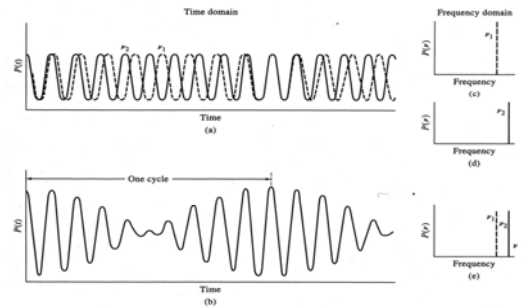


March 4, 2005

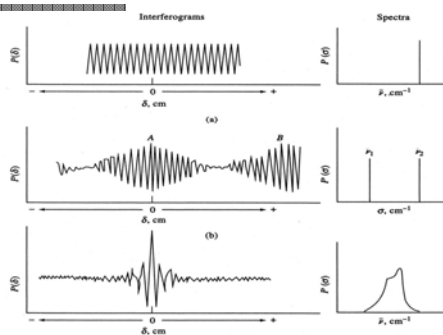
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To the Frequency Domain!



## From Interferogram to Spectrum



## Resolution

- It can be shown that for two "barely resolvable" spectral features:

$$\Delta \bar{\nu} = 1/\delta$$

-where  $\delta$  is the maximum retardation attainable with the interferometer.

So, to resolve two spectral features separated by  $0.1 \text{ cm}^{-1}$ , we need an interferometer with a maximum mirror displacement ( $x$ ):

$$x = \delta/2 = 10 \text{ cm}/2 = \underline{5 \text{ cm}}$$

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## Why Bother with FT-Interferometry?

### 1. Signal-to-Noise Enhancement

- Multiplex Advantage (" Fellgett's Advantage ")**
  - All wavelengths viewed *simultaneously*, so measurement time/resolution element is greater

If measurement is limited by detector noise:

$$S/N \text{ enhancement} \propto (n)^{1/2}$$

where  $n$  = number of resolution elements

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## Multiplex Advantage: S/N

- So, suppose we acquire a spectrum from  $500 - 3500 \text{ cm}^{-1}$  with an effective bandwidth of  $1 \text{ cm}^{-1}$

If we spend the same amount of time acquiring the spectrum via FT-Interferometry as we do via scanning spectrometry, we should see a S/N enhancement of:

$$n = 3000 \text{ resolution elements}$$

$$(3000)^{1/2} \approx \underline{55\text{-fold}} \text{ S/N enhancement}$$

This is the same as *signal averaging*: like averaging the signal 3000 times at each resolution element

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## Multiplex Advantage: *Time*

- Suppose we spent 6000 seconds acquiring the spectrum and we really don't need the enhanced S/N:

*We can get the same S/N as with a dispersive system in  $1/(n)^{1/2}$  of the time*

In this case, this means it would take:

$$6000 \text{ sec}/54.8 \approx \mathbf{110 \text{ sec}}$$

*So, 100 minutes (dispersive) versus 2 minutes (FT-interferometry)!*

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## Other Advantages

- **Throughput Advantage ("Jacquinot's Advantage")**  
Increased light throughput (no limiting apertures) independent of resolution, results in an increase in S/N.  
  
About a 100x S/N enhancement is claimed (not just for systems limited by detector noise)
- 2. **Precise Wavenumber Calibration**  
-due to internal standardization to laser  
-wavenumbers known to about  $10^1 - 10^2 \text{ cm}^{-1}$
- 3. **Sheer Elegance and Simplicity!**

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## Spectroscopy: Infrared Absorption Spectrometry

Chem 221  
Instrumental Analysis  
Spring 2005

## Origins of IR Absorption

- Due to transitions between *vibrational* and/or *rotational* energy states of molecules
  - **A molecule can absorb IR photons if:**
    - ✓ there is a *change* in the dipole moment of the molecule during a vibrational or rotational motion
- AND**
- ✓ The frequency associated with the photon matches the *frequency* of the vibrational motion
- So, *almost all molecules absorb in the IR* (except for homonuclear diatomics)

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