

March 7, 2005

➤ **Change Happens!**

- Probs added to Prob Set #3
- Schedule Adjustment

➤ **Exam #2: Wed., March 16th, 7pm**

- Review Session: Sunday? Monday? Tuesday?

1

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

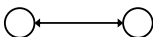
- ✓ The frequency associated with the photon matches the *frequency* of the vibrational motion
- So, *almost all molecules absorb in the IR* (except for homonuclear diatomics)

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* (ν_m) for the system:

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

where the *reduced mass* (μ) is given as:

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

- ν_m depends only on k and μ 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
 - ν_m is the frequency of a fundamental vibrational mode
- So, if the frequency of EMR = ν_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

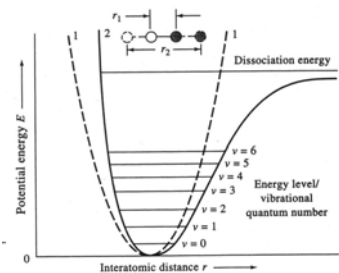
The Anharmonic Oscillator (AHO) Model

Limitations of SHO:

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

Solution: AHO Model

- Results similar to SHO for low energies
- ΔE *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)

$3N - 6$ vibrational DOF

($3N - 5$ 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