Time-Dependent Perturbation Theory

III.1 <u>First order perturbation theory</u>

When a molecule interacts with electromagnetic radiation, a photon may be absorbed, leading to an excited state. This may be an electronically (UV), vibrationally (IR) or a rotationally (microwave) excited state. All these processes may be described by first-order perturbation theory, where the radiation plays the part of the perturbation. By applying this method we find the <u>resonance</u> <u>condition</u> and the <u>selection</u> <u>rules</u> (including the Franck-Condon factor). The resonance condition is the condition that the frequency of the radiation (energy of the photon) must match with the energy difference between the two stationary states (the ground state and the excited state). The selection rules determine whether the transition is allowed or not. These rules derive from the properties of the molecule, which determine the intensity of the absorption. They are independent of the radiation.

Because electromagnetic radiation is time dependent, we need the time dependent Schrödinger equaton :

$$\hat{H}(q,t)\Psi(q,t) = -\frac{\hbar}{i}\frac{\partial}{\partial t}\Psi(q,t) \tag{3.1}$$

In the case of a <u>time-independend</u> Hamiltonian we find as solutions the stationary states

$$\Psi(q,t) = \psi_k e^{-\frac{iE_k t}{\hbar}}$$
$$with\, H\psi_k = E_k\psi_k \tag{3.2}$$

Not only stationary states are solutions, but also linear combinations of them, i.e. a superposition of stationary states.

$$\Psi(q,t) = \sum_k c_k \Psi_k(q,t) \tag{3.3}$$

If $\hat{H}$ does not depend on the time any wavefunction of the form (3), with coefficients that are constant in time, is a solution of (3.1).

Exercise 3.1

Verify that the (un)normalised superposition

$$\Psi(q,t) = \psi_1(q)\, e^{-iE_1 t/\hbar} + \psi_2(q) e^{-iE_2 t/\hbar} \tag{3.4}$$

is a solution of (1), if $\hat{H}$ does not contain the time. Check that the probability $\Psi^*\Psi$ is not constant in time, but that the energy $\langle H \rangle$ is. There is conservation of energy; the system is "conservative".

Because $\Psi^*\Psi$ depends on the time t the wavefunction in equation (3.4) is not a stationary state. The probability to find the particles on a position in space changes all the time. Using the example in exercise 3.1 and assuming that $\psi_1(q)$ and $\psi_2(q)$ are real, for simplicity, we get (use $e^{iZ} = \cos Z + i \sin Z$):

$$\Psi^*\Psi = \psi_1^2(q) + \psi_2^2(q) + 2\,\psi_1(q).\,\psi_2(q).\cos\left[2\pi\frac{(E_1-E_2)t}{h}\right] \tag{3.5}$$

The cosine varies from $+1$ (for $t = 0$, $t = \dfrac{h}{E_1-E_2}$, $t = 2\dfrac{h}{E_1-E_2}$, ...) to -1 (for $t =$

$\dfrac{1}{2}\dfrac{h}{E_1-E_2}$, $t = \dfrac{3}{2}\dfrac{h}{E_1-E_2}$) , ...),   so $\Psi^*\Psi$ varies from

