

# Spectroscopy: Infrared Absorption Spectrometry

Chem 221  
Instrumental Analysis  
Spring 2005

## Origins of IR Absorption

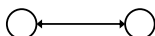
- Due to transitions between *vibrational* and/or *rotational* energy states of molecules
  - **A molecule can absorb IR photons if:**
    - ✓ there is a **change** in the dipole moment of the molecule during a vibrational or rotational motion
- AND**
- ✓ The frequency associated with the photon matches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

2

## Modeling Molecular Vibrations

### ■ Simple Harmonic Oscillator (SHO) Model

Consider two objects connected by a spring:



The *potential energy* of the system will vary with the **displacement** ( $y$ ) and the **force constant** ( $k$ ) of the spring:

$$E = \frac{1}{2}ky^2$$

3

## More SHO

- It can be shown that there is a *natural vibration frequency* ( $\nu_m$ ) for the system:

$$\nu_m = \left(\frac{1}{2}\pi\right)(k/\mu)^{1/2}$$

where the *reduced mass* ( $\mu$ ) is given as:

$$\mu = (m_1m_2)/(m_1 + m_2)$$

- $\nu_m$  depends only on  $k$  and  $\mu$  and is independent of the energy added to the system (affects only the vibrational amplitude)

4

## SHO Model and Molecules

### ■ As applied to molecular systems:

- $k$  is the *bond strength*
  - $m_1$  and  $m_2$  are the masses of the atoms
  - $\nu_m$  is the frequency of a fundamental vibrational mode
- So, if the frequency of EMR =  $\nu_m$ , absorption can occur

### ■ From a quantum mechanical viewpoint:

Molecular vibrational energies are *quantized*:

$$E = \left(v + \frac{1}{2}\right)h\nu_m \quad (v = 0, 1, 2, 3, \dots)$$

- Allowed transitions involve:  $\Delta v = \pm 1$
- So, only a *single absorption frequency* for each fundamental vibration ( $\Delta E = h\nu_m$ )

5

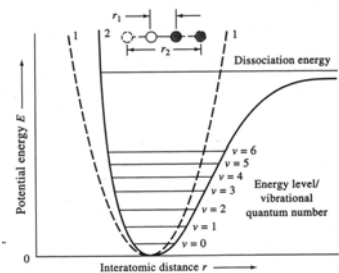
## The Anharmonic Oscillator (AHO) Model

### Limitations of SHO:

- Ignores effects of Coulombic repulsion
- Ignores effects of bond dissociation

### Solution: AHO Model

- Results similar to SHO for low energies
- $\Delta E$  *decreases* at higher values of  $v$
- $\Delta v = \pm 2, 3$  "less forbidden" (overtone bands)



6

## Vibrational Modes

- How many *fundamental vibrations* in a molecule?  
Related to the number of *degrees of freedom*:

**TOTAL #DOF:**  $3N$  (where  $N$  = # atoms in molecule)

**#Translational:** 3

**#Rotational:** 3 (only TWO for linear molecules)

$$3N - 6 \text{ vibrational DOF}$$

( $3N - 6$  vibrational modes)

- Not all vibr. modes will give IR absorption peaks

- no dipole moment change during vibration
- degenerate vibrational mode energies
- too low intensity to detect

7

## Vibrational Coupling

- Vibration frequency also depends on the *chemical environment* of the molecule

- due to interactions between two vibrating portions of the molecule

**Requires:**

- common atom or bond
- similar energies
- same symmetry

- Gives *structural information* on molecule (qualitative analysis applications)

8

## Instrumentation

■ **Sources**

- Blackbody radiators at 1500 - 2000 K give:

$$\lambda_{\max} \approx 1.7 - 2.0 \mu\text{m} \text{ (ca. } 5500 \text{ cm}^{-1}\text{)}$$

$$\lambda_{\text{range}} \approx 1 - 15 \mu\text{m} \text{ (ca. } 10,000 - 700 \text{ cm}^{-1}\text{)}$$

- Nernst Glower** (cylinder of rare earth oxides)
- Globar** (SiC rod) - better at shorter wavelengths

- High-Pressure Hg Arc** (far-IR)

9

## Sample Cells

- Cell windows made of alkali-metal halide (KBr, CsI, NaCl, etc.); largely transparent in IR

- **Solids** (particulates should be *smaller* than  $\lambda_{\text{IR}}$ )

- mix with KBr and press into a pellet

**OR**

- grind with *heavy hydrocarbon oil* (Nujol®) or *halogenated polymer* (Fluorolube®)

- view resulting mull as a film between salt plates

- **Gases**

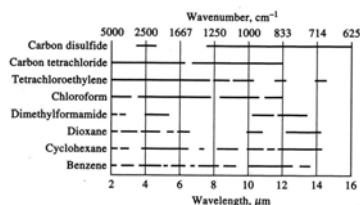
- use *long pathlength* (up to 1000 meters!) to get adequate sensitivity

