

The image shows the front cover of a spiral-bound notebook. The cover is a solid, textured blue color. At the top, there is a black spiral binding with silver-colored metal loops. The text is centered on the cover in a white, sans-serif font.

CHEM*3440

Chemical Instrumentation

Topic 10

Infrared Spectroscopy

Infrared is Rovibrational Spectroscopy

- Wavelengths between 0.8 μm to 1 mm.
- Associated with changes in nuclear motion (vibrations and rotations).
- In gas phase, rotational transitions are resolved; in liquid phase, they are broadened. Usually only focus on vibrational character.
- Energy is usually reported in wavenumbers (cm^{-1}); also proportional to frequency.

$$\bar{\nu} = \frac{1}{\lambda}$$

$$\nu = c\bar{\nu}$$

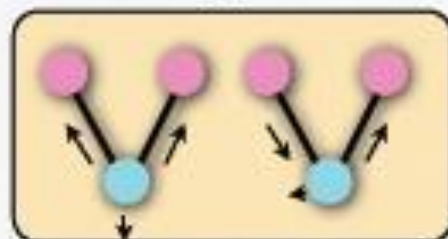
most commonly studied region

Near IR	0.8 - 2.5 μm	12800 - 4000 cm^{-1}
Mid-IR	2.5 - 50 μm	4000 - 200 cm^{-1}
Far IR	50 - 1000 μm	200 - 10 cm^{-1}

Types of Vibrations

- molecular dipole moment must change during a vibration to be IR active.
- this oscillating dipole interacts with the oscillating E-M field of the photon, leading to absorption.

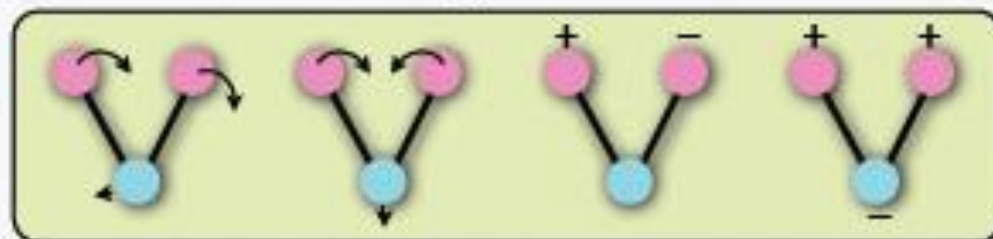
Stretching Vibrations



symmetric anti-symmetric

Changes in bond length

Bending Vibrations



rocking

scissoring

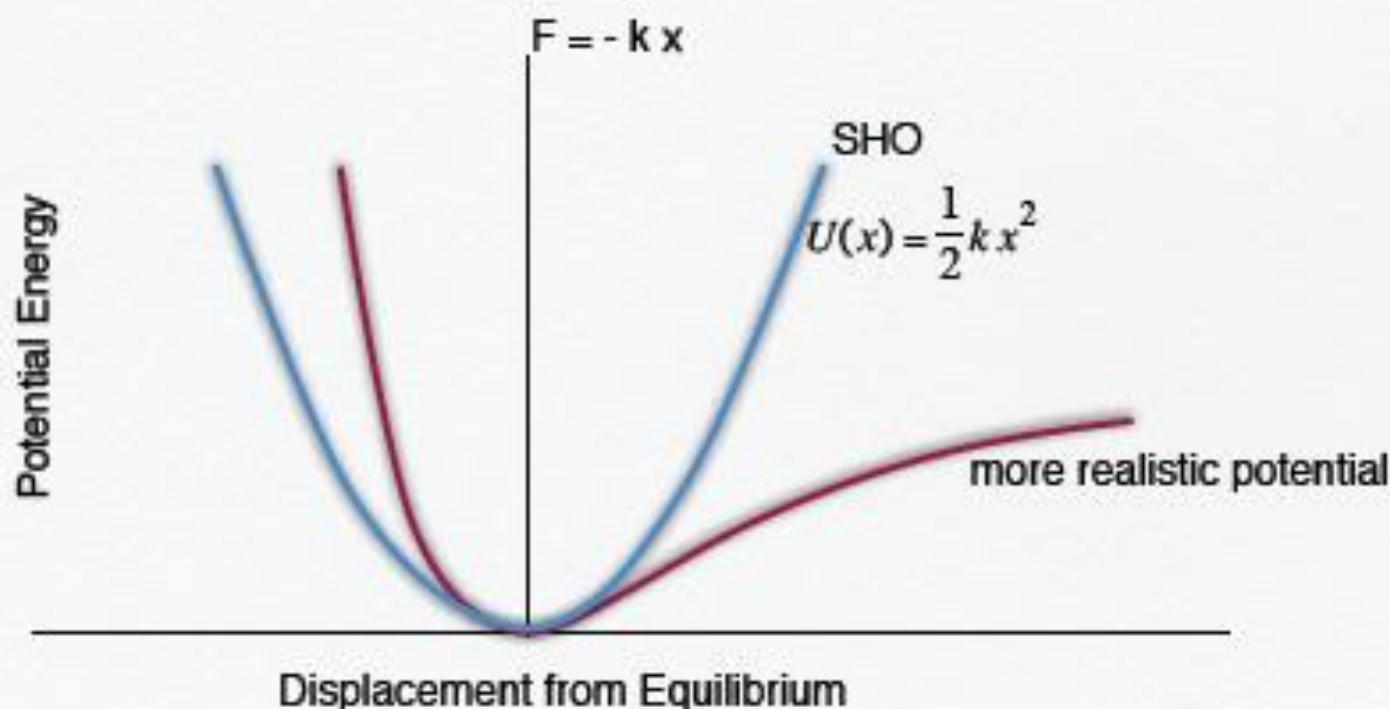
twisting

wagging

Changes in bond angle

Simple Harmonic Oscillator

- vibrations are successfully modeled as simple harmonic oscillator.
- based on Hooke's Law: restoring force is proportional to displacement



Sinusoidal Motion in SHO

By comparing Newton's Second Law with Hooke's Law, we obtain a differential equation.

$$F = ma = -kx \quad a = \frac{d^2x}{dt^2}$$
$$m \frac{d^2x}{dt^2} = -kx \quad \Rightarrow \quad \frac{d^2x}{dt^2} = -\frac{k}{m}x$$

A solution to this equation can be written as

$$x(t) = A \cos(2\pi \nu t) \quad \omega = \sqrt{\frac{k}{m}} = \sqrt{\frac{k}{\mu}}$$

ω is called the angular frequency. It is related to the frequency ν by $\omega = 2\pi\nu$.
The μ is reduced mass and is used when both ends of the bond can move (always).

Quantum Vibrational Motion

- molecular motion is quantized which leads to vibrational quantum levels indexed by a quantum number "v".

$$E_v = \left(v + \frac{1}{2}\right) \hbar \omega = \left(v + \frac{1}{2}\right) h \nu$$

$$\hbar = \frac{h}{2\pi} \quad \omega = 2\pi \nu \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

- energy absorbed is energy difference between two levels. In the SHO, the spacing is same between ALL adjacent levels

$$\Delta E_{v \rightarrow v+1} = \hbar \omega = h \nu = h \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

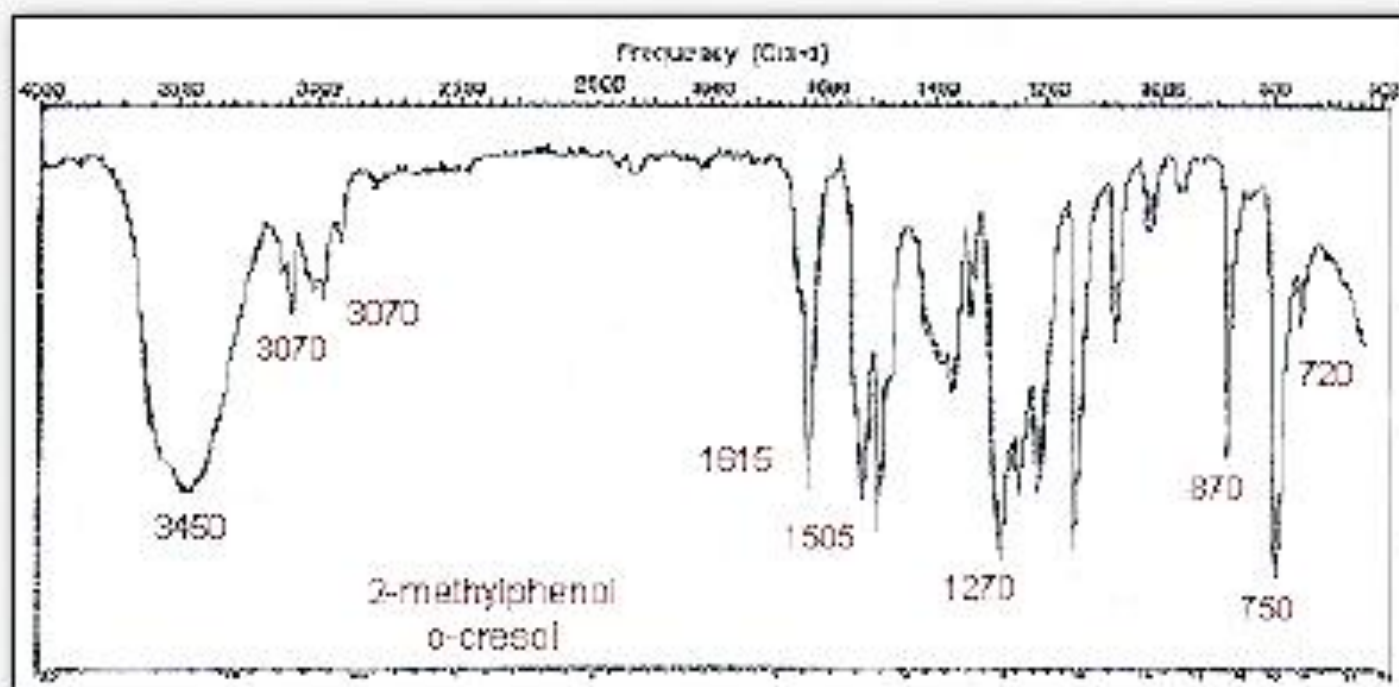
- selection rules: $\Delta v = \pm 1$ for electric dipole transitions (i.e. infrared transitions)

Anharmonic Oscillator

- real molecules, vibrations "close to being" harmonic.
- relaxes the selection rules (overtones and combination bands)
- distorts the intensities of the transitions
- changes spacings so that they are not all the same, but come closer together as you go up the vibrational ladder.
- bond can "break"; not so with SHO.

Typical Spectra

- spectra are usually presented as %transmittance against wavenumber. Mid-IR is usual scan range. Widely used as an aid in organic molecule identification.



Quick IR Analysis Algorithm

Infrared spectra: It is important to remember that the absence of an absorption band can often provide more information about the structure of a compound than the presence of a band. Be careful to avoid focusing on selected absorption bands and overlooking others. Use the examples linked to the table to see the profile and intensity of bands. Remember that the absence of a band may provide more information than the presence of an absorption band.

