

CHM 305 - Lecture 11 - Molecular Spectroscopy

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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:

$$E = h\nu = \hbar\omega = \frac{hc}{\lambda} \quad (1)$$

is resonant with the gap in energy between two molecular states. It is also necessary that the transition between those states is “allowed” by selection rules.

In this lecture, we will introduce rotational, vibrational, and ro-vibrational molecular spectroscopy by considering the “spectra” or sets of allowed transitions of diatomic molecules. This material is covered in Chapters 5 and 6 of McQuarrie, alongside the coverage of the harmonic oscillator and rigid rotor.

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 transitions between these levels. We learned that the energy levels of the quantum harmonic oscillator are given by:

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

where $\omega = \sqrt{\frac{k}{\mu}}$.

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 $\Delta E = E_{n'} - E_n$. Within the harmonic oscillator approximation, **transitions are only allowed between adjacent energy levels**, with $\Delta n = \pm 1$:

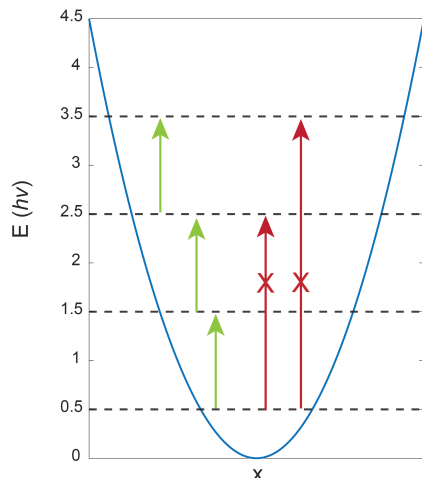
- for *absorption* of light, $n \rightarrow n' = n + 1$
- for *emission* of light, $n \rightarrow n' = n - 1$.

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 $\frac{d\mu}{dR} > 0$.

To give a concrete example, homonuclear diatomic molecules like H_2 or O_2 have a dipole moment of zero, which remains zero as they vibrate. Homonuclear diatomics therefore have no infrared spectrum.

While we do not derive them here, these vibrational selection rules are derived in McQuarrie Section 5.12 for those interested.



For an IR-active vibration, the allowed transition energies for absorption of light are:

$$\Delta E = E_{n+1} - E_n = h\nu\left(n + 1 + \frac{1}{2}\right) - h\nu\left(n + \frac{1}{2}\right) = h\nu \quad (3)$$

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:

$$\nu_{obs} = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2} \quad (4)$$

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

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

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.

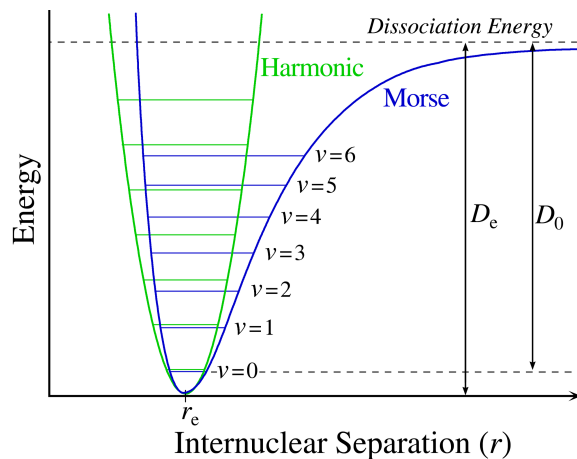
Practice Problem 1: Sketch the vibrational absorption spectrum of the HCl molecule, which has a harmonic vibrational frequency of 2886 cm^{-1} .

2 Beyond the Harmonic Oscillator

Let's now briefly consider 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 harmonic 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. Note that the Morse potential levels grow closer together as energy increases.

