

Practical Aspects

1. Calculating Transition Moments

a. *Electronic: hydrogen atom (allowed transitions 1s → 2p, 3p, 4p etc.)*

$$\Psi_{1s} = \left(\frac{2}{a_0^3}\right) e^{-r/a_0}$$

$$\Psi_{2pz} = \left(\sqrt{\frac{1}{24}} \frac{r}{a_0^{5/2}}\right) e^{-r/2a_0}$$

The integral also involves the angular part.

This is the same math as the rotational wave function below.

The volume element is

$$dV = r^2 dr \sin \theta d\theta d\phi$$

For example, if the transition is z – polarized

$$\mu = ez = e \cos\theta$$

b. *Electronic: particle in a box*

Consider the transitions from level n to n+1. The dipole moment operator is ex for a box along x. Recall that the normalized wave function is:

$$\Psi = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

The general transition moment is:

$$\frac{2e}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) x \sin\left(\frac{(n+1)\pi x}{L}\right) dx = \frac{2eL}{\pi^2(2n+1)^2}$$

c. *Electronic: particle on a circle*

d. *Electronic: π- π* model*

Calculate the transition moment for a π-π* transition using a simple model

The magnitude of the transition moment for C₂H₄ can be calculated from a simple model

The π and π* states are:

$$\Psi_{\pi} = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \text{ and } \Psi_{\pi^*} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

The transition moment is:

$$M_{\pi-\pi^*} = e \int \Psi_{\pi} x \Psi_{\pi^*} d\tau$$

$$\begin{aligned} M_{\pi-\pi^*} &= \frac{e}{2} \int (\phi_1 + \phi_2)x(\phi_1 - \phi_2) d\tau \\ &= \frac{e}{2} \left(\int \phi_1 x \phi_1 d\tau - \int \phi_2 x \phi_2 d\tau \right) \\ &= \frac{e}{2} (x_1 - x_2) \end{aligned}$$

where x₁ - x₂ is the C=C bond length of 1.35 Å. One charge displaced through 1 Å has a dipole moment of 4.8 D. M_{π-π*} = 3.24 D for C₂H₄.

e. *Vibrational transitions*

The vibrational wave functions are Gaussians times polynomials (Hermite).

$$\chi_0(Q) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha Q^2/2}$$

$$\chi_1(Q) = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2\alpha} Q e^{-\alpha Q^2/2}$$

...

The selection rule is $v = +1$ or $v = -1$ so

$$\begin{aligned}\mu_{10} &= \left(\frac{\partial\mu}{\partial Q}\right)\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \sqrt{2\alpha} Q e^{-\alpha Q^2/2} Q e^{-\alpha Q^2/2} dQ \\ &= \left(\frac{\partial\mu}{\partial Q}\right)\left(\frac{\alpha}{\pi}\right)^{1/2} \sqrt{\alpha} \int_{-\infty}^{\infty} e^{-\alpha Q^2} Q^2 dQ \\ &= \left(\frac{\partial\mu}{\partial Q}\right)\left(\frac{\alpha}{\pi}\right)^{1/2} \sqrt{2\alpha} \frac{1}{2} \frac{\pi^{1/2}}{\alpha^{3/2}} = \left(\frac{\partial\mu}{\partial Q}\right) \frac{1}{\sqrt{2\alpha}}\end{aligned}$$

using the following relations

$$\begin{aligned}I_0(\alpha) &= \int_{-\infty}^{\infty} e^{-\alpha Q^2} dQ = \left(\frac{\pi}{\alpha}\right)^{1/2} \\ -\frac{I_0(\alpha)}{\partial\alpha} &= \int_{-\infty}^{\infty} e^{-\alpha Q^2} Q^2 dQ = \frac{1}{2} \frac{\pi^{1/2}}{\alpha^{3/2}}\end{aligned}$$

f. Rotational transitions

The rotational wave functions are the spherical harmonics.

We have treated the case of the $J = 1 \rightarrow J = 2$ transition.

For $J = 0, M = 0$

$$Y_{00}(\theta, \phi) = \sqrt{\frac{(1+0)(0)!}{4\pi(0)!}} P_{00}(\cos\theta) = \sqrt{\frac{1}{4\pi}}$$

For $J = 1, M = 0$

$$Y_{10}(\theta, \phi) = \sqrt{\frac{(2+1)(1)!}{4\pi(1)!}} P_{10}(\cos\theta) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

Assuming that the dipole operator is $ez = eR\cos\theta$, the transition moment is:

$$\begin{aligned}&\int_0^{2\pi} d\phi \int_{-1}^1 Y_{10}^*(\theta, \phi) ez Y_{00}(\theta, \phi) dx \\ &= eR_0 \frac{\sqrt{3}}{4\pi} (2\pi) \left(\int_{-1}^1 x^2 dx \right) \\ &= eR_0 \frac{\sqrt{3}}{2} \left(\frac{1}{3} - \frac{-1}{3} \right) = \frac{1}{\sqrt{3}} eR_0 = 0.577 eR_0\end{aligned}$$

and the case of the $J = 1 \rightarrow J = 2$ transition.