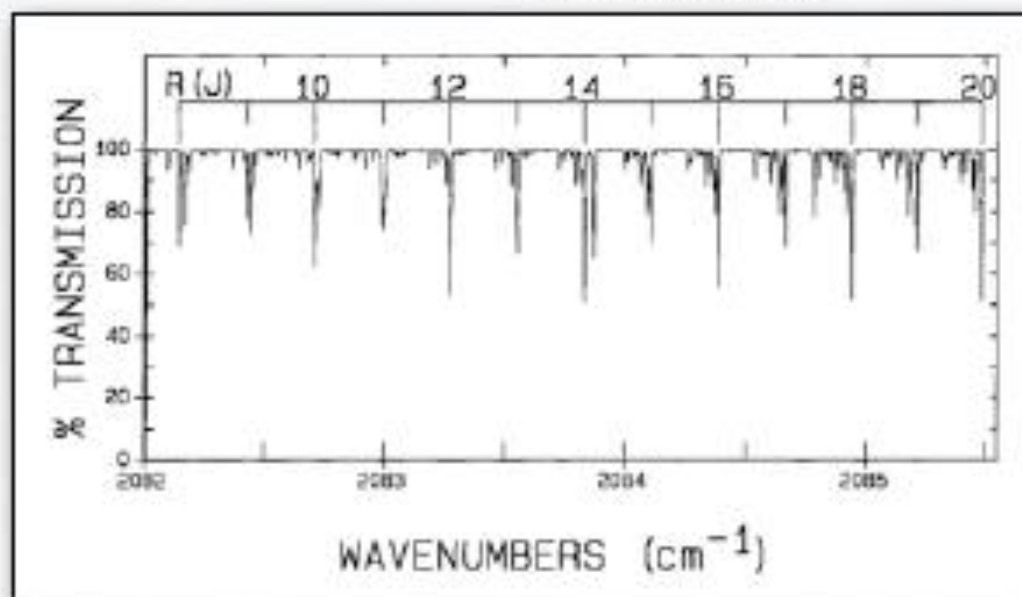
Look for absorption bands in decreasing order of importance:

1. the C-H absorption(s) between 3100 and 2850 cm^{-1} . An absorption above 3000 cm^{-1} indicates C=C, either alkene or aromatic. Confirm the aromatic ring by finding peaks at 1600 and 1500 cm^{-1} and C-H out-of-plane bending to give substitution patterns below 900 cm^{-1} . Confirm alkenes with an absorption at 1640-1680 cm^{-1} . C-H absorption between 3000 and 2850 cm^{-1} is due to aliphatic hydrogens.
2. the carbonyl (C=O) absorption between 1690-1760 cm^{-1} ; this strong band indicates either an aldehyde, ketone, carboxylic acid, ester, amide, anhydride or acyl halide. The an aldehyde may be confirmed with C-H absorption from 2840 to 2720 cm^{-1} .
3. the O-H or N-H absorption between 3200 and 3600 cm^{-1} . This indicates either an alcohol, N-H containing amine or amide, or carboxylic acid. For -NH₂ a doublet will be observed.
4. the C-O absorption between 1080 and 1300 cm^{-1} . These peaks are normally rounded like the O-H and N-H peak in 3. and are prominent. Carboxylic acids, esters, ethers, alcohols and anhydrides all containing this peak.
5. the CC and CN triple bond absorptions at 2100-2260 cm^{-1} are small but exposed.
6. a methyl group may be identified with C-H absorption at 1380 cm^{-1} . This band is split into a doublet for isopropyl (gem-dimethyl) groups.
7. structure of aromatic compounds may also be confirmed from the pattern of the weak overtone and combination tone bands found from 2000 to 1600 cm^{-1} .

This is a little recipe from Stanislaw State University (California).

High Resolution Gas Phase

This is a portion of the spectrum of completely isotopically substituted cyanogen
 $^{15}\text{N} \ ^{13}\text{C} \ ^{13}\text{C} \ ^{15}\text{N}$

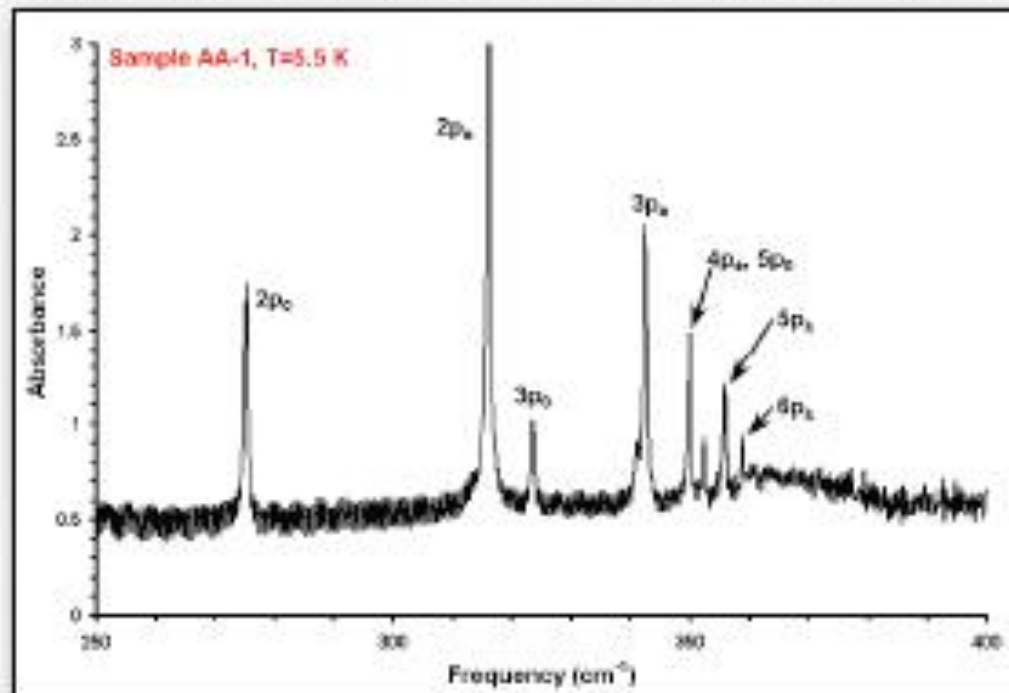


Quapp, Maki, Klee, Mellau,
J. Molec. Spectro. 187,
126 (1998).

We are observing the various rotational levels associated with ν_3 . The intensity variation confirms a unique quantum mechanical effect. Note that the entire spectrum seen here spans less than 4 cm^{-1} .

IR of Solid State - Silicon

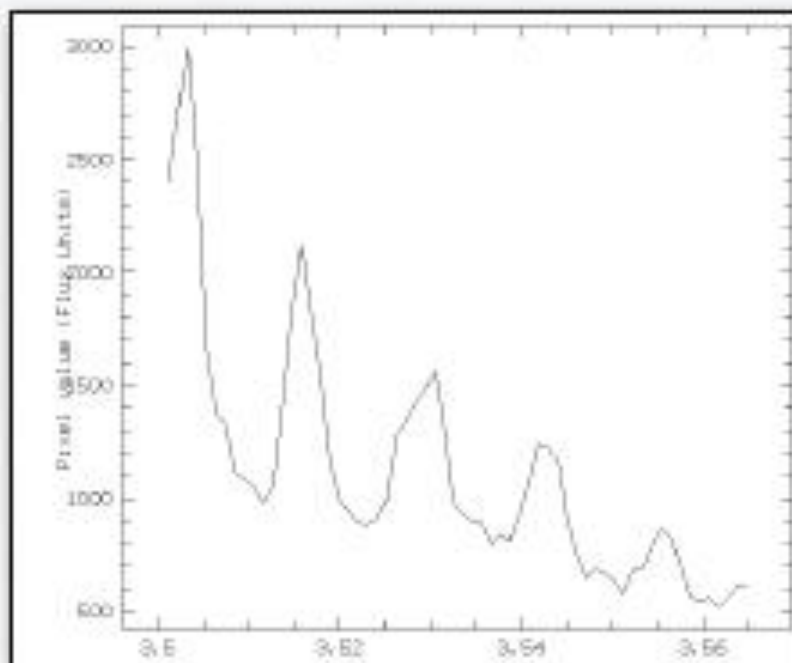
The solid state vibrates also. This is a sample of Si that has been annealed using acoustic shock waves rather than heat. Note the temperature and the sharpness of the peaks. The authors also use absorbance rather than %T; it spreads out the data better (absorbance over 3 orders of magnitude here).



Donnelly et al., Appl. Phys. Lett.
78, 2000 (2001).

IR in Space

The Shoemaker-Levy 9 comet that crashed into Jupiter in 1994. This is the infrared spectrum taken by the European Southern Observatory of the H-collision.



This is a spectrum of the S-band emission from methane. They are not usually seen on Jupiter but are seen here because of the high temperatures arising from the explosion of the collision.

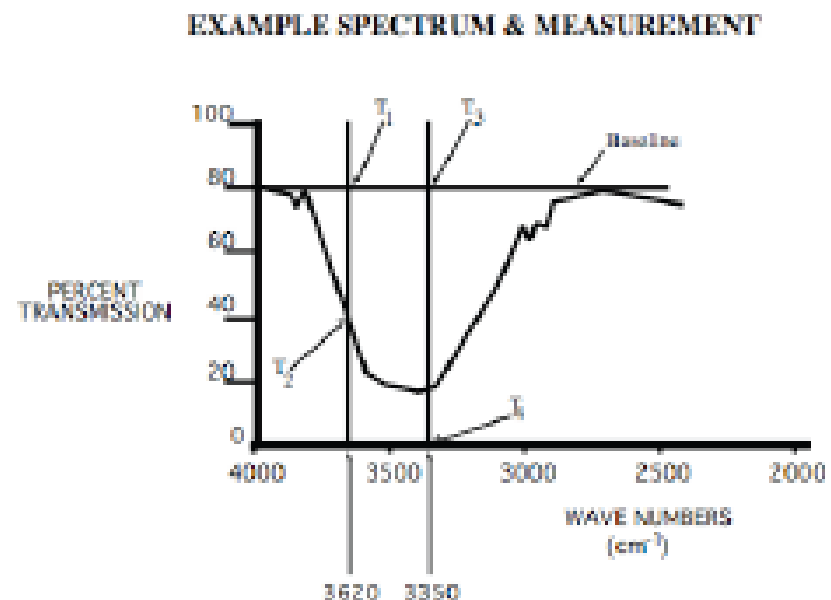


...and other applications.

Found this article:

"Infrared Spectra Alteration in Water Proximate to the Palms of Therapeutic Practitioners", Schwartz, De Mattei, Brame, Spottiswoode, published in many places, including "Research in Parapsychology" (1986).

They study water that was close to the hands of faith healers and determined that there was something different in the spectra in the $2.5\ \mu\text{m}$ to $3.5\ \mu\text{m}$ region. Specifically suggest that the ratio of the intensity at the two positions on the H-bonding peak change with exposure to the healers.



Infrared Sources

The **Nernst Glower** or Nernst Lamp. An early light bulb which did not need to operate in vacuum like Edison's W filament bulb. A $\text{ZrO}_2\cdot\text{Y}_2\text{O}_3\cdot\text{Er}_2\text{O}_3$ (90:7:3) mixed oxide. A current passing through it would heat it to glowing. Needed an external filament to get it hot to begin, but then it could continue on its own.

Gives a good spectrum from 1 to $10\ \mu\text{m}$; intensity varies over 3 orders of magnitude.



