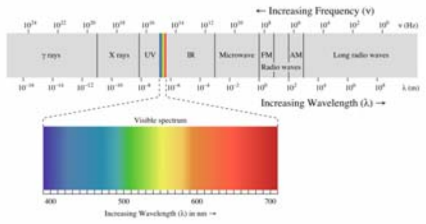
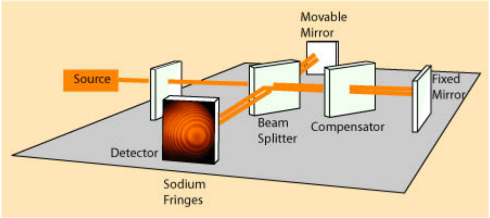


Phys 774:
IR spectroscopy

Fall 2007



Dielectric function contributions

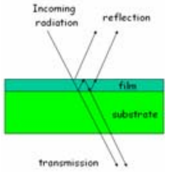
- ❖ Optical vibrations (phonons)
- ❖ Free electrons (plasma)
- ❖ Electronic transitions (valence → conduction band)
- ❖ Dielectric function and refractive index are generally complex:

$$\varepsilon_r = \varepsilon_r' + i\varepsilon_r'' ; \qquad ; \quad \varepsilon_r' = n_R^2 - n_I^2 \quad ; \quad \varepsilon_r'' = 2n_R n_I$$

absorption coefficient $\alpha = 2k_0 n_\mathrm{I}$ n_I - extinction coefficient

Direct transformation between R, T, A and $\varepsilon(\omega)$

is not always possible (no layered structures, wide spectral range, etc)



$$\chi_1(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} d\omega' \frac{\chi_2(\omega')}{\omega' - \omega}$$

and

$$\chi_2(\omega) = -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} d\omega' \frac{\chi_1(\omega')}{\omega' - \omega}.$$

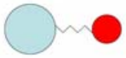
$$\mathcal{R} = \left|\frac{1 - \tilde{N}_\mathrm{complex}}{1 + \tilde{N}_\mathrm{complex}}\right|^2 = \frac{(1-\tilde{n})^2 + \tilde{k}^2}{(1+\tilde{n})^2 + \tilde{k}^2}$$

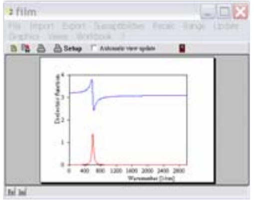
<u>Solution:</u>
Model for dielectric function
for each part of the sample

Dielectric function contributions

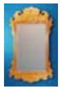
$$\varepsilon(\omega) = 1 + \chi_{Ph}(\omega) + \chi_{FC}(\omega) + \chi_E(\omega) = \varepsilon_\infty + \chi_{Ph}(\omega) + \chi_{FC}(\omega)$$

$$\chi_{ph}(\omega) = \sum_j \left(\frac{S_j^{\,2}}{\omega_{TO_j}^2 - \omega^2 + i\omega\gamma_j} \right)$$

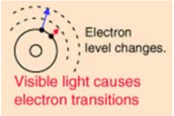




$$\chi_{FC}(\omega) = \frac{\Omega_p^{\,2}}{-\omega^2 + i\omega\gamma} \qquad \Omega_p^{\,2} = \frac{ne^2}{\varepsilon_0 m^*}$$

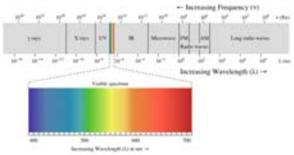


$$\chi_E(\omega) = \sum_j \frac{P_j^{\,2}}{\omega_{0j}^2 - \omega^2 + i\omega\gamma_j}$$



Spectroscopic Measurements in IR

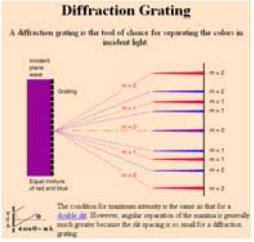
10 – 10000 cm^{-1}



Fourier Transform InfraRed Spectroscopy

Advantages:
1. Multiplexing
2. Throughput

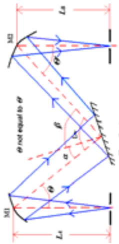
Disadvantages of grating spectrometers in IR

