

Lecture 25

Overview of Molecular Spectroscopy

Study Goal of This Lecture

- Hierarchy of molecular spectroscopy
- Einstein's A/B coefficients
- Temperature effects in spectroscopy

25.1 Hierarchy of Molecular Spectroscopy

We have discussed the interactions of matters and light in the perspective of the time-dependent Schrödinger equation. The resulting “Fermi's Golden Rule” includes many important aspects in quantum transitions, i.e. transition between two quantum states.

The key concepts are:

- Resonant transitions occur between eigenstates of the molecular system.
- Light induced transition rates depends on the transition dipole moment:

$$k_{m \leftarrow n} \simeq |\mu_{mn}|^2, \quad \mu_{mn}^{\vec{}} = \langle \psi_m | \sum_i q_i \hat{r}_i | \psi_n \rangle. \quad (25.1)$$

- Transition occurs only when energy is conserved.

- Absorption and emission “lines” reveal energy levels of molecular systems → molecular spectroscopy.
- From one state to the other state → involves different motions in the molecule.

Very generally, we can separate the molecular Hamiltonian into different degrees of freedom:

$$\hat{H}_{total} = \hat{H}_e + \hat{H}_v + \hat{H}_r + \hat{H}_s. \quad (25.2)$$

These motions normally are well separated in time scales, so we can properly apply the Born-Oppenheimer approximation by assuming non-correlated wave functions:

$$\Psi_{total} = \Psi_e \times \Psi_v \times \Psi_r \times \Psi_s, \quad (25.3)$$

and the energy will be

$$E_{total} = E_e + E_v + E_r + E_s. \quad (25.4)$$

Since EM waves probe energy levels in molecular systems, a hierarchy of spectroscopy methods exist in correspondence to the separation of energy scale in molecular system. i.e.

$$E_e > E_v > E_r > E_s. \quad (25.5)$$

Let's start by drawing the electronic PES:

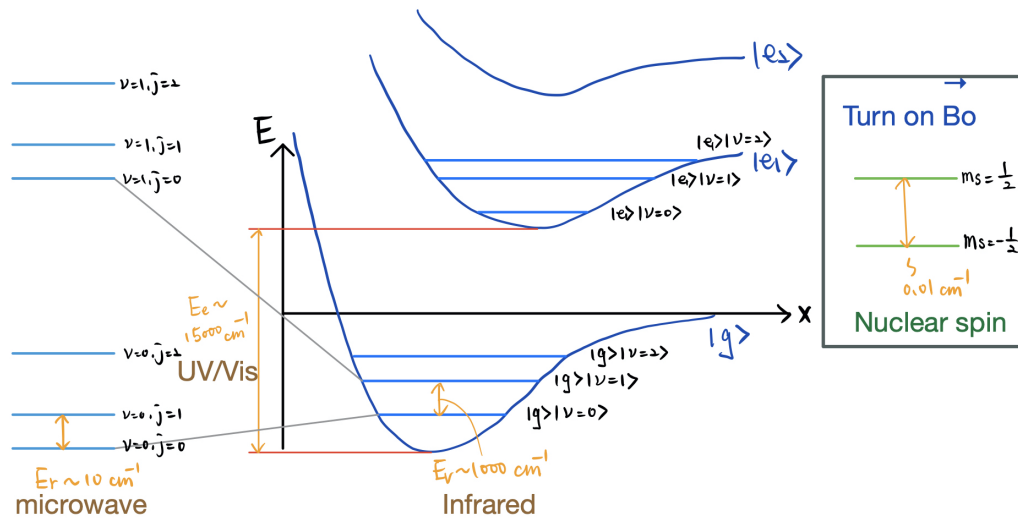


Figure 25.1: Potential energy surface.

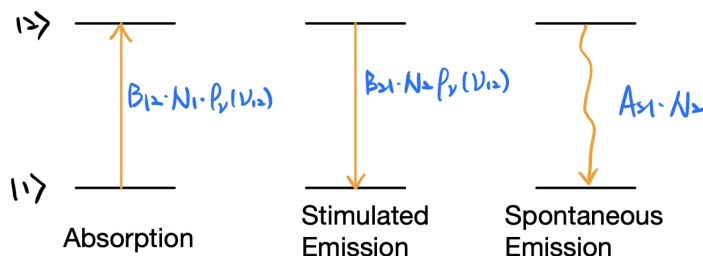
The room temperature thermal energy: $k_B T \simeq 200 \text{ cm}^{-1}$.