Infrared Sources con't

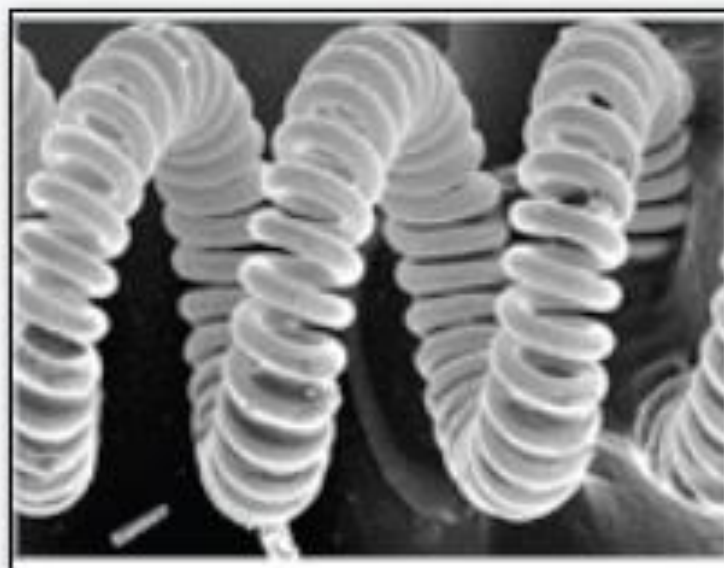
The **Globar** is a competitor of the Nernst Glower. Similar concept, but uses SiC instead of metal oxides. Can start heating from room temperature. Globar is a bit better for wavelengths below $5\text{ }\mu\text{m}$; also the Globar requires water cooling of the filament supports.



Infrared Sources con't

Incandescent wire sources are longer lasting but lower intensity than the glower or global. A nichrome wire or rhodium wire heated to around 1100 K is a good IR source.

A tungsten filament lamp can also work as a good source in the near-IR region.



Infrared Sources con't

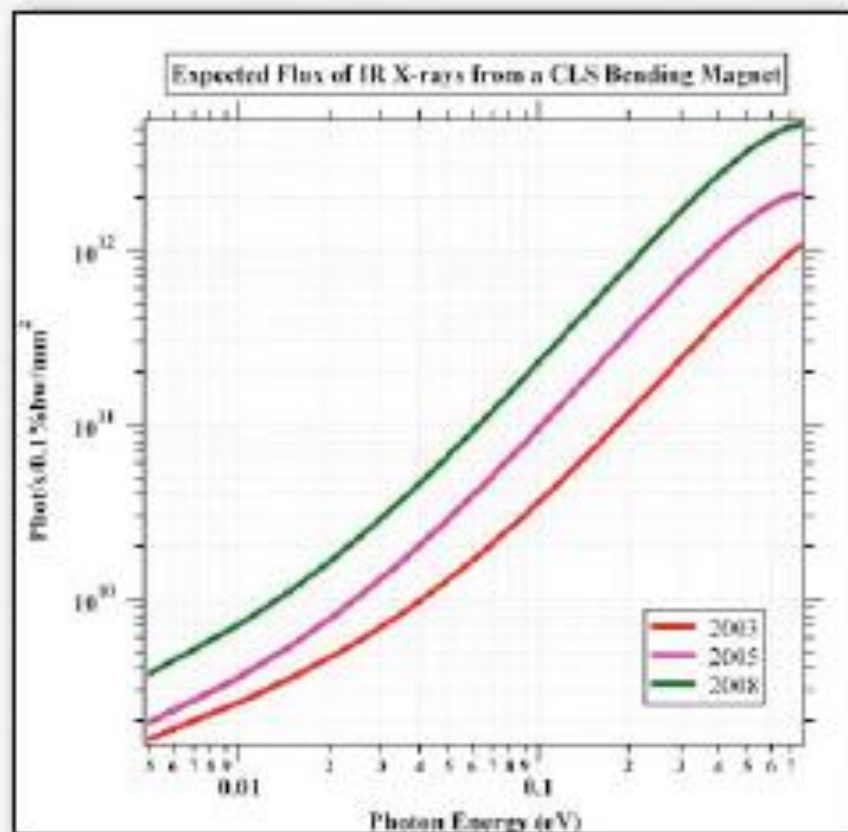
The most difficult spectral region in which to function is the Far-IR. Few sources are available. The mercury arc lamp does provide some Far-IR radiation and has been used as a source for this type of experimentation.



Infrared Sources con't

Most exciting is a new source coming on-line: the Canadian Light Source (CLS) is a **synchrotron** being built at the University of Saskatchewan. It is an extremely bright source of light and has, by comparison, a lot of light in the Far-IR. Experiments never before possible are being planned.

Also have projects using mid-IR to do spectromicroscopy - spectroscopy with microscopic spatial resolution. One project focusing especially on biological samples, involves doing IR work on a single cell.



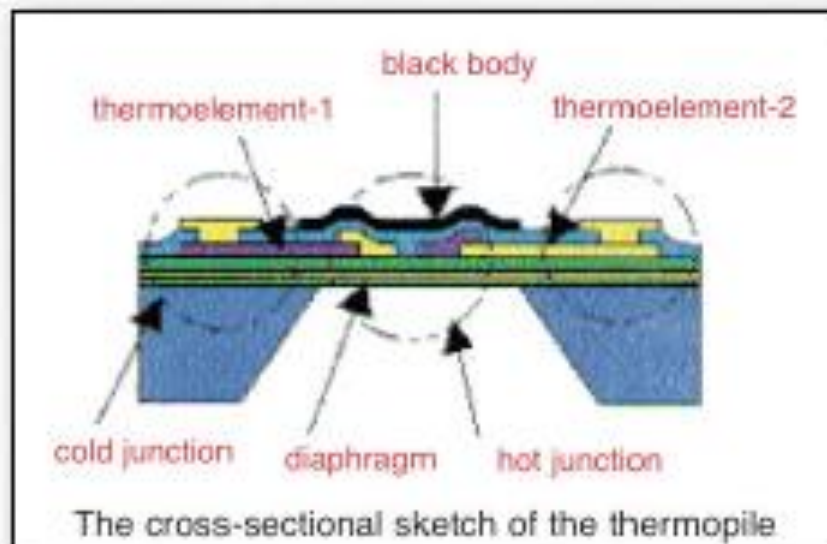
Infrared Detectors

An infrared photon carries a lot less energy than a visible photon. It is more difficult to detect, particularly with background radiation to worry about.

- **Thermocouple** is a thermal transducer; it measures the temperature rise because of the absorbed light.
- Heat capacity must be small since incoming is so small (10^{-7} to 10^{-9} W). Detector must be small. Temperature changes amount to a few thousandths of a K.
- Detector must be housed in vacuum to minimize thermal losses.
- Must be shielded from nearby objects which radiate IR (surround with liquid N_2 heat shields).
- Modulate the signal to further discriminate against noise.

Infrared Detectors con't

- **thermopiles** are thermocouples stacked together to achieve gain in the signal.
- measure difference in temperature between hot junction and cold junction.
- response is slow and weak compared to other systems. Coupled with a good amplifier can still give a good response.



A typical thermopile from Thermometrics.

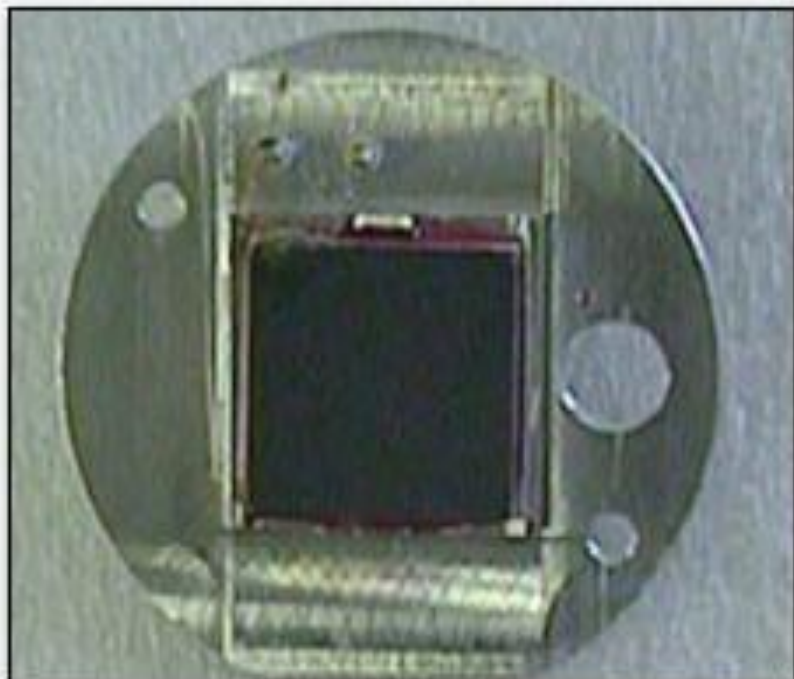
Infrared Detectors con't

- A **bolometer** is a sensitive resistance thermometer; material's resistance changes with changing temperature.
- Can be metallic. Platinum is a common, sensitive resistance thermometer.
- Can be semiconductors. These often called thermistors.
- Not as widely used, but a Ge bolometer at 1.5 K is an excellent Far-IR detector.



Infrared Detectors con't

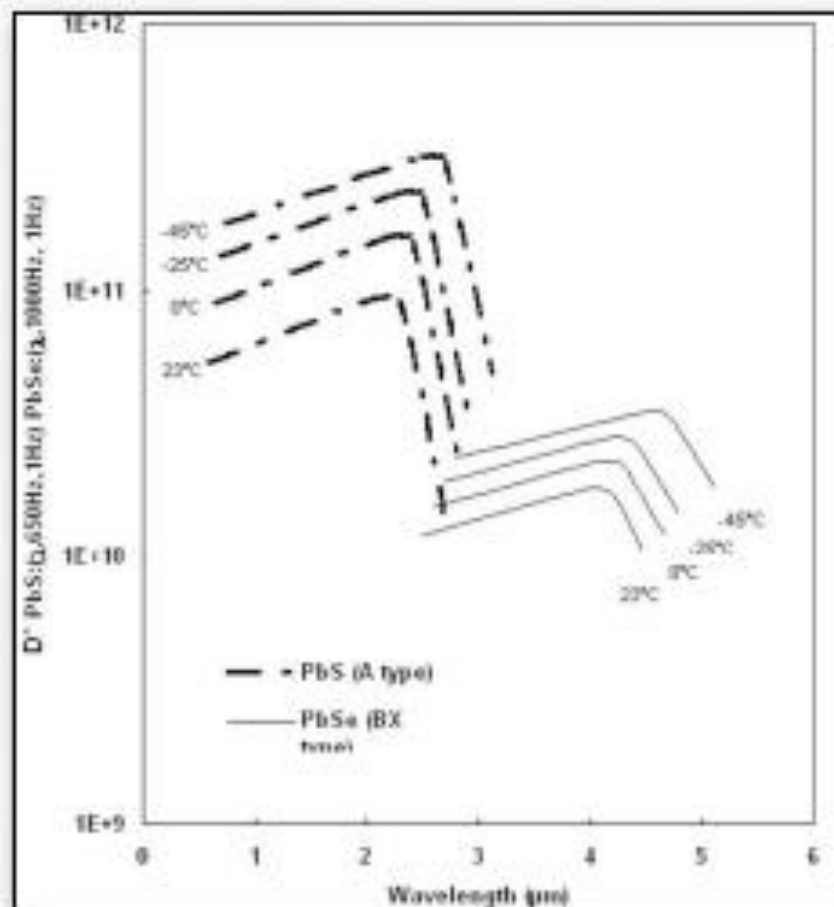
- Pyroelectric detectors have a potential which changes with temperature.
- Made from materials which demonstrate ferroelectricity.
- Sandwich the thin film between two metal electrodes, one of which is IR transparent. It becomes a temperature dependent capacitor. Changing capacitance requires current flow to adjust charge . Detect this current flow.



