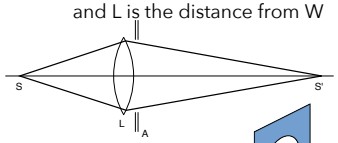
Tim May 

Microscopy
- spectromicroscopy -

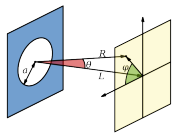
Resolution
Fraunhofer diffraction

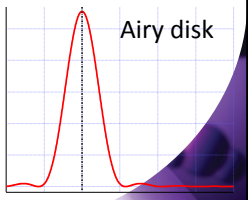
Occurs in the "far field" $\frac{W^2}{\lambda} << L$,

where W is the size of the entrance aperture, λ is the wavelength and L is the distance from W



$$I(\theta) = I_0 \left(\frac{2J_1(x)}{x} \right)^2$$



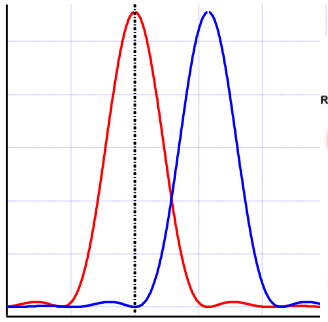


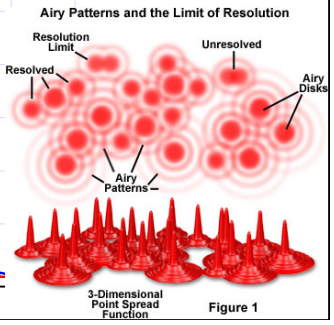
In case of a circular aperture

Rayleigh criterion

Two objects are resolved if:

The first object's Airy disk's maximum coincides with the second's firs minimum

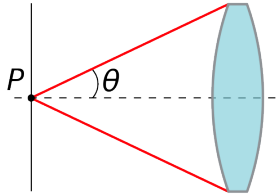




http://goo.gl/cp6WGT

In practice

Rayleigh resolution limit: $R = \dfrac{1.22\lambda}{NA_{cond} + NA_{obj}}$

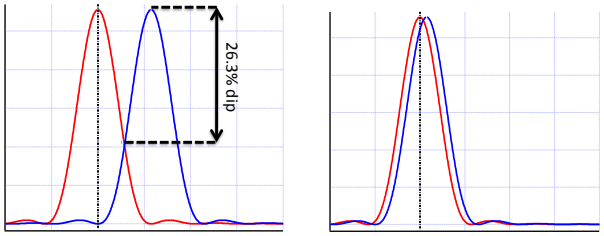


$$NA = n \cdot \sin(\theta)$$

n – refractive index of the medium the objective is looking into

But…

Beyond Rayleigh

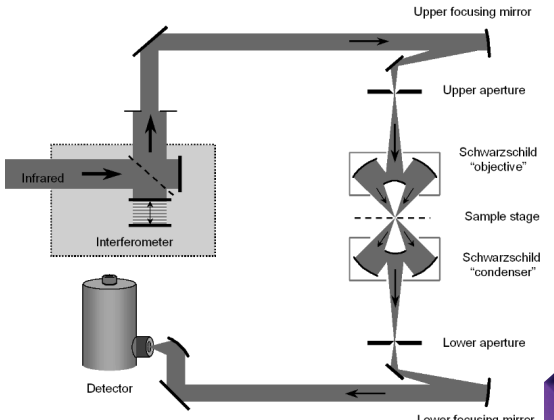


Σ: Higher resolution possible

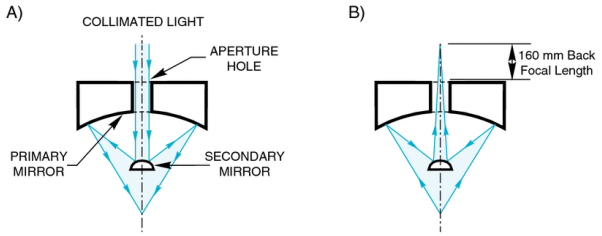
Image processing algorithms, 2D deconvolution techniques with PSF model or Bayesian (model free)

Oversampling!

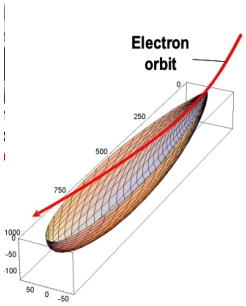
General IR microscope Layout



The Schwarzschild objective

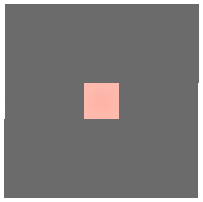




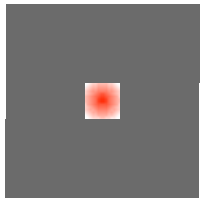


Globar SR

Why use a synchrotron?

