The absorption of light can cause molecules to change their internal states, undergoing transitions from one electronic, vibrational, and/or rotational state to another. These transitions occur when the energy carried by the photon:

\[ E = h\nu = \hbar\omega = \frac{hc}{\lambda} \]  

is resonant with the gap in energy between two molecular states, provided that the transition between those states is optically allowed.

In this lecture, we will discuss rotational, vibrational and ro-vibrational molecular spectroscopy by considering the “spectra” or sets of allowed transitions of diatomic molecules.

1 The Harmonic Oscillator and Vibrational Spectroscopy

The infrared spectrum of a diatomic molecule can be modeled by treating its vibrational levels as a quantum harmonic oscillator and considering optical transitions between these levels. We learned that the energy levels of the quantum harmonic oscillator are given by:

\[ E_n = h\nu \left( n + \frac{1}{2} \right) = \hbar\omega \left( n + \frac{1}{2} \right) \quad n = 0, 1, 2, \ldots \]  

where \( \nu = \frac{1}{2\pi} \sqrt{\frac{E}{\mu}} \).

The molecule can make a transition from one vibrational energy level \( n \) to another \( n' \) by absorbing or emitting radiation whose frequency matches the difference in energy levels \( E_n \) and \( E_{n'} \).

While we won’t derive it here, within the harmonic oscillator approximation, transitions are only allowed between adjacent energy states, with \( n' = n \pm 1 \). For absorption of light in particular, \( n' = n + 1 \). This rule for which states can undergo optical transitions to other states is called a selection rule. An additional rule for infrared spectroscopy is that the dipole moment of the molecule must change as it undergoes vibrational motion – otherwise that vibration is not infrared-active. As an example, homonuclear diatomic molecules like H\(_2\) or O\(_2\) have a dipole moment of zero, which remains zero as they vibrate. They therefore have no infrared spectrum. These vibrational selection rules are derived in McQuarrie Section 5.12 for those interested.

In any event, for an IR-active vibration, the allowed transition energies are:

\[ \Delta E = E_{n+1} - E_n = h\nu(n' + 1 + \frac{1}{2}) - h\nu(n + \frac{1}{2}) = h\nu \]
which is independent of $n$! Because the harmonic oscillator has evenly spaced vibrational levels, all transitions fall at the same frequency, and our diatomic molecule can therefore only absorb light with the frequency (in Hertz) of:

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

(4)

This frequency will also commonly be expressed in wavenumbers (cm$^{-1}$) as:

$$\tilde{\nu} = \frac{\nu_{obs}}{c} = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2}$$

(5)

Measuring a vibrational frequency in an infrared spectrum serves as a diagnostic, or fingerprint, of that molecule, since $\tilde{\nu}$ depends on the masses involved, as well as the bond strength $k$, which encodes whether the molecule features a single, double or triple bond.

**Practice Problem:** Calculate the energy of light absorbed by the H$^{35}$Cl molecule in wavenumbers (cm$^{-1}$) when its vibrational motion is excited, given that it has a force constant of $k = 478$ N/m. Note that you will need to calculate the reduced mass $\mu$.

### 2 Beyond the Harmonic Oscillator

Let’s briefly mention two ways in which the vibrational structure of “real molecules” is more complicated than what we’ve seen for the harmonic oscillator.

#### 2.1 Anharmonicity

First, real vibrational motions involve “anharmonicity,” e.g. their potentials deviate from perfect quadratic potential energy surfaces. We’ve already touched on this by looking at the Morse potential:
The harmonic oscillator is a reasonable approximation of this potential near the equilibrium geometry, but deviates substantially for \( x \) far from the center of the well. Correspondingly, the vibrational levels of the Morse potential will deviate from those of the HO model.

We can attempt to address this fact by adding in higher-order polynomial terms in our model potential to account for this additional curvature of the well, like a Taylor expansion:

\[
V(x) = \frac{k x^2}{2} + c \cdot x^3 + d \cdot x^4 + \ldots
\]  

The new energy levels of this anharmonic potential can be found using perturbation theory. We’ll just write down the result here, that we find higher-order corrections to the energy according to:

\[
E_{\text{vib}}(n) = \tilde{\omega}_e (n + \frac{1}{2})^2 - \tilde{x}_e \tilde{\omega}_e (n + \frac{1}{2})^2 + \ldots
\]  

where \( \tilde{\omega}_e \) is the anharmonic oscillator frequency, and \( \tilde{x}_e \) is called the anharmonicity constant and is much smaller than \( \tilde{\omega}_e \). Typically, one would measure the anharmonicity in the IR spectrum experimentally, then fit \( \tilde{\omega}_e \) and \( \tilde{x}_e \tilde{\omega}_e \) to the data.