For $J = 2, M = 0$

$$Y_{20}(\theta, \phi) = \sqrt{\frac{(4+1)(2)!}{4\pi(2)!}} P_{20}(\cos\theta) = \sqrt{\frac{5}{4\pi}} \frac{(3\cos^2\theta - 1)}{2}$$

Assuming that the dipole operator is $ez = eR\cos\theta$, the transition moment is:

$$\begin{aligned}&\int_0^{2\pi} d\phi \int_{-1}^1 Y_{20}^*(\theta, \phi) ez Y_{10}(\theta, \phi) dx \\ &= eR_0 \frac{\sqrt{15}}{8\pi} (2\pi) \left(3 \int_{-1}^1 x^4 dx - \int_{-1}^1 x^2 dx \right) \\ &= eR_0 \frac{\sqrt{15}}{4} \left(\frac{6}{5} - \frac{2}{3} \right) = eR_0 \frac{\sqrt{15}}{4} \left(\frac{8}{15} \right) = \frac{2}{\sqrt{15}} eR_0 = 0.52 eR_0\end{aligned}$$

The terms in $e^{iM\phi}$ must cancel (i.e. $\Delta M = 0$) since otherwise the ϕ integral is zero. This will always happen if you use the complex conjugate since $e^{-iM\phi} e^{iM\phi} = 1$ for all values of M . This is one of the only places in the course where we have actually used the complex conjugate (i.e. where the function is complex).

2. Calculating Dot Product and Orientation Average

In essence what we have done above is calculate the projection of the transition moment along a direction (usually the z-direction because that has the easiest math). However, this is in the molecular frame. The connection between the molecular frame and the lab frame is an entire topic, but simply put we can calculate the dot product of the transition moment with incoming radiation. In order to determine the interaction energy and also to determine the transition probability.

A. Isotropic distribution (i.e. solution or frozen solution)

Orientation average of $\cos^2\theta$

The orientation average of $\cos^2\theta$ is $1/3$.

$$\langle \cos^2\theta \rangle = \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} \cos^2\theta \sin\theta d\theta d\phi$$

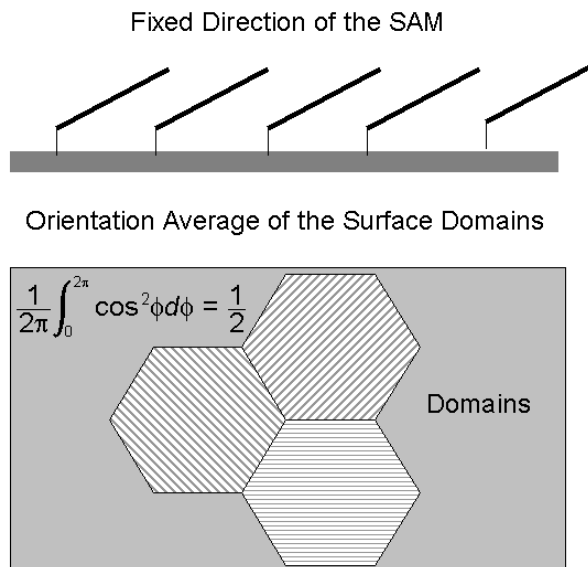
$$\langle \cos^2\theta \rangle = \frac{1}{2} \int_0^\pi \cos^2\theta \sin\theta d\theta$$

$$\langle \cos^2\theta \rangle = \frac{1}{2} \int_{-1}^1 x^2 dx = \frac{1}{2} \left. \frac{x^3}{3} \right|_{-1}^1 = \frac{1}{3}$$

Note that you could also treat this as the common sense solution. There are three directions of space so the average projection onto one of those directions (i.e. the direction of the incoming electromagnetic wave) is $1/3$.

B. Self-assembled monolayer

Imagine instead you have a surface adsorbed layer that has a fixed angle χ with respect to the surface.



The fixed direction will be given by a dot product between the transition moment and the incoming radiation. There will still be an orientation average over surface orientations, which shown as domains on the surface in the figure above. The integral can be done using integration by parts (hard) or using exponentials (easy).

$$\begin{aligned} \int_0^{2\pi} \cos^2 \phi d\phi &= \frac{1}{4} \int_0^{2\pi} (e^{i\phi} + e^{-i\phi})^2 d\phi = \frac{1}{4} \int_0^{2\pi} (2 + e^{i2\phi} + e^{-i2\phi})^2 d\phi \\ &= \frac{1}{2} \int_0^{2\pi} d\phi = \pi \end{aligned}$$

So if the normalization of 2π is used the integral is $\frac{1}{2}$.

3. Calculating Excited State Rate Constants and Quantum Yields

Keep in mind that when measuring fluorescence lifetimes or any excited state lifetimes one is measuring the rate process, which is the sum of all of the processes that deactivate the excited state. For example, if there is a quencher molecule Q, then the effective rate constant is:

$$k_{obs} = k_{rad} + k_{non-rad} + k_Q[Q]$$

The fluorescence quantum yield is

$$\Phi_f = \frac{k_{rad}}{k_{rad} + k_{non-rad} + k_Q[Q]}$$

Thus you can obtain all of the information about the system by measuring both the quantum yield and the rate constant (lifetime). The lifetime is just the inverse of the rate constant.

$$\tau_{rad} = \frac{1}{k_{rad}}$$

4. Calculating Practical Photon Fluxes

Practical formulae are

$$\sigma = 1000 \in N_A \text{ cm}^2 \text{ (cross section)}$$

$$I = \frac{1}{2}cu = \frac{1}{2}c\epsilon_0 E_0^2 \text{ (intensity)}$$

$$N = \frac{\text{Energy (J)}}{h\nu} \text{ (number of photons)}$$

$$N/\text{sec} = \frac{\text{Power (W)}}{h\nu} \text{ (number of photons per second)}$$

$$N/\text{sec}/\text{m}^2 = \frac{\text{Intensity (W/m}^2\text{)}}{h\nu} \text{ (photons flux)}$$