Chemistry 431

Lecture 5

The harmonic oscillator
Classical and quantum mechanical
As was the case for rotation, we can consider a simple model of a mass on a spring attached to a wall of infinite mass and a diatomic molecule as two simple examples.

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

\( k \) is the force constant
Harmonic approximation

\[ V(Q) = V(Q_0) + \left( \frac{\partial V}{\partial Q} \right)(Q - Q_0) + \frac{1}{2} \left( \frac{\partial^2 V}{\partial Q^2} \right)(Q - Q_0)^2 + \ldots \]

At equilibrium \( \left( \frac{\partial V}{\partial Q} \right) = 0 \)

Assume terms higher than quadratic are zero

By definition \( \left( \frac{\partial^2 V}{\partial Q^2} \right) = k, \text{ the force constant} \)
Classical approach to vibration

Solution is oscillatory
Any energy is possible

\[ \frac{\mu}{2} \left( \frac{\partial Q}{\partial t} \right)^2 + \frac{k}{2} Q^2 = 0 \]
Classical vibrational motion

- A particle undergoes harmonic motion if it experiences a restoring force that is proportional to its displacement, \( x \).
- \( F = -kQ \) (\( k \) is a force constant)
- \( F = -\frac{dV}{dQ} \) and \( V = \frac{1}{2}kQ^2 \).
- The classical harmonic oscillator can also be written as:
  \[
  ma = kQ, \quad -\mu\frac{\partial^2 Q}{\partial t^2} + kQ = 0
  \]
- Solutions have the form of \( \sin(\omega t) \) or \( \cos(\omega t) \) depending on the initial conditions.
- These solutions imply that
  \[
  \omega = \sqrt{\frac{k}{\mu}}
  \]
Classical potential function

- The potential is $V = \frac{1}{2} k Q^2$, which is a parabolic function.
- This potential is called a harmonic potential.

![Graph of classical potential function](image)

- The force constant $k$ has units of Newtons/meter (N/m) or Joules/meter$^2$ (J/m$^2$).
- The angular frequency $\omega = 2\pi \nu$, $\nu$ is the frequency in Hz.
Quantum approach to vibration

Solution is Gaussian
Energy is quantized

\[- \frac{\hbar^2}{2\mu} \frac{\partial^2 \Psi}{\partial Q^2} + \frac{k}{2} Q^2 \Psi = E \Psi\]

\[E = \left( v + \frac{1}{2} \right) \hbar \nu\]

\(\hbar\) is Planck's constant
\(\mu\) is the reduced mass
\(E\) is the energy
\(\Psi\) is the wave function
\(v\) is the quantum number

Allowed transitions:

\(v' \rightarrow v + 1, \quad v' \rightarrow v - 1\)
Vibrational wavefunctions

- Energy levels are given by $E_v = (v + 1/2)\hbar \omega$
- Wavefunctions are $\chi_v = N_v H_v e^{-y^2/2}$ where $H_v$ is the Hermite polynomial
- Typical energies are of the order of 0 - 3000 cm$^{-1}$
Solutions to harmonic oscillator

The Hermite polynomials are derivatives of a Gaussian, \( y = \alpha^{1/2}Q \)

\[ \alpha = \frac{\sqrt{\mu k}}{\hbar} \]

\[ H_v(y) = (-1)^v e^{y^2} \left( \frac{d}{dy} \right)^v e^{-y^2} \]

The normalization constant is

\[ N_v = \frac{1}{\sqrt{2^v v!}} \left( \frac{\alpha}{\pi} \right)^{1/4} \]

<table>
<thead>
<tr>
<th>( v )</th>
<th>( H_v(y) )</th>
<th>( N_v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>((\alpha/\pi)^{1/4})</td>
</tr>
<tr>
<td>1</td>
<td>2y</td>
<td>(1/\sqrt{2}(\alpha/\pi)^{1/4})</td>
</tr>
<tr>
<td>2</td>
<td>4y^2 - 2</td>
<td>(1/\sqrt{8}(\alpha/\pi)^{1/4})</td>
</tr>
<tr>
<td>3</td>
<td>8y^3 - 12y</td>
<td>(1/\sqrt{48}(\alpha/\pi)^{1/4})</td>
</tr>
</tbody>
</table>
The bonding electronic state gives rise to a potential energy surface for the nuclear motion.

