

March 7, 2005

➤ Change Happens!

- Probs added to Prob Set #3
- Schedule Adjustment

➤ Exam #2: Wed., March 16th, 7pm

- Review Session: Sunday? Monday? Tuesday?

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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

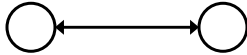
- ✓ The frequency associated with the photon matches the *frequency* of the vibrational motion
- So, *almost all molecules absorb in the IR* (except for homonuclear diatomics)

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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:

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

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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)

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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*:

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

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

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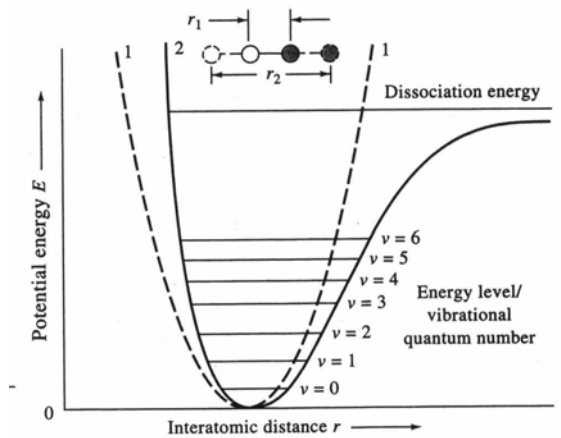
The Anharmonic Oscillator (AHO) Model

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 ν
- $\Delta\nu = \pm 2, 3$ "less forbidden" (overtone bands)



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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

($3N - 6$ 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

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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)

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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)