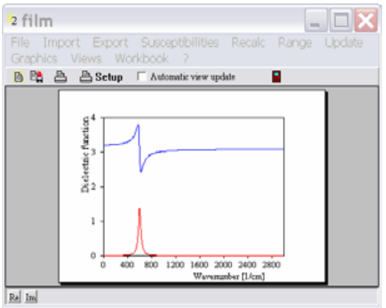


Diffraction Grating

A diffraction grating is the tool of choice for separating the colors in incident light

The condition for maximum intensity is the same as that for a double slit. However, angular separation of the maxima is generally much greater because the slit spacing is so small for a diffraction grating.





FWHM=0.1 nm for
Slit width of 100 μm

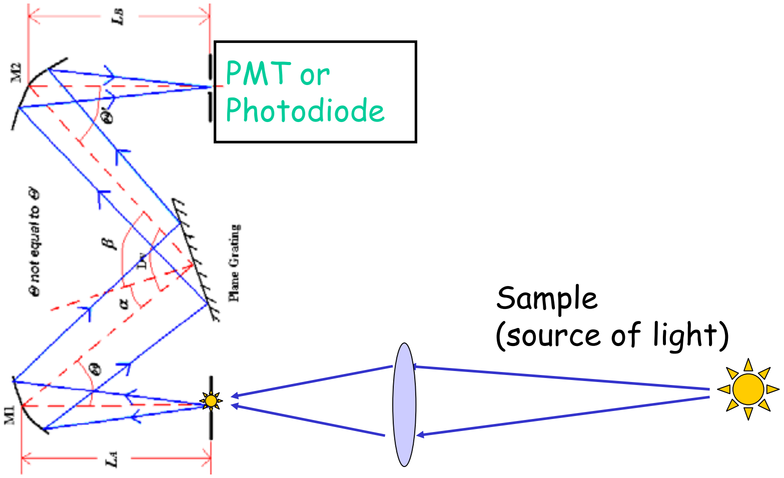
For 500 cm^{-1}
λ=20 μm

For 50 cm-1
λ=200 μm

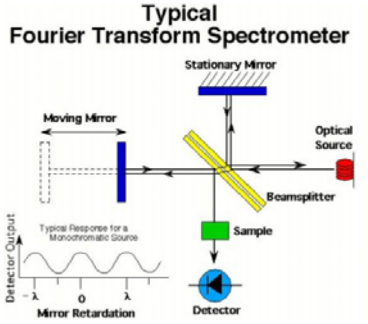
Slit width?
How to focus on the slit?

Grating Spectrometer / Spectrograph /Monochromator

Czerny-Turner Configuration



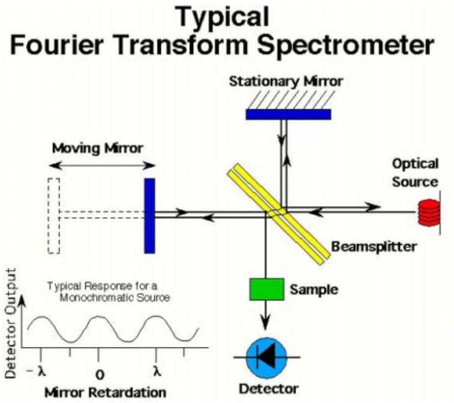
Fourier Transform InfraRed Spectroscopy

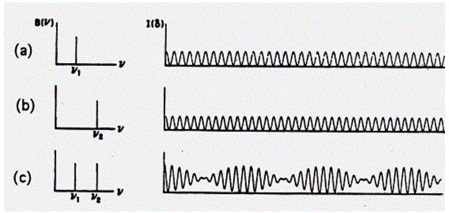


10 – 10000 cm^{-1}

Advantages:
1. Multiplexing
2. Throughput (no slits needed)