Harmonic approximation

\[ V(Q) = \frac{1}{2} k Q^2 \]

\[ \chi_0(Q) = \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha Q^2} \]

\[ \chi_1(Q) = \left( \frac{\alpha}{\pi} \right)^{1/4} 2\alpha Q e^{-\alpha Q^2} \]

... 

\[ E_v = \left( v + \frac{1}{2} \right) \hbar \omega \]
There is a potential energy surface that corresponds to each electronic state of the molecule. The shift in the nuclear displacement arises from the fact that the bond length increases in the $\sigma^*$ state compared to the $\sigma$ state. We will show that the overlap of the vibrational wave functions is key to understanding the shape of absorption bands.
The zero point energy

- The lowest level is $E_0 = \frac{1}{2}\hbar\omega$
- The lowest vibrational level is not zero in energy.
- This is consistent with the uncertainty principle. If atoms were completely still at absolute zero then we would know both their position and moment to arbitrary accuracy.
- The width of the wavefunction is related to positional uncertainty of an atom.
- We call $E_0$ the zero point energy.
Polyatomic Molecules

- There are $3N$ total degrees of freedom in a molecule that contains $N$ atoms.
- There are three translational degrees of freedom. These correspond to motion of the center of mass of the molecule.
- In a linear molecule there are two rotational degrees of freedom. In a non-linear molecule there are 3 rotational degrees of freedom.
- The remaining degrees of freedom are vibrational.
There are $3N-6$ vibrational degrees of freedom in a molecule with $N$ atoms.

Three degrees of freedom are required for translation.
Three degrees of freedom are required for rotation.

For example, in $\text{H}_2\text{O}$ there are 9 total degrees of freedom and 3 vibrational degrees of freedom.
In $\text{C}_6\text{H}_6$ there are 36 degrees of freedom and 30 vibrational degrees of freedom.

Exception: In linear molecules there are only 2 rotational degrees of freedom and therefore the number of vibrations is $3N - 5$. 
The vibrational degrees of freedom can be expressed as normal modes.

All normal modes have the same form for the harmonic oscillator wavefunction and differ only in the force constant $k$ and mass $m$. The total wavefunction is a product of normal modes. The total nuclear wavefunction for water is $\chi_1 \chi_2 \chi_3$. The normal mode wavefunctions of water correspond to the symmetric stretch, bend, and asymmetric stretch. These are linear combinations of the stretching and bending internal coordinates of $\text{H}_2\text{O}$. 
Normal modes - water

There are 3 normal modes (3N - 6). All of them are infrared active since all show a dipole moment change in their motion. The harmonic approximation can be applied to each normal mode.
There are 4 normal modes (3N - 5). Three of them are infrared active since they show a dipole moment change in their motion.
Vibrational Transitions
Vibrational transitions arise because of the oscillation of the molecule about its equilibrium bond configuration. As the molecule oscillates infrared radiation can interact to alter the quantum state.

\[
\mu(Q) = \mu_0 + \left( \frac{\partial \mu}{\partial Q} \right) Q + \ldots
\]

\[
M_{vib} = \left( \frac{\partial \mu}{\partial Q} \right) \int_{-\infty}^{\infty} \chi_{v+1}^* Q \chi_v dQ
\]
In order for infrared light to be absorbed the polarization must be aligned with the direction of the transition moment. For a vibrational mode this is determined by the directional change in the dipole moment. This is shown below for the bending mode of H$_2$O.
Transition dipoles

The change in ground state dipole moment during vibration interacts with light.

\[ \mu = \mu_g + \left( \frac{\partial \mu_g}{\partial Q} \right) Q + \]

The first term is static and does not contribute to the transition. Calling the vibrational wavefunctions \( \chi_i \) the transition moment is:

\[ \mu_{10} = \left( \frac{\partial \mu_g}{\partial Q} \right) \int \chi_1 Q \chi_0 dQ, \]
Dipole derivatives

The vibrational wavefunctions $\chi_i$ are Gaussians, thus the transition moment for transition from vibrational state 0 to vibrational state 1 is:

$$\mu_{10} = \left( \frac{\partial \mu_g}{\partial Q} \right) \int_{-\infty}^{\infty} e^{-\alpha Q^2/2} Q^2 e^{-\alpha Q^2/2} dQ = \frac{1}{\sqrt{2\alpha}} \left( \frac{\partial \mu_g}{\partial Q} \right)$$