Keep in mind this picture, and note that it is because of this separation of timescales/energy scale that allows us to investigate different types of spectroscopic methods, i.e. different molecule motions, separately. We will follow Silbey's arrangement and discuss the vibrational and rotational spectroscopies first. But, before we dive into it, we will briefly cover an important subject regarding the **population of states**.

Population of states: probability of finding a system in that specific state.

25.2 Einstein's A/B Coefficient and Population Effect

On last lecture we considered two process that will happen when a system is coupled to a EM field. Note that there is a third process that we did not mention, to describe it requires the use of quantum field theory. (So we will not cover it.) That is the spontaneous emission.



Spontaneous emission is responsible for fluorescence and radiation lifetimes of molecules.

Figure 25.2: Three light-induced transition, ρ is light intensity.

A_{21} , B_{12} and B_{21} are Einstein's A/B coefficients. For the process to occur, the initial states must be "populated". Let's assume the state populations are N_1 and N_2 , respectively. Total population is $N = N_1 + N_2$. From time-dependent Schrödinger equation treatment, we know the rate of the first two processes are the same. We have

$$\frac{dN_1}{dt} = -B_{12}N_1\rho_\nu + B_{21}N_2\rho_\nu + A_{21}N_2, \quad (25.6)$$

$$\frac{dN_2}{dt} = B_{12}N_1\rho_\nu - B_{21}N_2\rho_\nu - A_{21}N_2. \quad (25.7)$$

When in the steady-state, $\frac{dN_1}{dt} = \frac{dN_2}{dt} = 0$. Also, steady-state depends on light

Steady-state: satisfy Boltzmann distribution $P_s \simeq e^{-\frac{E_s}{k_B T}}$

intensity and requires that

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{\frac{N_1}{N_2} B_{12} - B_{21}} \quad (25.8)$$

\Rightarrow if $A = 0$, then no ρ_ν . This is why Einstein “guess” spontaneous emission. Note that in equilibrium, N_1, N_2 should also satisfy the Boltzmann distribution

$$\frac{N_1}{N_2} = \frac{e^{-\frac{E_1}{k_B T}}}{e^{-\frac{E_2}{k_B T}}} = e^{-\frac{E_1 - E_2}{k_B T}}, \quad (25.9)$$

therefore

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{e^{\frac{h\nu_{12}}{k_B T}} B_{12} - B_{21}}. \quad (25.10)$$

Compare to Plank’s blackbody distribution law,

$$\rho_\nu(\nu) = \frac{8\pi h(\nu c)^3}{e^{\frac{h\nu}{k_B T}} - 1}, \quad (25.11)$$

we have $B_{12} = B_{21}$ and $A_{21} = \frac{8\pi h\nu_{12}^3}{c^3} B_{21}$. Note that the relationship of $B_{12} = B_{21}$ can be derived from Fermi’s Golden rule. Einstein found this relationship before the birth of quantum mechanics!

All Einstein’s coefficients are related and a measurement of one yields the other two. Note that in our treatment on previous lecture, we have shown that $B_{12} = B_{21} = B$. A similar treatment with quantized field shows that

$$\begin{aligned} A &= \frac{16\pi^3 \nu^3 g_1}{3\epsilon_0 h c^3 g_2} |\mu_{12}|^2, \\ B &= \frac{2\pi^3 g_1}{3\epsilon_0 h^2 g_2} |\mu_{12}|^2, \end{aligned} \quad (25.12)$$

$$\text{where } \mu_{12} = \int \psi_1^* \hat{\mu} \psi_2 d\tau.$$

This discussion tells us that to have significant absorption between two states, say $|1\rangle \rightarrow |2\rangle$. By relation:

$$\frac{dN_2}{dt} = B\rho_2(\nu_{12})N_1, \quad (25.13)$$

therefore, the rate of absorption depends on two factors:

- Significant population on $|1\rangle$.
- Non-zero $\langle 1|\mu|2\rangle$, μ_{12} : transition dipole moment.

These are selection rule of light-induced transition.