New Dimensions in Synchrotron Infrared Spectroscopy and Imaging



Synchrotron Infrared Beamlines





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Introduction: SRIR

Introduction

Continuous spectrum - from infrared to hard x-rays



Synchrotrons produce useful IR too!

Introduction

10⁵

Continuous spectrum - from infrared to hard x-rays **ALS Bend Magnet Flux and Brightness Curves** Center Bend Magnet, 1.3 T 10¹⁶ **10**¹⁴ [Ph/(s mrad² mm ² 0.1% BVV)] Flux [Ph/(sec mrad 0.1% BVV)] 10¹⁶ Brightnes (**10**¹² **10**¹⁴ 10^{4}

 10^{1}

10⁻¹

10⁻²

10-3

 10^{2}

E_{photon} [eV]

 10^{3}



William Herschel

The discovery of infrared light

In 1800, Herschel studied the spectrum of sunlight with a prism. He measured the temperature of each color, and found the highest temperature was just beyond the red, what we now call the infrared ('below the red').



The Science Museum, UK



F.W. Herschel, Phil. Trans. Royal Soc. London 90, 49 (1800).





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What can we learn from IR spectroscopy?

- Atoms vibrate with frequencies in the IR range
- Chemical Analysis:
 - Match spectra to known databases
 - Identifying an unknown compound, Forensics, etc.
 - Monitor chemical reactions *in-situ*
- Structural ideas:
 - Can determine what chemical groups are in a specific compound
- Electronic Information:
 - Measure optical conductivity
 - Determine if Metal, Insulator, Superconductor, Semiconductor
 - Band Gaps, Drude model



A Simple Oscillator

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Imagine the mass is an atom, carrying a charge.
This will then couple to the electric field in light.

Ball & Spring equation: F = -k DxSpring constants for chemical bonds:

- k = 40 400 N/m for covalent bonds
 - k = 20 200 N/m for ionic bonds
- k = 0.5 4 N/m for Van der Waals bonds

Solution to resonance frequency for ball & spring:

$$\omega_0 = \sqrt{\frac{\kappa}{m}}$$

A hydrogen atom has a mass of 1.6735 x 10⁻²⁷ kg An oxygen atom has a mass of 2.6561 X 10⁻²⁶ kg



(Has dipole moment so IR active)



A more complex example: Toluene



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From: http://www.cem.msu.edu/~parrill/AIRS/



Example infrared spectrum of a biological system



A good reference: Mantsch and Chapman, Infrared spectroscopy of biomolecules. 1996, New York: Wiley-Liss.



Monochomators

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Albert Michelson (1852-1931)

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Michelson wanted to measure the speed the the earth moves through the ether (the medium in which light travels). By measuring the interference between light paths at right angles, one could find the direction & speed of the ether.

Michelson's first interferometer (1881)



Michelson-Morley Experiment

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Still no fringes → No ether. The speed of light is constant. A new physics of light was needed.

"My honored Dr. Michelson, it was you who led the physicists into new paths, and through your marvelous experimental work paved the way for the development of the theory of relativity." – Albert Einstein, 1931.

Michelson-Morley interferometer (1887)





More about Michelson

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Michelson won the Nobel Prize in physics in 1907.

He continued pioneering optical measurements:
The speed of light
The size of stars
Using a particular wavelength of light as a distance standard

How an FTIR Spectrometer Works

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A Simple Spectrometer Layout



Pathlength difference = x

The intensity detected of two plane waves:

$$I = \left|\vec{E}\right|^{2} = \left|E_{1}\right|^{2} + \left|E_{2}\right|^{2} + 2\vec{E}_{1} \bullet \vec{E}_{2}\cos(\theta)$$

Normal incidence, $\theta = kx$, can simplify to:

$$I(x) = 2[1 + \cos(kx)]$$

For non-monochromatic light:

$$I(x) = \int_{0}^{\infty} [1 + \cos(kx)] G(k) dk$$
$$= \int_{0}^{\infty} G(k) dk + \int_{0}^{\infty} G(k) \frac{e^{ikx} + e^{-ikx}}{2} dk$$
$$= \frac{1}{2} I(0) + \frac{1}{2} \int_{-\infty}^{\infty} G(k) e^{ikx} dk$$



FTIR Math Continued

We can rewrite this to something more familiar:

$$W(x) \equiv \frac{2I(x) - I(0)}{\sqrt{2\pi}} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} G(k) e^{ikx} dk$$

A Fourier Transform!