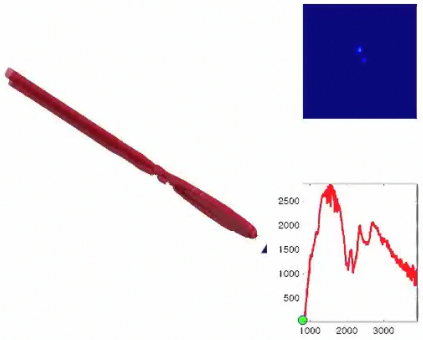


Globar Light Spot in Plane of Confocal Aperture

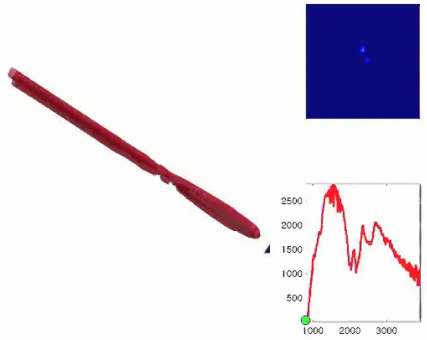


Synchrotron Light Spot in Plane of Confocal Aperture

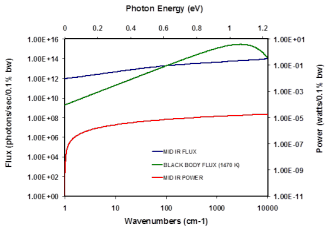
Beam spot in the CLS

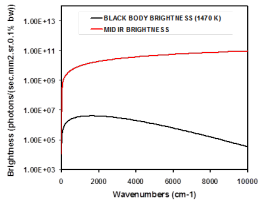


Beam spot in the CLS



Globar vs. Synchrotron





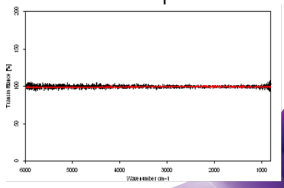
Globar vs. synchrotron

2x2 mm pinhole

5x5 mm pinhole

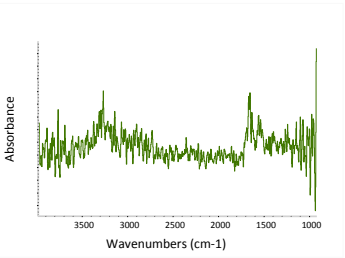
3x3 mm pinhole

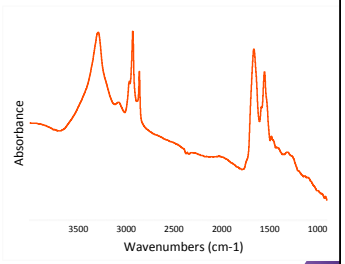
10x10 mm pinhole



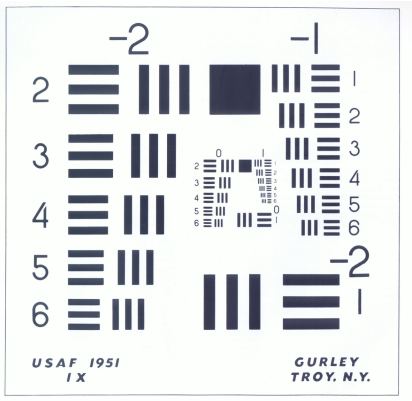
Globar vs. synchrotron

6x6 μm aperture (single cell)

