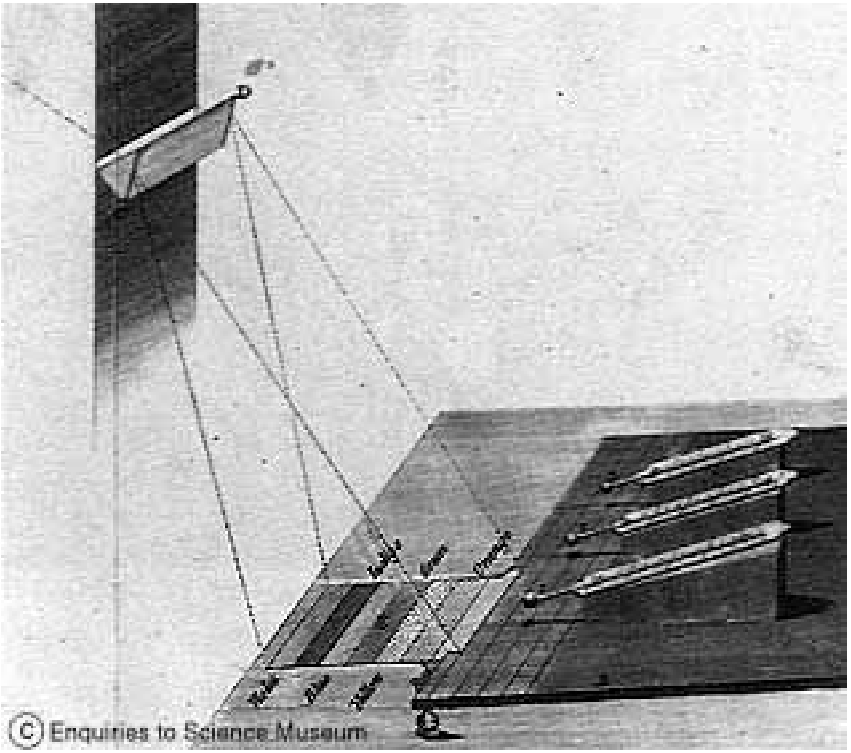
# Fourier-Transform Infrared Spectroscopy

- Introduction to infrared and IR spectroscopy
- How an FTIR bench works
- Why we use a synchrotron
- Some examples