Fourier Transform Infra-Red Spectroscopy

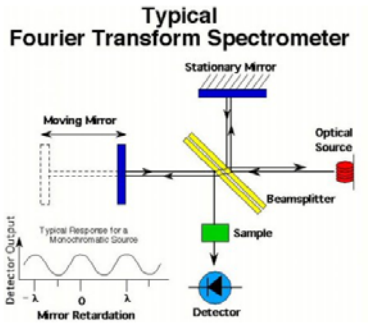


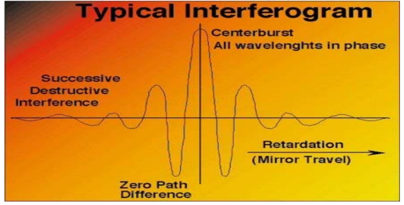


$$I_0 = B(\lambda_0)[1 + \cos(2\pi x/\lambda_0)] = B(\sigma_0)(1 + \cos 2\pi\sigma_0 x)$$

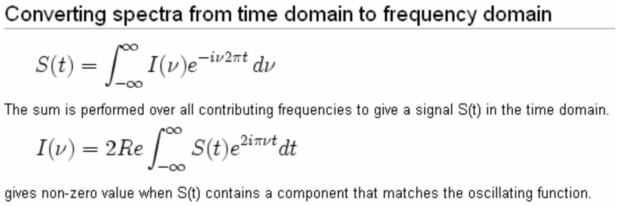
where σ = wavenumber = $1/\lambda_0 = \nu/c$
λ_0 = light source wavelength
$B(\lambda_0)$ = intensity
x = optical path difference between two beams
σ_0 = spatial frequency

Fourier Transform Infra-Red Spectroscopy





Path difference



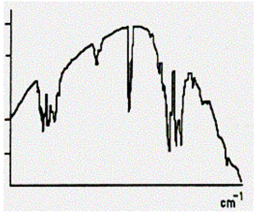
Converting spectra from time domain to frequency domain

$$S(t) = \int_{-\infty}^{\infty} I(\nu) e^{-i\nu 2\pi t}\, d\nu$$

The sum is performed over all contributing frequencies to give a signal S(t) in the time domain.

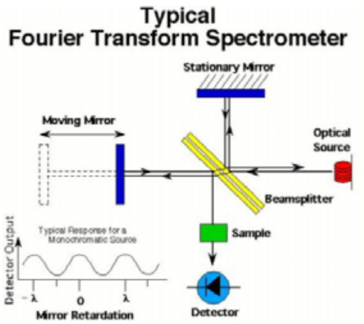
$$I(\nu) = 2Re \int_{-\infty}^{\infty} S(t) e^{2i\pi\nu t} dt$$

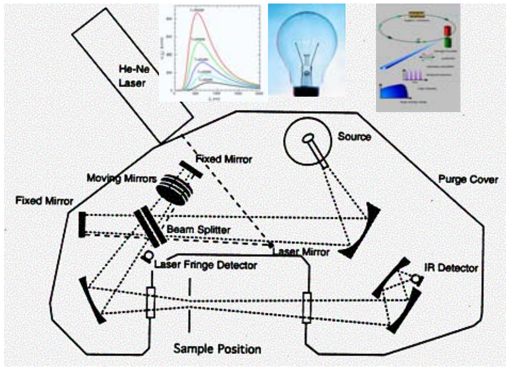
gives non-zero value when S(t) contains a component that matches the oscillating function.



Spectrum

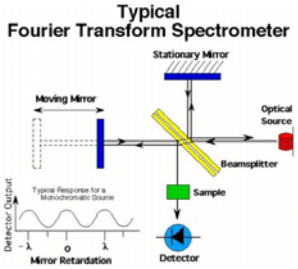
Fourier Transform Infra-Red Spectroscopy

