Lecture 30

Molecular Electronic Spectroscopy II

Study Goal of This Lecture

- Franck-Condon overlap and Franck-Condon principle
- Elementary photophysical process

30.1 Franck-Condon Overlap and Franck-Condon Principle

30.1.1 Franck-Condon Overlap

In the previous lecture, the selection rules of molecular electronic spectroscopy is presented. It depends on the transition dipole:

$$\begin{aligned} \mu_{12} &\simeq \int \Psi_1^*(R=R_e)\hat{\mu_e}\Psi_2(R=R_e)d\tau_e \int \Psi_{\nu=0}^*\Psi_{\nu'}d\tau_{vib} \times \int \Psi_s^*\Psi_s' d\tau_s \\ &= \mu_{0,12} \times \int \Psi_{\nu=0}^*\Psi_{\nu'}d\tau_{vib} \times \delta_{s,s'}. \end{aligned} \tag{30.1}$$

From above, we observe that the selection rules of molecular electronic transition are:

1. Non zero electronic transition dipole.

2. Overlap of vibrational wavefunctions between ground and excited electronic PES.

3. Spin function cannot change.

In this lecture, the first two rules will be well focused on. Let's look at the second point first. The overlap is called the "Franck-Condon overlap integral"

$$S_{\nu,\nu'} = \int \Psi_\nu \Psi_{\nu'} \tau_{vib}. \tag{30.2}$$

What does this mean and what this tells us about the "state" after excitation? It is explained by the following diagram:

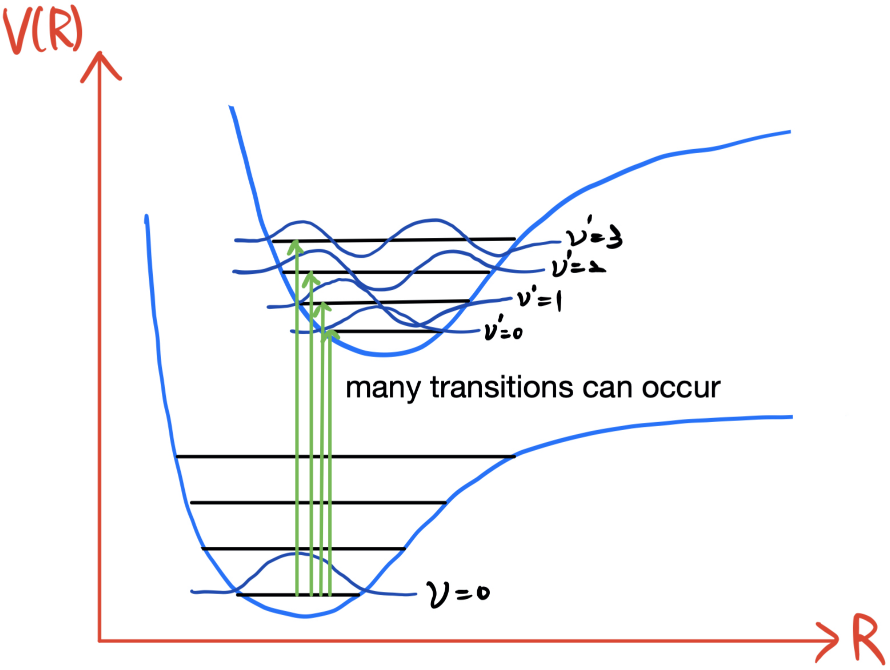


Figure 30.1: Potential energy surface of two electronic states and the first few vibrational states in electronic excited state.

In this case, the largest overlap $S_{0,\nu}$ occurs at $\nu = 0 \to \nu' = 2$.

30.1.2 Franck-Condon Principle

What is the physical meaning of this? Recall that in our treatment of excitation due to electromagnetic field, after excitation the new state can be written as a superposition

$$|\Psi_f\rangle = \sum_k b_k \left|\Psi'_k\right\rangle \tag{30.3}$$

where the coefficient are proportional to the transtion dipole $\mu_{f\to k}$. Therefore, after excitation the wavefunction of the excited state:

$$\Psi_1\Psi_{\nu=0} \longrightarrow \sum_k \mu_{0,12} S_{0,\nu'=k}\Psi_2\Psi_{\nu'} = \Psi_2 \sum_k S_{0,\nu'=k}\Psi_{\nu'}.$$

What is the vibrational part after excitation? Recall the rule for basis transform in QM:

> Any wavefunction $|\psi\rangle$ can be written as a superposition on a "basis" $\{\phi_i\}$,
>
> $$|\psi\rangle = \sum_n C_n \phi_{\phi_n} \tag{30.4}$$
>
> where
>
> $$C_n = \langle\phi_n|\psi\rangle = \int \phi_n^* \psi d\tau. \tag{30.5}$$

$\sum_k S_{0,v'=k}\Psi'_v$ is exactly $\Psi_{\nu=0}$ written in a different basis (vibrational states of the excited electronic state.) Therefore, in the excitation, the electronic wavefunction changes from $\Psi_1 \to \Psi_2$, but the nuclear wavefunction stays the same, because nuclei move much slower than electrons and have no time to respond to electronic transition. This is called the Franck-Condon principle. The principle is more general than just for optical transitions. It is everywhere in physical chemistry from excitation energy transfer(EET) to electron transfer(ET). I am making a living one of it.

> In an electronic process, nuclei have no time to move, so the nuclear wavefunction stays the same!

The electronic contribution is also important:

$$\mu_{0,12} = \int \Psi_1^*(R = R_e)\hat{\mu}_e\Psi_2(R = R_e)d\tau_e, \tag{30.6}$$

electronic transition dipole at the molecular equilibrium structure between two many electron states.

Note that both Ψ_1 and Ψ_2 are many-electron wavefunctions! From the inspection of the expression we inmediately know:

1. (Optional)For linear molucule: $\hat{\mu}_e$ has $\hat{z}$ character, i.e. is an odd function in z and both $\cos\theta$ character. Recall that for such molecules with cylidrical symmetry, we can define molecular terms.

   For many electrons:

   - Orbital angular momentum: $M_L = m_1 + m_2 + \cdots$
   - Axial quantum number: $\Lambda = |M_L| = 0, 1, 2, 3, \cdots$
   - Symbol: $1 \rightarrow \Sigma$, $2 \rightarrow \Pi$, $3 \rightarrow \Delta$, $4 \rightarrow \Phi$, $\cdots$
   - Axial spin quantum number: $\Sigma = S, S-1, \cdots, -S$
   - Total angular momentum: $\Omega = |\Lambda + \Sigma|$
   - Molecular term symbol: ${}^{2S+1}\Lambda_{\Omega}$

   the selection can be derived as:

   $$\Delta\Lambda = 0, \pm 1, \quad \Delta S = \Delta\Sigma = 0, \quad \Delta\Omega = 0, \pm 1$$

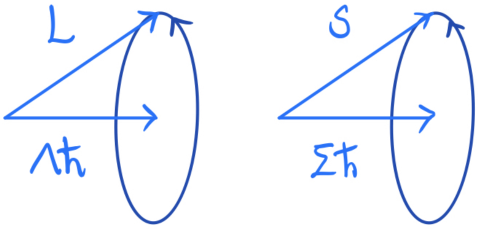
   

   Figure 30.2: Figure of molecular term symbol.

2. State symmetry selection rule I:

   For molecules with a symmetry plane containing $\vec{\mu}$ axis, then $+ \leftrightarrow +$, $- \leftrightarrow -$ transition are allowed, but $+ \leftrightarrow -$ are not due to $\hat{\mu}$ is symmetry.

3. State symmetry selection rule II:

   For molecules has an inversion center, $\hat{\mu}$ is odd(u), then $g \leftrightarrow u$ are allowed, but $u \leftrightarrow u$, $g \leftrightarrow g$ are not.

   For instance: absorption of polyenes, such as β-carotene

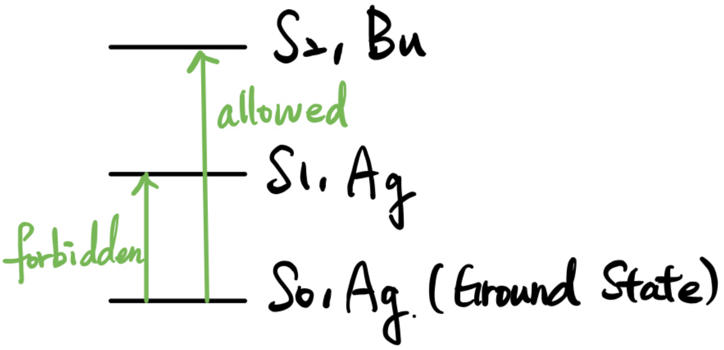


Figure 30.3: Transition rule of *beta*-carotene.

