Chemistry 3P51 – Fall 2013
# Quantum Chemistry

Lecture No. 14
Oct 7th, 2013

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Objectives

- To motivate the vibrational motion of diatomic molecules.

- To show how the vibrational motion of a diatomic molecule can be reduced to a one-body oscillatory motion.

- To introduce the concepts of relative coordinate and reduced mass and show their relevance in the vibrational motion of diatomic molecules.

- To show the vibrational spectra of diatomic molecules.

- To discuss the infrared and Raman vibrational transitions.

- To discuss the potential energy functions for nuclear motion and the vibrational zero-point energy.

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Vibrational motion of a diatomic molecule

Classically, a diatomic molecule can be thought of as a system of two masses (nuclei) connected by a spring.
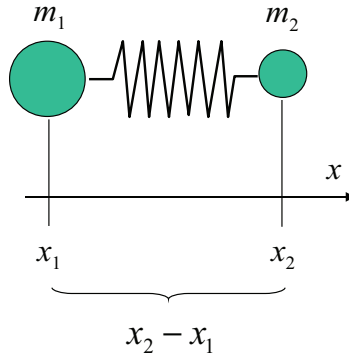
We will denote by x_e the equilibrium distance between m_1 and m_2.

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Classical treatment of a vibrating diatomic molecule

The equation of motion for the first mass (nucleus) is:

$$m_1 \frac{d^2 x_1}{dt^2} = -k\left(x_1 - x_2 + x_e\right) \qquad (1)$$

By Newton's third law, the restoring force acting on m_2 must be equal and opposite to the restoring force acting on m_1

$$m_2 \frac{d^2 x_2}{dt^2} = -k\left(x_2 - x_1 - x_e\right) \qquad (2)$$

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Dividing eq. (1) by m_1 and eq. (2) by m_2 and subtracting eq. (1) from eq. (2) we obtain

$$\frac{d^2x_2}{dt^2} = -\frac{k}{m_2}(x_2 - x_1 - x_e)$$

$$+ \quad -\frac{d^2x_1}{dt^2} = -\frac{k}{m_1}(x_2 - x_1 - x_e) \quad \Rightarrow$$

$$\frac{d^2(x_2 - x_1)}{dt^2} = -k\left(\frac{1}{m_1} + \frac{1}{m_2}\right)(x_2 - x_1 - x_e)$$

After introducing the **relative coordinate** and the **reduced mass**

$$x = x_2 - x_1 - x_e \quad , \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

we obtain

$$\boxed{\mu \frac{d^2x}{dt^2} = -kx}$$

Oscillating motion of a **single** particle of mass μ in the potential $V(x) = \frac{x^2}{2}$

The two-body problem is reduced to a one-body problem.

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Quantum mechanical treatment of a vibrating diatomic molecule

The Hamiltonian operator for a diatomic molecule is obtained by taking the Hamiltonian for a harmonic oscillator and substituting

$$m \rightarrow \mu$$

where

masses of the nuclei

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \text{reduced mass}$$

The Schrödinger equation for the vibrating diatomic molecule is:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x)$$
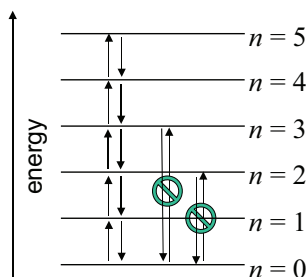
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Vibrational spectra of diatomic molecules

The energy levels of a diatomic molecule are:

$$E_n = h\nu\left(n+\tfrac{1}{2}\right) = \hbar\omega\left(n+\tfrac{1}{2}\right), \quad n = 0, 1, 2, 3, \dots$$

A diatomic molecule undergoes transitions from one vibrational state (energy level) to another by absorbing or emitting a photon of light.

Selection rule for allowed transitions:

$$\boxed{\Delta n = \pm 1}$$

The transition $n = 0 \rightarrow 1$ is called the **fundamental transition**.

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Vibrational frequencies and wavenumbers

The frequency (in Hz) of the fundamental and all other allowed transitions is

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

Here μ is the reduced mass of the diatomic molecule

In molecular vibrational spectroscopy, transition energies are often expressed in **wavenumbers** (m^{-1} or cm^{-1})

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

Since the energy gap between two adjacent energy levels of a harmonic oscillator is constant, all other allowed transitions have the same energy as the fundamental transition. Therefore, the spectrum of a harmonic oscillator consists of a single peak.

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Simple application of the harmonic oscillator model to chemistry

One can determine the rigidity of a chemical bond from the IR spectrum of a diatomic molecule if the masses of the atoms (nuclei) are known.