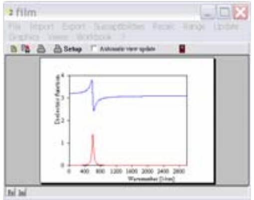


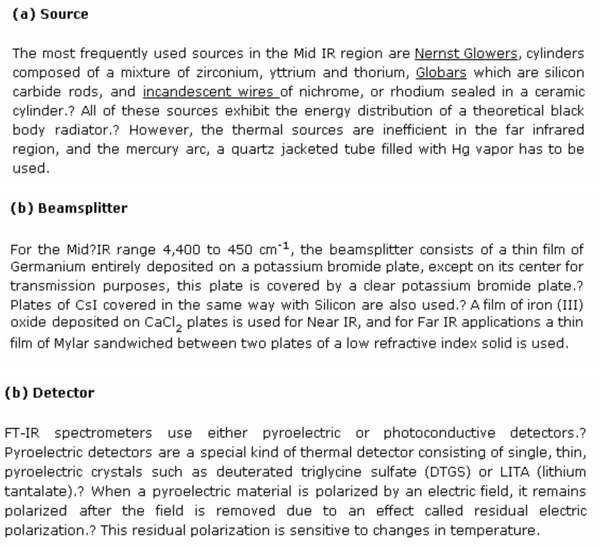


Transmission configuration

Fourier Transform Infra-Red Spectroscopy







(a) Source

The most frequently used sources in the Mid IR region are Nernst Glowers, cylinders composed of a mixture of zirconium, yttrium and thorium, Globars which are silicon carbide rods, and incandescent wires of nichrome, or rhodium sealed in a ceramic cylinder.? All of these sources exhibit the energy distribution of a theoretical black body radiator.? However, the thermal sources are inefficient in the far infrared region, and the mercury arc, a quartz jacketed tube filled with Hg vapor has to be used.

(b) Beamsplitter

For the Mid?IR range 4,400 to 450 cm^{-1}, the beamsplitter consists of a thin film of Germanium entirely deposited on a potassium bromide plate, except on its center for transmission purposes, this plate is covered by a clear potassium bromide plate.? Plates of CsI covered in the same way with Silicon are also used.? A film of iron (III) oxide deposited on $CaCl_2$ plates is used for Near IR, and for Far IR applications a thin film of Mylar sandwiched between two plates of a low refractive index solid is used.

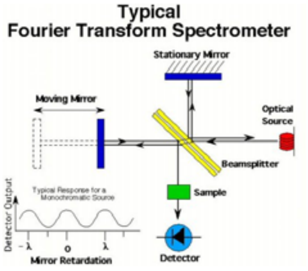
(b) Detector

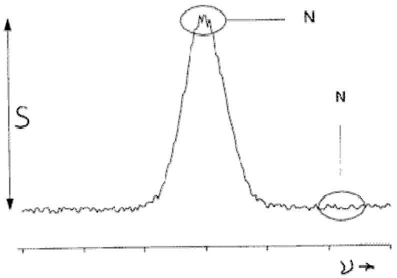
FT-IR spectrometers use either pyroelectric or photoconductive detectors.? Pyroelectric detectors are a special kind of thermal detector consisting of single, thin, pyroelectric crystals such as deuterated triglycine sulfate (DTGS) or LITA (lithium tantalate).? When a pyroelectric material is polarized by an electric field, it remains polarized after the field is removed due to an effect called residual electric polarization.? This residual polarization is sensitive to changes in temperature.

