### Lecture B3 Vibrational Spectroscopy

Molecular bonds can vibrate. We model this motion with a "Simple Harmonic Oscillator" (SHO) using Hooke's law as a linear restoring force.



Classically:

$$F = ma = m\frac{d^2x}{dt^2} = -kx$$

The exact classical solution depends upon the initial conditions, but can sometimes take the form:

$$x(t) = A\sin(2\pi v t) = A\sin(\omega t)$$

$$\omega = 2\pi\nu = \sqrt{\frac{k}{m}}$$

where k is the force constant of the spring in units of N/m).

The frequency of oscillation is given by V:

$$\omega = 2\pi\nu = \sqrt{\frac{k}{m}}$$



v does not depend on the displacement, A.

Quantum Mechanical SHO. To get the QM solution, we need the potential energy stored in the SHO:





Hamiltonian:

 $H = \frac{p^2}{2m} + \frac{1}{2}kx^2$ 

These equations are true for both the Classical and QM SHO.

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 a set of eigenstates, |ψ<sub>n</sub>>.
 a set of eigenstate energies, E<sub>n</sub> (that is, a set of allowed values for the energy).

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$$E_n = h\nu(n+\frac{1}{2})$$

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$$\begin{aligned} |\psi_n\rangle \\ n &= 0.12 \end{aligned} \qquad E_n = h\nu(n + \frac{1}{2}) \end{aligned}$$

QM predicts the existence of discrete, evenly spaced, vibrational energy levels for the SHO.



#### **SHO** Wavefunctions



The SHO wavefunctions that are solutions to the one dimensional Schrödinger equation are known as the "Hermite Polynomials."

They alternate even/odd symmetry/asymmetry about zero (parity).

#### SHO Probability Densities



The SHO probability density for the ground state (n=0) is centered in the middle of the potential.

For high energy states, the probability density moves to the edge of the potential window, or the classical turning point. Let's start by looking at the IR absorption spectrum from a diatomic molecule, such as HCI:



## diatomic



We define the reduced mass,  $\mu$ , as:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

If  $m_2 = \infty$ , then  $\mu = m_1$ . (Just like the SHO).

If  $m_2 = m_1$ , then  $\mu = \frac{1}{2}m_1$ .

For diatomics, we can replace  $p^2/2m$  in the SHO Hamiltonian with  $p^2/2\mu$  and get the same result for the energies and eigenstates:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad H \qquad Cl$$

$$\omega = 2\pi v = \sqrt{\frac{k}{\mu}} \qquad m_1 \cup 0 \cup 0 \cup m_2$$

$$|\psi_n\rangle \qquad E_n = hv(n + \frac{1}{2})$$

The IR absorption spectrum for a diatomic molecule, such as HCI:





Optical selection rule I -- SHO can absorb or emit light with a  $\Delta n = \pm I$ 



Optical selection rule 2 -- a change in molecular dipole moment ( $\Delta\mu/\Delta x$ ) must occur with the vibrational motion.

(Note:  $\mu$  here means dipole moment).

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 $I/\lambda = 2888.59 \text{ cm}^{-1}$ Characteristic group frequenciesI eV = 8065 cm^{-1}CH stretches - 3000 cm^{-1}C=O stretches - 1800 cm^{-1}

CN streches - 2100 cm<sup>-1</sup>

CC stretches - 1000 cm<sup>-1</sup>



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 $\mu = (0.9796 \text{ amu})(1.661 \times 10^{-27} \text{ kg/amu}) = 1.627 \times 10^{-27} \text{ kg}$ 

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Then calculate k:

 $k=(1.627 \times 10^{-27} \text{ kg})(2\pi)^2(8.660 \times 10^{13} \text{s}^{-1})^2 = 481.6 \text{ N m}^{-1}$ 

IV. Calculate the IR absorption band frequency (in  $cm^{-1}$ ) you expect for the isotope H<sup>37</sup>Cl.

<sup>37</sup>Cl has an atomic wt of 36.966.

$$\omega = 2\pi\nu = \sqrt{\frac{k}{\mu}}$$
  $\mu = 0.9796 \text{ amu for H}^{35}\text{Cl}$   
 $\mu = 1.626 \times 10^{-27} \text{ kg for H}^{35}\text{Cl}$ 

 $\mu$  = 0.9811 amu for H<sup>37</sup>Cl  $\mu$  = 1.629 x 10<sup>-27</sup> kg for H<sup>37</sup>Cl

 $v(H^{37}CI) = (8.660 \times 10^{13}s^{-1})(1.626/1.629)^{\frac{1}{2}} = 8.652 \times 10^{13}s^{-1}$  $\lambda = c/v = (2.998 \times 10^8 \text{ m s}^{-1})/(8.652 \times 10^{13}s^{-1}) = 3.465 \text{ microns}$  $1/\lambda = 2885.9 \text{ cm}^{-1}$  This is lower by 2.6 cm<sup>-1</sup> than  $v(H^{35}CI)$  If a more realistic Morse potential is used in the Schrödinger Equation, these energy levels get scrunched together...