10

## Solution Samples

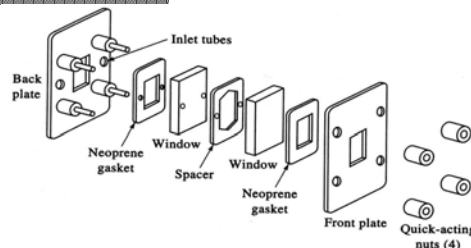
■ **Solvents**

- choose carefully, based on IR absorption and reactivity with salt windows (avoid water, alcohols)



11

## More Solution Samples

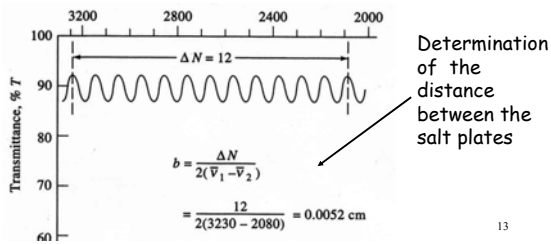


- narrow cell pathlengths (10 μm - 1 mm) needed to minimize absorption due to solvent

12

## Determining Cell Pathlength

- Get interference pattern due to constructive/destructive interference of EMR waves that are reflected between the salt plates:



13

## Detectors

- **Thermal** - based on temperature detection

- **Thermocouple**

- poor sensitivity
    - *slow* (>ms response time) - *not suitable for FT-IR*

- **TGS (Triglycine Sulfate)**

- based on *pyroelectric effect* (temperature dependant capacitance)
    - *fast enough for FT-IR* (but less sensitive than thermocouple)
    - most common detector for FT-IR

14

## More Detectors

- **Photoconductive**

- semiconductors (e.g., Ge, Si, CdSe, PbS, CdS, etc.)
  - resistance decreases with increased photon flux (due to promotion of electrons to conduction band)
  - *slow (ms) and limited to visible and NIR unless:*
    - Cooled to N<sub>2</sub>(l) temps (μs response in IR)

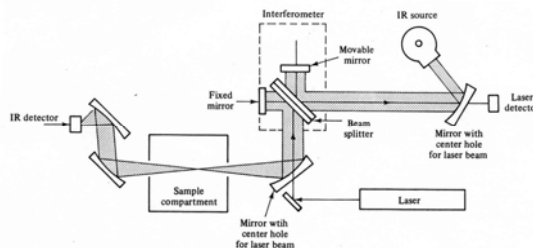
- **MCT (Mercury/Cadmium Telluride) Detector**

- cooled with liquid nitrogen
    - about 100x more sensitive than TGS detector
    - expensive* (k\$), limited wavelength coverage, popular option

15

## IR Instruments

- *Almost exclusively based on FT-interferometry:*



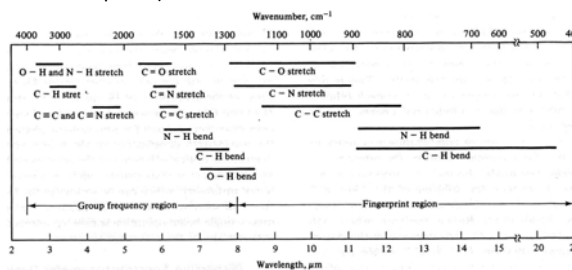
## FT-IR Advantages

- ✓ **S/N Enhancement & Rapid Scanning**
  - Due to Fellgett's and Jacquinot's Advantages
- ✓ **Precise Wavenumber Calibration**
  - Due to laser reference
- **Facilitates:**
  - Signal averaging
  - Spectral Subtraction
  - Computer-based spectral I.D.
- ✓ **High-Resolution Capability**
- ✓ **No Stray Radiation Problems**
  - Each IR frequency has a unique modulation frequency

17

## Qualitative Analysis

- **Group Frequencies:**



18

## More Qual Analysis

- Must have spectrum of a *pure compound*
- Use group frequencies as a guide
- Use *correlation chart* for more compound specific functional group analysis
- Use computerized spectral search engines
- Use IR assignments *in conjunction with other info* (e.g., chemical, physical, spectroscopic)

19

## Quantitative Analysis

### ■ The Good Side:

- Almost all compounds absorb in IR
- solids, liquids and gases are all accessible

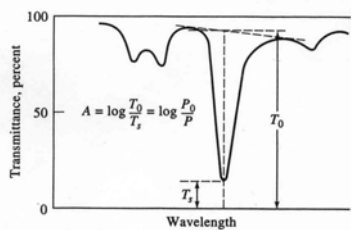
### ■ The Problems:

- Poor sensitivity and short cell pathlengths mandate relatively high solution concentrations (1-2% or more) results in *Beer's Law deviations*
- Narrow absorption bands and complex spectra (with overlapping bands) can cause polychromatic errors

20

## Accurate Absorbance Measurements

- Solution cells are difficult to match exactly, so 100%T is not necessarily an absorbance of zero:



21

## IR Spectrometry Applications

### ■ Qualitative Analysis

- Most significant use of IR spec: *structural analysis*
- Computerized spectral I.D.
- Use in conjunction with other methods for confirmation

### ■ Quantitative Analysis

- Limited use but, with care, can obtain reasonable results
- Can get trace (ppm) detection limits with gases (with excellent *selectivity*)

22