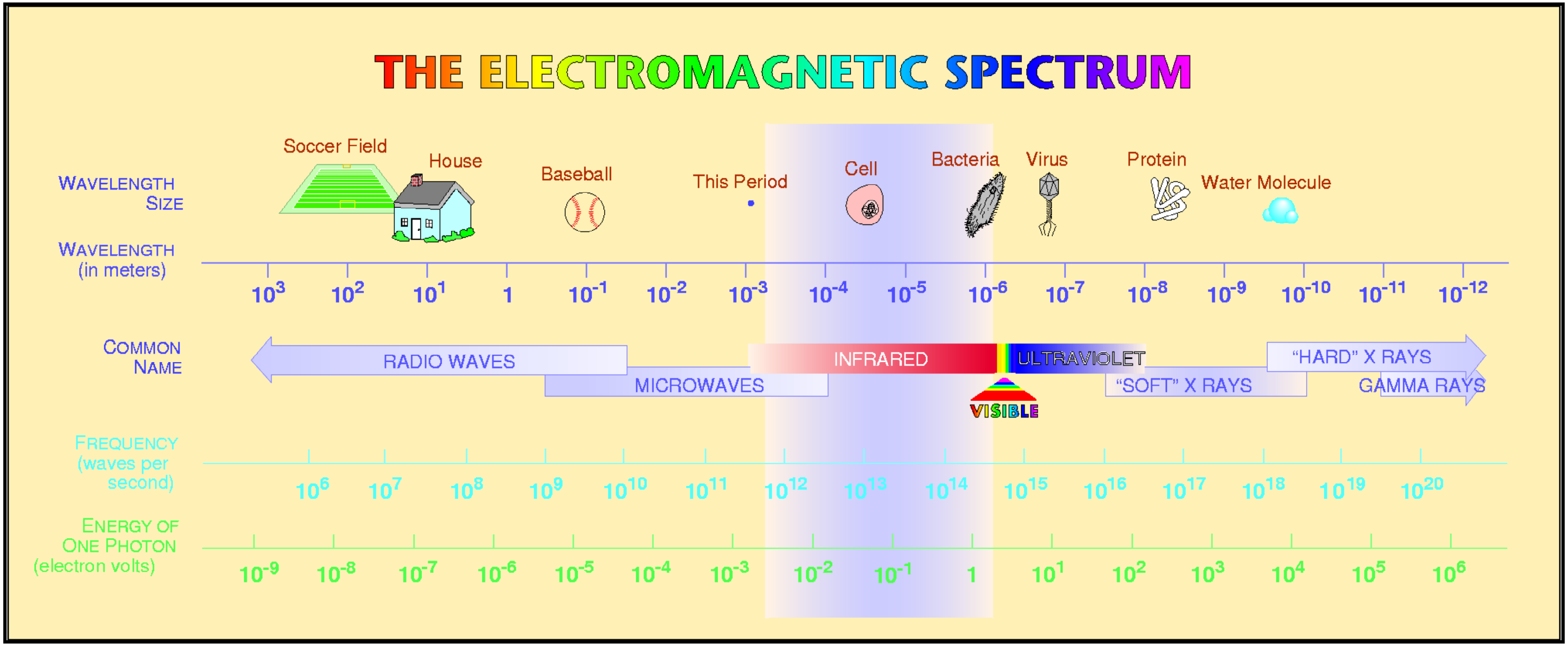
# William Herschel

Around 1800, Herschel studied the spectrum of sunlight using 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'.


The Science Museum, UK

# The Infrared Part of the EM Spectrum




IR units: wavenumbers ($cm^{-1}$),

10 micron wavelength = 1000 $cm^{-1}$

1 eV ≈ 8100 $cm^{-1}$

1 THz ≈ 33 $cm^{-1}$

300 Kelvin ≈ 210 $cm^{-1}$

Near-IR: 4000 – 14000 $cm^{-1}$

Mid-IR: 500 – 4000 $cm^{-1}$

Far-IR: 5 – 500 $cm^{-1}$

IR covers ~ 1 meV to 1 eV

# What can we learn from IR spectroscopy?

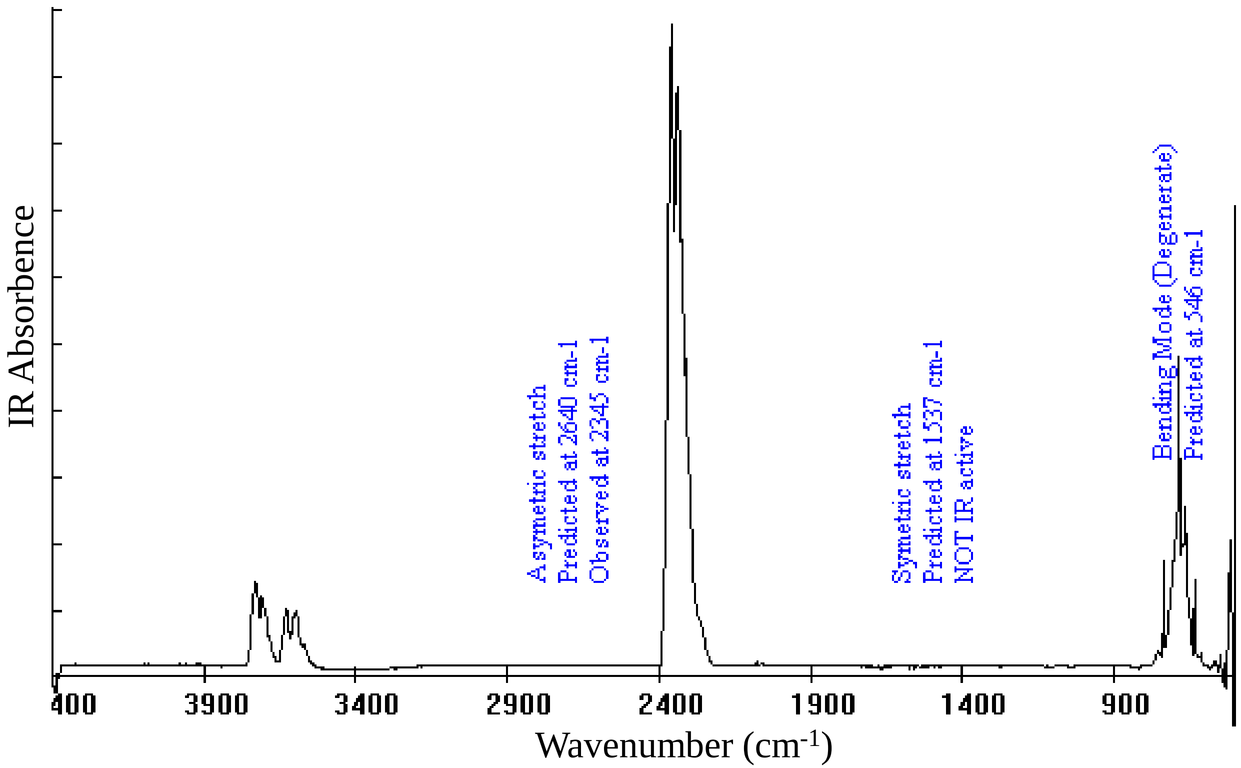
- **Atoms vibrate with frequencies in the IR range**