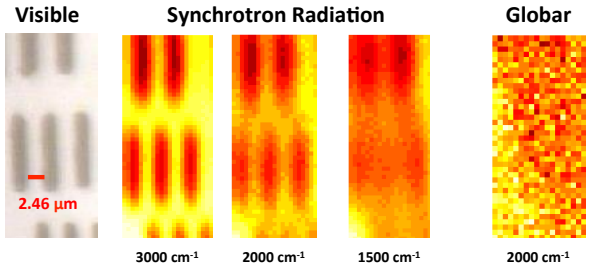




Spatial resolution

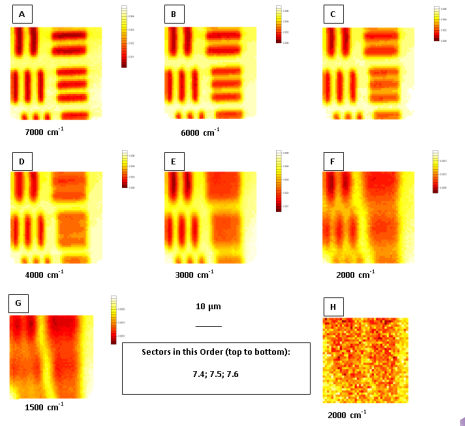


Spatial resolution…



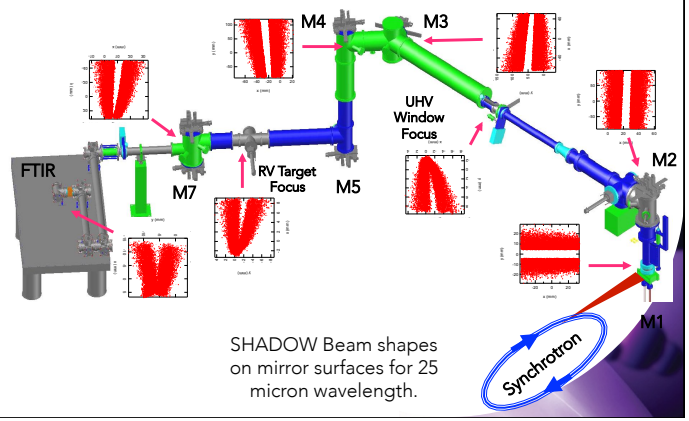
Diffraction limited resolution can be achieved only by SR

…diffraction limited



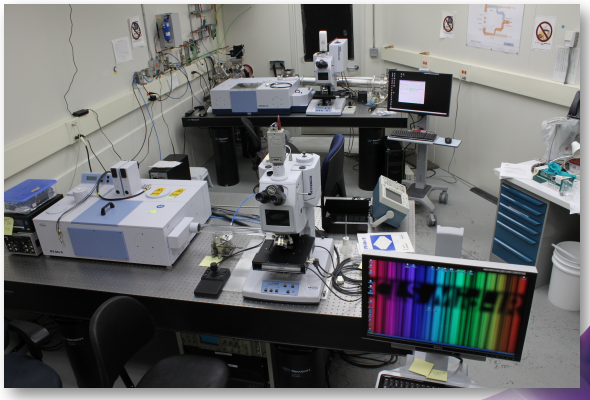
Infrared beamlines - some examples -

Canadian Light Source Mid-IR

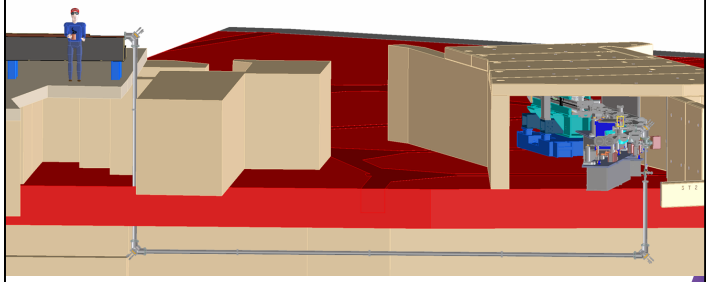


SHADOW Beam shapes on mirror surfaces for 25 micron wavelength.

Canadian Light Source Mid-IR



Advanced Light Source, Bl 5.4



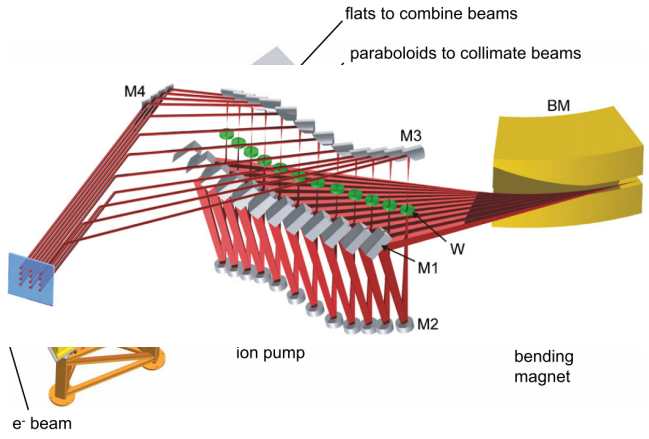
+ Beamline 1.4

NSLS VUV-IR ring

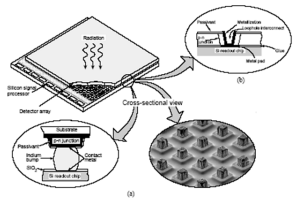
U2A	Geophysics, materials at extreme pressures and microspectroscopy
U2B	Mid-IR microspectroscopy
U4IR	Instrumentation development
U10A	Far-IR microspectroscopy
U10B	Mid-IR microspectroscopy
U12IR	Far-IR, THz and millimeter wave spectroscopy. Materials physics

