Lecture 26

Rotational and Vibrational Spectroscopy

Study Goal of This Lecture

- Rotational spectrum

- non-rigid rotor: centrifugal distribution

- Vibrational spectrum

26.1   Preface

Now we explicitly consider molecular spectrum, starting from rotations (rigid rotors) and vibrations (harmonic oscillator) that are related to nuclear motions. Note that in spectroscopy we concern:

- position of the peaks $\rightarrow$ energy level, spectrum

- intensity of the peaks $\rightarrow$ absorption coefficient

- selection rules

The first point relates to eigenstate (energy levels) and the second and third one relate to coupling square ($|\mu_{12}|^2$).

26.2   Molecular Spectroscopy

The nuclear Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_R^2 + E(R). \tag{26.1}$$

In general, nuclear motions can be seperated into three different categories:

$$\hat{H} = \hat{H}_{tr} + \hat{H}_{rot} + \hat{H}_{vib}, \tag{26.2}$$

translational, rotational and vibrational part correspond to free electron, rigid rotor and harmonic model respectively. The wave function can be written as:

$$\Psi = \psi_e \times \psi_{tr} \times \psi_{rot} \times \psi_{vib}. \tag{26.3}$$

For general non-linear molecules, there are 3 translational, 3 rotational and $3N-6$ vibrational motions. For diatomic or linear molecule, there are one rotational mode disappears and thus, 3 translation, 2 rotational and $3N-5$ vibrational motions.

26.3   Diatomic Molecule

In the following, we will focus on diatomic molecule:

Figure 26.1: Diatomic molecule.

for diatomic molecule, there is two rotational motions and one vibrational motion. Note that two rotational motions are degenerate. Thus, the respective Hamiltonians are:

$$\hat{H}_{rot} = \frac{\hat{L}^2}{2I}, \tag{26.4}$$

$$\hat{H}_{vib} = \frac{-\hbar^2}{2\mu}\nabla_r^2 + V(r), \tag{26.5}$$

$V(r)$ is determined by electronic energy, and the rotational Hamiltonian is independent of $\hat{H}_e$. (Rotational motions do not affect electronic motion.)

Let's discuss the rotational transitions first. In general, I is a function of r Rotational spectroscopy can be used to measure bond length and bond angles.

and thus rotational motions are coupled to vibrational motions, it should also be clear that I should depends on the rotational states, because of the centrifugal force. However, to a first approximation, the rigid rotor approximation that treats I as a constant is a very good one.

26.3.1 Ideal Rigid Rotor

For ideal rigid rotor, I is fixed, then

$$\hat{H}_{rot}Y_J^m = E_r Y_J^m, \tag{26.6}$$

$$E_r(J) = \frac{\hbar}{2I}J(J+1) \tag{26.7}$$

J is spectroscopic symbol and l is angular momentum.

with $J = 0, 1, 2, \cdots$, it is angular momentum quantum number,

$$M = -J, \cdots, J.$$

The energy levels are $(2J+1)$-fold degenerate!! In spectroscopy we like to use "wavenumbers" cm^{-1} as the unit, then

$$\tilde{F}(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 Ic}J(J+1) = \tilde{B}J(J+1). \tag{26.8}$$

$\tilde{F}(J)$ is term values and $\tilde{B}$ is rotational constant $\simeq 10cm^{-1}$. This equation gives the rotational energy levels for rotational transitions. Next, we would like to ask: How about the selection rules?

26.3.2 Selection Rules

Consider a transition from $\psi_{J,M} \to \psi_{J',M'}$, the transition rules are determined by the transition dipole moment:

$$\mu_{12} = \iiint \psi_{J',M'}^* \psi_\nu^* \psi_e^* \hat{\mu} \psi_e \psi_\nu \psi_{J,M} d\tau_e d\tau_{vib} d\tau_{rot}. \tag{26.9}$$

Define

$$\hat{\mu}_0 = \iint \psi_\nu^* \psi_e^* \hat{\mu} \psi_e \psi_\nu d\tau_e d\tau_{vib} \tag{26.10}$$

as permanent dipole moment of a molecule in the electronic and vibrational state. Then we can write:

$$\mu_{12} = \int \psi_{J',M'}^* \hat{\mu}_0 \psi_{J,M} d\tau_{rot}, \tag{26.11}$$

therefore, the selection rules:

1. The molecule has permanent dipole moment $\hat{\mu}_0 \neq 0$(i.e. polar)

2. specific selection rule: $\Delta J = \pm 1,\ \Delta M = 0$

We take a close look on point 2:

previously, we use the conservation of angular momentum arguement to argue that $\Delta J = \pm 1$, but it is already included in the expression for the transition dipole moment. Recall that $\hat{\mu}_0$ is a vector along "some" axis $\rightarrow$ say z. Then $\vec{\mu_0} \sim z \sim \mu_0 \cos\theta$, therefore

$$\mu_{12} = \int Y_{J'}^{M'}(\theta,\phi)\cos\theta Y_J^M(\theta,\phi)d\Omega_{\theta,\phi}. \tag{26.12}$$

The mathematcial properties of spherical harmonics:

$$\cos\theta Y_l^m(\theta,\phi) = \sqrt{\frac{l^2-m^2}{4l^2-1}}Y_{l-1}^m(\theta,\phi) + \sqrt{\frac{(l+1)^2-m^2}{4(l+1)^2-1}}Y_{l+1}^m(\theta,\phi), \tag{26.13}$$

coefficient are not important, so we rewrite

$$\cos\theta Y_l^m(\theta,\phi) = c_1 Y_{l-1}^m(\theta,\phi) + c_2 Y_{l+1}^m(\theta,\phi) \tag{26.14}$$

$$\Rightarrow \int Y_{J'}^{M'}(\theta,\phi)\cos\theta Y_J^M(\theta,\phi)d\Omega$$

$$= c_1 \int Y_{J'}^{M'}(\theta,\phi)Y_{J-1}^M(\theta,\phi)d\Omega + c_2 \int Y_{J'}^{M'}(\theta,\phi)Y_{J+1}^M(\theta,\phi)d\Omega$$

$$= c_1\delta_{J',J-1}\delta_{M',M} + c_2\delta_{J',J+1}\delta_{M',M} \Rightarrow \Delta J = \pm 1,\ \Delta M = 0.$$

Thus, absorption occurs from $J \rightarrow J+1$ and absorption peaks locate at
$\tilde{\nu} = \tilde{F}(J+1) - \tilde{F}(J) = 2\tilde{B}(J+1),\ J = 0,1,2,\cdots$
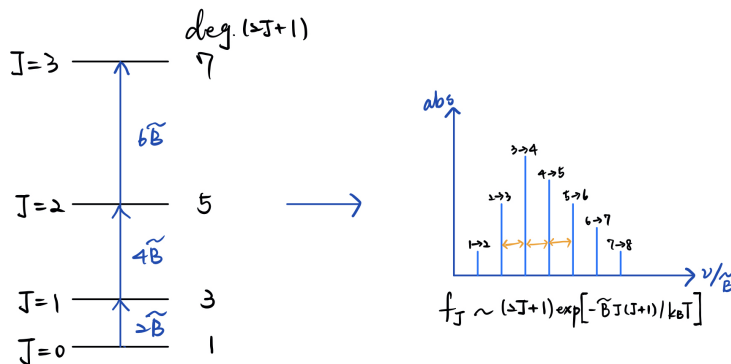

Figure 26.2: Energy levels and rotational spectrum

Above is the energy level between different allowed transition and the rotational spectrum. Notice that the spacing between two adjacent lines is equal and that the profile of spectrum is due to the competing between Boltzmann distribution and number of degeneracy

$$f_J \sim (2J+1)e^{-\frac{\tilde{B}J(J+1)}{k_B T}}. \tag{26.15}$$

26.3.3 Non-rigid Rotor, Centrifugal Distribution

Now consider non-ideal case, where the moment of inertia increases as J increases, due to the effects of centrifugal distribution

$$I \simeq I_0(1 + \alpha \hat{L}^2), \tag{26.16}$$

$\alpha \hat{L}^2$ is the leading term in the expansion of the rotational velocity. With above equation, we obtain:

$$
\begin{aligned}
\hat{H}_r = \frac{\hat{L}^2}{2I} &= \frac{\hat{L}^2}{2} \times \frac{1}{I_0} \times \frac{1}{1 + \alpha \hat{L}^2} \\
&= \frac{\hat{L}^2}{2} \times \frac{1}{I_0} \times 1 - \alpha \hat{L}^2 \\
&= \frac{\hat{L}^2}{2I_0} - \underbrace{\frac{\alpha}{2I_0}\hat{L}^4}_{\substack{\text{Leading} \\ \text{correction term.} \\ \text{Shift the energy.}}} .
\end{aligned}
\tag{26.17}
$$

