CHM 305 - Lecture 13 - Molecular Spectroscopy (Part 1)

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In this lecture, we will recap our quantum model systems of the harmonic oscillator and the rigid rotor to understand the available energy levels in simple diatomic molecules and how light can be used to measure the frequencies of transitions between these levels. In the next lecture (Part 2), we will explore in more detail how and why real molecular spectra deviate from the predictions of our simple models. This material is covered in Chapters 5 and 6 of McQuarrie, alongside the coverage of the harmonic oscillator and rigid rotor.

1 The Electromagnetic Spectrum & the Basics of Molecular Spectroscopy

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 to be absorbed:

$$E = h\nu = \hbar\omega = \frac{hc}{\lambda} \tag{1}$$

is resonant with the gap in energy between two molecular states. It is also necessary that the transition between those states is "allowed" by certain rules, called "selection rules," which we will discuss shortly.

There are several different kinds of light-induced transitions we might observe in molecules:

- **Electronic transitions** correspond to excitation of electrons from one electronic orbital to another, e.g. a HOMO to LUMO transition. We typically detect these transitions using UV-vis absorption spectroscopy with light whose wavelengths fall in the visible ($400 - 700$ nm) to ultraviolet ($200 - 400$ nm) region of the electromagnetic spectrum. One popular unit for the energy axis in UV-vis spectroscopy is wavenumbers (cm^{-1}). Electronic transitions typically fall in the range of 15,000 to 45,000 cm^{-1}.

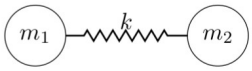
- **Vibrational transitions** correspond to excitation of the motion of nuclei in a molecule. These transitions are lower in energy than electronic excitations, corresponding to wavelengths in the infrared (1000 to 10,000 nm or 1 to 10 μm) or wavenumbers of 1,000 to 4,000 cm^{-1}. For this reason, vibrational spectroscopy is often called infrared (IR) spectroscopy.

- **Rotational transitions** correspond to excitation of the orientational tumbling motion of a molecule. Rotational transition energies fall even lower in energy than vibrations, and typically fall in the microwave region of the electromagnetic spectrum around $0.1 - 10$ cm^{-1}. Rotational spectroscopy is thus often referred to as microwave spectroscopy.

- A final note on **nuclear magnetic resonance (NMR)**. NMR is another popular form of molecular spectroscopy that you may have used in your lab classes or research lab. We won't cover NMR at the moment, but it's worth noting here that it uses even lower-frequency electromagnetic radiation in the form of radiowaves to drive transitions between nuclear spin states of molecules split in an external magnetic field.

2 The Harmonic Oscillator and Vibrational Spectroscopy

In an earlier lecture, we saw that we can use the quantum harmonic oscillator with a potential of $V(x) = \frac{1}{2}kx^2$ as a model for the vibration of a diatomic molecule connected by a chemical bond that acts as a spring with force constant k.



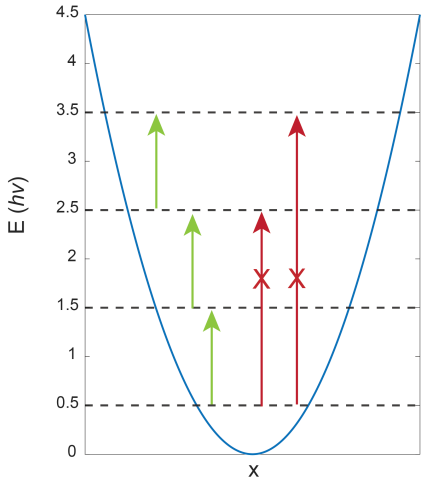
We learned that the quantized energy levels of the harmonic oscillator are given by:

$$E_n = h\nu\left(n + \frac{1}{2}\right) = \hbar\omega\left(n + \frac{1}{2}\right) \qquad n = 0, 1, 2, \ldots \tag{2}$$

where $\omega = \sqrt{\frac{k}{\mu}}$. We can use the spring constant k to model the bond strength (a larger k represents a stiffer bond), while μ is the reduced mass of a diatomic molecule, defined as $\mu = \frac{m_1 m_2}{m_1 + m_2}$.

2.1 Vibrational spectrum of a diatomic molecule

Our diatomic 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 $\Delta E = E_{n'} - E_n$. Importantly, however, not all transitions are "allowed," or probable, even if the photon energy satisfies this energy difference requirement. Within the harmonic oscillator approximation, ***transitions are only allowed between adjacent energy levels***, with $\Delta n = \pm 1$:



- for *absorption* of light, $n \rightarrow n' = n + 1$
- for *emission* of light, $n \rightarrow n' = n - 1$.