One other note is that anharmonicity also changes the selection rules for IR transitions. For absorption of IR light, we can now have:

\[
\Delta n = +1, +2, +3 \ldots
\]  

where \( \Delta n = +1 \) are fundamental transitions and \( \Delta n = +2, +3 \ldots \) are called overtones, and can occur but are much weaker in intensity than the fundamental.

### 2.2 Polyatomic molecules have multiple vibrational modes

We have limited our discussion here to diatomic molecules, which only have one vibrational degree of freedom. Even a simple molecule with three atoms, like water, has several vibrational degrees of freedom, which we describe with vibrational normal modes that involve motion of the whole molecule, rather than just one bond. These vibrations will have different frequencies, which act as fingerprints in the IR spectrum for functional groups present in a molecule.
The Rigid Rotor and Microwave Spectroscopy

The microwave spectrum of a diatomic molecule can be modeled by treating its rotational levels as a rigid rotor and considering optical transitions between these levels. We learned that the energy levels of the rigid rotor are given by:

\[ E_J = \frac{\hbar^2}{2I} J(J + 1) \quad J = 0, 1, 2, \ldots \]  
\[ = BJ(J + 1) \]  

where \( B = \frac{\hbar^2}{2I} \) is the rotational constant in Joules and \( J \) is the angular momentum quantum number.

When considering optically allowed transitions between rotational levels, our selection rule is that \( \Delta J = \pm 1 \), and for absorption of light between states \( J \) and \( J' \) we must have \( J' = J + 1 \). The molecule must also have a non-zero dipole moment in order to undergo pure rotational transitions by absorbing light, so, for instance, homonuclear diatomic molecules like \( \text{H}_2 \) or \( \text{O}_2 \) have no microwave spectrum! These selection rules are derived in McQuarrie Section 6.7 for those who want to know more.

Let’s consider transition energies for absorption now:

\[ \Delta E = E_J - E_{J'} \]  
\[ = E_{J+1} - E_J \]  
\[ = \frac{\hbar^2}{2I} [(J + 1)(J + 2) - J(J + 1)] \]  
\[ = \frac{\hbar^2}{2I} (J + 1)(J + 2 - J) \]  
\[ = \frac{\hbar^2}{I} (J + 1) = 2B(J + 1) \]  

The series of rotational transitions from lower state \( J \) are therefore evenly spaced by \( 2B = \frac{\hbar^2}{I} \), in Joules. We aren’t usually measuring spectra in Joules, however, so let’s write down some expressions for energy in more convenient units:

\[ \nu(\text{Hz}) = \frac{\Delta E}{\hbar} = \frac{\hbar}{I} \nu(J + 1) = \frac{h}{4\pi^2 Ic} (J + 1) \]  
\[ \tilde{\nu}(\text{cm}^{-1}) = \frac{\nu}{c} = \frac{h}{4\pi^2 Ic} (J + 1) \equiv 2\tilde{B}(J + 1) \]  

and

\[ \tilde{\tilde{B}}(\text{cm}^{-1}) = \frac{h}{8\pi^2 Ic} \]  

Practice Problem: The bond length of the \( \text{H}^{35}\text{Cl} \) molecule is 129 pm. What is the line spacing in its rotational spectrum in wavenumbers?
4 Beyond the Rigid Rotor

In reality, chemical bonds are not perfectly rigid. As the molecule spins more quickly, with larger angular momentum at larger values of $J$, the bond distorts. In particular, the centrifugal force pulls the atoms further apart and extends the bond at high $J$. If $r$ increases, then the moment of inertia $I = \mu r^2$ increases, and the effective rotational constant $B = \frac{\hbar^2}{2I}$ will decrease at high $J$, causing the rotational states of a real molecule to be more closely spaced together as $J$ increases.

This effect can be captured using a mathematical method called perturbation theory, and the end result is that the energy levels of a nonrigid-rotor can be approximated as:

$$E_J = \tilde{B}J(J + 1) - \tilde{D}J^2(J + 1)^2$$

(19)

where $\tilde{D}$ is called the centrifugal distortion constant, which corrects the energy levels for this effect. It is typically much much smaller than $\tilde{B}$.