Infrared Detectors con't

Photoconducting detectors; absorbed radiation generates excess electrons and holes which increases the substances conductivity. Many semiconductors employed here. Different materials have a different absorption bandwidth.

Here is the spectral response for PbS and PbSe detectors at different temperatures.

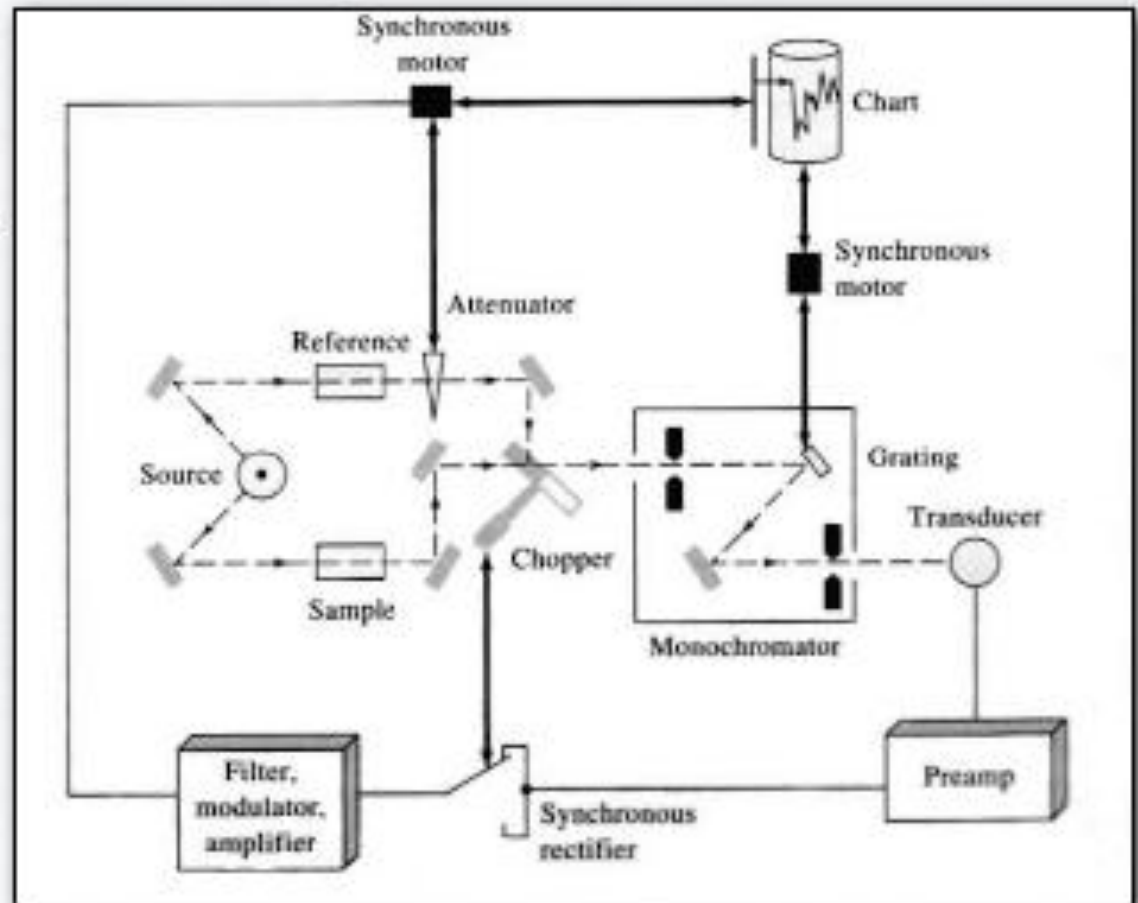


Dispersive IR Systems

- Formerly the real workhorse in IR spectroscopy.
- Used gratings with smaller grating count than in UV-Vis.
- Use low frequency choppers to modulate signal for background discrimination (low chopping rate because of slow detector response).
- Detectors usually cooled (LN_2 , thermoelectric, ice bath)
- Sample compartments before the monochromator (opposite for UV-vis). Diminishes stray/scattered light problems. Possible because IR radiation does not tend to photodecompose compounds.
- Often a null system is used (see next)

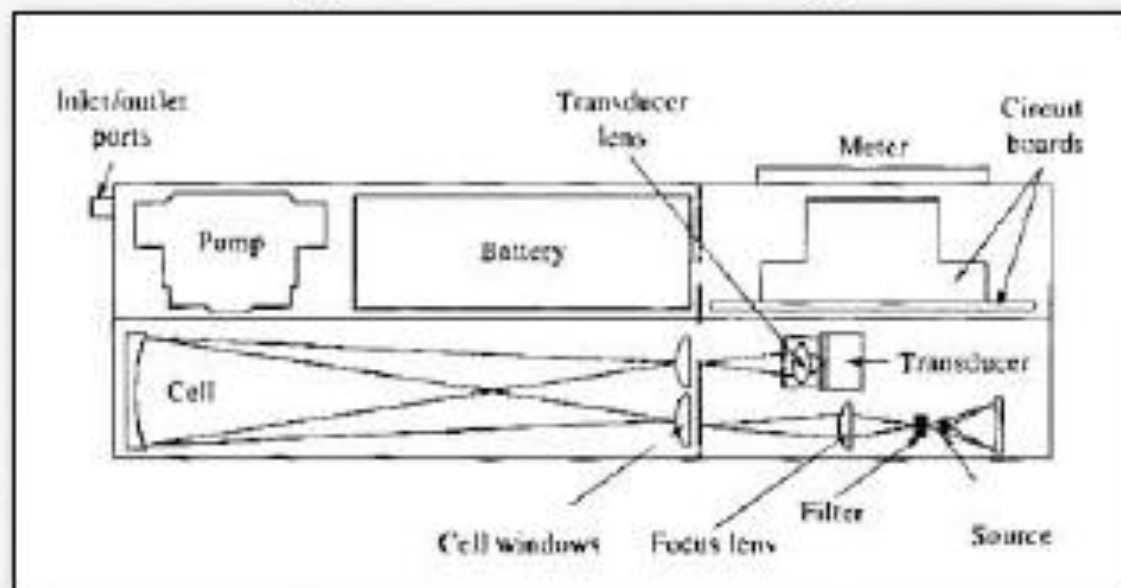
Dispersive IR Systems con't

The light is alternately directed through the monochromator by the chopper wheel. Any difference in the power of the two is detected and a motor drives a wedge attenuator into the reference beam until there is no difference. The drive signal is also the spectrum; another drive synchronously drives the grating and the recorder.



Non-Dispersive/FTIR Systems

- Rugged and inexpensive system to perform very specific tasks have been developed.
- A light source, a detector, and sometimes or not a filter.
- Often can be used for sensing of gas components. For instance, CO detector.
- Filter photometers can be designed to detect numerous organic substances.



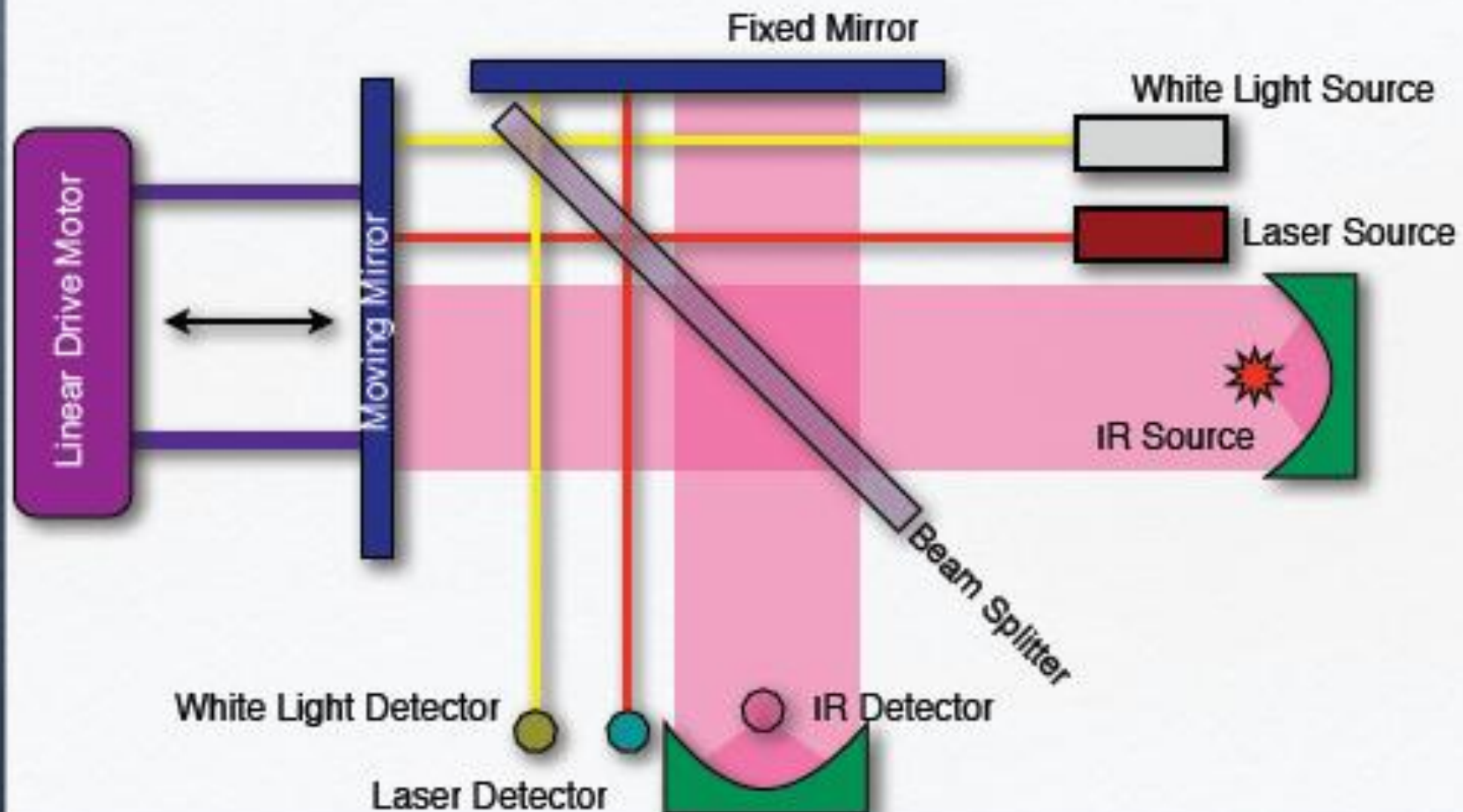
FTIR Systems

- Everything at the research level is now a Fourier Transform device.
- There are many transforms that have been used (Hadamard, Hartley, cosine, Blackwell, etc.) but none have achieved the universal application of Fourier (though all have some application – there are Hadamard Transform spectrometers, for instance).
- Most common to encode the spectral information using a Michelson interferometer.
- Computer processing of encoded information produces the spectrum.