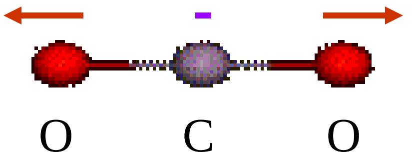
- **Chemical Analysis:**
  - Match spectra to known databases
    - Identifying an unknown compound, Forensics, etc.
  - Monitor chemical reactions *in-situ*
- **Structural ideas:**
  - Can determine what chemical groups are in a specific compound
- **Electronic Information:**
  - Measure optical conductivity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

# Contact-less Measurements

- **Much easier to mount & measure samples**
- **Can work with solids, liquids, gases**
- **Is easier to vary other sample properties via**
  - Temperature (cryostats, heaters)
  - Pressure (Diamond Anvil Cells)
  - Magnetic Field

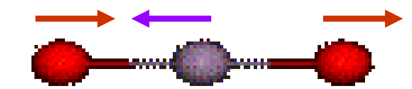
# An Example: $CO_2$



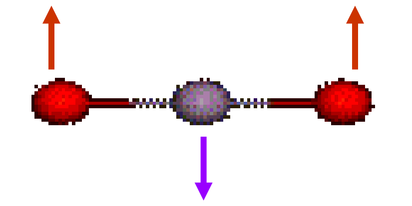

## Symmetric Stretch

(Dipole moment = 0 so **not** IR active)



## Asymmetric Stretch

(Has dipole moment so IR active)