These rules that determine which states can be reached by optical transitions are called *selection rules.*

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. This rule is usually summarized as $\frac{d\mu}{dR} > 0$. This means that homonuclear diatomic molecules like N_2 or O_2 lack any infrared-active transitions because they have a dipole moment of zero, which remains zero as they vibrate. While we do not derive them here, these vibrational selection rules are derived in McQuarrie Section 5.12 for those interested.

The allowed transition energies for absorption of light by an IR-active vibration are therefore:

$$\Delta E = E_{n+1} - E_n = h\nu(\cancel{n} + 1 + \cancel{\tfrac{1}{2}}) - h\nu(\cancel{n} + \cancel{\tfrac{1}{2}}) = h\nu \tag{3}$$

which is independent of n! Because the harmonic oscillator has evenly spaced vibrational levels, all allowed transitions fall at the same frequency. Our diatomic molecule can therefore only absorb light with the frequency of:

$$\nu_{obs} = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \qquad [Hz] \tag{4}$$

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

$$\tilde{\nu} = \frac{\nu_{obs}}{c} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{5}$$

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 1: Sketch the vibrational absorption spectrum of the HCl molecule, which has a harmonic vibrational frequency of $2886\,\mathrm{cm}^{-1}$.

2.2 Polyatomic molecules have multiple vibrational modes

We have so far limited our discussion here to diatomic molecules, which only have one vibrational degree of freedom. The simplest polyatomic molecule with three atoms, like the water molecule, has three 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.

While we won't go further with this here, in general, a molecule with N atoms has $3N - 6$ vibrational modes – although for the special case of a linear molecule with N atoms, there are $3N - 5$ vibrational modes. These modes of a polyatomic molecule can include stretching modes (symmetric and asymmetric) as well as in-plane and out-of-plane bending motions (e.g., scissoring, rocking, wagging).

Practice Problem 2: Sketch the vibrational absorption spectrum of the water molecule, treating it as a harmonic oscillator. Water has three IR-active vibrations with frequencies near 1595, 3652, and 3756 cm^{-1}.



3 The Rigid Rotor and Microwave Spectroscopy

We saw previously how we could use the rigid rotor model to describe the rotational behavior of a rigid diatomic molecule. For our diatomic with reduced mass μ, we express the moment of inertia, I, as $I = \mu r^2$, where r is the total distance between the two masses.

We discussed the rigid rotor eigenfunctions, often called spherical harmonics, $\psi(\theta, \phi) \equiv Y_J^m(\theta, \phi)$, which are functions of the two angles θ and ϕ in spherical coordinates and are indexed by two quantum numbers J and m, where $J = \{0, 1, 2, ...\}$ and $m = \{0, \pm 1, \pm 2, ..., \pm J\}$. The energy eigenvalues corresponding to these eigenfunctions depend only on the total angular momentum quantum number J:

$$\hat{H}\, Y_J^m(\theta, \phi) = E_J Y_J^m(\theta, \phi) \tag{6}$$

$$E_J = \frac{\hbar^2}{2I} J(J+1) \equiv BJ(J+1), \qquad J = 0, 1, 2, \ldots \tag{7}$$

where $B = \frac{\hbar^2}{2I}$ is the rotational constant specific to this molecule, given here in Joules. The J^{th} energy level has a degeneracy of $2J + 1$ due to the lack of m dependence in the form of the energy.

3.1 Rotational spectrum of a diatomic molecule

Let's now consider light-driven transitions between the discrete rigid rotor energy levels. Similar to the case of the harmonic oscillator, we also have selection rules that govern which rotational transitions are allowed within the rigid rotor approximation. We won't derive these rules here, but there is a full derivation provided in Section 6.7 of McQuarrie.