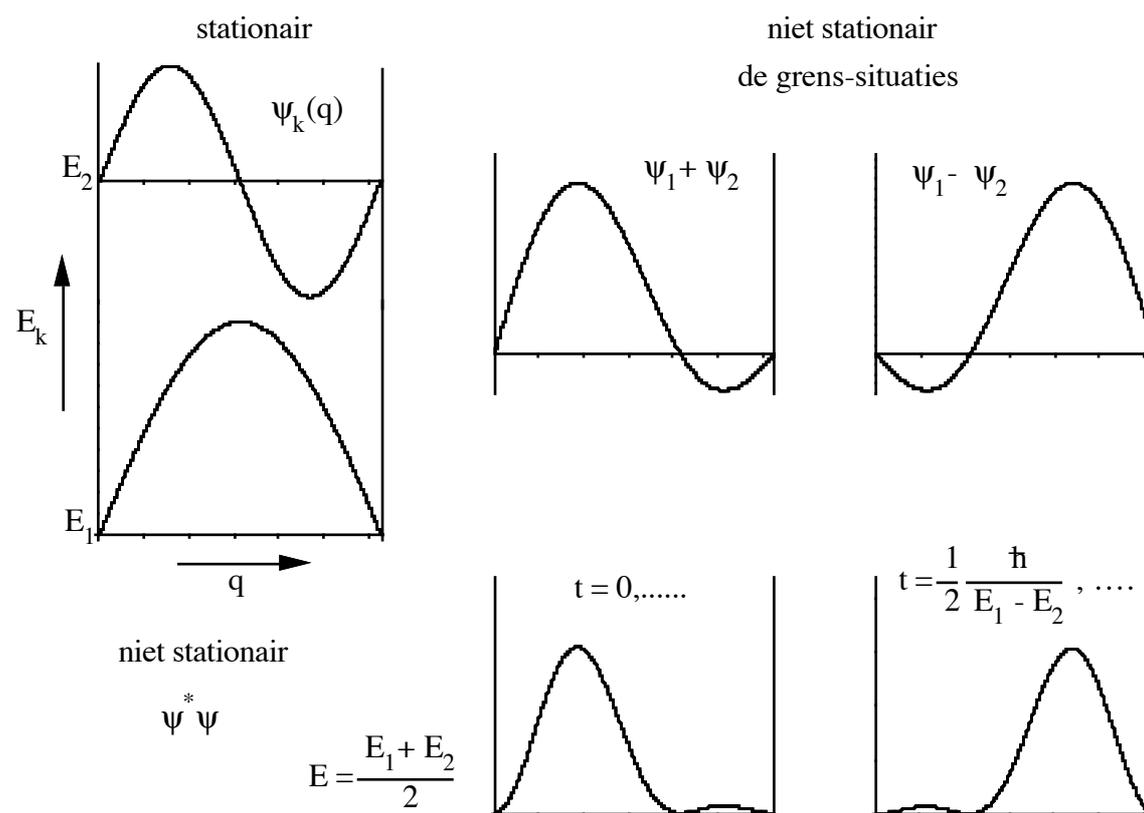$$\Psi^*\Psi = \psi_1^2(q) + \psi_2^2(q) + 2\,\psi_1(q).\,\psi_2(q) = (\,\psi_1(q) + \psi_2(q)\,)^2 \tag{3.6a}$$

for $t = (n-1).\dfrac{h}{E_1-E_2}$,   and

$$\Psi^*\Psi = \psi_1^2(q) + \psi_2^2(q) - 2\,\psi_1(q).\,\psi_2(q) = (\,\psi_1(q) - \psi_2(q)\,)^2 \tag{3.6b}$$

for $t = (n-\dfrac{1}{2}).\dfrac{h}{E_1-E_2}$,.

As an example we plot the superposition of the lowest two solutions for the "particle in the box" problem.:

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So in this example the probability density varies $\dfrac{E_1 - E_2}{h}$ times per second between de

extremes $\psi_1+\psi_2$ and $\psi_1-\psi_2$. A consequence is that the system may interact with

electromagnetic radiation of this frequency ($\nu = \dfrac{E_1 - E_2}{h}$). Thus $h\nu$ (the energy of the

photon) = E_1-E_2 (the energy difference of the stationary states involved), the Planck

(resonance) condition.

Now we will apply perturbation theory in the framework of the time-dependent

Schrödinger equation (3.1) It is assumed that the time-dependent part of H, which

represents the radiation, induces a small change in the molecule. The zero-order

Hamiltonian $H_0(q)$ represents the isolated molecule and $H_1(q,t)$ represents the

radiation :

$$H(q,t) = H_0(q) + H_1(q,t) \tag{3.7}$$

The eigenfunctions of $H_0(q)$ are the time independent part of the stationary states Φ_0

for the ground state and Φ_k for the excited state, which are assumed to be normalised.

The complete stationary states are solutions of the Schrödinger equation (3.1) :

$$\Psi_0 = \Phi_0 e^{-iE_0 t/\hbar} \tag{3.8a}$$

$$\Psi_k = \Phi_k e^{-iE_k t/\hbar} \tag{3.8b}$$

The perturbed wave function is written as :

$$\Psi(q,t) = \Psi_0(q,t) + C_k(t)\Psi_k(q,t) \tag{3.9}$$

where "intermediate normalization" is used, i.e. the coefficient of Ψ_0 equals 1, The 1st order correction to the wave function is orthogonal to Ψ_0 (cf. quantumchemistry reader). Only the 1st order change in the wave function will be considered.

For t = 0 we take $C_k = 0$, i.e. we start with the ground state at the moment that the perturbation is switched on. The probability that at the point in time t the molecule has been excited to the state Ψ_k is given by $|C_k(t)|^2$.