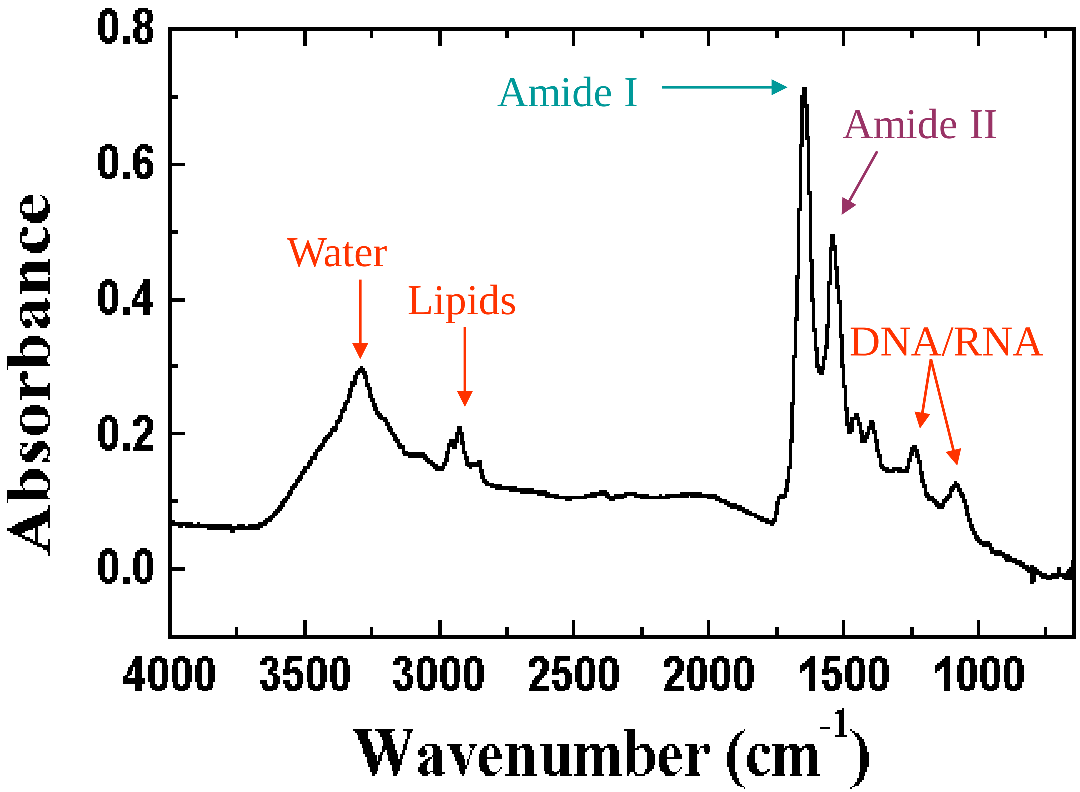


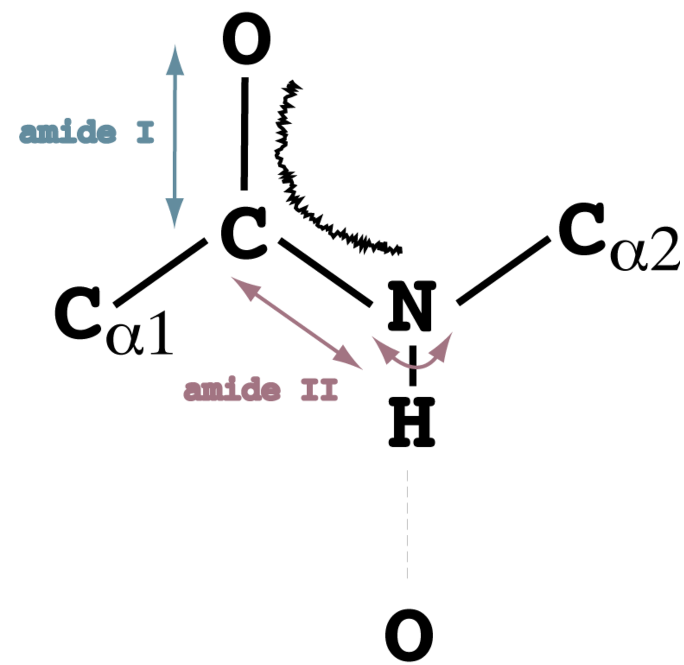
## Bending Mode

(Has dipole moment so IR active)

A Dipole Moment = charge imbalance in the molecule

# Example infrared spectrum of a biological system



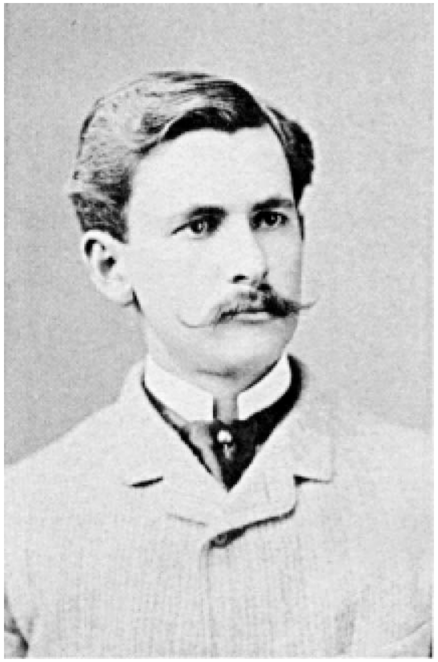

Typical IR absorbance positions:

| | |
|---|---|
| Protein Amide I: | 1690-1600 |
| Protein Amide II: | 1575-1480 |
| Lipid $=CH_2$: | 3100-3000 |
| Lipid $-CH_2$, $-CH_3$: | 3000-2850 |
| Nucleic Acid $-PO_2^-$: | 1225, 1084 |

The peak positions of Amide I and II are sensitive to the protein secondary structure (α-helix, β-sheet, random coils, etc.)