We have two selection rules that govern which pure rotational transitions are optically allowed within the rigid rotor approximation:

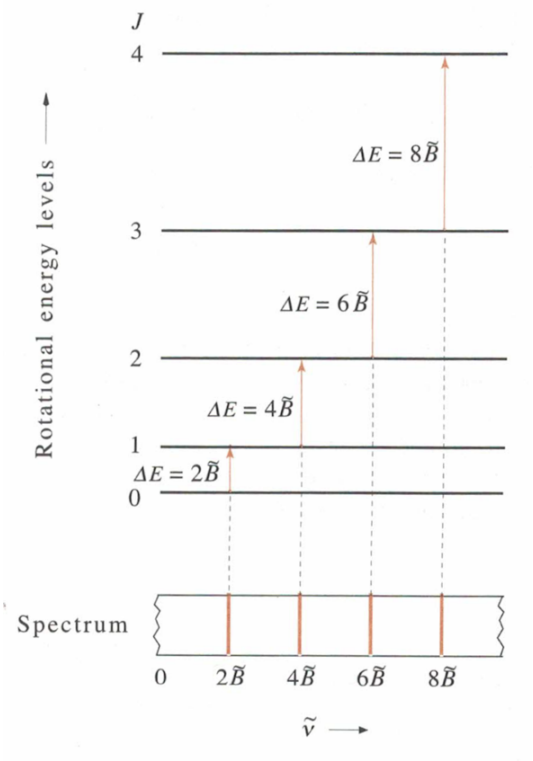
- $\Delta J = \pm 1$. For absorption of light between states J and J' we must have $J' = J + 1$.
- The molecule must also have a non-zero permanent dipole moment. Therefore, homonuclear diatomic molecules like N_2 or O_2 do not feature a pure rotational spectrum!

Given these rules, the energies of light that can be absorbed during an allowed transition between a rotational state with quantum number J and an adjacent state with $J' = J + 1$ are:

$$\Delta E = E_J - E_{J'} \tag{8}$$
$$= E_{J+1} - E_J \tag{9}$$
$$= \frac{\hbar^2}{2I}\left[(J+1)(J+2) - J(J+1)\right] \tag{10}$$
$$= \frac{\hbar^2}{2I}(J+1)(J+2-J) \tag{11}$$
$$= \frac{\hbar^2}{I}(J+1) = 2B(J+1) \tag{12}$$

The transition energies are therefore a function of J, and the *series* of rotational transitions from a lower state J are evenly spaced by $2B = \frac{\hbar^2}{I}$, in Joules.

Let's make sure we understand what this means: when we measure a rotational spectrum, we will see a series of lines that correspond to individual $J \rightarrow J+1$ transitions, such as $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$; and so on. Therefore, $\Delta E_{0\rightarrow1} = 2B$, $\Delta E_{1\rightarrow2} = 4B$, $\Delta E_{2\rightarrow3} = 6B$, and so on. If we make a plot of absorption signal versus the energy of incident light, we will see lines in the spectrum at energy values of $2B, 4B, 6B, \ldots$ which are evenly spaced by $2B$. Molecular rotational energies typically fall in the microwave region of the electromagnetic spectrum around $0.1 - 10$ cm^{-1}, and thus rotational spectroscopy is often referred to as microwave spectroscopy.



The rotational constant B is given above units of Joules, but we can convert to the more

convenient units of wavenumbers:

$$\nu\ [\text{Hz}] = \frac{\Delta E}{h} = \frac{2B(J+1)}{h} = \frac{\hbar^2}{I}\frac{1}{h}(J+1) = \frac{h}{4\pi^2 I}(J+1) \tag{13}$$

$$\tilde{\nu}\ [\text{cm}^{-1}] = \frac{\nu}{c} = \frac{h}{4\pi^2 Ic}(J+1) \equiv 2\tilde{B}(J+1) \tag{14}$$

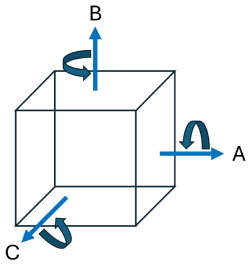
$$\tilde{B}\ [\text{cm}^{-1}] = \frac{h}{8\pi^2 Ic} \tag{15}$$

In these conversions, we can use Planck's constant h (Joule $\cdot$ s) as a way to convert between energy in Joules and frequency in Hz. We can similarly convert between Hz and wavenumbers using the speed of light, c.

Practice Problem 3: Sketch the microwave spectrum of the HCl molecule within the rigid rotor approximation, given that it has a rotational constant $B = 10.6\,\text{cm}^{-1}$.