Shutting down soon because of NSLS II

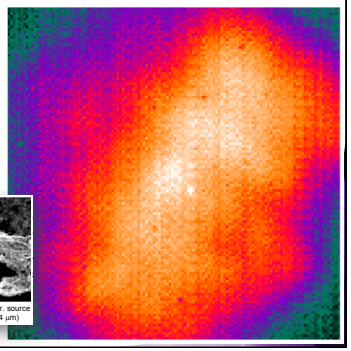
IRENI beamline, SRC



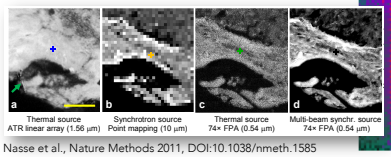
IRENI beamline, SRC



Shutting down in November 2013



Focal Plane Array

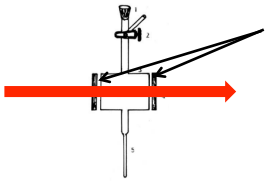


Nasse et al., Nature Methods 2011, DOI:10.1038/nmeth.1585

IR spectroscopy
- samples and measurement techniques -

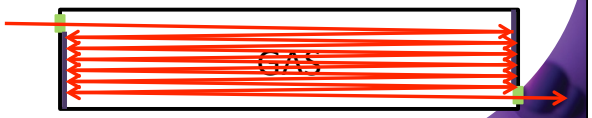
Sample forms

Gases



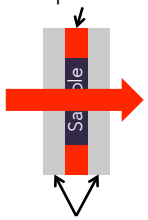
IR transparent windows

Multi-pass cells



Sample forms

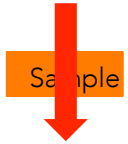
Liquids





Sample forms

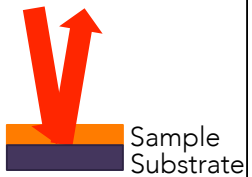
Solids



Transmission



Reflection



Reflection-absorption
Transflecion

Self supporting
Lying on substrate
Suspended in carrier
- KBr
- Nujol

Reflection setups

Regular
Convenient



Special microscope objectives
Increases optical pathlength
Monolayers
Sub-monolayers

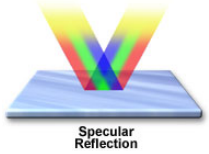
Very thin samples
Grazing angle incidence



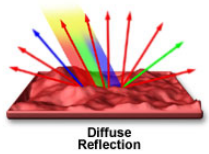


Reflection setups

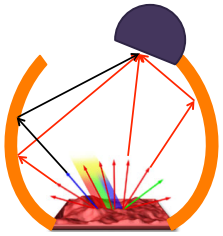
We are happy



Not so lucky



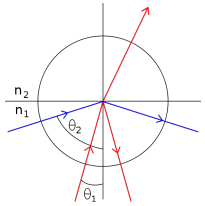
DRIFTS
Diffuse reflection
Integrating sphere



Application:
- Powders
- Catalysis!!!

Reflection setups

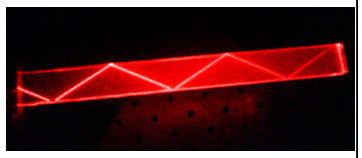
Total internal reflection

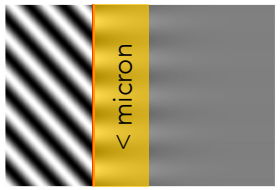


$$\Theta_c = sin^{-1}(\frac{n_1}{n_2})$$

$$E_T = E_0 e^{-z/d_p}$$

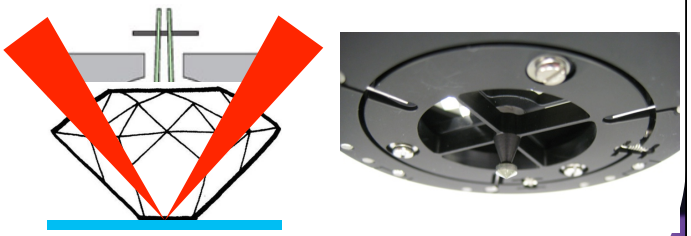
$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{sin^2\theta - n_{21}^2}}$$





