Lecture 27

More on Vibrational Spectroscopy

Study Goal of This Lecture

- Vibrational spectrum
  - anharmonicity
  - Morse oscillator
  - vibrational term values
- vibration-rotation spectrum

27.1 Preface

So far we have discussed rotational and vibrational spectroscopy with focus on their respective simple (approximated) model Hamiltonians (energy levels) and selection rules. Here we emphasize that the respective rigid rotor/harmonic oscillator model used are clearly "approximations" and require modifications to describe real experiments. We have discussed such modifications for rotational spectroscopy in centrifugal distortions. Now we will discuss about modifications for vibrational spectroscopy.

27.2 Morse Oscillator

Consider the experimental vibrational absorption of HCl:

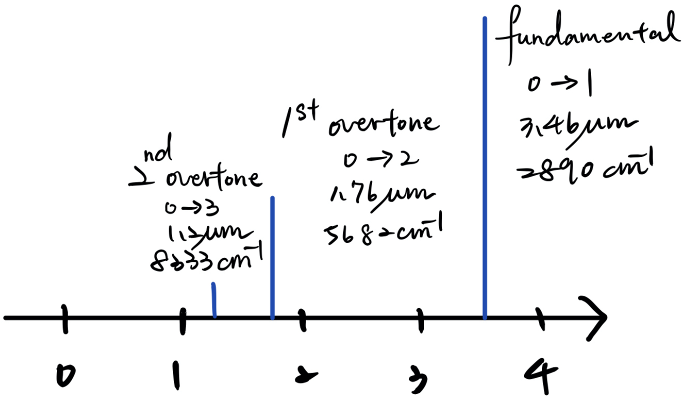

Figure 27.1: Vibrational spectrum of HCl.

We observed that

1. Overtone transitions do occur, with much lower amplitude.
2. $E_{0\to 2} < E_{0\to 1}$, energy levels are not equally spaced.

These are the results of the “anharmonicity” of the potential energy surface. A more realistic model for nuclear motions of diatomic molecules is the “Morse potentail model”.

Morse potential:

$$V(R) = D_e\{1 - e^{-a(R-R_e)}\}^2. \tag{27.1}$$

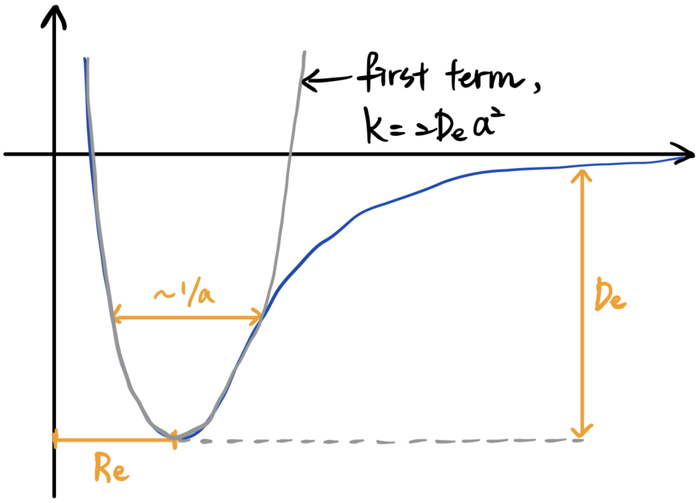

Figure 27.2: Morse potential.

R is the internuclear distance. Notice that as $R \to \infty$, $V(R) \to D_e$ and the minimum $\frac{\partial V(R)}{\partial r} = 0$ is located at $R = R_e$. This potential describes dissociation and anharmonic effect, also, this model can be solved exactly to yield the energy levels. The energy levels of Morse oscillator is:

$$E_n = \hbar\omega_0(n + \frac{1}{2}) - \frac{[\hbar\omega_0(n+\frac{1}{2})]^2}{4D_e}, \; n = 0, 1, 2, 3, \cdots, n_{max}, \tag{27.2}$$

where $\omega_0 = a\frac{2D_e}{\mu}$. We find that quantum number n can't reach infinity now. The energy levels indicates that

$$Z.P.E. \Rightarrow n = 0 \Rightarrow E_0 = \frac{\hbar\omega_0}{2} - \frac{\hbar^2\omega_0^2}{16D_e}. \tag{27.3}$$

Meaning of a: $k = 2D_ea^2$, verified in Silbey's problem 13.24. Note that $D_e >> \hbar\omega_0$.