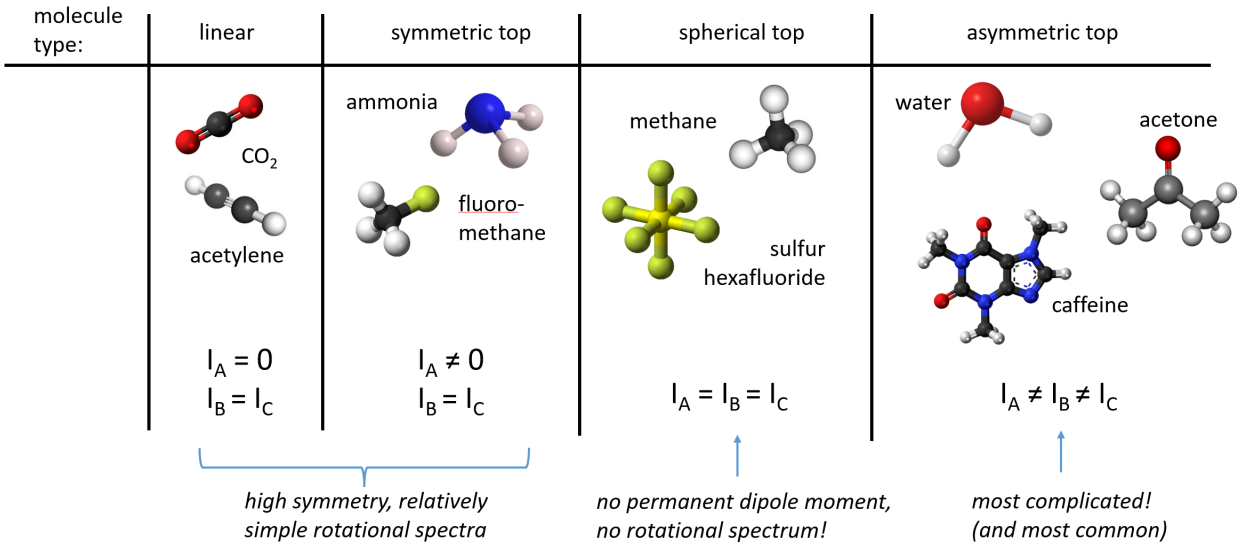
3.2 Rotations of polyatomic molecules

We can extend our rigid rotor framework to describe polyatomic molecules, but to do so, we need to consider rotation in 3 dimensions. Unlike a linear molecule, a polyatomic molecule can be spun around three different orthogonal axes – the so-called principle axes often denoted with A, B, and C labels. Rotating the molecule around each of these axes involves to a unique moment of inertia, labeled I_A, I_B, I_C.



As an analogy: you can imagine that it might be easy to spin a football about its long, pointy axis, but it would take more energy to send it tumbling end-over-end. A 3D object with may therefore have three different rotational constants, with $A[\text{Hz}] = \frac{h}{8\pi^2 I_A c}$, $B[\text{Hz}] = \frac{h}{8\pi^2 I_B c}$, and $C[\text{Hz}] = \frac{h}{8\pi^2 I_C c}$.

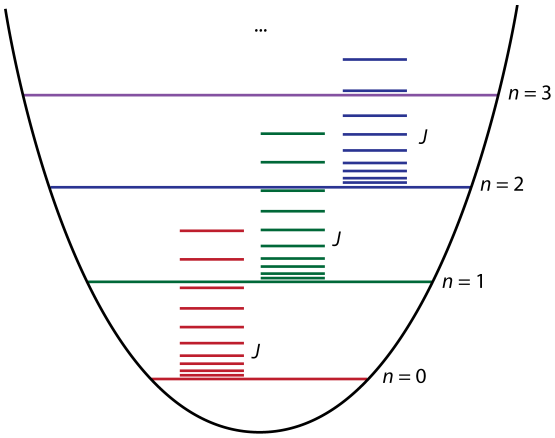
The details of rotational spectroscopy of polyatomic molecules can get complicated very quickly. See the chart on the next page for some examples of how the molecular symmetry matters quite a bit here. Depending on its symmetry, a molecule may have one, two, or three distinct moments of inertia and therefore one, two, or three rotational constants, respectively, governing where the microwave spectral lines. That's all the detail we will go into here!



4 The Rigid-Rotor-Harmonic-Oscillator (RR-HO) and Rovibrational Transitions

Finally, let's talk about the combined rotational and vibrational motion of a diatomic molecule by combining the rigid rotor and harmonic oscillator approximations.

In reality, when a molecule absorbs infrared radiation, the vibrational transition is also accompanied by transitions between rotational levels associated with that vibrational level, since these rotational transitions are much more closely spaced than the vibrational transitions.