The detected intensity as a function of moving mirror position, I(x), can therefore be converted into G(k), the intensity spectrum as a function of frequency by a simple Fourier transform.





Infrared Spectroscopy Measurements



Why use a synchrotron for IR?

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High brightness

- Essentially a point source
- Can focus light to a diffractionlimited size: <u>Microscopy</u>

More far-IR flux

- Smaller samples
- Better signal-to-noise

Pulsed source

- Light is from electron bunches
- Fast timing measurements (nsec)

Synchrotron IR is 1000x *brighter* than a conventional blackbody source



Advantages

• Diffraction-limited spot sizes for microscopy (2-10 μm) Levenson, Lerch & Martin, *J. Synch. Rad.* (2008)

- Superior collimation for high spectral resolution
- Smaller samples
- Better signal to noise ratios
- Faster data acquisition

Holman et al., Spectroscopy - An International Journal 17(2-3), 139-159 (2003).

High Brightness = Better Biology

Better Signal-to-Noise and Faster Collection



Absorbance

Globar: $6x6 \ \mu m^2$ 1000 scans = 500s

Synchrotron: $6x6 \ \mu m^2$ 32 scans = 16 s

3000 2500

Wavenumbers (cm⁻¹)

3500

2000 1500

1000





High Brightness = Better for small samples

Better Signal-to-Noise and Faster Collection



Panero, Benedetti, Jeanloz

Synchrotron Light Sources with IR beamlines worldwide



Conclusions

- High-impact science with a cost-effective beamline.
- Diffraction-limited spot size: analysis of micron-scale cells, tissues, particles, novel materials, fibers, heterogeneity, etc.

Science and Applications of SR IR

Beamtime allocated for the ALS IR Beamlines









Graphene work done by



Prof. Feng Wang, Yuanbo Zhang, Tsung-Ta Tung, Cheol-Hwan Park, Baisong Geng, Caglar Girit



Dimitri Basov, Zhiqiang Li, UC San Diego



E. A. Henriksen, Z. Jiang, P. Kim, H. L. Stormer, Colombia 🔛 Columbia University



Michael C. Martin, Hans Bechtel, ALS, LBNL Zhao Hao, Earth Sciences Division, LBNL



Synchrotron Infrared Beamlines

Fascinating Graphene



$$E = v_F \cdot P$$

Massless Dirac fermion. Ballistic Transport. Attractive for both fundamental physics and technological applications.

Tunable via:

Electrical Field

Layer-Layer interactions

Nanopatterning



devices

Field effect



Bilayer





We can vary temperature and gate voltage



SR-FTIR spectromicroscopy with Oxford microstat for samples at 4 - 400 Kelvin at ALS beamline 1.4.4.





Dual-Gate Bilayer Graphene Devices





Top View

Side View

Tunable Bandgap in Bilayer Graphene



Tunable Bandgap in Bilayer Graphene



A bandgap over 250 meV can be achieved.

Zhang, Tang, Girit, Hao, Martin, Zettl, Crommie, Shen, and Wang, Nature, **459**, 820-823 (2009). (Currently the highest cited paper from our beamline with >1200 citations)

Science and Applications of SR IR

Beamtime allocated for the ALS IR Beamlines



Gulf of Mexico Oil Disaster

•On April 20, 2010 the *Deepwater Horizon* exploded.

•The floating rig burned for 2 days then sank, shearing the 21-inch riser pipe 600 ft above the BOP.

•Leak estimated at ~65,000 barrels per day

•87 days of flow into Gulf until containment.

•Largest offshore oil spill in history.

•Scientific Response:

Measurements revealed a large lens of oil
Deepest and largest lens was at 1,200m and measured approx. 15 km long
Oil aggregates and mousse floated





Sampling Gulf of Mexico Oil









A significant plume of oil was found at a depth of 1200 m.

Bacteria and oil droplets





Bright-field



Hazen, et al., Science 330(6001), 204-208 (2010).


Oil degradation by microbes within the 1200 m deep oil plume





Scale bars = 10 micrometers

Hazen, et al., Science 330(6001), 204-208 (2010).



Science and Applications of SR IR

Beamtime allocated for the ALS IR Beamlines



Lunar and Planetary Science





STARDUST flew threw comet WILD-2's tail...







...and landed January 15, 2006.