4. Orbital transition rules:

   Note that within the Hartree-Fock approximation, we can write Ψ_1, Ψ_2 as products of molecular orbitals, then the transition rule apply to MO level. Electronic transition can be considered as promoting an electron from an occupied MO to an unoccupied MO(virtual orbital).

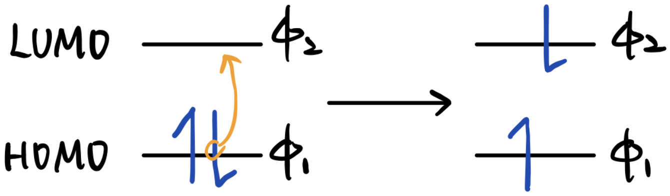


Figure 30.4: Left one is the HF groundstate, and the right one is the excited state. Note that the transition energy in left one is under the “frozen orbital” approximation.

Under this MO picture, we find two selection rules:

- ϕ_1 and ϕ_2 must have different parity.
- Note that between $\hat{\mu}$ is linear in electron coordinate. i.e. combination of single electron operators, it can only change one electron at a time, so all changes involving more than one electron are forbidden in the HF level.

These transition rules allow us to understand molecular electron(UV/Vis) spectrum and assign transitions to peaks. Nevertheless, what is the UV/Vis experiments tell us?

30.2 Absorption Pattern

Recall, absorption rate from $|1\rangle \to |2\rangle$ is

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = B\rho_\nu(\nu_{12})N_1, \tag{30.7}$$

therefore, absorption from the ground state tells us how many molecules are in the state. A method to measure concentration. This is Beer-Lambert Law:

$$\frac{dI}{I} = -\kappa \cdot c \cdot dx \tag{30.8}$$

$$\to \log \frac{I_0}{I} = A = \epsilon \cdot c \cdot L, \tag{30.9}$$

κ, ϵ, c and L are Napierian molar absorption coefficient, molar extinction coefficient, concentration and path length, respectively.

30.2.1 Shape of absorption "bond" reveals elementary photophysical process.

So far we have considered absorption, stimulated emission and spontaneous emission of molecular in ideal conditions. i.e. gas phase. Now we consider a displaced harmonic oscillator model:

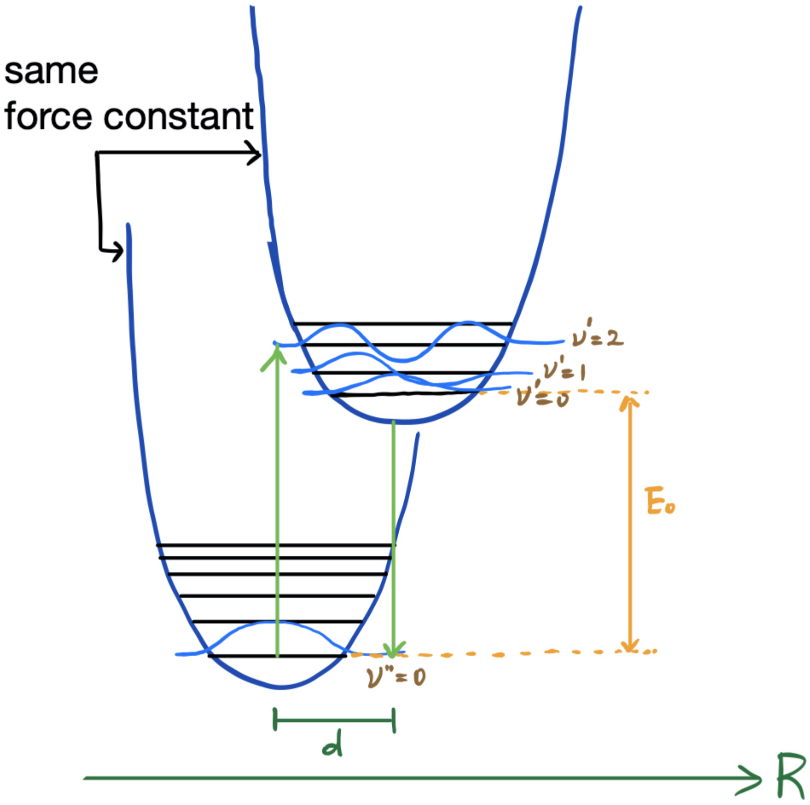


Figure 30.5: Displaced harmonic oscillator model

in this case, the Franck-Condon overlap is

$$\left|\int \Psi^*_{\nu''=0}\Psi_{\nu'=m}d\tau\right|^2 = \frac{s^m}{m!}e^{-s} \tag{30.10}$$

where $s = \frac{\mu\omega_0}{2\hbar}d^2$ and it is called Huang-Rhys factor, represent the coupling strength between nuclear and electronic degrees of freedom. Different s affect the absorption pattern.