By substituting (3.9 into (3.1), multiplying (on the left) by Φ_k and integrating we find :

$$< \Phi_k | H_0 + H_1 | \Psi_0 + C_k\Psi_k > = i\hbar < \Phi_k | \frac{\partial}{\partial t} | \Psi_0 + C_k\Psi_k > \tag{3.10}$$

After some algebraic manipulation this yields :

$$\frac{\partial C_k(t)}{\partial t} = -\frac{i}{\hbar} < \Phi_k | H_1 | \Phi_0 > e^{i(E_k - E_0)t/\hbar} \tag{3.11}$$

Exercise 3.2

By using (3.8a) show that (3.10) may be rewritten as :

$$C_k < \Phi_k | H_0 + H_1 | \Psi_k > + < \Phi_k | H_1 | \Psi_0 > = i\hbar < \Phi_k | \frac{\partial}{\partial t} | C_k\Psi_k >$$

In the left hand side the contribution

$$C_k < \Phi_k | H_1 | \Psi_k >$$

is of 2nd order (C_k and H_1 are both small). It will be ignored in the 1st order treatment.

The right hand side yields two terms, since C_k and Ψ_k both depend on t.

From (3.8b) it follows that :

$$< \Phi_k | H_0 | \Psi_k > = i\hbar < \Phi_k | \frac{\partial \Psi_k}{\partial t} >$$

Now show that (3.11) holds

Eq (3.11) is a differential equation for C_k. It may be solved by integrating over t :

$$C_k(t_1) = -\frac{i}{\hbar}\int_0^{t_1} <\Phi_k \mid H_1(q,t) \mid \Phi_0> e^{i(E_k - E_0)t/\hbar}dt \qquad (3.12)$$

where the use of perturbation theory implies that t_1 should be small.

Until now the derivation is fairly general and (3.12) may be used for any kind of time-dependent potential energy perturbation. In order to perform the integration an explicit expression for $H_1(q,t)$ is needed.

III.2 The radiation field

$H_1(q,t)$ represents the interaction between the molecule and the electromagnetic radiation. Since the electric component is much stronger than the magnetic one, only the first component will be considered here. The electric field strength is given by F (a vector). The field interacts with all (charged) particles of the molecule. For visible light or UV the wave length of the radiation is of the order 10^3-10^4 Å (100-1000 nm), for infrared (IR) and for microwaves even much larger. Therefore the field strength is almost constant within the molecule and therefore we assume a <u>homogeneous</u> field. The expression for the potential energy of the molecule in a homogeneous field in the x-direction (x-polarised light) is:

$$V_x(q,t) = -F_x(t)\sum_{i=1}^{N} Q_i x_i \qquad (3.13)$$

where

> N = number of nuclei + electrons
>
> Q_i = charge of particle i
>
> x_i = x-coordinate of particle i
>
> $F_x(t)$ = x-component of the field strength at point of time t

The position dependent part in (3.13) corresponds to the x-component of the dipole moment operator :

$$\mu_x = \sum_{i=1}^{N} Q_i x_i \qquad (3.14)$$

Therefore for x-polarised light H_1 may be written as :

$$H_1(q,t) = V_x(q,t) = -F_x(t)\mu_x(q) \qquad (3.15a)$$

where the time dependence is given by :

$$F_x(t) = F_x^0 \sin \omega t. \tag{3.15b}$$

Here F_x^0 is the amplitude of the radiation (maximum field strength) in the x direction and $(F_x^0)^2 = I_0$ is the intensity. Analogous formulas hold for the other components and in the complete expression the inner product of the vectors F and μ is used. However, in the following the suffix x will be dropped.

By substituting (3.15) into (3.12) we find :

$$C_k(t) = -\frac{i}{\hbar} < \Phi_k \mid \mu(q) \mid \Phi_0 > \int_0^{t_1} F_0 \sin \omega t \, e^{i(E_k - E_0)t/\hbar} dt \tag{3.16}$$

By invoking the homogeneous field approximation we have been able to separate the spatial and the time-dependent parts of $H_1(q,t)$: since $H_1(q,t)$ is expressed as a <u>product</u> of a spatial and a time-dependent part, the two effects are now <u>independent</u> of each other. The spatial part in (3.16) is called the <u>transition moment</u> T_{k0} :

$$T_{k0} = < \Phi_k \mid \mu(q) \mid \Phi_0 > \tag{3.17}$$

The time dependent part leads to the resonance condition.