Albert Michelson and Albert Einstein



Michelson Interferometer



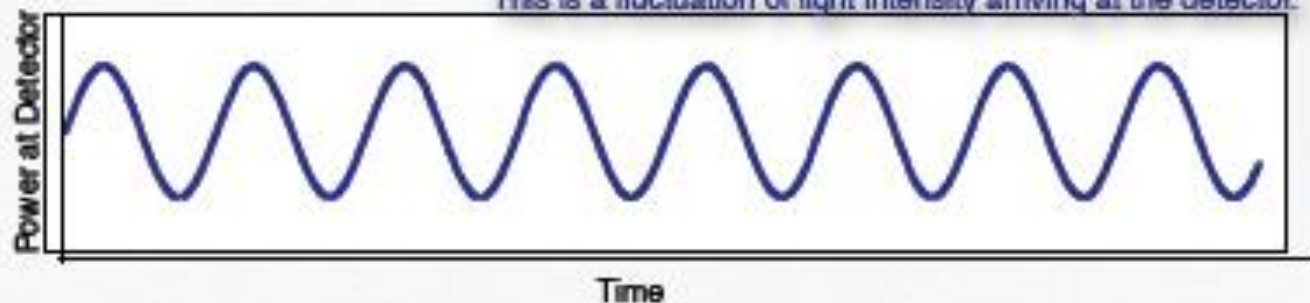
Photon Interference

- A photon is "split" and travels down the two legs of the interferometer, reflects off the two mirrors, returns to the beam splitter, is "recombined" and reflected off towards the detector. By recombining, the two "photon-parts" interfere with each other. If the paths taken are identical, or are different by a integral number of wavelengths, then constructive interference occurs. The photon has a probability of 1 of heading off to the detector.
- If the paths differ by exactly $1/2$ of a wavelength of the light, the two parts will destructively interfere and the photon has a probability of 0 of coming out and heading to the detector.
- Any other path difference, the photon has a probability between 0 and 1 of reaching the detector.
- The detector does not know about interference; any photon that reaches it deposits energy that gives rise to a signal. The sum of a large number of photons, each one having been subjected to an interference event, constitutes the signal reaching the detector at any point in time.

Monochromatic Light

- Consider a monochromatic light source. For a given path difference, the output beam's intensity is given by the probability of a given photon making it through.
- The path difference is continually changing because the moving mirror is being scanned.
- Record the detector intensity vs. time. Note that time is directly correlated to mirror position by the scan velocity, which corresponds directly to any path difference.

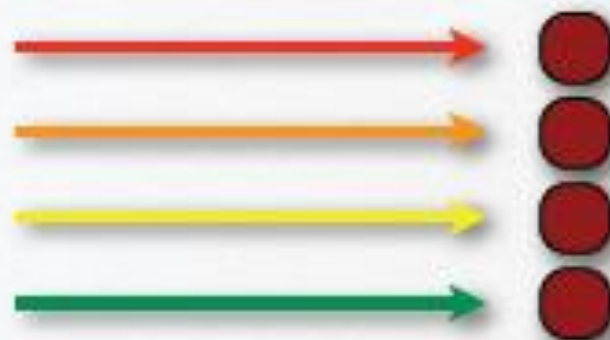
N.B. Don't confuse this wavelength with the wavelength of the light.
This is a fluctuation of light intensity arriving at the detector.



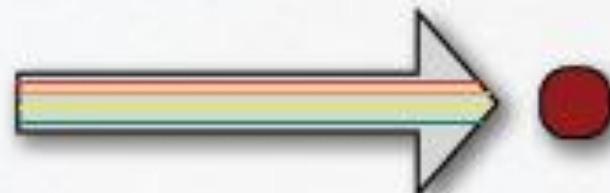
FTIR is a Multiplex Experiment

When a spectrometer uses an array detector, it has a large number of similar detectors functioning simultaneously. It is a multichannel detection system. By contrast, the FTIR encodes the many channels with different frequencies and they impinge upon the same detector simultaneously. It is a multiplex experiment.

Multichannel

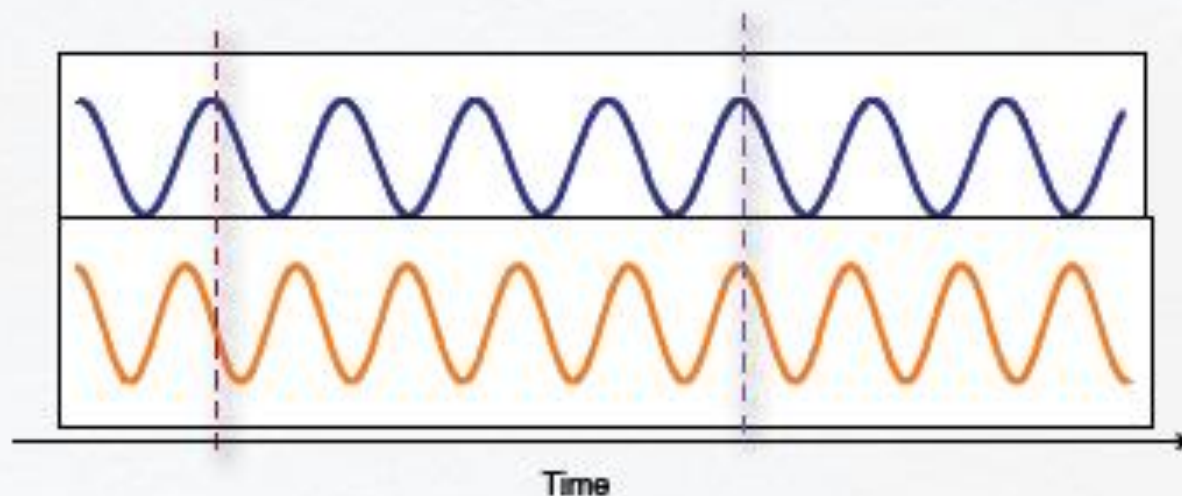


Multiplex



Bichromatic Light

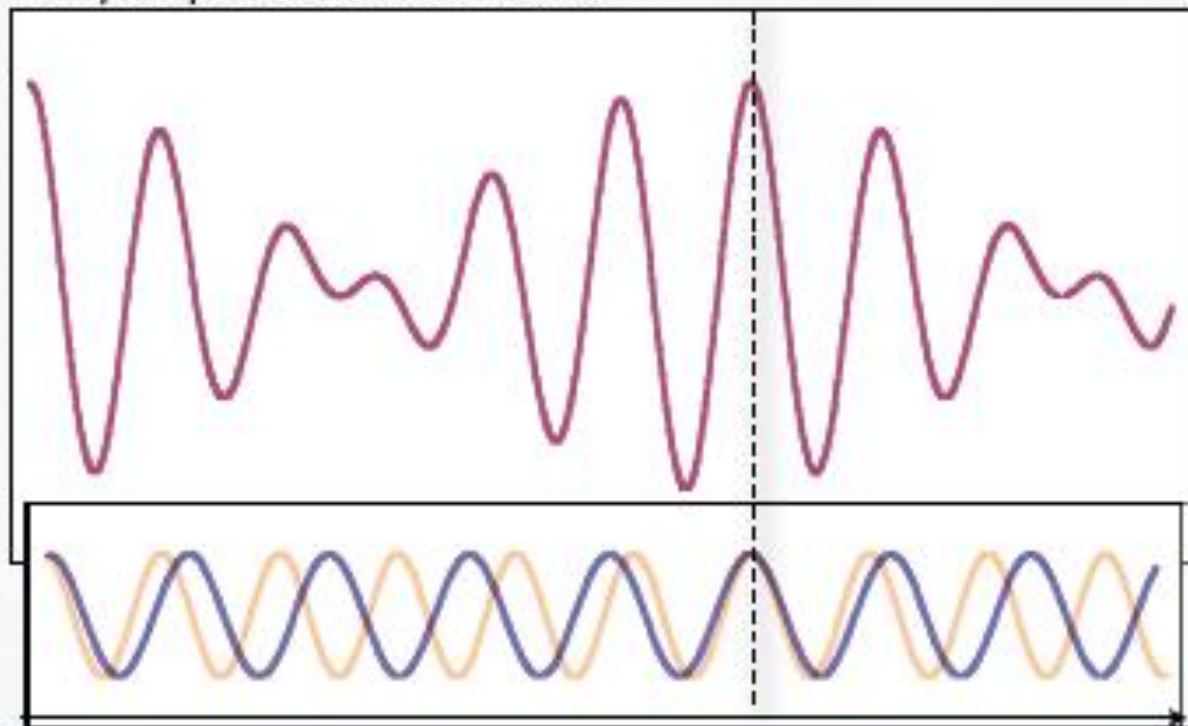
When two light wavelengths traverse the interferometer, both come in and out of phase with themselves, but they do so at different times because of the different wavelengths involved.



Higher frequency light comes in- and out-of-phase more quickly and modulates the power arriving at the detector more quickly.

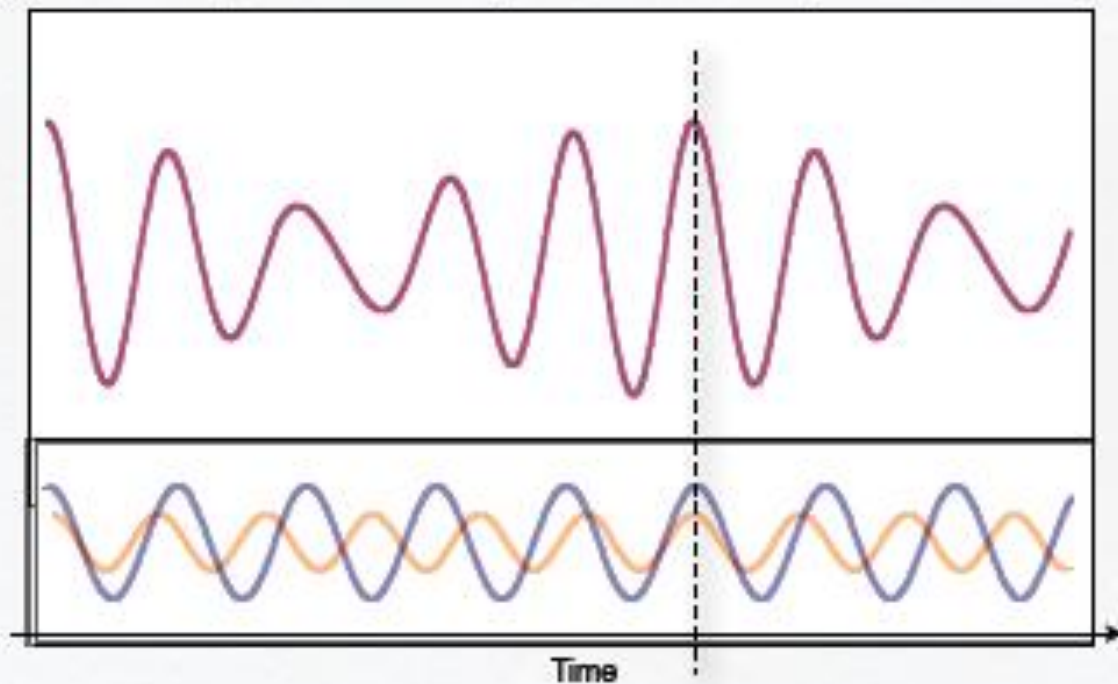
Detector Sees the Sum

The detector sees the sum of the power delivered by the two beams. When both have a maximum power, then the signal is doubled; when both are at a minimum, the signal is at a minimum. When one is at a maximum and the other at a minimum, the power is in the middle.