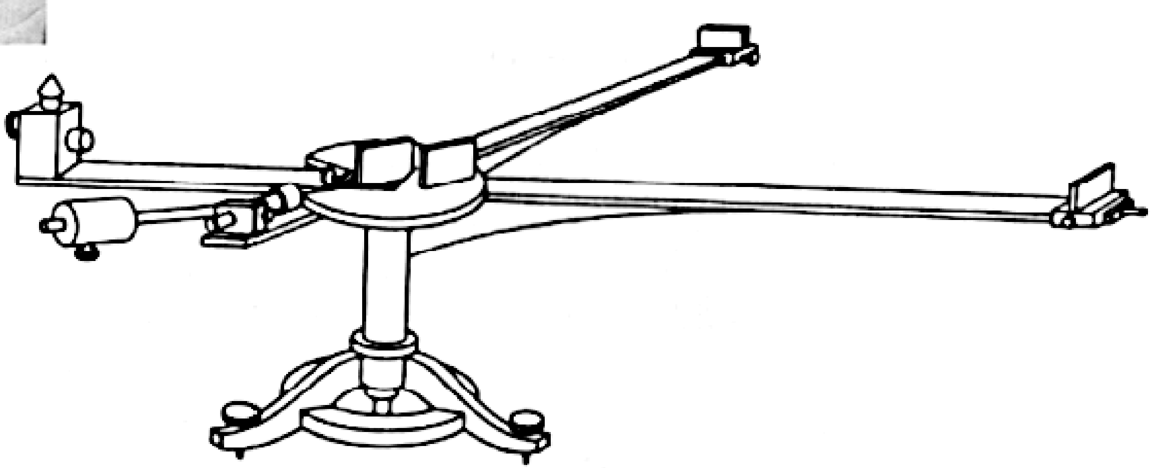
A good reference: Mantsch and Chapman, *Infrared spectroscopy of biomolecules*. 1996, New York: Wiley-Liss.

# **Albert Michelson** (1852-1931)

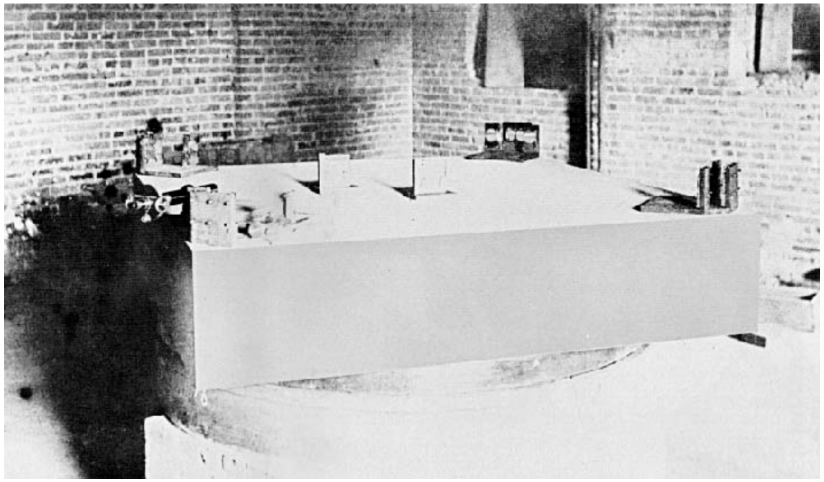


Michelson wanted to measure the speed the earth moves through the ether (the medium in which light travels). By measuring the interference between light paths at right angles, one could find the direction & speed of the ether.

Michelson's first interferometer (1881)