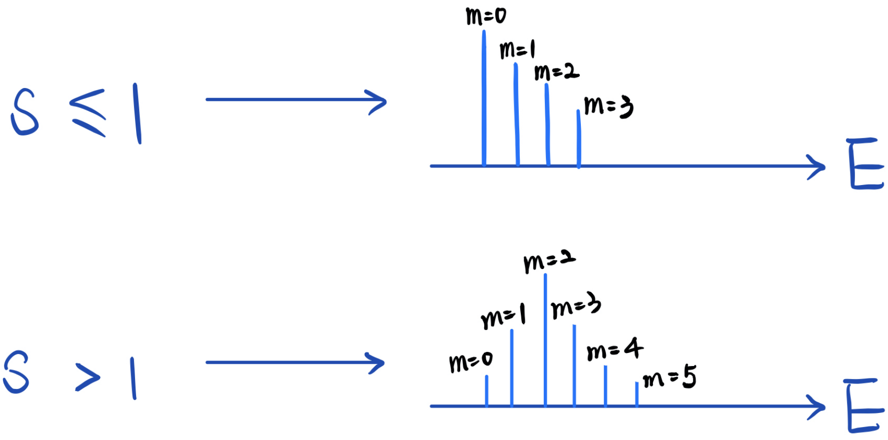
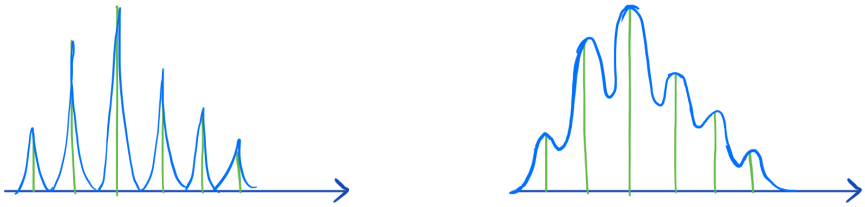


Figure 30.6: Huang-Rhys factor and absorption pattern.

When the upperstate can “relax”, the linewidth contains information about the life time.


gas phase
(collisional dephasing)

condensed phase

Figure 30.7: Absorption lineshpae under different phase.

The bandwidth/linewidth tells the lifetime of the excited states and can reveal information about many elementary photophysical process.

30.2.2 Stoke's Shift

There is one famous phenomena called Stokd's shift, it worths a notice. When we plot the absorption spectrum and the emission spectrum together in the same graph, we will find that the two highest peaks do not coincide. The shift between it is called Stoke's shift

It is stemed from that the most stable geometry of the molecule in the ground state and excited state are generally not the same . So, when we excite a molecule from electronic ground state to the electronic excited state, this excited state have the higher energy than it is in equilibrium(The most stable geometry.) And while a molecule are going to radiate its excess energy and transfer to the electronic ground state from electronic excited state, the energy of this electronic ground state will also have higher energy than it is in equilibrium. Thus, the absorption enrgy will be larger than the emission energy in general.

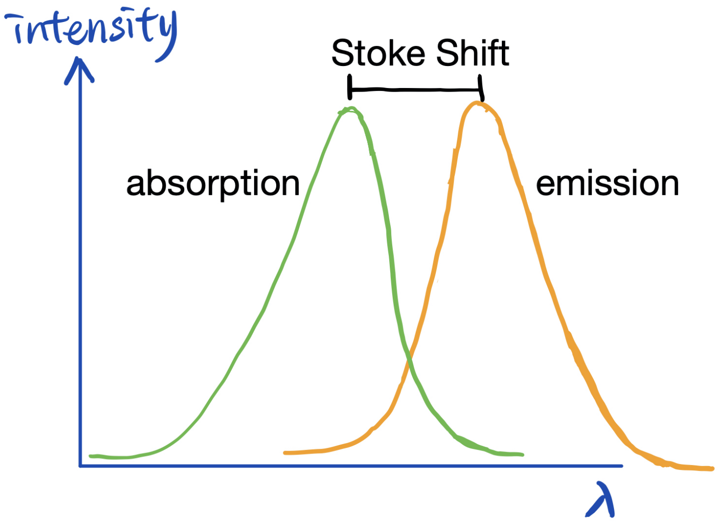


Figure 30.8: Stoke's shift

30.3 Jablonski Diagram

After the molecule be excited to the excited state, there are lots of processes can happen. It is useful to describe those process via the Jablonski diagram.