The transition dipole moment is proportional to the dipole derivative. This is true for any normal mode of vibration (i.e. harmonic).
Vibrational transitions

As an example we can calculate the transition moment between the state $v = 0$ and $v = 1$.

\[ \chi_0 = \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha Q^2/2}, \quad \chi_1 = \left( \frac{\alpha}{\pi} \right)^{1/4} \sqrt{2\alpha} Q e^{-\alpha Q^2/2} \]

\[ M_{vib} = \left( \frac{\partial \mu}{\partial Q} \right) \left( \frac{\alpha}{\pi} \right)^{1/2} \sqrt{2\alpha} \int_{-\infty}^{\infty} e^{-\alpha Q^2/2} Q^2 e^{-\alpha Q^2/2} dQ \]

\[ = \left( \frac{\partial \mu}{\partial Q} \right) \left( \frac{\alpha}{\pi} \right)^{1/2} \sqrt{2\alpha} \frac{\sqrt{\pi}}{2\alpha^{3/2}} = \left( \frac{\partial \mu}{\partial Q} \right) \frac{1}{\sqrt{2\alpha}} \]
Vibrational transitions

Note that this result is a statement of the vibrational selection rule. Within the harmonic approximation transitions can only occur between states separated by one quantum number ($\Delta v = 1$ or $\Delta v = -1$).

This general rule can be seen by considering integrals of the type shown in the previous slide.
Vibrational Transition
Vibrational Transition
Vibrational Selection Rule

$v' = v + 1$
$v' = v - 1$

$v = 0$
$v = 1$
$v = 2$
Comparison of harmonic and anharmonic potentials
Overtones of water

Even in water vapor \( \nu_1 \approx \nu_3 \), but symmetries are different, \( \Gamma_1 \neq \Gamma_3 \). However, the third overtone of mode 1 has the same symmetry as the combination band \( \Gamma_1 \Gamma_1 \Gamma_1 = \Gamma_1 \Gamma_3 \Gamma_3 \).

Strong anharmonic coupling leads to strong overtones at 11,032 and 10,613 cm\(^{-1}\). These intense bands give water and ice their blue color.
Frequency shift due to molecular interactions

Hydrogen bonding lowers O-H force constant and H-O-H bending force constant.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Vapor Frequency</th>
<th>Liquid Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>3825</td>
<td>3657</td>
</tr>
<tr>
<td>$v_2$</td>
<td>1654</td>
<td>1595</td>
</tr>
<tr>
<td>$v_3$</td>
<td>3935</td>
<td>3756</td>
</tr>
</tbody>
</table>
Question

Which expression is correct?

A. \( k = \sqrt{\frac{\mu}{\omega}} \)
B. \( k = \sqrt{\frac{1}{\mu \omega}} \)
C. \( k = \mu \omega \)
D. \( k = \mu \omega^2 \)
Question

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C. \( k = \mu\omega \)
D. \( k = \mu\omega^2 \)

\[ \omega = \sqrt{\frac{k}{\mu}} \]

\[ \omega^2 = \frac{k}{\mu} \]

\[ k = \mu\omega^2 \]
Question

How many normal modes of vibration does methane have?

A. 15
B. 12
C. 9
D. 6
How many normal modes of vibration does methane have?

A. 15  
B. 12  
C. 9  
D. 6
Analysis of isotope effects

Vibrational spectra are analyzed within the harmonic approximation.

Classical harmonic oscillator equation

\[ \mu \frac{\partial^2 x}{\partial t^2} + kx = 0 \]

Reduced mass

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

\[ x = A \cos(\omega t) \]

\[ \omega = \sqrt{\frac{k}{\mu}} \]
The vibrational partition function

The vibrational energy levels are evenly spaced with a separation of $\hbar \nu$ or $\hbar \omega$. If we take the zero-point level as our “zero of energy” then $\varepsilon_v = v \hbar \omega$.

$$q_v = \sum_{v=1}^{\infty} e^{-\beta \hbar c \nu v} = \sum_{v=1}^{\infty} \left( e^{-\beta \hbar c \nu} \right)^v = \frac{1}{1 - e^{-\beta \hbar c \nu}}$$

This is the partition function that we found for an infinite ladder of energy levels.

For high frequency modes $\varepsilon >> kT$ and $q_v \approx 1$

For very low frequency modes $\varepsilon << kT$ and