Reflection setups

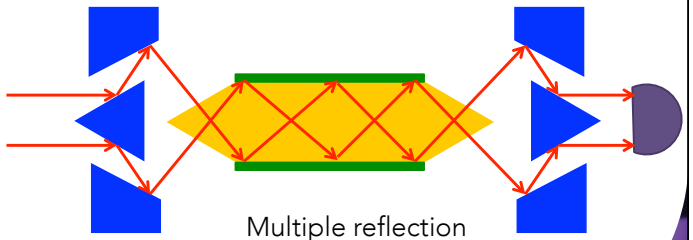
Attenuated total internal reflection



Single reflection
Surface sensitive
Microscopy

Reflection setups

Attenuated total internal reflection



Multiple reflection
Very sensitive

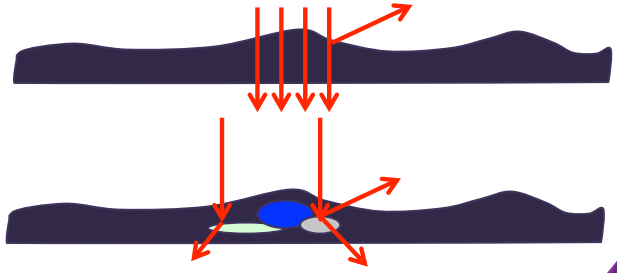
Number of reflections:

$$N_{bounces} = \frac{length_{crystal}}{thickness_{crystal}} ctg\theta$$

Possible problems

Artifacts?

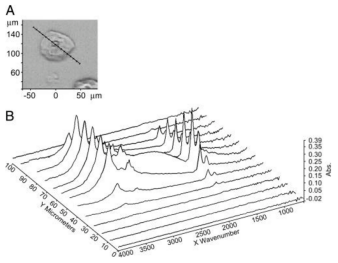
Samples are not ideal…thickness/roughness



Life gets very complicated

Artifacts?

Samples are not ideal…



Mie Scattering

$$Q = 2 - \frac{4}{p}\sin p + \frac{4}{p^2}(1 - \cos p)$$

$$p = 4\pi a \frac{n-1}{\lambda}$$

$$a : r_{sphere}$$

$$n = \frac{n_{inside}}{n_{outside}}$$

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

Artifacts?

Samples are not ideal…scattering.

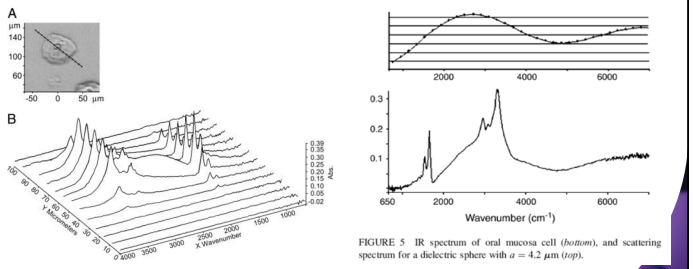


FIGURE 5 IR spectrum of oral mucosa cell (*bottom*), and scattering spectrum for a dielectric sphere with $a = 4.2\ \mu m$ (*top*).

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?

- Statistical analysis
  - Cluster analysis
  - Principal Component Analysis
  - Partial Least Squares regression

Cytospec
R, Matlab,
Eigenvetcor
The Unscrambler

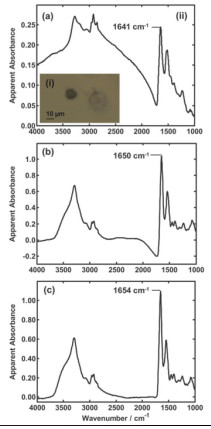
Artifacts? – RMieSc

Samples are not ideal…
resonant scattering.

Amide I – 1641 cm^{-1}
b-sheet, random

Amide I – 1650 cm^{-1}
random, turns

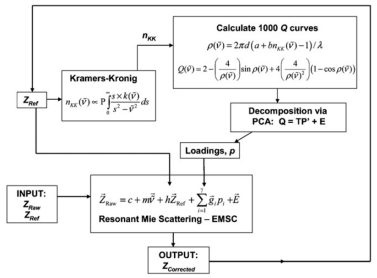
Amide I – 1654 cm^{-1}
a-helix



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

Artifacts? – RMieSc…

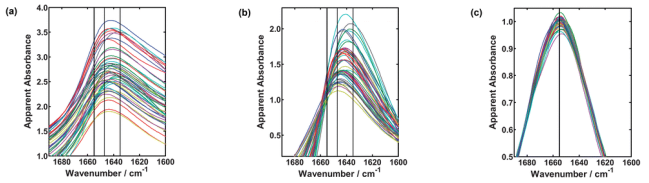
Samples are not ideal…resonant scattering.