III.3   <u>Electronic and vibrational excitations</u>

The dipole moment operator contains a sum over <u>all</u> particles in the molecule. It can also be written as :

$$\mu = \mu_x = \sum_{K=1} Z_K X_K + e \sum_{i=1} x_i = \mu_X^{nuc} + \mu_x^{el} \tag{3.18}$$

The Born-Oppenheimer approximation assumes that the molecular wave functions may be factorised into an electronic and a nuclear part :

$$\begin{aligned} \Phi_0 &\Rightarrow \Phi_{0,m} = \Phi_0^{el} \chi_{0,m}^{vib} \\ \Phi_k &\Rightarrow \Phi_{k,n} = \Phi_k^{el} \chi_{k,n}^{vib} \end{aligned} \tag{3.19}$$

For the contribution of the <u>electronic</u> part of the dipole moment operator to (3.17) we find

$$< \Phi_{k,n} \mid \mu_x^{el} \mid \Phi_{0,m} > \ = \ < \Phi_k^{el} \mid \mu_x^{el} \mid \Phi_0^{el} > \ < \chi_{k,n}^{vib} \mid \chi_{0,m}^{vib} > \tag{3.20}$$

The first part in (3.20) is the <u>electronic</u> <u>transition</u> <u>moment</u>. Since the electronic excitation process is much faster than the nuclear motions it may be assumed that the geometry of the molecule does not change during the excitation. This is called a <u>vertical</u> excitation. Therefore both electronic energies have to be evaluated at the equilibrium geometry of the ground state of the molecule. The second part is the <u>Franck-Condon</u> <u>factor</u>. This factor shows that for an intense absorption the vibrational functions should have a large overlap.

For the contribution of the <u>nuclear</u> part we have :

$$< \Phi_{k,n} | \mu_X^{nuc} | \Phi_{0,m} > \ = \ < \Phi_k^{el} | \Phi_0^{el} > \ < \chi_{k,n}^{vib} | \mu_X^{nuc} | \chi_{0,m}^{vib} > \qquad (3.21)$$

Since the electronic wave functions are orthonormal, the nuclear part can only contribute if $k = 0$, i.e. for vibrational transitions within the <u>same</u> electronic state. In that case we have :

$$< \Phi_{0,n} | \mu_X^{nuc} | \Phi_{0,m} > \ = \ < \chi_{0,n}^{vib} | \mu_X^{nuc} | \chi_{0,m}^{vib} > \qquad (3.22)$$

This is the <u>vibrational</u> (or rotational) <u>transition</u> <u>moment</u>.

III.4   <u>The resonance condition</u>

In order to evaluate the time dependence of $C_k(t)$ in (3.16) the excitation energy E_k-E_0 is replaced by :

$$\omega_k = \frac{E_k - E_0}{\hbar} \qquad (3.23)$$

By substituting (3.23) into the time-dependent part of (3.16) and integrating the following result is found. The coefficient for <u>absorption</u> is given by :

$$C_{0 \to k}(t) = \frac{iF_0}{2\hbar} T_{k0} \frac{e^{i(\omega - \omega_k)t} - 1}{\omega - \omega_k} \qquad (3.24a)$$

and for <u>stimulated</u> (or <u>induced</u>) <u>emission</u> :

$$C_{k \to 0}(t) = \frac{iF_0}{2\hbar} T_{k0} \frac{e^{i(\omega + \omega_k)t} - 1}{\omega + \omega_k} \qquad (3.24b)$$

This is the coefficient for the de-excitation process, where the excited state emits a photon and returns to the ground state, in the presence of the radiation.

The final result for the <u>transition</u> <u>probability</u> per second for <u>absorption</u> is given by

$$w_k(t) = \frac{1}{t} |C_k(t)|^2 = \frac{\pi I_0}{2} |T_{k0}|^2 \delta(\omega - \omega_k) \qquad (3.25)$$

This is the "**Fermi Golden Rule**"

Here $I_0 = F_0{}^2$ is the intensity of the radiation, T_{k0} is the transition moment and the δ-function corresponds to the resonance condition, which states that the probability for a transition vanishes unless the energy of the radiation (of a photon) ω equals the energy difference between the two states ω_k as defined by (3.23) ($\delta(\omega-\omega_k) = 0$ unless $\omega = \omega_k$). The transition moment T_{k0} determines the selection rules, which have to be satisfied in order to get a non-zero transition probability : if T_{k0} vanishes the transition is forbidden. The transition moment is in fact given by (3.20) for electronic transitions (UV) or (3.22) (IR/vibrations or microwave/rotations). The Dirac δ-function will be discussed in more detail in the next section.