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 its vibrational quantum number, n, and a rotational quantum number J:

$$E_{n,J}[\mathrm{J}] = (n+\tfrac{1}{2})\hbar\omega_0 + BJ(J+1) \tag{16}$$

$$\tilde{E}_{n,J}[\mathrm{cm}^{-1}] = \frac{E_{n,J}}{hc} = (n+\tfrac{1}{2})\tilde{\nu}_0 + \tilde{B}J(J+1) \tag{17}$$

$$\tilde{\nu}_0[\mathrm{cm}^{-1}] = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}, \quad \tilde{B}[\mathrm{cm}^{-1}] = \frac{h}{8\pi^2 cI} \tag{18}$$

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 rovibrational transitions of a diatomic molecule, we are subject to the *combined* selection rules for the rigid rotor and harmonic oscillator.

In particular, for absorption of light, we have both

$$\Delta n = +1 \qquad \text{and} \qquad \Delta J = \pm 1 \tag{19}$$

The fact that ΔJ can be either $+1$ or -1 during a rovibrational transition leads to two "branches" of transitions in the resulting spectrum, one branch with *increasing* J and one with *decreasing* J:

$$\textbf{R-branch:} \quad n \to n+1, \quad J \to J+1 \qquad \text{"richer" in } J \tag{20}$$

$$\textbf{P-branch:} \quad n \to n+1, \quad J \to J-1 \qquad \text{"poorer" in } J \tag{21}$$

Let's consider the energies of these transitions in cm^{-1}, where J always labels the lower state:

$$\textbf{R-branch:} \quad \tilde{E}_{n+1,J+1} - \tilde{E}_{n,J} = (n+1+\tfrac{1}{2})\tilde{\nu}_0 + \tilde{B}(J+1)(J+2) \tag{22}$$

$$- (n+\tfrac{1}{2})\tilde{\nu}_0 - \tilde{B}J(J+1) \tag{23}$$

$$= \tilde{\nu}_0 + 2\tilde{B}(J+1), \quad J = 0, 1, 2, \ldots \tag{24}$$

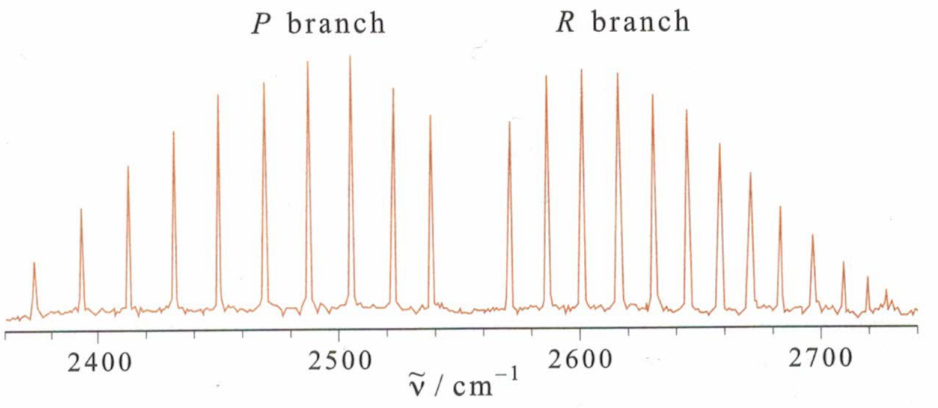
$$\textbf{P-branch:} \quad \tilde{E}_{n+1,J-1} - \tilde{E}_{n,J} = (n+1+\tfrac{1}{2})\tilde{\nu}_0 + \tilde{B}(J-1)J \tag{25}$$

$$- (n+\tfrac{1}{2})\tilde{\nu}_0 - \tilde{B}J(J+1) \tag{26}$$

$$= \tilde{\nu}_0 - 2\tilde{B}J, \quad J = 1, 2, 3, \ldots \tag{27}$$

We therefore find a manifold of evenly spaced rotational transitions clustered around the central frequency of the "bare" vibrational transition at wavenumber $\tilde{\nu}_0$. Note there is no allowed transition precisely at which is "empty" in the measured spectrum since there is there is no allowed $\Delta J = 0$ transition.

Below, we provide as an example the experimental rovibrational spectrum for the $n = 0 \to n = 1$ vibrational transition of HBr gas (McQuarrie Figure 6.4). The "gap" in the middle of the spectrum near 2555 cm^{-1} is the missing "forbidden" $\Delta J = 0$ transition that is not allowed by the selection rules and thus does not appear in the spectrum. One thing you may notice in looking at this spectrum that it appears that the R-branch line spacing starts to get closer together for larger values of J, whereas the P-branch lines appear to be spaced slightly further apart for increasingly large values of J. We will explore the effects that underlie these interesting observations in the next lecture!


P branch
R branch
2400
2500
2600
2700
$\tilde{\nu}$ / cm^{-1}