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

Artifacts? – RMieSc…

Samples are not ideal…resonant scattering.



Uncorrected

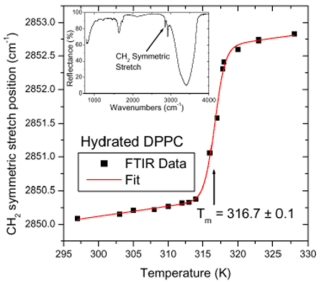
Mie scattering corrected

Resonant Mie scattering corrected

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

Artifacts?

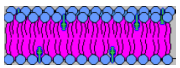
Does the synchrotron light heat the sample?



Synchrotron source:
Measured 1 mW focused onto ~10 X 10 μm²

DPPC = dipalmitoylphosphatidylcholine, a phospholipid bilayer

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



Observed < 0.5˚ C temp rise on sample

Important: No Evidence for Cytotoxic Effects on Living Cells

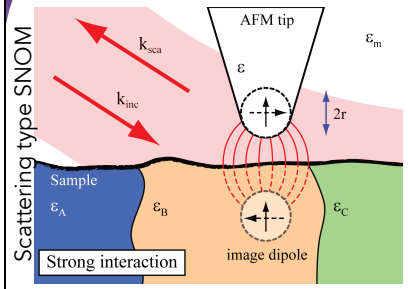
M.C. Martin et al., Applied Spectroscopy 55, 111 (2001)

SR IR spectroscopy - applications -

Courtesy of H. A. Bechtel, ALS LBNL

IR SNOM

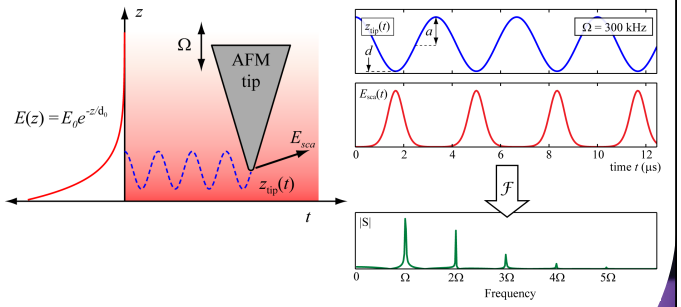
Scanning Near-field Optical Microscopy



Nanometer spatial resolution
Wavelength independent
Soft and hard matter
Amplitude and phase of optical field