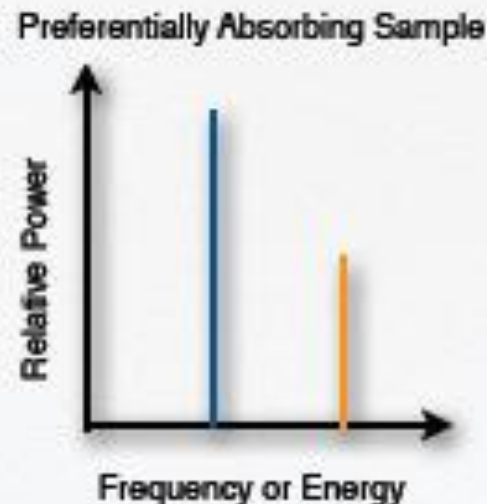
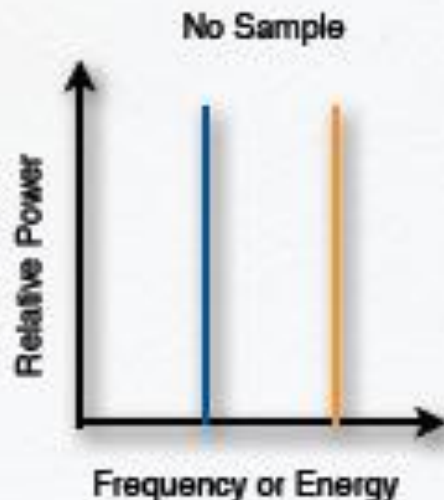
Then One is Absorbed

Then a sample is placed in the beam; it has the property that it has a certain probability (let's say 50%) of absorption of the higher frequency photon. The beat pattern changes due to the preferential absorption of the one frequency.



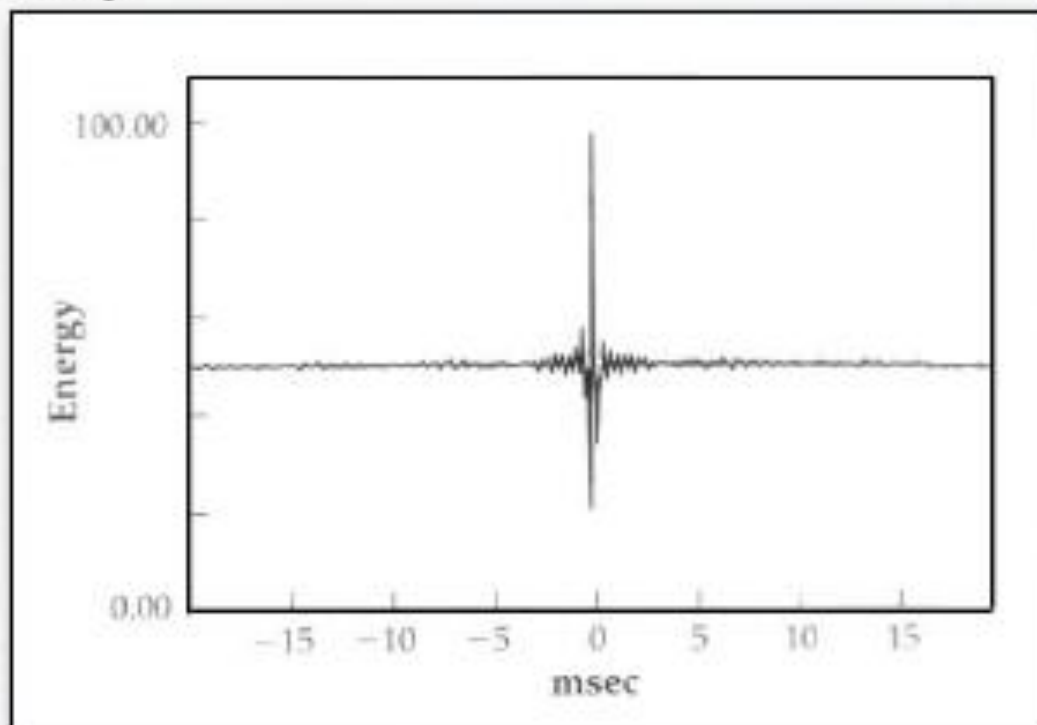
The Frequency Domain

- The detector observes and reports the variation of photon power in time arriving at the detector. Such a graph of time vs. power is said to be a time domain representation of the data.
- The spectrum with which we are more familiar is that which reports the relative amplitude of each contributing signal.



The Time Domain

The time domain signal is called an "interferogram". It contains all of the frequency spectral information, but we need to extract that information mathematically.



Retardation

Usually plot interferogram in terms of a distance - the path difference between the moving and stationary arms of the interferometer. Propagation down the moving mirror path is "retarded" by this distance. Since the motion is down and back again, the total retardation is twice the path difference.

$$\delta = 2 (d_{\text{moving}} - d_{\text{fixed}})$$

- When $\delta = \lambda/2$, destructive interference occurs ($\Delta d_{\text{moving}} = \lambda/4$).
- When $\delta = \lambda$, constructive interference occurs ($\Delta d_{\text{moving}} = \lambda/2$).

This holds true for any integer multiples of λ or $\lambda/2$.

Mirror Scan Velocity

The mirror is scanned at a constant velocity, v_m (in the range of a few cm/s).

The time (τ) for the mirror to move a distance of $\lambda/2$ is

$$\tau = \frac{\lambda/2}{v_m}$$

Since this retardation distance is exactly the amount needed to bring the wave back into constructive interference, this represents the time between maxima of the power reaching the detector. Hence the modulation frequency at the detector is

$$f = \frac{1}{\tau} = \frac{2v_m}{\lambda}$$

Detector Frequency Proportional to Light Frequency

The relationship between the light's wavelength, wavenumber, and frequency is

$$\frac{1}{\lambda} = \bar{\nu} = \frac{\nu}{c}$$

The frequency at the detector is then given by

$$f = \frac{2\nu_m}{\lambda} = 2\nu_m \bar{\nu} = \frac{2\nu_m \nu}{c}$$

Note how the power fluctuation frequency at the detector is directly proportional to the incident light frequency, except scaled by a huge factor. For a mirror velocity of 1.5 cm/s, we have $f = 10^{10} \text{ n}$.

For 2000 cm^{-1} ($5.0 \text{ }\mu\text{m}$ or $6 \times 10^{13} \text{ Hz}$) light, the power fluctuates at 6 kHz. This is why the experiment works. We can measure kHz frequencies electronically, but not terahertz frequencies.

A Jumble of Frequencies

- The IR source emits a continuum of frequencies over its wide emission bandwidth. These all interact simultaneously with the sample. How do we sort it out?
- Consider the radio frequency broadcast spectrum in a major city. Attach an antenna to an amplifier and observe with an oscilloscope the signal in time. The sum of all radio and television stations broadcast signals are observed; the jumble is indecipherable.
- Introduce a tuning circuit that allows you to focus on a single frequency at a time. Measure the amplitude of the signal at that frequency, scan to the next, and so on. The end result is a table of signal and frequency - the spectrum.

The Cosine Transform

This jumble of frequencies is really a sum of whole bunch of cosine (or sine) waves. Look at the following integral:

$$\int_{-\infty}^{\infty} \cos \omega_1 t \cdot \cos \omega_2 t \, dt$$

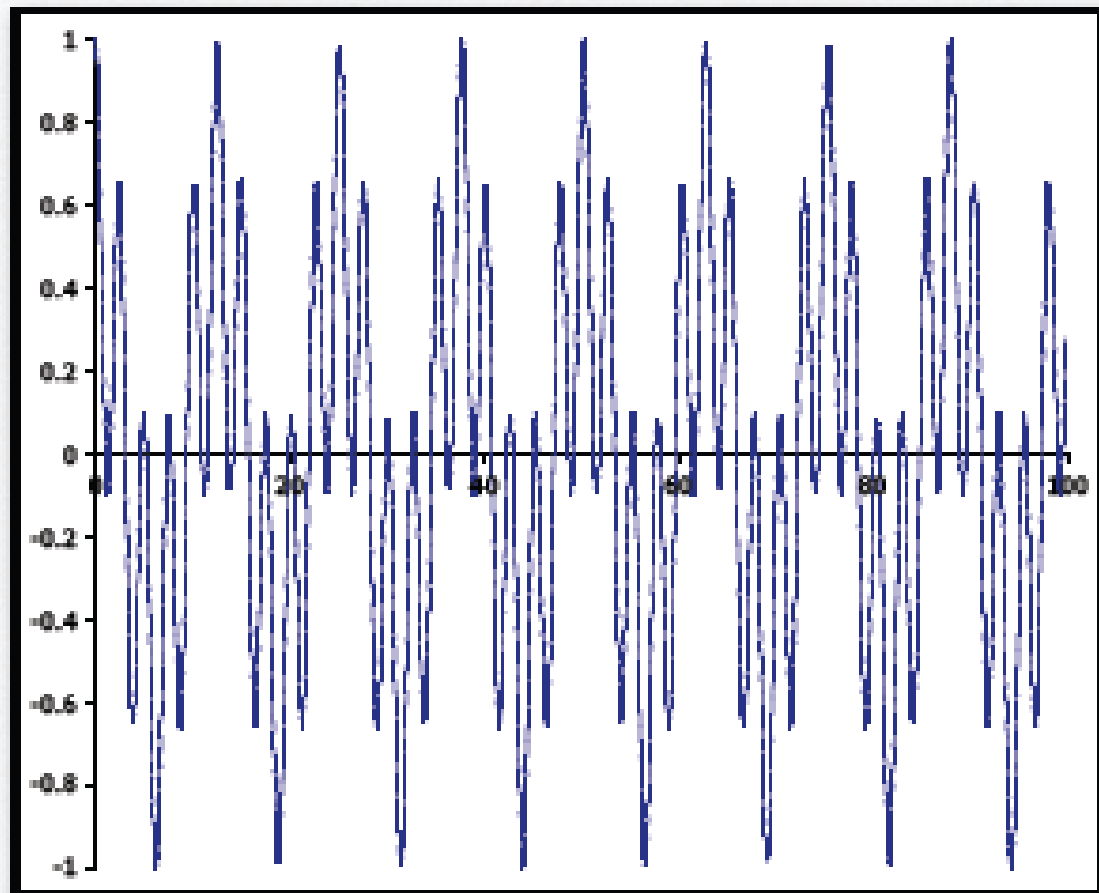
The following trig relation can expand the integral into

$$\cos x \cdot \cos y = \frac{1}{2} [\cos(x + y) + \cos(x - y)]$$

$$\therefore \int_{-\infty}^{\infty} \cos \omega_1 t \cdot \cos \omega_2 t \, dt = \frac{1}{2} \left[\int_{-\infty}^{\infty} \cos(\omega_1 + \omega_2)t \, dt + \int_{-\infty}^{\infty} \cos(\omega_1 - \omega_2)t \, dt \right]$$