Exercise 3.3

Show that singlet-triplet excitations are electronically forbidden for any 2-electron system if all magnetic interactions are ignored.

Comments.

1) If the magnetic component of the radiation is included in H_1, the transition moment contains a contribution of the magnetic moment of the molecule. This causes singlet-triplet transitions to be magnetically allowed. However, for most molecules the magnetic moment is much smaller than the electric dipole moment.

2) The excited state may also spontaneously fall back to the ground state (e.g. after switching off the perturbation). This is called spontaneous emission. This process also depends on the transition moment (Einstein), but the transition probability cannot be derived by this form of perturbation theory.

III.5   The general Dirac Delta function.

A more accurate evaluation of the resonance condition leads to the more general δ-function $\delta(\omega-\omega_k,t)$:

$$\delta(\omega - \omega_k, t) = \frac{1}{\pi} \frac{\sin^2[(\omega - \omega_k) t]}{[(\omega - \omega_k)]^2 t} \tag{3.26}$$

This function has a narrow peak at $\omega=\omega_k$ (see Fig. 3.1).

The width of the peak depends on t : the peak narrows if t increases. The δ-function in (3.25) is in fact the limit for t $\rightarrow\infty$ of (3.26), that is, a peak which in infinitely high and infinitely narrow. The width belonging to the time scale of the excitation process is called the <u>natural</u> <u>line</u> <u>width</u>. The peak cannot really be infinitely narrow (as (3.25) suggests) because of the "uncertainty relation"

$$\Delta E.\Delta t \geq \hbar \qquad\qquad\qquad (3.27)$$

In (3.27) ΔE corresponds to the spread in the energy of the excited state (or in $(\omega-\omega_k)$) and Δt corresponds to the time needed for the excitation process to complete. This time scale depends on the excitation energy : for electronic excitations the life span of an excited state $\tau \approx 10^{-8}$ sec $\approx 10^{9}$ atomic units. Therefore $\Delta E \approx 10^{-9}$ Hartree, whereas $\omega_k \approx 10^{-1}$ Hartree and we have a relative accuracy of 10^{-8}. Therefore the peak is very narrow. For IR and microwave spectra the relative accuracy is even larger. In practice the spectral lines are much wider, since several effects not discussed here (like temperature effects) increase the line widths.
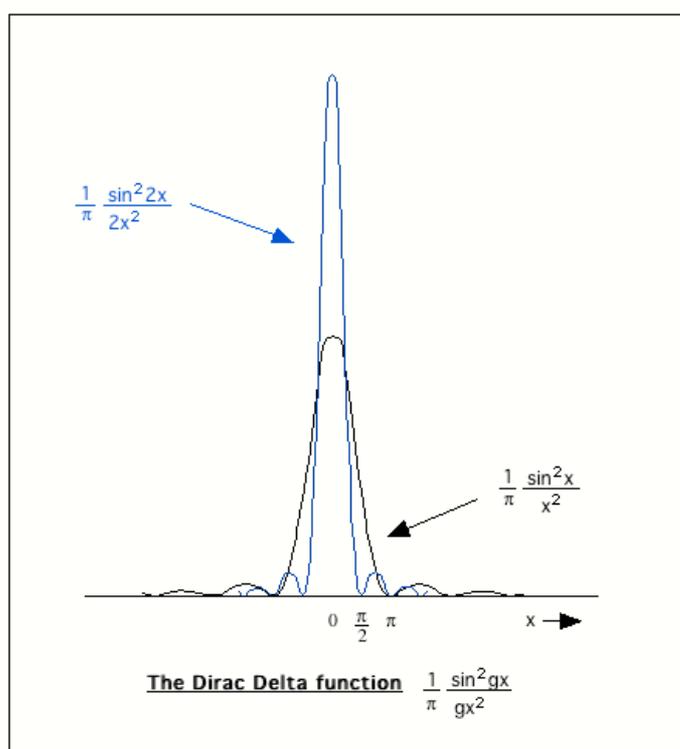