The $E_n = 0$ line indicates the dissociation limit. Also, as n increase, the correction increases, which is the anharmonic effects. In vibrational spectroscopy, the popular choice of unit is also the wavenumbers, so we often define vibrational term values (Morse Oscillator)

$$\tilde{G}(\nu) = \frac{E_\nu}{hc} = \tilde{\nu_e}(\nu + \frac{1}{2}) - \tilde{\nu_e}x_e(\nu + \frac{1}{2})^2, \tag{27.4}$$

$$\tilde{\nu_e} = \frac{\hbar\omega_0}{hc} = \frac{a}{2\pi c}\sqrt{\frac{2a}{\mu}},\ \tilde{\nu_e}x_e = \frac{\hbar a^2}{4\pi c\mu},\ x_e = \frac{\tilde{\nu_e}}{4D_e}hc, \tag{27.5}$$

$\tilde{\nu_e}$ and x_e are experimental measurables.
Therefore, the expression

$$D_e = \frac{\tilde{\nu_e}}{4x_e} \times hc \tag{27.6}$$

provides a means to estimate D_e, which can not be directly measured. In the anharmonic cases, vibrational spectrum can show more than one lines

$$\tilde{\nu_{abs}} = \tilde{G}(\nu+1) - \tilde{G}(\nu) = \tilde{\nu_e} - 2\tilde{\nu_e}x_e(\nu+1). \tag{27.7}$$

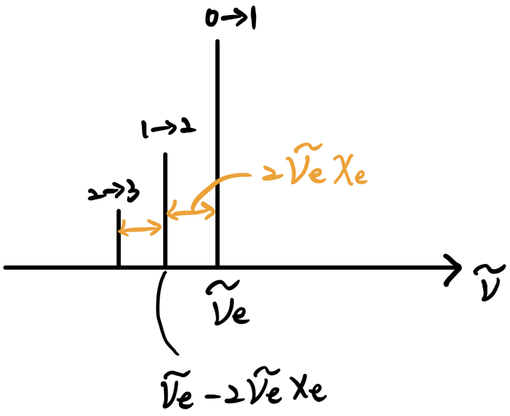

Figure 27.3: Morse spectrum.

The intensity depends on population on each vibrational levels, i.e.

$$P_\nu \simeq (1 - exp(-\frac{\hbar\omega_0}{k_BT}))exp(\frac{-\nu\hbar\omega_0}{k_BT}). \tag{27.8}$$

In real experiments, the higher order term were recorded

$$\tilde{G}(\nu) = \tilde{\nu_e}(\nu + \frac{1}{2}) - \tilde{\nu_e}x_e(\nu + \frac{1}{2})^2 + \tilde{\nu_e}y_e(\nu + \frac{1}{2})^3. \tag{27.9}$$

This shows us that Morse potential is still an approximation (but good one!) and in real applications, $\tilde{\nu_e}$, x_e and y_e are recorded and tabulated.

27.3 Vibration-Rotation Spectrum

Now combine the rotational and vibrational terms:

E, F, G, now you know where the symbols come from.

$$\begin{aligned}\tilde{E}(\nu, J) &= \underbrace{\tilde{G}(\nu)}_{vib.} + \underbrace{\tilde{F}_\nu(J)}_{rot.} \\ &= \tilde{\nu}_e(\nu + \frac{1}{2}) - \tilde{\nu}_e x_e(\nu + \frac{1}{2})^2 + \tilde{B}_\nu J(J+1).\end{aligned} \tag{27.10}$$

It is necessary to put ν on $\tilde{B}_\nu$ because the rotational constant depends clearly on the vibrational level, generally, increasing of ν means bond-length also increase(i.e. $\langle \Delta x^2 \rangle$ increases), that is, larger moment of inertia. The dependence can be described by introducing a vibrational-rotational coupling constant

$$\tilde{B}_\nu = \tilde{B}_e - \tilde{\alpha}_e(\nu + \frac{1}{2}). \tag{27.11}$$

This means that rotational constant. i.e. spacing between rotational peaks, decreases when vibrational excitation level ν increases. (Physically, it is due to increasing of I.)

Now we consider the selection rule, the rule of vibrational and rotational spectrum is combined now, that is $\Delta J = \pm 1, \Delta\nu = \pm 1$.