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:

$$V(x) = \frac{k}{2} \cdot x^2 + c \cdot x^3 + d \cdot x^4 + \dots \quad (6)$$

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:

$$E_{vib}(n) = \tilde{\omega}_e(n + \frac{1}{2}) - \tilde{x}_e \tilde{\omega}_e(n + \frac{1}{2})^2 + \dots \quad [\text{in cm}^{-1}] \quad (7)$$

where $\tilde{\omega}_e$ is the anharmonic oscillator frequency, and \tilde{x}_e is the *anharmonicity constant*, which is typically 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:

$$\Delta n = +1, +2, +3 \dots \quad (8)$$

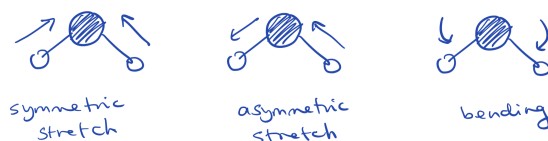
where $\Delta n = +1$ are *fundamental transitions* and $\Delta n = +2, +3 \dots$ are called *overtones*, and can occur but are much weaker in intensity than the fundamental.

Practice Problem 2: Sketch the vibrational absorption spectrum of the HCl molecule, but now treating it as a Morse oscillator.

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. 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 (though for the special case of linear molecules, there are $3N - 5$ vibrational modes).



Practice Problem 3: 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, 3657, and 3756 cm^{-1} .

3 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:

$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2, \dots \quad (9)$$

$$= BJ(J+1) \quad (10)$$

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 $\Delta J = \pm 1$. For absorption of light between states J and J' we must have $J' = J + 1$.

A 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 H_2 or 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 the transition energies for absorption of microwave light now:

$$\Delta E = E_J - E_{J'} \quad (11)$$

$$= E_{J+1} - E_J \quad (12)$$

$$= \frac{\hbar^2}{2I} [(J+1)(J+2) - J(J+1)] \quad (13)$$

$$= \frac{\hbar^2}{2I} (J+1)(J+2-J) \quad (14)$$

$$= \frac{\hbar^2}{I} (J+1) = 2B(J+1) \quad (15)$$

The transition energies are therefore a function of J . The series of rotational transitions from lower state J are 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:

$$\nu(\text{Hz}) = \frac{\Delta E}{h} = \frac{\hbar^2}{I} \frac{1}{h} (J+1) = \frac{h}{4\pi^2 I} (J+1) \quad (16)$$

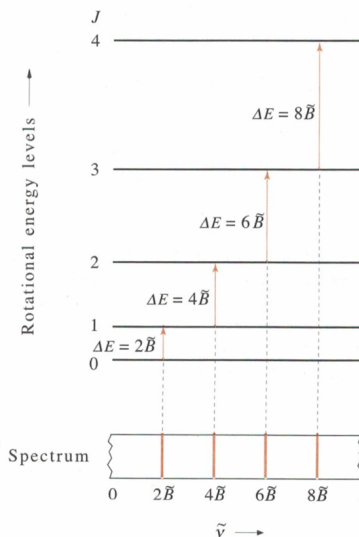
$$\tilde{\nu}(\text{cm}^{-1}) = \frac{\nu}{c} = \frac{h}{4\pi^2 I c} (J+1) \equiv 2\tilde{B}(J+1) \quad (17)$$

and

$$\tilde{B}(\text{cm}^{-1}) = \frac{h}{8\pi^2 I c} \quad (18)$$

Note that in the above conversions, we can think of Planck's constant h (Joule · sec) as a means to convert between energy in Joules and frequency in Hertz. We can similarly convert between Hertz and wavenumbers using the speed of light, c .

Practice Problem 4: Sketch the microwave spectrum of the HCl molecule, given that it has a rotational constant $B = 10.6 \text{ cm}^{-1}$.



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 $B = \frac{h^2}{2I}$ 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 with the addition of higher-order terms in J :

$$E_J = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2 \quad (19)$$

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} .

Practice Problem 5: Sketch the microwave spectrum of the HCl molecule, assuming that it is subject to some centrifugal distortion.