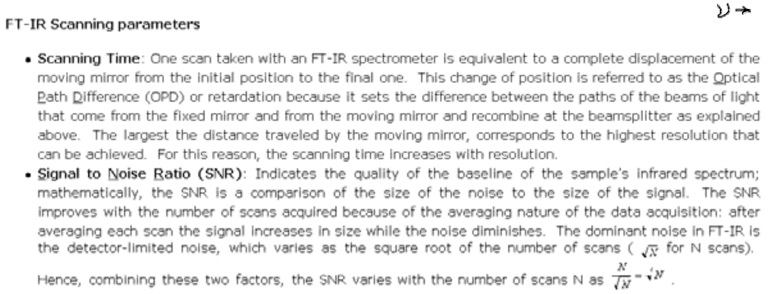
Materials for

Beam splitters Si, Ge, diamond

Fourier Transform Infra-Red Spectroscopy





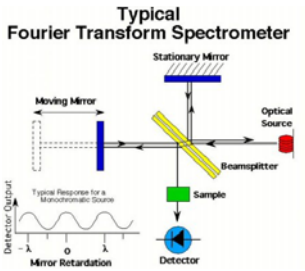


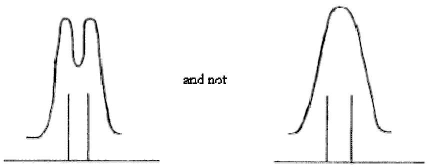
FT-IR Scanning parameters

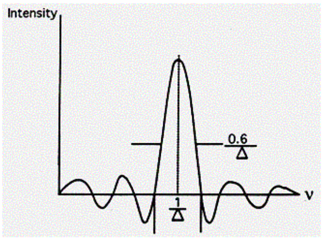
- **Scanning Time**: One scan taken with an FT-IR spectrometer is equivalent to a complete displacement of the moving mirror from the initial position to the final one. This change of position is referred to as the Optical Path Difference (OPD) or retardation because it sets the difference between the paths of the beams of light that come from the fixed mirror and from the moving mirror and recombine at the beamsplitter as explained above. The largest the distance traveled by the moving mirror, corresponds to the highest resolution that can be achieved. For this reason, the scanning time increases with resolution.
- **Signal to Noise Ratio (SNR)**: Indicates the quality of the baseline of the sample's infrared spectrum; mathematically, the SNR is a comparison of the size of the noise to the size of the signal. The SNR improves with the number of scans acquired because of the averaging nature of the data acquisition: after averaging each scan the signal increases in size while the noise diminishes. The dominant noise in FT-IR is the detector-limited noise, which varies as the square root of the number of scans ($\sqrt{N}$ for N scans).

Hence, combining these two factors, the SNR varies with the number of scans N as $\frac{N}{\sqrt{N}} = \sqrt{N}$.

Resolution:

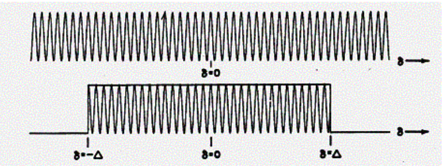


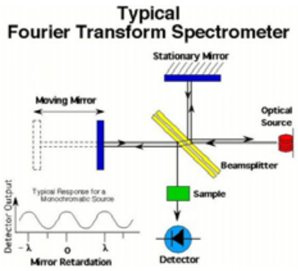


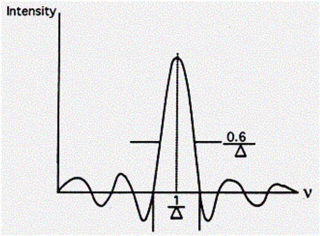


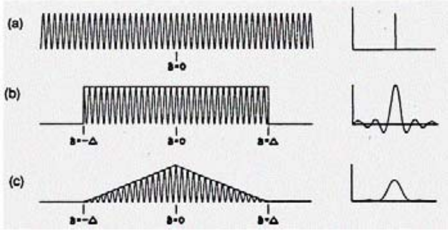
Effect of boxcar truncation on an infinitely narrow line

Effect of the finite scanning distance



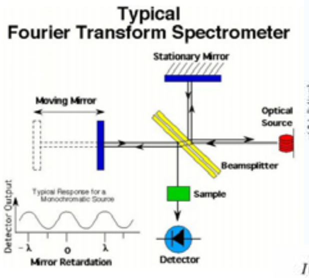


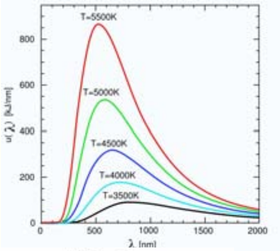




Effect of boxcar truncation on an infinitely narrow line

Fourier Transform Infra-Red Spectroscopy





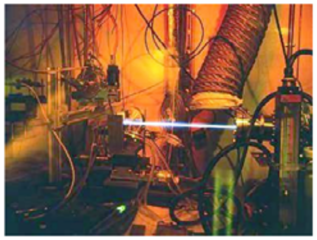
$$I(\nu,T) = \frac{2h\nu^3}{c^2}\frac{1}{e^{\frac{h\nu}{kT}}-1}. \quad [1]$$

As a function of wavelength λ it is written as:

$$I(\lambda,T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda kT}}-1}. \quad [2]$$

Why Synchrotron-radiation ?