Organics in Stardust

Organics Captured from Comet Wild 2 by the Stardust Spacecraft Sandford et al. Science, 314, 1720-1724 (December 2006)

Fig. 2. IR transmittance spectra obtained along a line perpendicular to cometary impact tracks (**A**) track 59 and (**B**) track 61. In addition to aerogel features, the spectra of track 59 (A) display peaks at 3322 (broad), 2968, 2923, 2855, and 1706 cm⁻¹ (not shown), both inside the track and extending outward into the aerogel. (B) track 61 exhibits only the aliphatic CH stretching feature dominated by the 2968 cm⁻¹ peak and (Si-O) bands (not shown) characteristic of the flight aerogel. The optical images of the same tracks, with corresponding maps to the same scale showing the intensity distribution of the 2923 cm^{-1} peak (–CH₂–), are displayed in (C) and (D). The false-color image scale shown at



the bottom is used in both maps, and the black scale bars correspond to 100 µm. In both cases, the entrance of the cometary particle is on the left side. The false-color map in (C) shows an increase in intensity of the 2923 cm^{-1} –CH₂– peak in and near the track. The distributions of other organics peaks are similar. In contrast, the second track shown in (D) shows almost uniform distribution of the peak area centered at 2923 cm^{-1} ; that is, the track shows only the features of aerogel.



Lunar and Planetary Science

Assessment and control of organic and other contaminants associated with the Stardust sample return from comet 81P/Wild 2

Scott A. Sandford, Sasa Bajt, Simon J. Clemett, George Cody, Bradley T. Degregorio, Vanessa De Vera, Jason P. Dworkin, Jamie E. Elsila, George J. Flynn, Daniel P. Glavin, Antonio Lanzirotti, Thomas Limero, Mildred P. Martin, Christopher J. Snead, Maegan K. Spencer, Thomas Stephan, Andrew J. Westphal, Sue Wirick, Richard N. Zare, Michael Zolensky *Meteoritics & Planetary Science*, **45(3)**, 406-433 (March 2010).





Fig. 1. Infrared spectrum of an approximately 10 μ m × 10 μ m spot on C2115,23,21, a keystone extracted from the C2115 Stardust aerogel flight cell. The strong Si-O, C=O, aliphatic -CH₂- and -CH₃, structural –OH, and adsorbed H₂O absorption features were seen at all the spots examined and their presence is typical of Stardust flight aerogels.



How can we go beyond diffraction-limited spectro-microscopy?

> 3D FTIR Spectro-Microtomography

Martin *et al.*, Nature Methods **10**, 861-864 (2013)

Synchrotron Infrared Nano Spectroscopy

Bechtel et al., PNAS 111(20), 7191–7196 (2014).



3D Imaging with Infrared Spectral Microtomography

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Carol Hirschmugl, Miriam Unger *Physics Department, University of Wisconsin-Milwaukee*

Julia SedImair, Barbara IIIman Forrest Products Laboratory and SRC, Madison

Jonathan M. Castro, Institute of Geosciences, University of Mainz

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Brief primer on Tomography

Measure projected transmission image:



In a single 2D projection, cannot tell the depth or 3D extent of each object.

Rotate sample and measure many projection images.

Then computed tomography algorithms reconstruct slices through the sample, revealing the 3D nature.

3D picture remains gray scale: can observe different densities.

Full-color Spectral Tomography

Can we do this in "Full-Color"??



Use the power of **FTIR spectroscopy** to provide meaningful colors based on full spectral identification.

What's needed:

- A fast FTIR imaging instrument with complete spectral images obtained in ~1 minute so a full 180 degrees of sample rotation can be measured within a reasonable time.
 - 2. A sample rotation stage.

3. Tomography reconstruction algorithms that are spectroscopy aware.

Fast Imaging + Rotation = 3D IR Tomography

Proof of principle experiments, 2012



We removed the x-y sample stage at the IRENI beamline and installed a test sample rotation stage.

The combination of the tip-tilt stage and the x-y-z stage allows us to place the center of rotation at any sample location of interest.

Fast Imaging + Rotation = 3D IR Tomography



3D FTIR Tomography Demonstration

Test sample: MiTeGen protein crystallography microloop holder.







1574-1655 cm⁻¹ Polyimide absorption 2287-2415 cm⁻¹ Edge scattering

3D FTIR Tomography Demonstration





Fast Imaging + Rotation = 3D IR Tomography

Better automation at IRENI, 2013



Programmed macro automates tomographic data acquisition. Reconstruction programs coded to be spectroscopy aware.