Forbidden transition:

$$\begin{gathered}(\nu, J) \to (\nu, J \pm 1) \text{ pure rotational} \\ (\nu, J) \to (\nu + 1, J) \text{ Q band}\end{gathered}$$

Allowed transition:

$$\begin{gathered}(\nu, J) \to (\nu + 1, J + 1) \text{ R band} \\ (\nu, J) \to (\nu + 1, J - 1) \text{ P band}\end{gathered}$$

Because often $h\tilde{\nu}_e >> k_B T$, we only have to consider the vibrational transition from $\nu = 0 \to \nu = 1$. The vibrational transition is now described by the following energy diagram:

Note that the spacing:

$$\begin{aligned}|\Delta\tilde{\nu}_e(J)| &= |\tilde{\nu}_R(J+1) - \tilde{\nu}_R(J)| \\ &= |\underbrace{3\tilde{B}_1 - \tilde{B}_0}_{>0} + \underbrace{(\tilde{B}_1 - \tilde{B}_0)}_{<0}(2J+1)|,\end{aligned} \tag{27.12}$$

$$\begin{aligned}|\Delta\tilde{\nu}_p(J)| &= |\tilde{\nu}_p(J+1) - \tilde{\nu}_p(J)| \\ &= |\underbrace{-(\tilde{B}_1 + \tilde{B}_0)}_{<0} + \underbrace{(\tilde{B}_1 - \tilde{B}_0)}_{<0}(2J+1)|.\end{aligned} \tag{27.13}$$

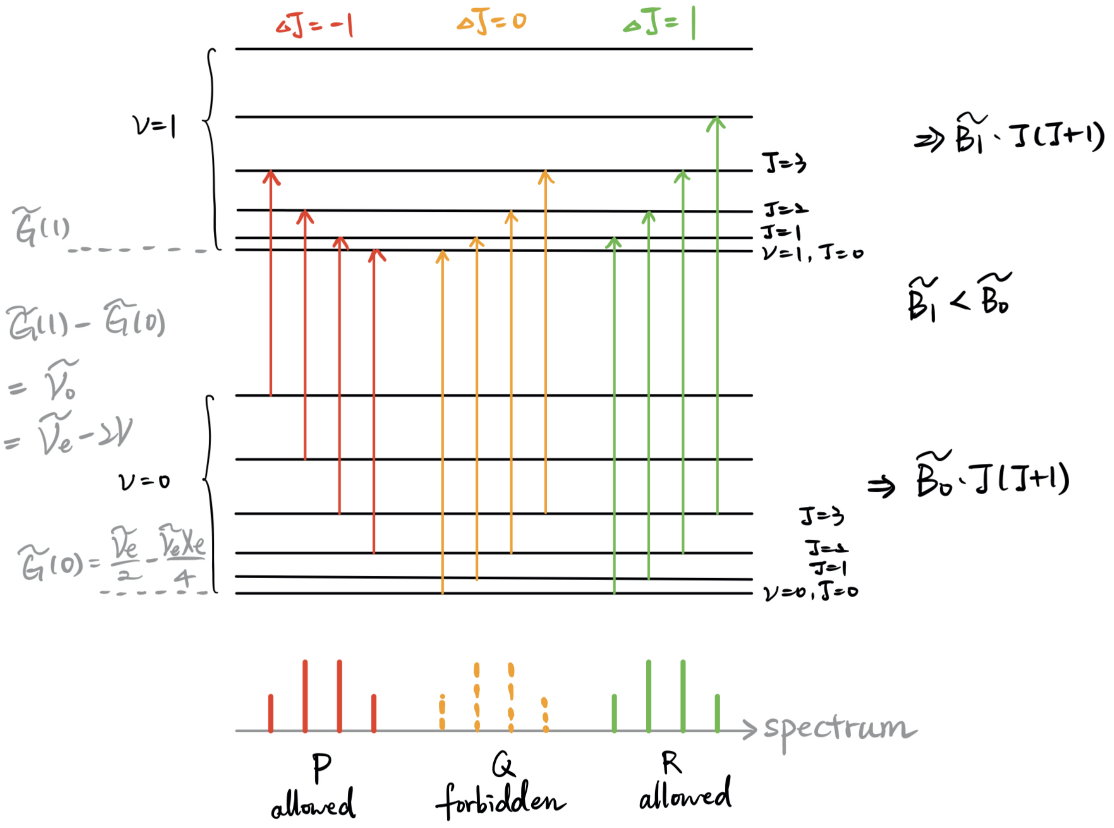

Figure 27.4: Rotational and vibrational energy diagram.

Note that $\tilde{B}_1 < \tilde{B}_0$, therefore, $\tilde{B}_1 - \tilde{B}_0 < 0$ is negative. Therefore, the spacing decreases with J increasing for R band and the spacing increases with J increasing for P band.

The difference $\tilde{B}_1 - \tilde{B}_0$, $\tilde{\alpha}_e$, can be evaluated from the change of the spacing. This tell us the vibration-rotation spectra can be used to probe molecular potentail energy surface! When there comes to more than one vibrational mode, we still can handle it via normal mode analysis, for details, see Silbey.