Note that $\hat{L}^4$ commute with $\hat{L}^2$, so Y_J^M is still the eigenfunction of $\hat{L}^4$. We put spherical harmonic into the correction term and obtain:

$$\hat{L}^4 Y_J^M = J^2(J+1)^2 Y_J^M, \tag{26.18}$$

thus, the corrected $\tilde{F}(J) = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2$, where $\tilde{D}$ is centrifugal distortian constant. The corrected spectrum:

$$\nu = \tilde{F}(J+1) - \tilde{F}(J) = 2\tilde{B}(J+1) - \underbrace{4\tilde{D}(J+1)^3}_{\text{decreasing spacing}} . \tag{26.19}$$

26.4   Vibrational Spectra

26.4.1   Harmonic Oscillator

Now we turn our attentions to vibrational motion. The Potential energy surface, $V(r)$, generally looks like as we have discussed, the motions around the equilibrium

point R_e. An it can always be approximated by a Harmonic osillator:

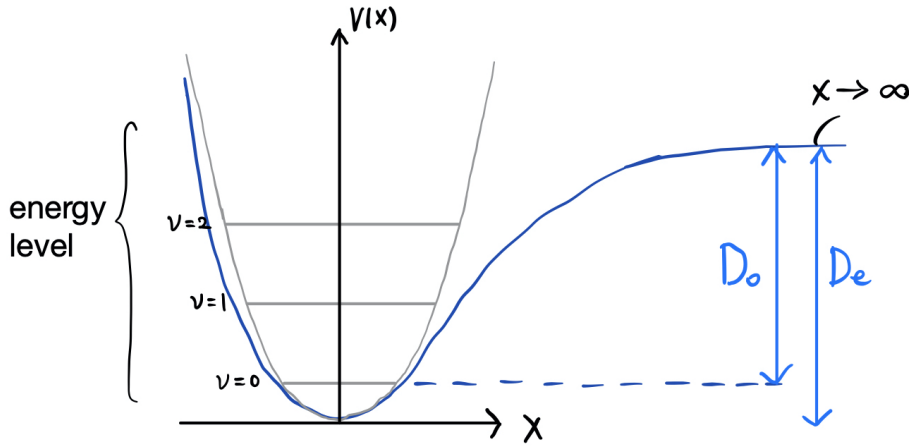$$V(R) = \frac{1}{2}k(R - R_e)^2 = \frac{1}{2}m\omega_0^2 x^2.$$ (26.20)

Figure 26.3: Vibrational Motion

We have already known that the energy levels $E_\nu = (\nu + \frac{1}{2})\hbar\omega, \ \nu = 0, 1, 2, \cdots$. Note that the zero point energy $E_0 = \frac{1}{2}\hbar\omega$, which helps to define the spectroscopic dissociation energy D_0.

26.4.2 Selection Rule

Now, the selection rule for vibrational transition from $\nu \to \nu'$ dependents on the transition dipole moment:

$$\mu_{12} = \int \psi_{\nu'}^* \mu_0^{(e)} \psi_\nu d\tau,$$ (26.21)

recall that $\mu_0 = \int \psi_e^* \hat{\mu} \psi_e d\tau_e$. It is electric permanent dipole and is a function of x, therefore, if we expand it around $x = 0$(set the origin at equilibrium position):

$$\mu^{(e)} = \mu_0 + (\frac{\partial\mu}{\partial x})|_{x=0} \cdot x + \frac{1}{2}(\frac{\partial^2\mu}{\partial x^2})|_{x=0} \cdot x^2 + \cdots,$$ (26.22)

therefore,

$$\mu_{12} = \mu_0 \cdot \int \psi_{\nu'}^* \psi_\nu d\tau^{\,0} + (\frac{\partial\mu}{\partial x})|_{x=0} \cdot \int \psi_{\nu'}^* x \psi_\nu d\tau + \cdots.$$ (26.23)

Thus, the selection rules are:

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1. Gross: $\frac{\partial \mu}{\partial x} \neq 0$, i.e. dipole moment changes with the vibrational coordinate.

2. Specific: $\Delta \nu = \pm 1$ (recall $x \propto (a^\dagger + a)$)

now we see that the vibrational absoption occurs at a single frequency!

Of course, the ideal harmonic osscillator model is an approximation. The true vibrational spectrum can contain additional lines, for example, the $0 \rightarrow 2$ transition which is called the "overtone" transitions, but they are generally much weaker. In next lecture, we will discuss about rotational and vibrational spectra for polyatomic molecules and some finer points about rotational and vibrational spectroscopy. Especially the non-harmonic, termed "anharmonic" effects or "anharmonicity".