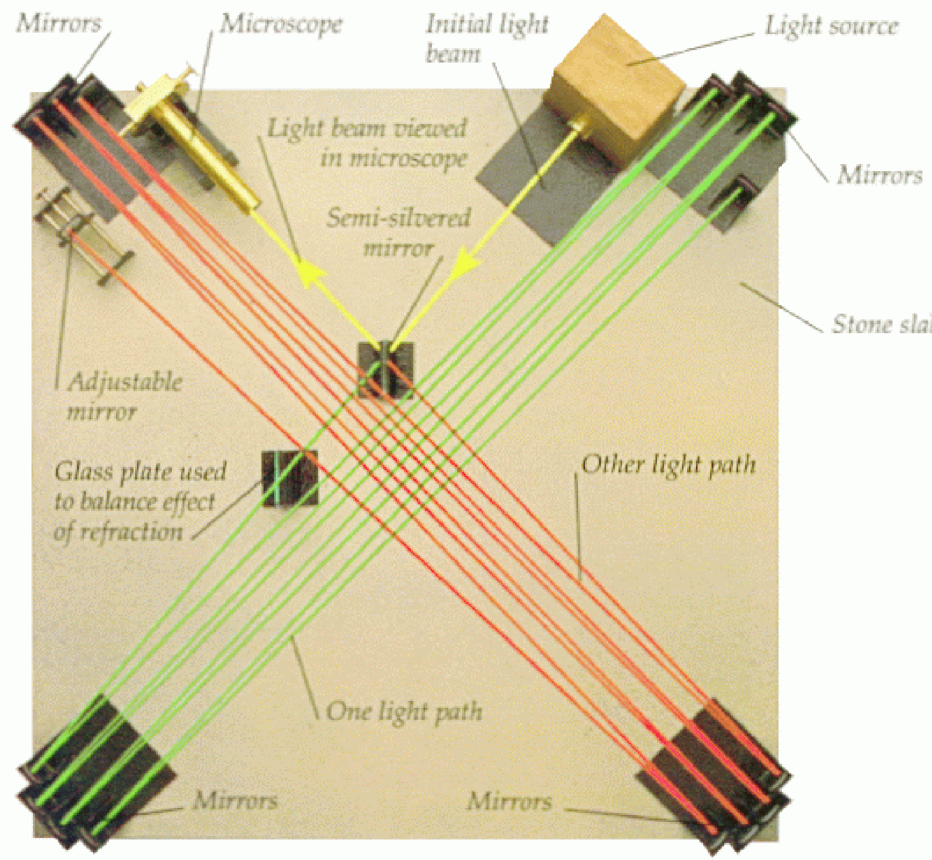
# Michelson-Morley Experiment



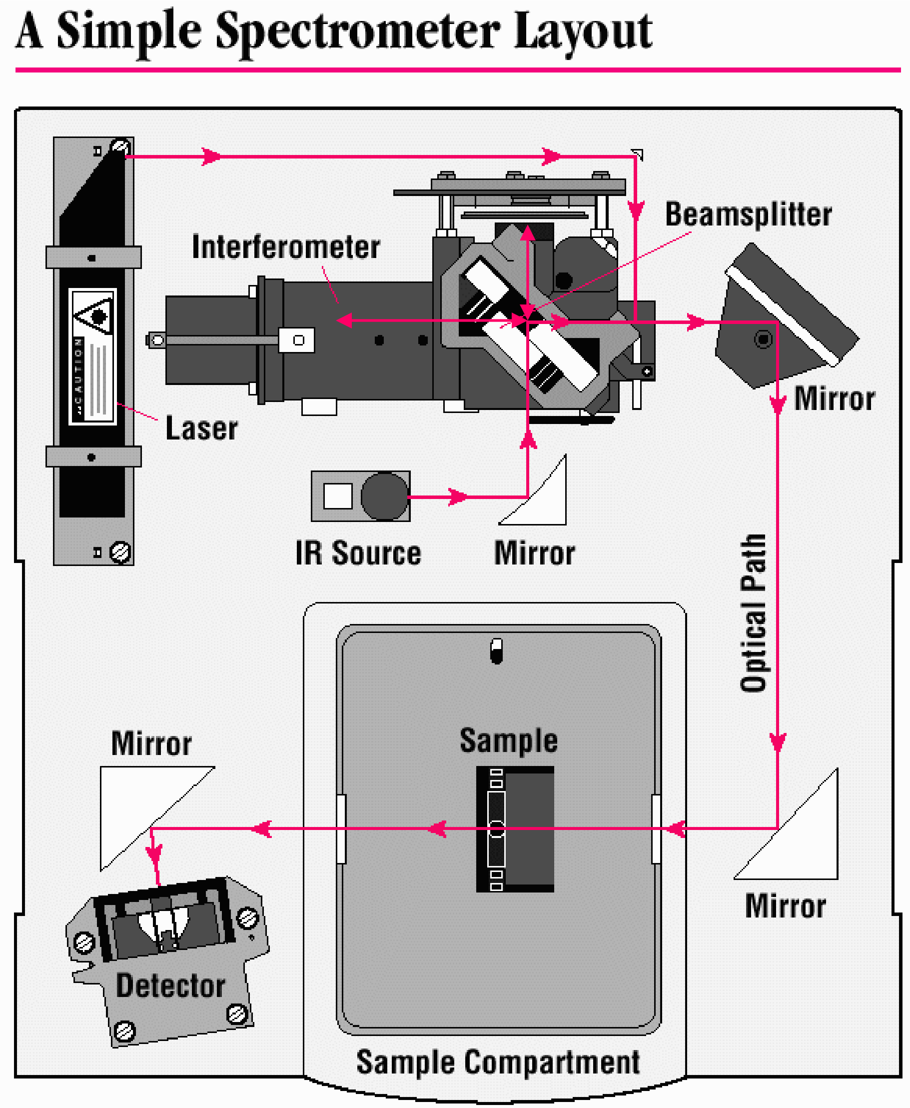
Still no fringes → No ether.
The speed of light is constant.
A new physics of light was needed.

