Physical Chemistry

Lecture 27

Spectroscopic Transitions

Nature of spectroscopic transition

- Change in the state of a system due to transfer of energy
- Wave function reflects this change
- Time-dependent process

Ψ_f

ΔE

Ψ_i

$$c_i = 1,\ c_f = 0 \Leftrightarrow \text{before transition} \qquad c_i = 0,\ c_f = 1 \Leftrightarrow \text{after transition}$$

$$\psi(t) = c_i(t)\psi_i + c_f(t)\psi_f = a_i e^{iE_i t/\hbar}\psi_i + a_f e^{iE_f t/\hbar}\psi_f$$

Time-dependent process

- Must use Schroedinger's time-dependent equation
- Hamiltonian consists of two parts
  - Stationary part that determines the energy levels
  - Time-dependent part that determines coupling that induces transition
- Gives the time-dependent coefficients, c_i and c_f

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar}\hat{H}\Psi$$

$$\hat{H} = \hat{H}_0 + \hat{H}_1(t)$$

Resonance

- For a coupling, such as a coupling of the dipole moment to a time-dependent electric field, to have a strong effect on the coefficients, it must have the "proper" time dependence (given by its frequency, ω)
- Resonant absorption occurs if matching occurs

$$\omega = \frac{\Delta E}{\hbar} = \frac{E_f - E_i}{\hbar}$$

Transfer rate

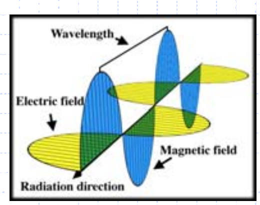
- Under resonant conditions, the rate of transfer is proportional to an integral over the states
- Fermi's Golden Rule

$$\textit{Rate proportional to} \quad |<\psi_i|\hat{H}_1|\psi_f>|^2$$

- Basis for selection rules in spectroscopy

Light and radiation

- Light radiation is a time- and space-dependent energy field
- A system may couple to either the electric or magnetic field
  - Mostly consider coupling to the electric field of light



Electric-dipole coupling

- An electric dipole couples to an electric field
- The energy of the dipole in the field depends on orientation

$$\hat{H}_1(t) \quad = \quad \hat{\mathbf{d}} \bullet \mathbf{E}(t)$$

- A mechanism for coupling between the spectroscopic system and the light

$$Rate \;\propto\; |<\psi_i\,|\,\hat{\mathbf{d}}\cdot\mathbf{E}(t)\,|\,\psi_f>|^2$$

Selection rules

- Is the integral of the Golden Rule zero?
- Must know dipole form
  - A vector (the dipole moment) which can be shown to have components proportional to the cartesian co-ordinates
- Evaluation of integral becomes an evaluation of integral of x, y and z
- Can often evaluate integrals by knowing only certain properties of the wave functions

$$\int \psi_i^* \hat{x} \psi_f \, d\tau$$

$$\int \psi_i^* \hat{y} \psi_f \, d\tau$$

$$\int \psi_i^* \hat{z} \psi_f \, d\tau$$

Summary

- Transitions are time-dependent processes
- Must use Schroedinger's time-dependent equation
- Rate of transition determined by an integral over the states
  - Fermi's Golden Rule
  - Electric dipole and magnetic dipole transitions
- Evaluation of whether integrals are zero can sometimes be without knowledgeable of the total mathematical form of the wave functions
  - Selection rules