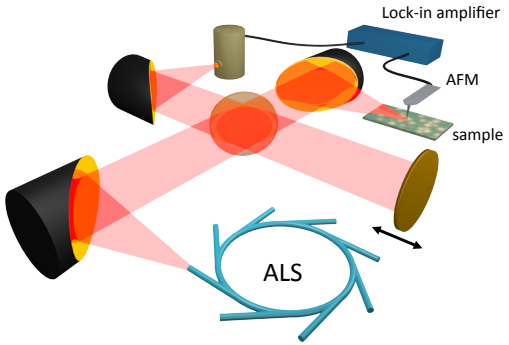
Courtesy of H. A. Bechtel, ALS LBNL

Background suppression in s-SNOM



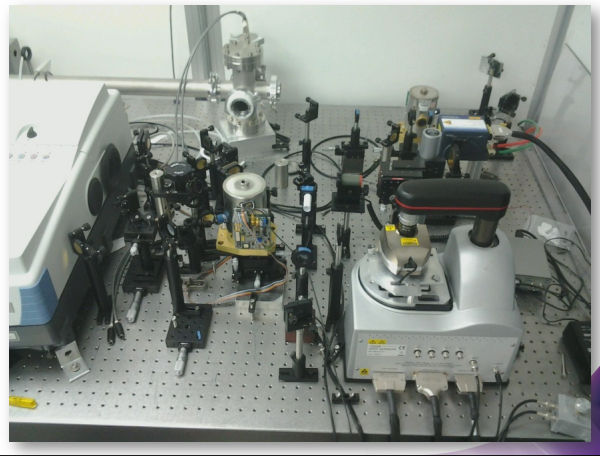
Courtesy of H. A. Bechtel, ALS LBNL

Experimental setup



Courtesy of H. A. Bechtel, ALS LBNL

Experimental setup



Courtesy of H. A. Bechtel, ALS LBNL

Approach curves

Courtesy of H. A. Bechtel, ALS LBNL

Broadband nano-imaging

Courtesy of H. A. Bechtel, ALS LBNL

Broadband nano-spectroscopy: interferograms

Courtesy of H. A. Bechtel, ALS LBNL

Broadband nano-spectroscopy

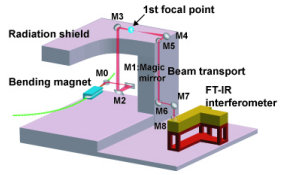
Courtesy of H. A. Bechtel, ALS LBNL

Linescans

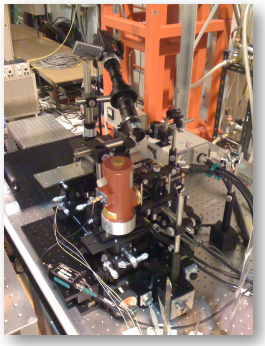
Courtesy of H. A. Bechtel, ALS LBNL

Biological Samples

SPring-8, BL43B



Three IR endstations



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

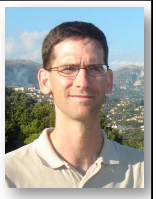
Commercial, non SR system



NeaSNOM
from
NeaSpec
www.neaspec.com

Uses QCL sources
Possible with Globar

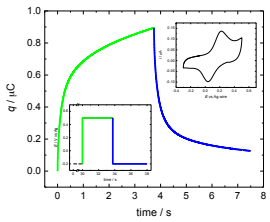
The Burgess Research Group



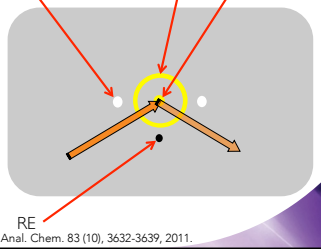
Kinetics: problem RC time constant of the electrode
solution: decrease size

Small electrode size ~ 10 µm

Need for SR

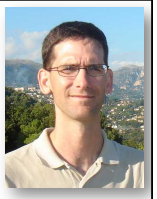


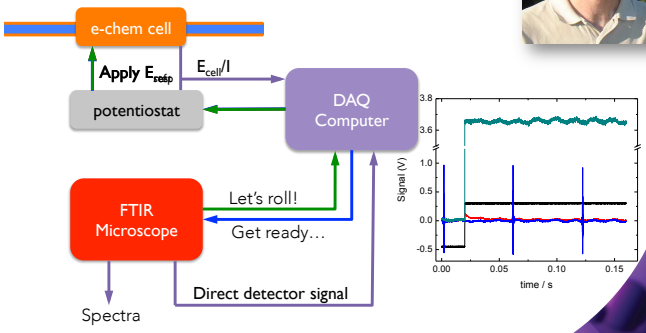
Flow Through Holes



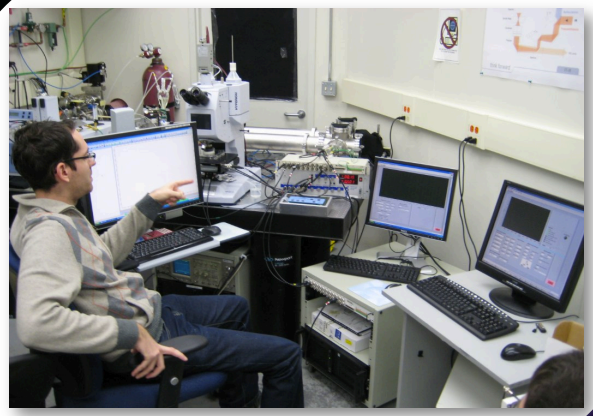
Rosendahl SM; Borondics F; May T; Pedersen T; Burgess I, Anal. Chem. 83 (10), 3632-3639, 2011.

The Burgess Research Group





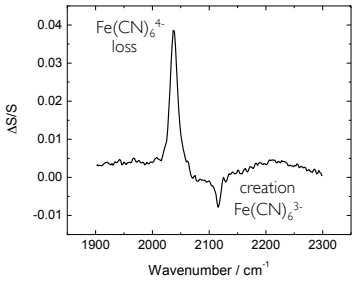
Rosendahl SM; Borondics F; May T; Pedersen T; Burgess I, Anal. Chem. 83 (10), 3632-3639, 2011.

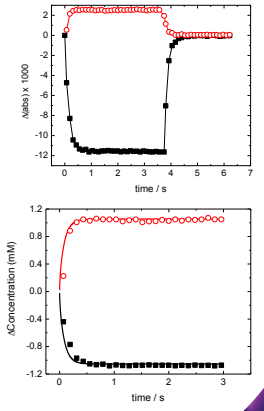


Rosendahl SM; Borondics F; May T; Pedersen T; Burgess I, Anal. Chem. 83 (10), 3632-3639, 2011.