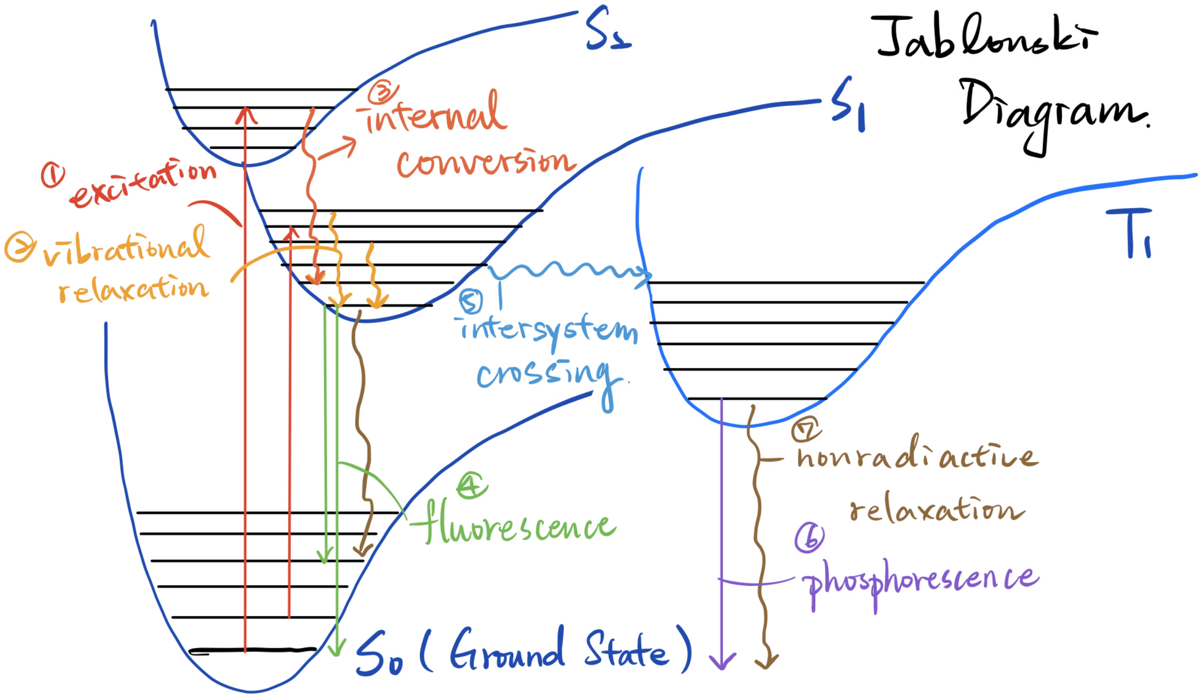


Figure 30.9: Jablonski diagram.

1. **Excitation** ($\sim 10^{-15}s$)

   A state absorbs the energy and transfer to a higher energy state.

2. **Vibrational relaxation** ($\sim 10^{-14} - 10^{-11}s$)

   The system loss its energy and transfer to a lower energy state via vibrational motions.

3. **Internal conversion** ($\sim 10^{-14} - 10^{-11}s$)

   Nonradiative transition between two state with the same multiplicity.

4. **Fluorescence** ($\sim 10^{-9} - 10^{-7}s$)

   Radiative transition between two states with the same multiplicity.

5. **Intersystem crossing**

   Nonradiative transition between two states with the different multiplicity.

6. **Phosphorescence** ($\sim 10^{-3} - 10^{-2}s$)

   Radiative transition between two states with different multiplicity.

7. **Nonradiative relaxation**

   The system loss its energy and transfer from high energy state to low energy state via nonradiative processes.(Not necessary via vibrational motion, other processes such as dipole-dipole interaction or Coumlomb interaction can cause relaxations.)

The approximated life time of those processes are given, one should have a vague memory about it. There still other processes can occur after an system was excited such as excitation energy transfer, $\cdots$. Those contents are beyond this course but every student has already equipped enough abilities to study those contents by themselevs.