"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)



# How an FTIR Spectrometer Works




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, θ = kx, can simplify to:

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

For non-monochromatic light:

$$I(x) = \int_0^\infty \left[1 + \cos(kx)\right] G(k)\,dk$$

$$= \int_0^\infty G(k)\,dk + \int_0^\infty G(k)\frac{e^{ikx} + e^{-ikx}}{2}\,dk$$

$$= \frac{1}{2} I(0) + \frac{1}{2}\int_{-\infty}^{\infty} G(k) e^{ikx}\,dk$$

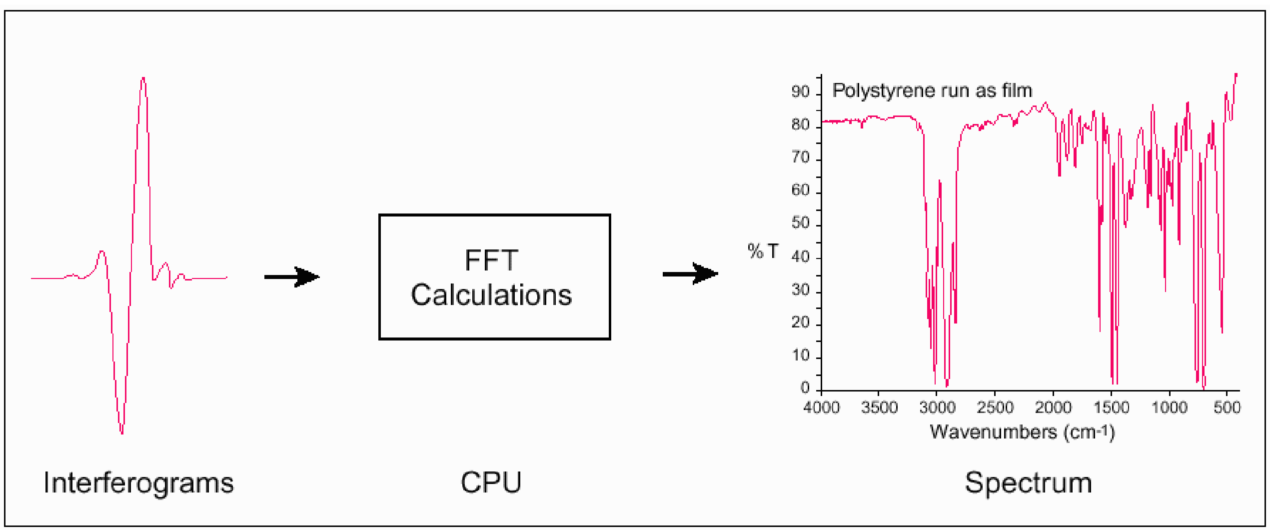
# FTIR Math Continued

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.



# FTIR Spectrometers

In practice one cannot measure from -∞ to ∞. The resolution of a measurement is simply given by how far in x you measure.

$$resolution \propto \frac{1}{2\pi x_{\max}}$$

**Rapid-Scan measurements:**

- Sweep mirror quickly, average many interferograms
  - Very fast & easy
  - Not high resolution
  - Not for quickly changing signals or very low signal

**Step-Scan measurements:**

- Step to each x position, then measure (long average, or triggered time series). Can have very long path length.
  - Excellent for fast time resolution, low signals (lock-in)
  - Harder to run stably.

# Infrared Spectroscopy Measurements