Human Hair in 3D



Human Hair in 3D



Microtomography of Volcanic Glass



Volcanic glass filament from the Puyehue volcano, Chile. Sample collected by Jon Castro, Jan 2012.

IR image shows density variations and water concentration changes along darker stripes relevant to mechanism of eruption.

Microtomography of Volcanic Glass



Brown = 1789 cm⁻¹ = Silicate glass Blue = 3495 cm⁻¹ = Water O-H



Correlation between glass and water can be seen well.

Poplar wood fibers





2800 – 3000 cm⁻¹ C-H region



1524 – 1628 cm⁻¹ region: Shows channels made of lignin





Poplar wood fibers





1689 – 1782 cm⁻¹ region (red) Hemicellulose: Outlines channels 1524 – 1628 cm⁻¹ region (blue) Lignin: Fills channels

Zinnia elegans plant cells



Cellulose microfibrils arranges in a parallel orientation.

2360 cm⁻¹ region (red) Scatter outline of holder

3330 cm⁻¹ region (blue-green): Shows water in Zinnia



A





acayo et al., Plant Physiology (2010).

Embryonic Stem Cell Colony



1650 cm⁻¹ region (red-blue) Proteins

2850 cm⁻¹ region (yellow-orange): Lipids





PVOH: 2928-2966 cm⁻¹

PAA: 1684-1759 cm⁻¹

NFC: 1151-1181 cm⁻¹

Nano Fiber Cellulose composite

PVOH: 2928-2966 cn PAA: 1684-1759 cm⁻¹ NFC: 1151-1181 cm⁻¹



Partnership for Data analysis

4D spectral hypercube:

1.6 Million voxels, each with a fully reconstructed FTIR spectrum = 1.3 Billion datapoints

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

Fast data pipeline to super computer center

Web portal to reconstructed spectral 3D data

3D Data Visualization and Analysis room at the ALS



Absorbance



with Dula Parkinson, Craig Tull



Broadband vibrational nano-spectroscopy with a synchrotron infrared source

Hans A. Bechtel and Michael C. Martin Advanced Light Source

Robert L. Olmon, Eric A. Muller, Benjamin Pollard, and Markus B. Raschke University of Colorado, Boulder







Beating the diffraction limit

Far-field





 $R = \frac{\lambda}{2 n \sin \theta}$



 $S \propto \left(\frac{d}{\lambda}\right)^4$

Apertureless



R = tip size

Scattering-type scanning near-field optical microscopy (s-SNOM)



Advantages

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

Laser s-SNOM of purple membrane protein



S. Berweger, D.M. Nguyen, E. A. Muller, H. A. Bechtel, T. T. Perkins, and M. B. Raschke, JACS 135, 18292 (2013).

Broadband sources for s-SNOM

Broadband sources

- More efficient spectral collection
 - Improved spectral accuracy

Synchrotron IR

- Ultra-broadband
- High spectral irradiance
 - Spatially coherent
- Good spectral stability





Bechtel et al., PNAS 111(20), 7191–7196 (2014).

ALS Beamline 5.4 SINS



Key Components

- •Floating table
- •Modified Bruker Innova AFM
- •Zurich Instruments lock-in amplifier
- Commercial Thermo FTIR
- •Kolmar MCT (100 um)



SiO₂ Microstructures: Si response



SiO₂ Microstructures: Interferrograms


SiO₂ Microstructures: spectra



SiO₂ spatio-spectral imaging



SiO₂ spatio-spectral imaging









Antenna near-field imaging

Eric Muller, Benjamin Pollard, and Markus Raschke (U. Colorado)

Topography



Infrared





Antenna near-field imaging

Eric Muller, Benjamin Pollard, and Markus Raschke (U. Colorado)













S. Dai et al., Science 343, 1125-1129 (2014)





Surface Phonon Polaritons in Boron Nitride

Zhiwen Shi and Feng Wang (UC Berkeley)



Surface Phonon Polaritons in Boron Nitride

λ at ω=1440cm⁻¹

100 120 140 160

80

d(nm)

Zhiwen Shi and Feng Wang (UC Berkeley)

40 nm

160 nm



Summary

Exciting new directions for synchrotron infrared science.





3D FTIR Tomography

Synchrotron Infrared Nano-Spectroscopy