The Cosine Transform con't

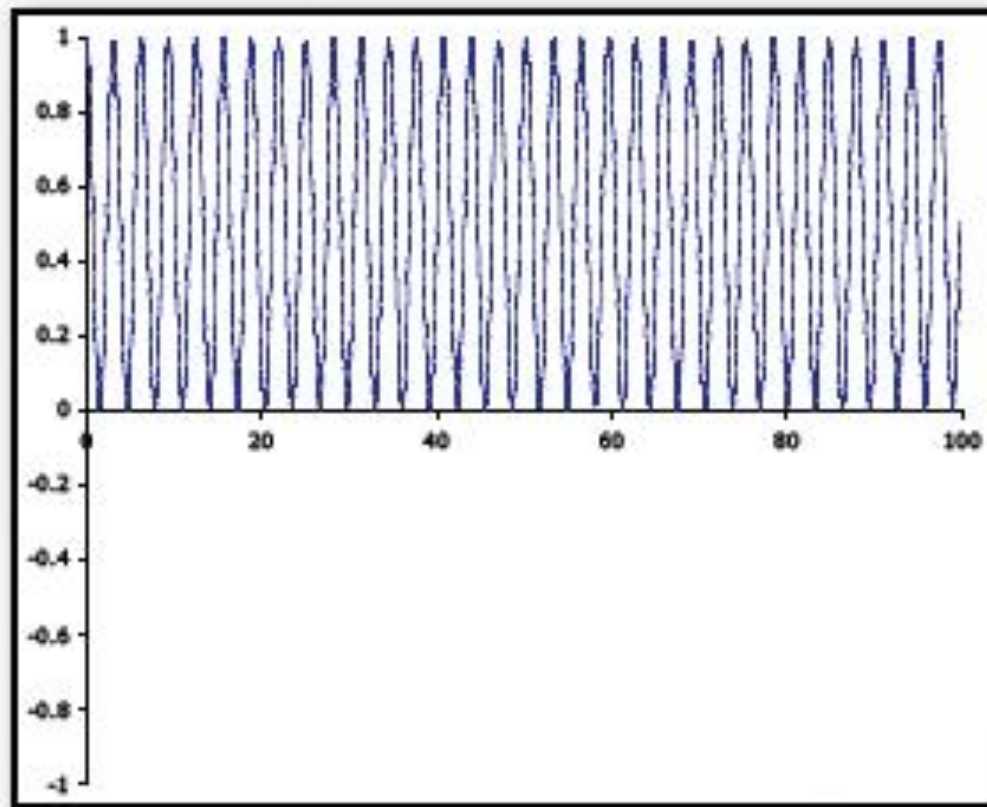
Consider the situation with $\omega_2 = 1.5 \omega_1$. The product of the two functions is



Now take the integral of this function. Note how the symmetry forces the integral to be exactly 0. This is true for ALL values of the two frequencies except...

The Cosine Transform con't

... the case where the two frequencies are the same. Then the product looks like



Everything is positive.
The integral must have a
non-zero value.

With this integral, the $\cos \omega_2 t$ function selects its own frequency from all other possible frequencies; all other frequencies are zero.

The Cosine Transform con't

Apply this integral's property to the jumble of frequencies discussed earlier. Let $f(t)$ be the time domain signal we would collect. It is, recall, the sum off all frequencies being broadcast. We can calculate $C(\omega_2)$

$$C(\omega_2) = \int_{-\infty}^{\infty} f(t) \cos(\omega_2 t) dt$$

The value of $C(\omega_2)$ is related to that part of $f(t)$ which is oscillating at ω_2 . In fact, it is the amplitude of the signal at that frequency. This integral is the Cosine Transform of $f(t)$.

By sequentially solving the integral for different ω_2 we eventually determine the amplitude for all frequencies - we have the spectrum.

Euler's Identity

Both amplitude and phase are important in analyzing the "jumble of frequencies". Analyzing for cosine AND sine functions simultaneously is a way of recovering all the information. To treat two components simultaneously, we use the complex number system. When the cosine and the sine are, respectively, the real and imaginary parts of a complex number, there is a remarkable identity (first proven by Leonard Euler) that arises

$$e^{ix} = \cos x + i \sin x$$

You can prove this by just taking the series expansions for each term and comparing them term by term. It really works.

Fourier Decodes the Time Domain

The Fourier Transform is written as follows:

$$F(\omega) = \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt$$

This integral will decode the phase and amplitude for each frequency component in $f(t)$. $F(\omega)$ is the spectrum. This is called the Forward Fourier Transform. It is also possible to take the frequency spectrum and transform it back into the time domain. The Inverse Fourier Transform is written as

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) e^{-i\omega t} d\omega$$

FFT - Fast Fourier Transform

Our data is actually digital; the time domain is known only at discrete time intervals. Transforming this discrete time domain into a discrete frequency spectrum is done by a Discrete Fourier Transform; the integration is replaced by a series of sums, tailored made for a computer. A famous algorithm published by Cooley and Tukey provided what is known as the Fast Fourier Transform, applicable to a discrete data set which has a power of 2 for its elements. This is the basis for most FFT calculations today.

FFT calculations are subject to the aliasing problems mentioned earlier; we must sample at such a rate that we have at least two data points per period of the highest frequency component. The Nyquist frequency is at $1/2$ of the sampling frequency. An anti-aliasing filter can help to keep the spectrum "clean".

Interferometry and Fourier

An interferometer encodes the frequency spectrum of the source – as *modified by the adsorption of a sample* – by downscaling into a more accessible frequency range and recording its behaviour in the time domain, or rather the detector power as a function of mirror retardation δ .

A Fourier Transformation of the time domain provides a frequency spectrum. (It actually gives a spectrum with both real and complex components; we want the power spectrum which is the complex square of the transform, but don't worry about that now.)

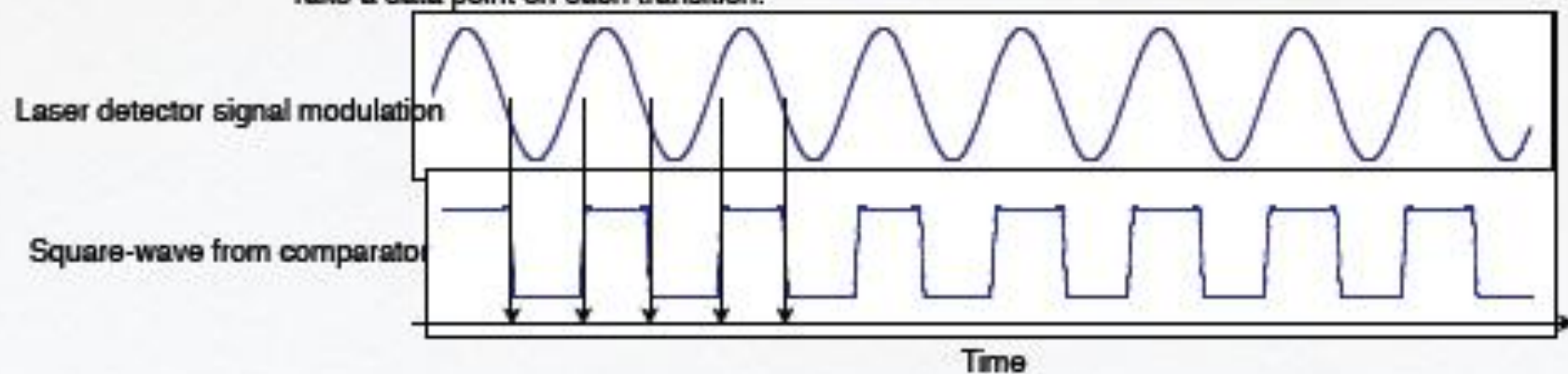
Then with our knowledge of the mirror scan velocity and its retardation, we can convert the frequency spectrum into the frequency or energy of the original components of the infrared spectrum.

What's the Laser Doing There?

Why is there a laser, complete with its own interferometric system in the spectrometer?

- Used to stabilize mirror scan; triggers a data acquisition event.
- Use 632.8 nm (red) He:Ne laser light. It gives a single wavelength interferogram that oscillates much more quickly than anything in the IR (shorter wavelength). Use the zero-crossings to trigger a data acquisition event.

Take a data point on each transition.

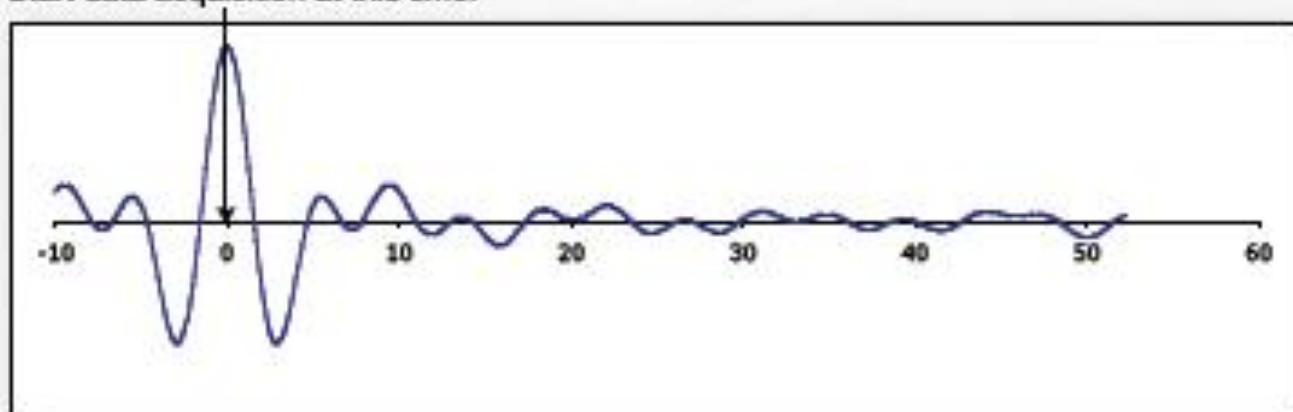


What's the White Light Doing There?

There is also another interferometer. But this time using a white light source.

- Used to initialize the data acquisition process for each mirror scan.
- The interferogram for white light is extremely sharp at $\delta = 0$ (no retardation), but everywhere else, it has complete destructive interference. A pulse on that channel alerts the controller that the mirrors are now at 0 retardation; the scan acquisition can start.

Start data acquisition at this time.



Digital Concerns

FTIR is always done digitally. There are three things to choose; any two can be independent:

Rate of Sampling



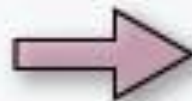
The Spectral Range

Total Time Spent Sampling



The Spectral Resolution

Total Number of Data Points

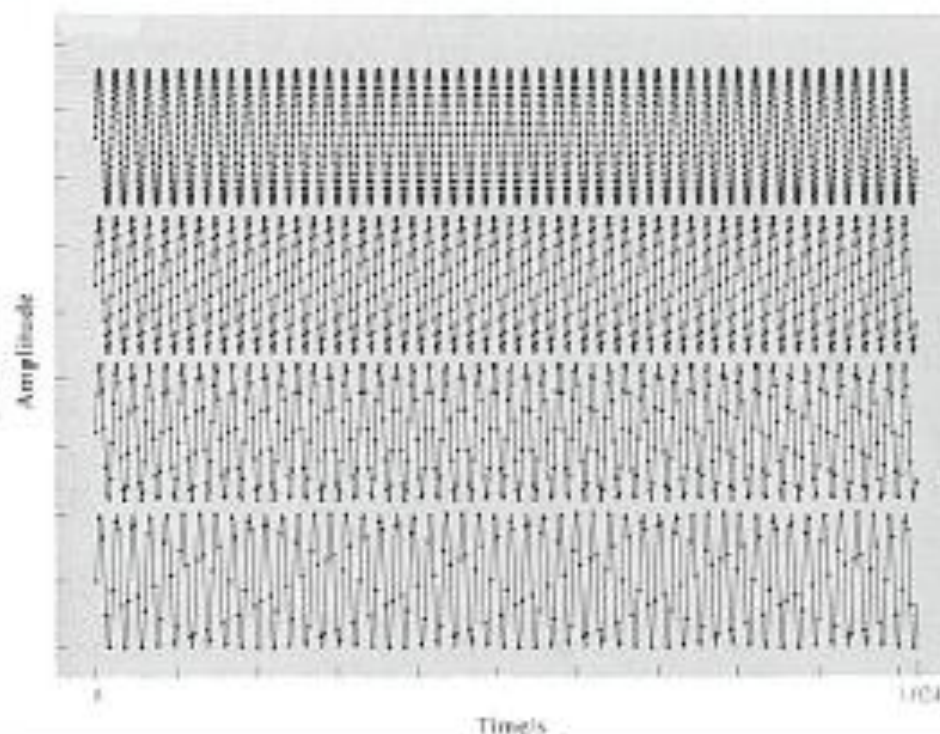


Memory Requirements

... and remember the Nyquist sampling theorem. You can only measure frequency components up to $1/2$ the sampling frequency (without aliasing).

