

motivate w/ solid vib, Einstein
QM problem

wavefunctions, energies, ZPE

application to vib spectrum

diatomic

frequency
population

Bohr condition

selection rules

- gross
- specific

Raman

polyatomic

$$3n-5 / 3n-6$$

distinct ν_j

CO_2 example

Harmonic oscillator

Recall Einstein solid model, assumed vibrating atoms have energy $E = nh\nu$. to explain heat capacity. Can we understand why?

Recall treated vibrating atom as a harmonic oscillator:

$$F = -kx \rightsquigarrow V = \frac{1}{2}kx^2$$

where x is displacement from equilibrium point.

Schrödinger eq

$$\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right\} \psi(x) = E\psi(x)$$

$$KE$$

$$V$$

$$\lim_{x \rightarrow \pm\infty} V(x) = \infty \rightarrow \lim_{x \rightarrow \pm\infty} \psi(x) = 0$$

Mathematical solution a bit messy (asymptotic analysis + Hermite eq)

Solutions simple

$$E_v = (v + \frac{1}{2}) \hbar \omega, \quad v = 0, 1, 2, \dots$$

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \alpha = \left(\frac{\hbar^2}{mk} \right)^{1/2} \text{ distance}$$

$$\psi_v = N_v H_v(x/\alpha) e^{-x^2/2\alpha^2}$$

normalization $\int \psi_v^2 dx$ $\int H_v^2(x/\alpha) e^{-x^2/2\alpha^2} dx$ Gaussian polynomial of order v
assures orthogonality

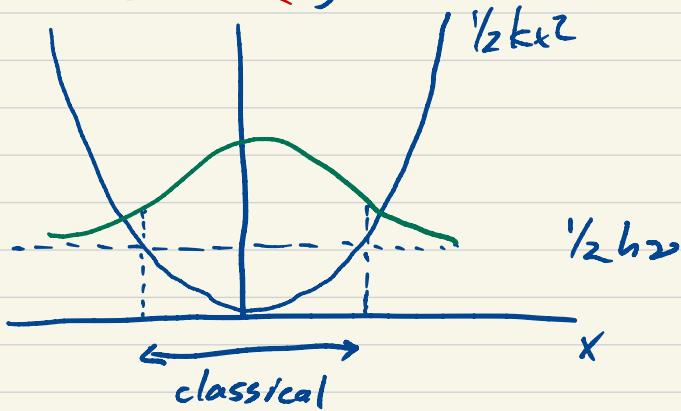
Energy spectrum matches Einstein assumption, with one tiny addition

$$ZPVE = \frac{1}{2} \hbar \omega$$

Like PIAB, consequence of confinement

Wavefunctions look similar to PLSB
nodes grows linearly w/v
(even/odd alternation)

wavefunction spills into forbidden region — tunneling



Wavefunction spreads out as $v \uparrow$

$$\langle x^2 \rangle = \alpha^2 (v + \frac{1}{2})$$

grows linearly w/v

At very large v , approaches classical limit. — MO spends most of its time at boundaries !!

Particularly useful application is to describe vibrational spectrum of a molecule

Bond connecting two atoms behaves like a harmonic spring (as long as it isn't stretched too much!)

$$A \text{---} B = \frac{1}{\mu} \pi^2 n^2 \text{ cm}^{-1}$$

$$\frac{1}{\mu} = \frac{1}{m_a} + \frac{1}{m_b} \quad \text{reduced mass}$$

Ex ${}^1\text{H} - {}^{35}\text{Cl}$ vibrates at a frequency
 $\nu = 8.963 \times 10^{13} \text{ s}^{-1}$.

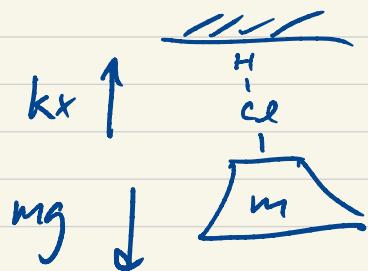
Q1. What is the H-Cl spring const?

$$m_H = 1.0078 \text{ amu}$$

$$m_{\text{Cl}} = 34.968 \text{ amu} \rightarrow \mu = 0.9796 \text{ amu}$$

$$k = \mu (2\pi\nu)^2 = 515.9 \text{ N/m}$$

(2) mass necessary to stretch this spring 1 cm?



