

Lecture 29

Molecular Electronic Spectroscopy I

Study Goal of This Lecture

- Briefly understanding of molecular electronic and vibrational transitions
- Electronic selection rules

29.1 Introduction to Molecular Electronic Spectroscopy

Now we go up on the energy ladder to consider electronic spectroscopy, which involves transition between electronic and vibrational states in molecular systems and are much higher in energy than vibration and rotational transition.

Consider the transition between eigenstates of hydrogen atom, from $n = 1 \rightarrow n = 2$. The energy difference is

$$\Delta E = E_2 - E_1 = 13.6 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \simeq 10.2 \text{ eV}, \quad (29.1)$$

it is about 120nm, in the UV range.

For a molecule to absorb light at UV/Vis region, it requires long conjugated system or d-orbitals to have smaller spaced electronic states to absorb light in the visible regime. The well known chromophores adapts this kind of structures.

Let's again, consider the principle using model diatomic molecules, by considering energy levels and selection rules. For diatomic molecules, electronic transition

almost always involves, at the same time, varies vibrational levels. Following Silbey's symbols, if we consider \tilde{E} is the sum of vibrational and electronic energy for the higher electronic state (in cm^{-1})

Here, we utilize two Morse Potentials.

$$\tilde{E}' = \underbrace{\tilde{\nu}_{e1}}_{\text{electronic energy}} + \tilde{\nu}_e(n' + 1/2) - \underbrace{\tilde{\nu}_e\chi_e(n' + 1/2)^2}_{\text{anharmonicity correction}}, \quad (29.2)$$

and consider the energy for ground electronic state \tilde{E}''

$$\tilde{E}'' = \tilde{\nu}''_{e1} + \tilde{\nu}''_e(n'' + 1/2) - \tilde{\nu}''_e\chi_e''(n'' + 1/2)^2. \quad (29.3)$$

Normally, $\tilde{\nu}''_e \gg k_B T/hc$, so we can consider the system is in ground vibrational state, that is

$$\tilde{E}'' = \tilde{\nu}''_{e1} + \frac{\tilde{\nu}''_e}{2} - \frac{\tilde{\nu}''_e\chi_e''}{4}. \quad (29.4)$$

The transition occurs at

$$\tilde{\nu}_{abs} = \tilde{E}' - \tilde{E}'' = \tilde{\nu}_{0,0} + \tilde{\nu}'_e n' - \tilde{\nu}'_e\chi'_e n'(n' + 1) \quad (29.5)$$

where

$$\tilde{\nu}_{0,0} = \tilde{\nu}'_{e1} - \tilde{\nu}''_{e1} + \left(\frac{\tilde{\nu}'_e}{2} - \frac{\tilde{\nu}'_e\chi'_e}{4} \right) - \left(\frac{\tilde{\nu}''_e}{2} - \frac{\tilde{\nu}''_e\chi_e''}{4} \right). \quad (29.6)$$

The spectrum gives rise to a progression, of vibrational lines, note that as n' increases, the spacing decreases.

29.2 Selection Rules

Now let's consider the selection rules. Let's first clearly determine the initial and final states in a UV/Vis transition:

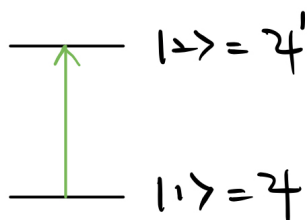


Figure 29.1: Two molecular electronic states.

If we assume Born-Oppenheimer approximation, which states that the electronic and vibrational wavefunctions are independent.

Recall that Ψ_1 and Ψ_2 are functions of R .

$$\Psi = \Psi_e \Psi_{vib} \Psi_{spin} = \Psi_1 \Psi_{\nu=0} \Psi_{spin}, \quad (29.7)$$

$$\Psi' = \Psi_2 \Psi_{\nu'} \Psi_{s'}, \quad (29.8)$$

note that ν denotes the vibrational state for $|1\rangle$ and ν' denotes the vibrational state for $|2\rangle$, they are different vibrational mode and they are NOT orthonormal to each other. We ignore rotational states because their energies are too small.

Why? Explain why to yourself.

We further recall that the dipole operator can be divided into electronic and nuclear parts:

$$\hat{\mu} = \sum_i q_i \hat{r}_i = \sum_j q_j \hat{r}_j + \sum_a q_a \hat{R}_a = \hat{\mu}_e + \hat{\mu}_n. \quad (29.9)$$

The transition dipole:

$$\begin{aligned} \mu_{12} &= \int \Psi_1^* \Psi_{\nu=0}^* \Psi_s^* (\hat{\mu}_e + \hat{\mu}_n) \Psi_2 \Psi_{\nu'} \Psi_{s'} d\tau_e d\tau_{vib} \tau_s \\ &= \int \Psi_1^* \Psi_{\nu=0}^* \Psi_s^* \hat{\mu}_e \Psi_2 \Psi_{\nu'} \Psi_{s'} d\tau_e d\tau_{vib} \tau_s \\ &\quad + \int \Psi_1^* \Psi_2 d\tau_e \int \Psi_{\nu=0}^* \hat{\mu}_n \Psi_{\nu'} d\tau_{vib} \\ &= \int \Psi_{\nu=0}^* \left[\int \Psi_1^* \hat{\mu}_e \Psi_2 d\tau_e \right] \Psi_{\nu'} d\tau_{vib} \times \int \Psi_s^* \Psi_{s'} \tau_s. \end{aligned} \quad (29.10)$$

Note that in the above equation, since both Ψ_1 and Ψ_2 depend on R , so $\int d\tau_e$ must be carried out first. We usually further define

$$\mu_{e,12} = \int \Psi_1^* \hat{\mu}_e \Psi_2 d\tau_e \quad (29.11)$$

as electronic transition dipole, $\mu_{e,12}$ is generally a function of R , so we can expand it around R_e

$$\mu_{e,12} \simeq \mu_{0,12} + \underbrace{\frac{\partial \mu_{e,12}}{\partial R} \Big|_{R=R_e} (R - R_e)}_{\text{higher order term, neglected}} + \dots \quad (29.12)$$

where

$$\mu_{0,12} = \underbrace{\int \Psi_1^*(R = R_e) \hat{\mu}_e \Psi_2(R = R_e) d\tau_e}_{\text{electronic transition dipole}} \quad (29.13)$$

The above expression for $\mu_{0,12}$ utilizes Condon approximation. The higher order term are only important when $\mu_{0,12} = 0$. In this case, the gradient term will generate change in both electronic and vibrational wavefunctions, it is called “vibronic excitation” (normally weak). We will neglect such vibronic excitations and only consider $\mu_{0,12}$ independent of R . This is Condon Approximation.

Let’s go back to see the transition dipole:

$$\begin{aligned} \mu_{12} &\simeq \int \Psi_1^*(R = R_e) \hat{\mu}_e \Psi_2(R = R_e) d\tau_e \int \Psi_{\nu=0}^* \Psi_{\nu'} d\tau_{vib} \times \int \Psi_s^* \Psi_s' d\tau_s \\ &= \mu_{0,12} \times \int \Psi_{\nu=0}^* \Psi_{\nu'} d\tau_{vib} \times \delta_{s,s'}, \end{aligned} \quad (29.14)$$

note that because ν and ν' correspond to vibrational states for the ground and excited potential energy surface respectively, in general the two states are not orthonormal. So the electronic transition depends on:

1. Non zero electronic transition dipole.
2. Overlap of vibrational wavefunctions between ground and excited electronic PES.
3. Spin function cannot change.

These three are the selection rules of molecular electronic transition. We will focus on the first two rules in the next lecture.