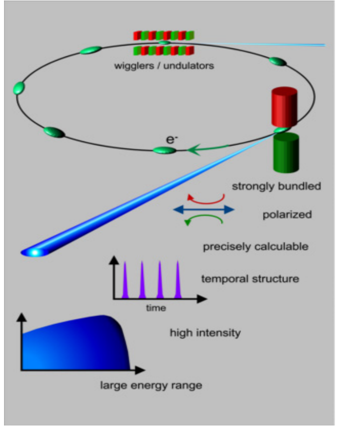
Intensity !!!



Application:
Far-IR Microscopy
Far-IR Ellipsometry
Far-Far-Far-IR

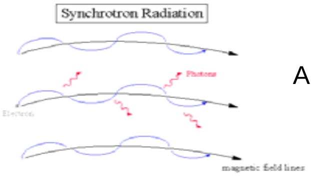
HW: find dependence of I(λ) for λ→∞

Synchrotron radiation

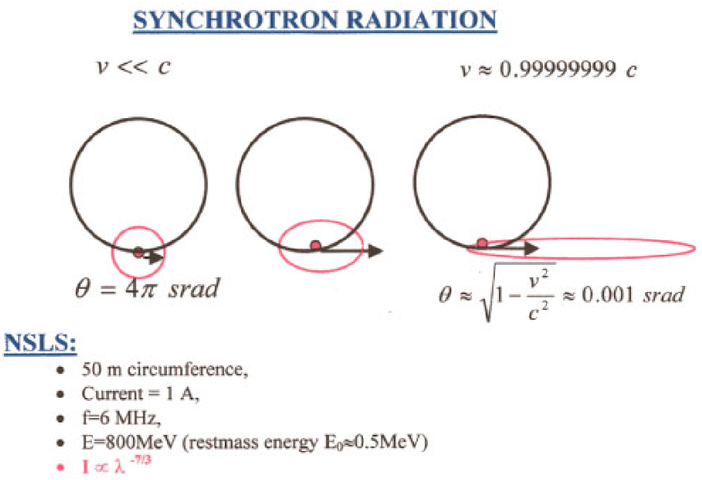


Natural Synchrotron Radiation

Stars and Galaxies



Accelerating electron emits light



SYNCHROTRON RADIATION

$v << c$

$v \approx 0.99999999\ c$

$\theta = 4\pi\ srad$

$\theta \approx \sqrt{1 - \frac{v^2}{c^2}} \approx 0.001\ srad$

NSLS:

- 50 m circumference,
- Current = 1 A,
- f=6 MHz,
- E=800MeV (restmass energy $E_0 \approx 0.5$MeV)
- $I \propto \lambda^{-7/3}$

Synchrotron Radiation produced by relativistic electrons in accelerators (since 1947)

•Synchrotron Radiation from a storage ring is the most bright manmade source of white light
•Useful for materials studies from Far Infrared and UV to X-ray

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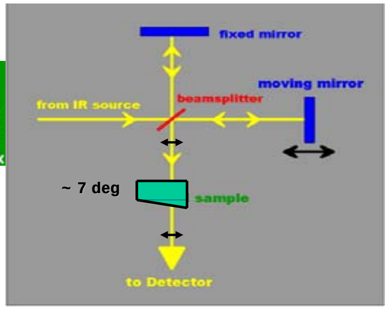
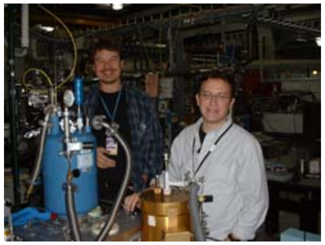
EXPERIMENTAL SETUP at NSLS, BNL