$$m = \frac{kx}{g} = \frac{515.9 \text{ N/m} \cdot 0.01 \text{ m}}{9.8 \text{ m/s}^2} = \underline{\underline{0.52 \text{ kg}}}$$

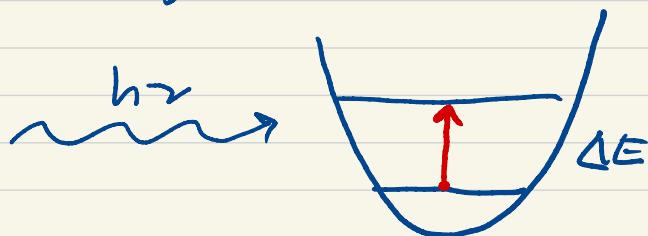
(3) ZPE? $\frac{1}{2}h\nu = 2.97 \times 10^{-20} \text{ J}$
 $= \underline{\underline{18 \text{ kJ/mol}}}$

(4) population of $v=1$ relative to $v=0$ @ 298 K?

$$\frac{P(v=1)}{P(v=0)} = \frac{e^{-\frac{3}{2}h\nu/kT}}{e^{-1/2h\nu/kT}} = e^{-h\nu/kT} = \underline{\underline{6 \times 10^{-7}}}$$

At ambient T, all HCl are in their ground vibrational state

How would we know ν ?
Use light!!



Bohr condition: if $\Delta E = h\nu$,
system can absorb photon

$$\Delta E_{\text{osc}} = h\nu_{\text{light}} \rightarrow h\nu_{\text{osc}} = h\nu_{\text{light}} \\ = 8.963 \times 10^{13} \text{ s}^{-1}$$

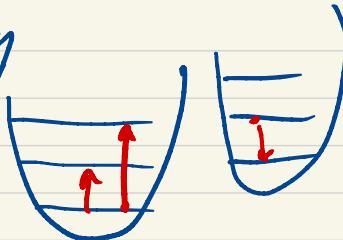
Commonly reported in wavenumbers

$$\frac{1}{\lambda} = \frac{\nu}{c} = 2990 \text{ cm}^{-1} \quad (\text{IR region})$$

Example of a spectroscopy expt,
where we use light to interrogate
energy states.

Spectroscopy

λ, ν 



Send light of specific λ, ν into a sample & observe how much is absorbed

Rules:

- Bohr condition

$$E_f - E_i = h\nu$$

- gross selection rule

For vib spec, vibration must change dipole moment



- specific selection rule

transition dipole moment must be non-zero

$$M = \langle \psi_i | \hat{x} | \psi_f \rangle$$

(doing on HW
4 for P1AB)

If ψ_i & ψ_f are harmonic oscillator wavefunctions, can show

$$\langle \psi_i | \hat{x} | \psi_f \rangle = \begin{cases} 0 & |i-f| \neq 1 \\ >0 & |i-f|=1 \end{cases}$$

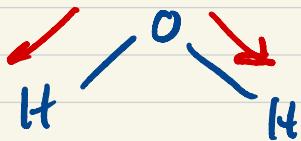
Steps of 1 are called "allowed"
" $\neq 1$ " " " " " forbidden"

- transitions can only start from states that are populated

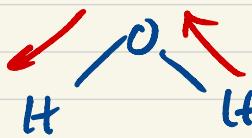
For HCl above, showed that all molecules at 298 K are in $v=0$. Thus, only possible IR transition is $v=0 \rightarrow v=1$!

Polyatomics

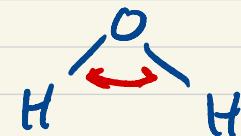
Some ideas apply to larger molecules. Speak of "normal modes" of a molecule.



symmetric
stretch



asymmetric
stretch



bend

Each will have its own force constant, own γ , and have to follow the same rules to be IR active.

In general, a molecule of N atoms will have

$3N-6$ normal modes

$3N-5$ non-linear

example



$$n = 3 \quad 3n - 5 = 4 \text{ normal modes.}$$

Look at spectrum.

Only 2 present. Why??

- gross selection rule
- degeneracy

Real spectra are seldom clean S
ftas:

- collisional broadening
gas or liquid
- Doppler broadening
- lifetime broadening
(uncertainty in ΔE)
- fine structure
eg rotational states