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

We can treat 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,

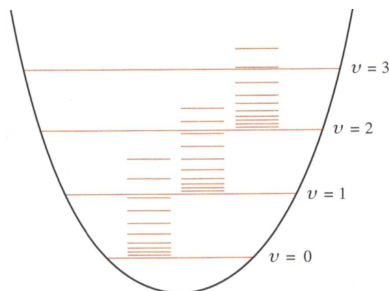
n , and a rotational quantum number J :

$$E_{n,J}(\text{Joules}) = (n + \frac{1}{2})\hbar\omega + BJ(J + 1) \quad (20)$$

$$\tilde{E}_{n,J}(\text{cm}^{-1}) = \frac{E_{n,J}}{hc} = (n + \frac{1}{2})\tilde{\nu} + \tilde{B}J(J + 1) \quad (21)$$

$$\tilde{\nu} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2}, \quad \tilde{B} = \frac{h}{8\pi^2 cI} \quad (22)$$

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.

For absorption of light, we have:

$$\Delta n = +1 \quad (23)$$

$$\Delta J = \pm 1 \quad (24)$$

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

$$\mathbf{R}\text{-branch: } n \rightarrow n + 1, \quad J \rightarrow J + 1 \quad \text{“richer”} \quad (25)$$

$$\mathbf{P}\text{-branch: } n \rightarrow n + 1, \quad J \rightarrow J - 1 \quad \text{“poorer”} \quad (26)$$

Let's consider the energies of these transitions, where J always labels the lower state:

$$\mathbf{R}\text{-branch: } \tilde{E}_{n+1,J+1} - \tilde{E}_{n,J} = (n + 1 + \frac{1}{2})\tilde{\nu} + \tilde{B}(J + 1)(J + 2) \quad (27)$$

$$- (n + \frac{1}{2})\tilde{\nu} - \tilde{B}J(J + 1) \quad (28)$$

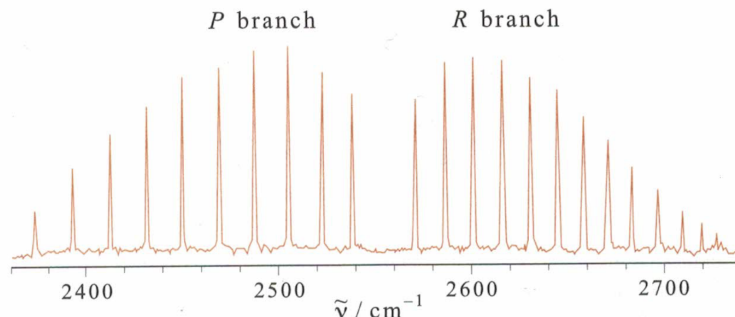
$$= \tilde{\nu} + 2\tilde{B}(J + 1), \quad J = 0, 1, 2, \dots \quad (29)$$

$$\mathbf{P}\text{-branch: } \tilde{E}_{n+1,J-1} - \tilde{E}_{n,J} = (n + 1 + \frac{1}{2})\tilde{\nu} + \tilde{B}(J - 1)J \quad (30)$$

$$- (n + \frac{1}{2})\tilde{\nu} - \tilde{B}J(J + 1) \quad (31)$$

$$= \tilde{\nu} - 2\tilde{B}J, \quad J = 1, 2, 3, \dots \quad (32)$$

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 write down the RR-HO energy again:

$$\tilde{E}_{n,J} = (n + \frac{1}{2})\tilde{\nu} + \tilde{B}J(J + 1) \quad (33)$$

$$\tilde{B} = \frac{h}{8\pi^2cI}, \quad I = \mu r^2 \quad (34)$$

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 label 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.

$$\tilde{B}_n = \tilde{B}_e - \tilde{\alpha}_e(n + \frac{1}{2}) \quad (35)$$

where \tilde{B}_e is known as the equilibrium rotational constant for the ground vibrational state. The constants \tilde{B}_e and $\tilde{\alpha}_e$ are found by fitting the above expression to the positions of spectral lines in 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.