Results

$Fe(CN)_6^{4-} = Fe(CN)_6^{3-} + e^-$

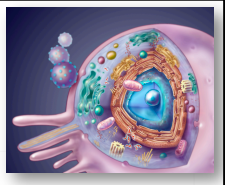


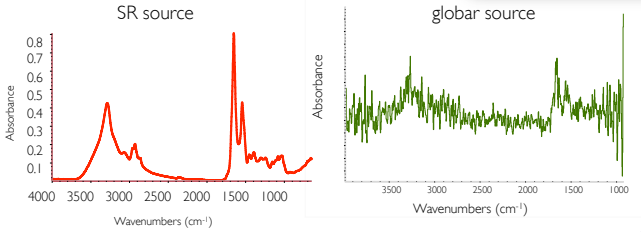


Rosendahl SM; Borondics F; May T; Pedersen T; Burgess I, Anal. Chem. 83 (10), 3632-3639, 2011.

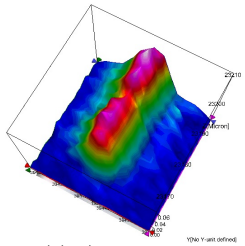
Biology

Ideal size range for resolution
Cells, tissues, bacteria, fungi

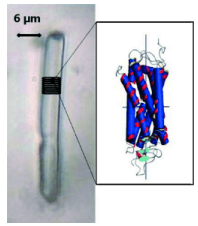




Spectromicroscopy in Rod Cells



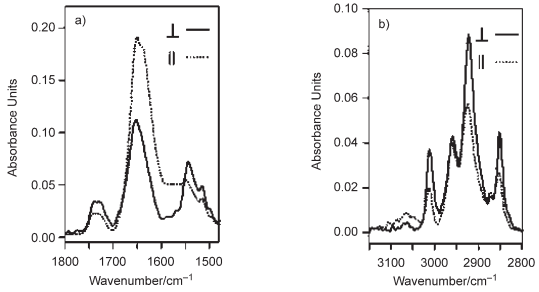
Lipid distribution:
absorbance at 2925 cm^{-1}



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

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

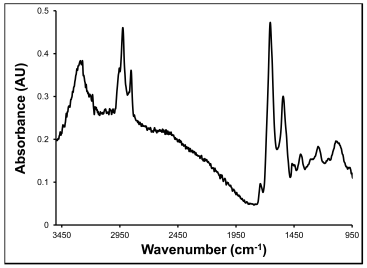
Results – polarization studies



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

Courtesy of M. J. Hackett

FPA imaging of brain samples for stroke research



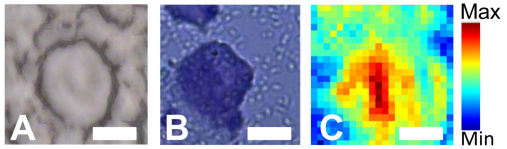
52x objective high res imaging. Representative Spectrum from a single 0.77 um pixel (512 scans) = 10 minute image time (20 minutes with BG). 180 mA beam current

Courtesy of M. J. Hackett

Courtesy of M. J. Hackett

Imaging Total Protein in Cerebellum Purkinje Neurons

Histochemistry provided evidence that Purkinje neurons have low protein content (relative to other neurons, and surrounding tissue), however, results were could have been misleading due to removal of proteins from cell during fixation/staining protocol. FTIR imaging at the cellular level revealed that the Purkinje neuron is rich in Protein. (A) Bright Field image of unstained tissue. (B) Bright field image of cresyl violet stained tissue showing neuron body (stained after FTIR). (C) FTIR image protein (amide I band, 1690 – 1610 cm^{-1})



Hackett et al. ACS Chemical Neuroscience 2013

Courtesy of M. J. Hackett

Subcellular imaging with SR/FPA

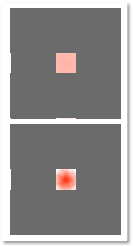
Something to remember

Synchrotron = high brightness

Diffraction limited resolution
Small samples!

High spectral resolution

Data processing…pay attention!



Resources

- CLS Mid-IR webpage http://midir.lightsource.ca
- ALS Infrared beamlines http://infrared.als.lbl.gov
- SPring-8 publications website https://user.spring8.or.jp/uisearch/publication2/
- 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 (http://demonstrations.wolfram.com)
- Synchrotron Simulator
  T. Shintake, Nuclear Instruments and Methods in Physics, 507 (1-2), 89-92 (2003) (http://www-xfel.spring8.or.jp/dlmonitor.html)

Thank you for your attention!

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