Spectral Range

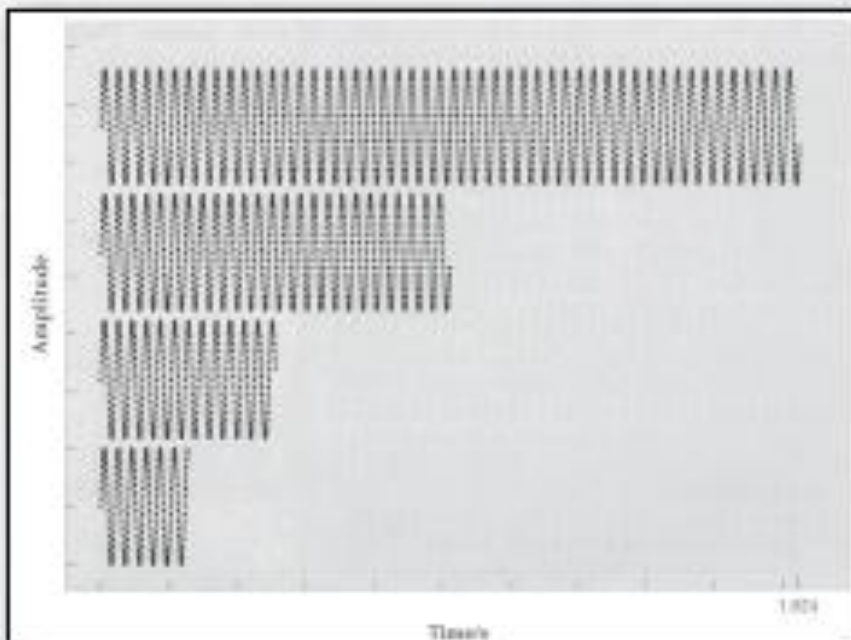
Here we sample for the same length of time (1.024 s) but acquire at different rates (which accumulates different numbers of data points). As the acquisition rate decreases, the useful (non-aliased) range decreases.



Sampling Frequency	# of points	Nyquist Limit
2000 Hz	2048	1000 Hz
1000 Hz	1024	500 Hz
500 Hz	512	250 Hz
250 Hz	256	125 Hz

Spectral Resolution

Here we sample data at the same rate (2000 Hz) so the spectrum goes to 1000Hz. However, we scan for different lengths of time (accumulating different total number of data points). The data is spread through the same total range, but with fewer points, they are farther apart. The frequency space between points increases as the sampling time decreases; this is a decreased resolution.



# of points	Frequency Spacing
2048	0.976 Hz
1024	1.953 Hz
512	3.906 Hz
256	7.812 Hz

Connes Advantage

Because the laser is used as an internal clock, it provides a frequency calibration to the spectrum that is far more accurate than is available for a scanning instrument.

Janine Connes was an astronomer at the University of Paris. As part of her Ph.D. thesis work, she developed the process of frequency calibration for the FTIR process and applied it to some spectroscopic studies of Mars and Venus.

...and almost no stray light!

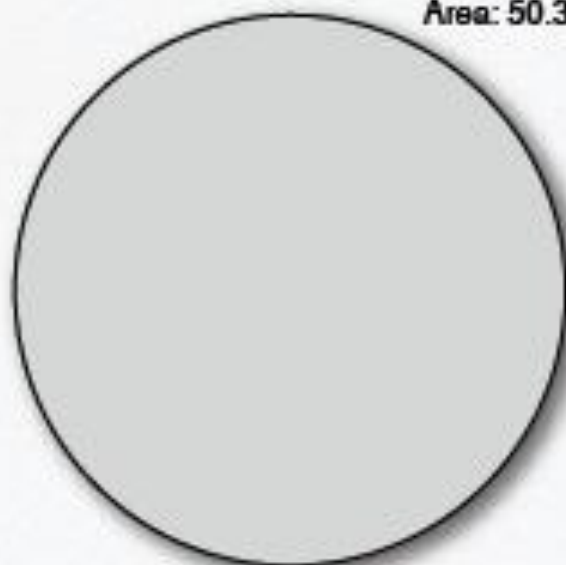
And finally, because the FT experiment modulates the source radiation and then detects only modulated radiation, there is essentially no stray light problems as there are with scanning instruments.

Any stray light that reaches the detector is not incorporated into the spectrum since it is unmodulated.

Jacquinet Advantage

The FT instrument does not use any slits; all the light falls on the detector all the time. A much larger fraction of the light is able to move through the instrument. This is known as the throughput advantage or the Jacquinet advantage.

FT: 8 mm diameter
Area: 50.3 mm²



FT advantage = 35

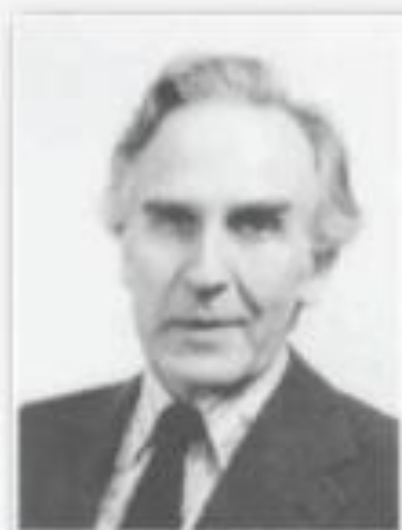
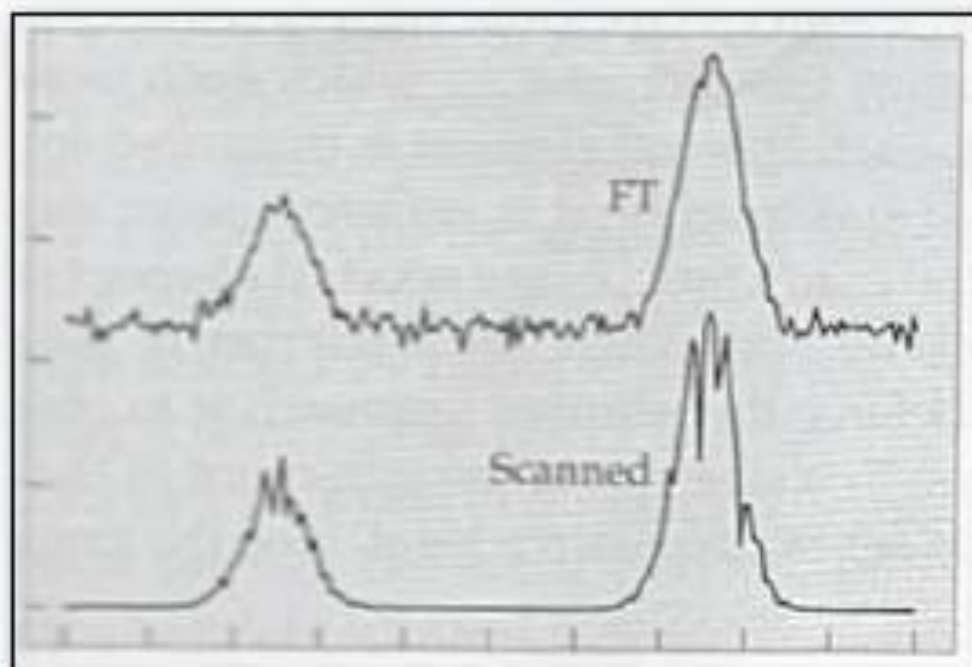
Slit: 12 mm x 120 μ m
Area: 1.44 mm²



Pierre
Jacquinet

Fellget Advantage

Because all spectral components are acquired simultaneously, the detector noise is spread over the entire spectrum, rather than being accumulated at each point. Each line has less noise than if it were measured individually. This S/N gain is called the multiplex advantage or the Fellget advantage.



Peter
Fellget

Mid-IR Region

The mid-IR region spans 4000 to ~ 500 cm^{-1} . Usually the region one is referring to when they say "IR spectroscopy".

- Cells for gases, solutions, gels (mulls), pellets, solids
- Long path length experiments (multipass or remote reflections)
- Remote sensing from emission sources

Most widely used for qualitative analysis. Innovations in microspectrometry are possible with bright sources such as the synchrotron.

Importance for quantitation is growing.

Qualitative Analysis

IR Spectroscopy is widely employed as an identification technique.

- many narrow peaks
- general peak position identifies chemical bonds in molecule
- subtle shifts are measurable with good resolution and provide details of the molecular bonding environment

Analyze wavenumber shifts in specific group

- CH stretches $3000 - 2800 \text{ cm}^{-1}$
- OH stretches $3600 - 3200 \text{ cm}^{-1}$
- CO stretch $1690 - 1760 \text{ cm}^{-1}$

Fingerprint region $1200 - 700 \text{ cm}^{-1}$

Computer search libraries >100,000 spectra

Quantitative Analysis

- Requires more careful work than in UV-visible region.
- FTIR instrumentation is more precise.
- Narrow peaks make for Beer's Law deviations in slit-based measurements.
- Multitude of peaks leads to likelihood of overlap.
- FTIR instruments are single beam; cannot simultaneously determine transmitted power with/without sample.
- Everything except homonuclear molecules has a unique infrared spectrum.
- Good for remote sensing applications.
- Near-IR used more for quantitative than Mid-IR.

Near IR Region

This region extends from the visible at about 770 nm to 2500 nm or 13,000 cm^{-1} down to 400 cm^{-1} . Generally consists of overtone and combinations bands from the fundamental stretches in the 3000 - 1700 cm^{-1} mid-IR region.

- Transitions are generally weak.
- Most applications are in quantitative analysis. Detection limits around 0.1%. Precision routinely around 1%. Clearly not a trace analysis technique.

Uses some transmission but mostly diffuse reflectance is used.

Canadian wheat analyzed for protein content for sale. Previously would run several hundred thousand chemical analyses/year; now use near-IR and saves millions in analysis costs.

Far IR Region

Region from 500 to 5 cm^{-1} . Bounded below by the microwave region.

Traditionally hard region to access. Synchrotron promises to re-energize the field.

- Stretching vibrations in inorganics (heavy atoms, slow vibrations).
- Bending vibrations when two atoms other than H involved.
- Pure rotational spectroscopy.

FT is particularly useful here, avoiding order sorting problems and retaining the Jacquinot advantage.