5 The Rigid-Rotor-Harmonic-Oscillator and Rovibrationl Transitions

We can discuss the combined rotational and vibrational motion of a diatomic molecule by combining the rigid rotor and harmonic oscillator approximations. We can express the total rotational-vibrational energy of a molecule within this approximation by simply taking the sum of the rotational and vibrational energies, and labeling each state with both a vibrational quantum number, $n$, and a rotational quantum number $J$:

$$E_{n,J} \text{(Joules)} = (n + \frac{1}{2})\hbar \omega + B J(J + 1)$$

(20)

$$\tilde{E}_{n,J} \text{(cm}^{-1}) = \frac{E_{n,J}}{h c} = (n + \frac{1}{2})\tilde{\nu} + \tilde{B} J(J + 1)$$

(21)

$$\tilde{\nu} = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2}, \quad \tilde{B} = \frac{\hbar}{8\pi^2 cI}$$

(22)

The rotational spacing is much finer than the vibrational spacing, leading to a manifold of energy levels that looks like:

Let’s now consider transitions between these rovibrational states. When we make an infrared vibrational transition, it will be accompanied by a simultaneous change in rotational state. In the
case of our diatomic molecule, the selection rules are the same as they were for the rigid rotor and
harmonic oscillator separately. In particular, for absorption of light, we have:

\[
\begin{align*}
\Delta n &= +1 \\
\Delta J &= \pm 1
\end{align*}
\]

The fact that \( J \) can increase or decrease by 1 during a rovibrational transition leads to two
“branches” of transitions:

**R-branch:** \( n \to n + 1, \quad J \to J + 1 \) “richer”

**P-branch:** \( n \to n + 1, \quad J \to J - 1 \) “poorer”

Let’s consider the energies of these transitions, where \( J \) always labels the lower state:

**R-branch:**

\[
\tilde{E}_{n+1,J+1} - \tilde{E}_{n,J} = \left( n + 1 + \frac{1}{2} \right)\tilde{\nu} + \tilde{B}(J + 1)(J + 2)
\]

\[
- \left( n + \frac{1}{2} \right)\tilde{\nu} - \tilde{B}J(J + 1)
\]

\[
= \tilde{\nu} + 2\tilde{B}(J + 1), \quad J = 0, 1, 2, \ldots
\]

**P-branch:**

\[
\tilde{E}_{n+1,J-1} - \tilde{E}_{n,J} = \left( n + 1 + \frac{1}{2} \right)\tilde{\nu} + \tilde{B}(J - 1)J
\]

\[
- \left( n + \frac{1}{2} \right)\tilde{\nu} - \tilde{B}J(J + 1)
\]

\[
= \tilde{\nu} - 2\tilde{B}J, \quad J = 1, 2, 3, \ldots
\]

We therefore find a manifold of evenly spaced rotational transitions clustered around the central
frequency of the “bare” vibrational transition at wavenumber \( \tilde{\nu} \).

6 Beyond the Rigid-Rotor-Harmonic-Oscillator

While the RR-HO approximation of rovibrational structure we discussed above is a fairly good
model, of course we can always consider a more complete, accurate model. One further step is
the fact that rotations and vibrational motions interact with one another. For instance, when a
molecule is spinning rapidly with high \( J \), we can imagine that its vibrational motion is impacted
by the centrifugal force. We can also imagine that when a molecule is highly vibrationally excited,
that may change its rotational energies and dynamics.
Let’s examine one of these examples a little more carefully. Let’s write down the RR-HO energy again:

\[ \tilde{E}_{n,J} = (n + \frac{1}{2})\tilde{\nu} + \tilde{B}J(J + 1) \]  
\[ \tilde{B} = \frac{\hbar}{8\pi^2 cI}, \quad I = \mu r^2 \]  

(33)  

(34)

In a vibrationally excited state, the amplitude of vibration is large, and the molecule effectively spends more time at a longer bond length \( r \). Therefore, the effective moment of inertia \( I \) is larger in this vibrational state, and the rotational constant \( \tilde{B} \) is effectively smaller. For a more careful treatment, we can measure our effective rotational constants as a function of vibrational state \( n \), and call each vibrational-state-dependent rotational constant \( \tilde{B}_n \).

You might see the approximation made that \( \tilde{B}_n \) decreases linearly for larger \( n \), e.g.

\[ \tilde{B}_n = \tilde{B}_e - \tilde{\alpha}_e(n + \frac{1}{2}) \]  

(35)

where the constants \( \tilde{B}_e \) and \( \tilde{\alpha}_e \) are fit to the data.

All the other complications we’ve discussed already – anharmonicity, centrifugal distortion, polyatomic molecules – can also be integrated into our description of rovibrational structure. We have really only scratched the surface here, and could spend an entire semester talking about molecular spectroscopy! But here is where we will stop in this course.