Problem: The infrared spectrum of H^{35}Cl has an intense line at

$$\widetilde{v} = 2886 \ \text{cm}^{-1}$$

What is the force constant of the H–Cl bond?

Solution: $$k = \mu(2\pi c \widetilde{v})^2$$

$$\mu = \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} = \frac{1.00 \times 35.0}{1.00 + 35.0} \ \text{amu} = 0.9722 \ \text{amu} = 1.614 \times 10^{-27} \ \text{kg}$$

$$k = 1.614 \times 10^{-27} \ \text{kg} \left[2\pi (2.9979 \times 10^{10} \ \text{cm/s})(2886 \ \text{cm}^{-1}) \right]^2$$
$$= 477 \ \text{N/m}$$

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Infrared and Raman vibrational transitions

A molecule can undergo a vibrational transition in two ways:

Infrared transitions: A photon of light is simply absorbed or emitted by a vibrating molecule.

Raman transitions: A photon of light is **scattered** (i.e., absorbed and re-emitted at a different energy) by a vibrating molecule.

Infrared (IR) and Raman spectroscopies both measure vibrational energies of molecules but according to different selection rules.

For a vibrational transition to be **IR active**, the dipole moment of the molecule must change in magnitude as the molecule vibrates. This means that the molecule must have a permanent dipole moment to be IR-active.

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Potential energy functions for nuclear motion

For a diatomic molecule near the equilibrium bond length, the potential energy of the nuclei can be approximated by a harmonic potential:
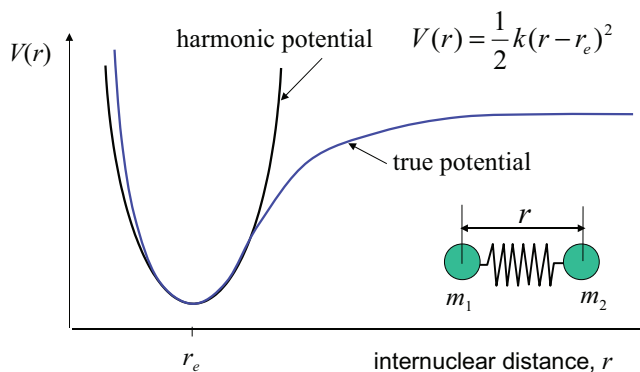
The internuclear forces in real molecules are not exactly harmonic. More sophisticated model potentials must be used if better agreement with experiment is desired.
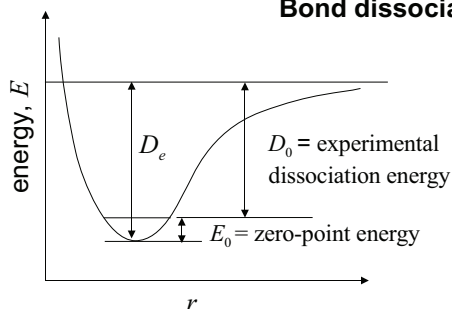
The vibrational zero-point energy

The zero-point energy (ZPE) of a harmonic oscillator is:

$$\text{ZPE} = E_0 = \frac{1}{2}h\nu = \frac{1}{2}\hbar\omega = \frac{\hbar}{2}\left(\frac{k}{\mu}\right)^{1/2}$$

The magnitude of E_0 is significant on a chemical energy scale.

Bond dissociation energies
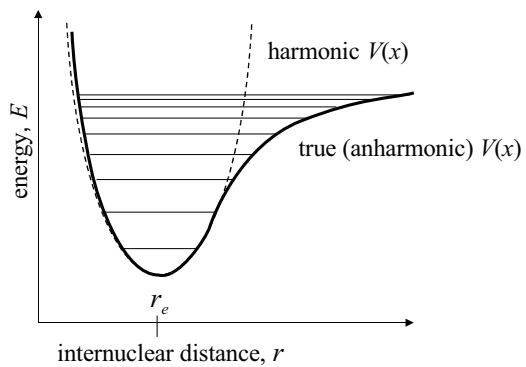

Example: H_2 molecule

$D_0 = 103.2$ kcal/mol

ZPE = 6.5 kcal/mol

$D_e = D_0 + \text{ZPE}$

Anharmonicity effects

1) Energy levels are not equally spaced: spacing decreases with n;
2) Selection rule $\Delta n = \pm 1$ is not rigorously obeyed: the vibrational spectrum consists of more than one peak

However, IR intensities of non-fundamental transitions are typically small which suggests that the harmonic oscillator model is adequate.