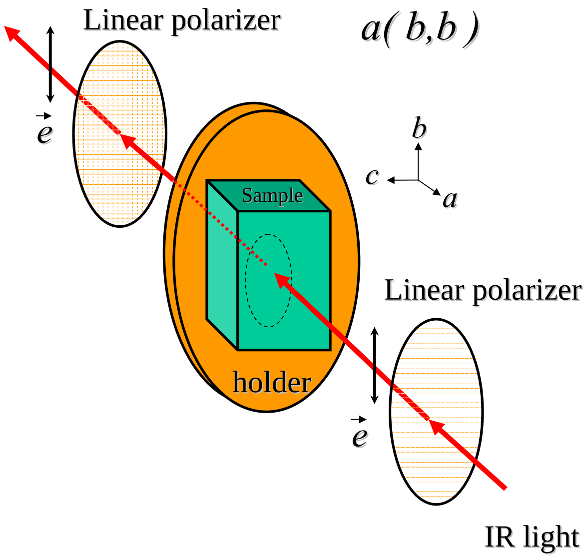


Sean O'Malley and Andrei Sirenko at U12IR, NSLS

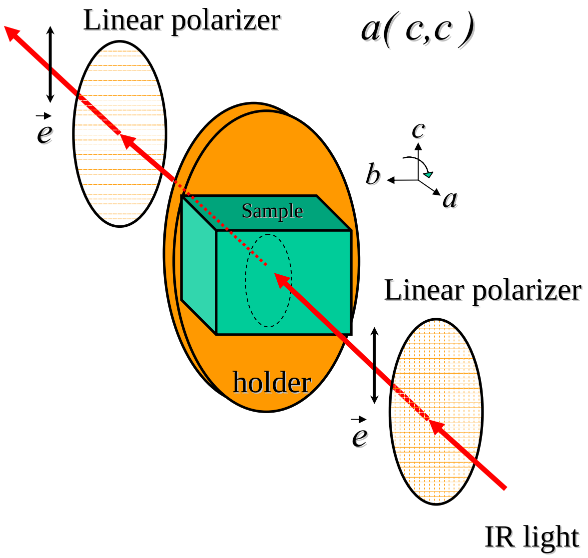
Spectral range: 8.5 – 105 cm^{-1} (~ 1 – 13 meV or ~ 0.25 – 3 THz)

Spectral resolution: 0.6 cm^{-1}

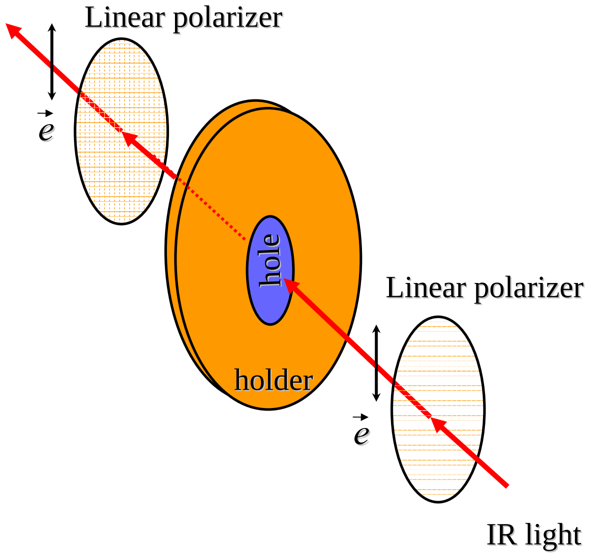
Transmission configuration:



Transmission configuration:

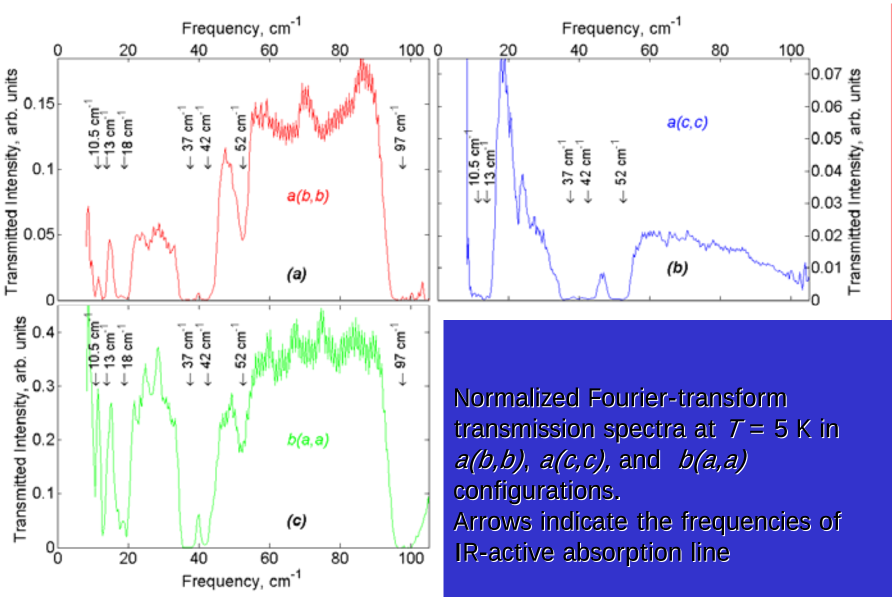


Normalization procedure:



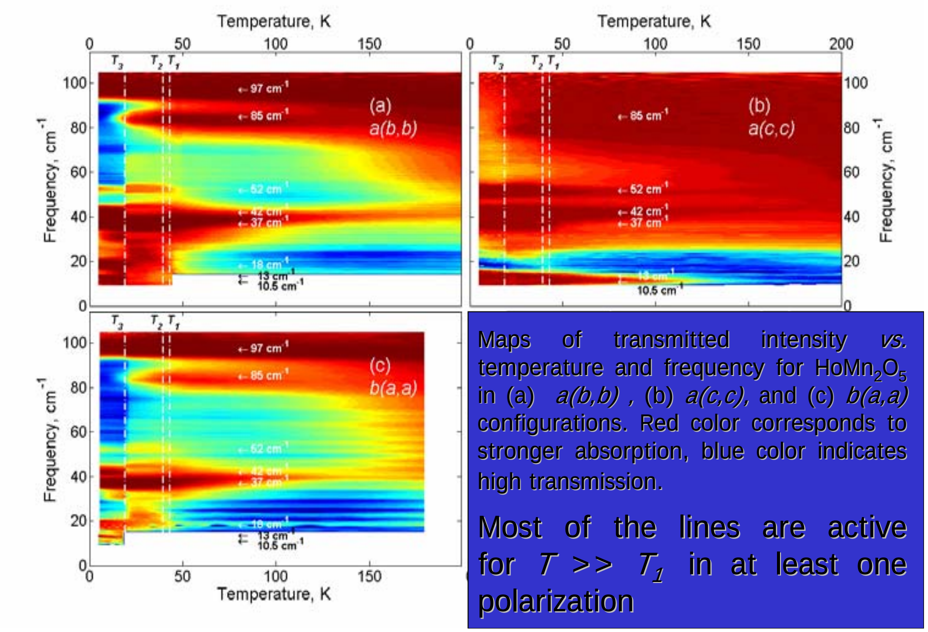
sirenko@njit.edu APS March Meeting, 2007

Far-IR transmission spectra for HoMn$_2$O$_5$



Normalized Fourier-transform transmission spectra at T = 5 K in *a(b,b)*, *a(c,c)*, and *b(a,a)* configurations.
Arrows indicate the frequencies of IR-active absorption line

IR transmission intensity maps for HoMn$_2$O$_5$



Maps of transmitted intensity *vs.* temperature and frequency for HoMn$_2$O$_5$ in (a) *a(b,b)*, (b) *a(c,c)*, and (c) *b(a,a)* configurations. Red color corresponds to stronger absorption, blue color indicates high transmission.

Most of the lines are active for $T >> T_1$ in at least one polarization