Fig 3.1 The Dirac δ-function $\delta(x,g)$

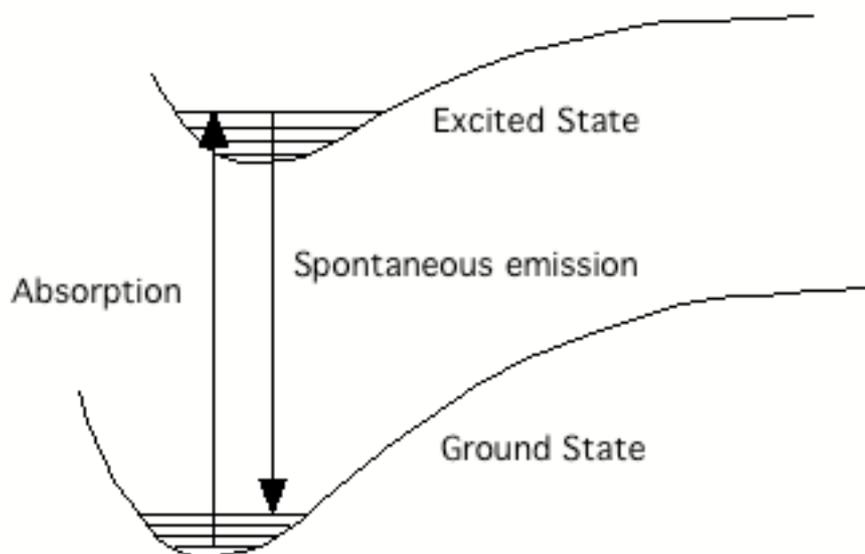### III.6   <u>Luminescence and Photochemistry</u>

Fig 3.2 Fluorescence

Luminescence contains the two phenomena <u>fluorescence</u> and <u>phosphorescence</u>. These processes are depicted in Fig 3.2 and Fig 3.3. Since the minima of the two electronic states do not coincide, the excitation leads to an excited vibrational mode in the electronically excited state. Which vibrational mode(s) will be selected depends on the Franck-Condon factors. In fluorescence the excited state falls back (spontaneously) to an excited vibrational level of the ground state. The emitted radiation has a lower energy than the absorbed radiation. This corresponds to a red shift (Stokes' law).

Exercise 3.4

Why will no absorption take place if the equilibrium geometries of the two states are very different?

In phosphorescence (Fig 3.3) there is a transition to another excited state before it falls back to the ground state. This is a radiationless singlet-triplet transition at the geometry where the two excited states are degenerate. Such a transition is called an <u>intersystem</u> <u>crossing</u>. Since this transition is forbidden (in first order), phosphorescence is a much slower process than fluorescence.
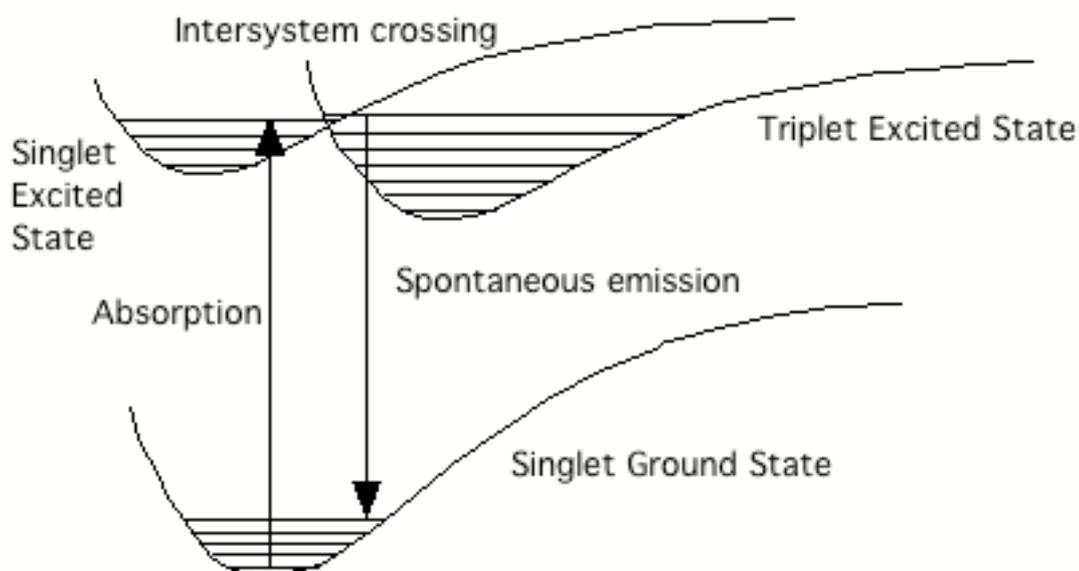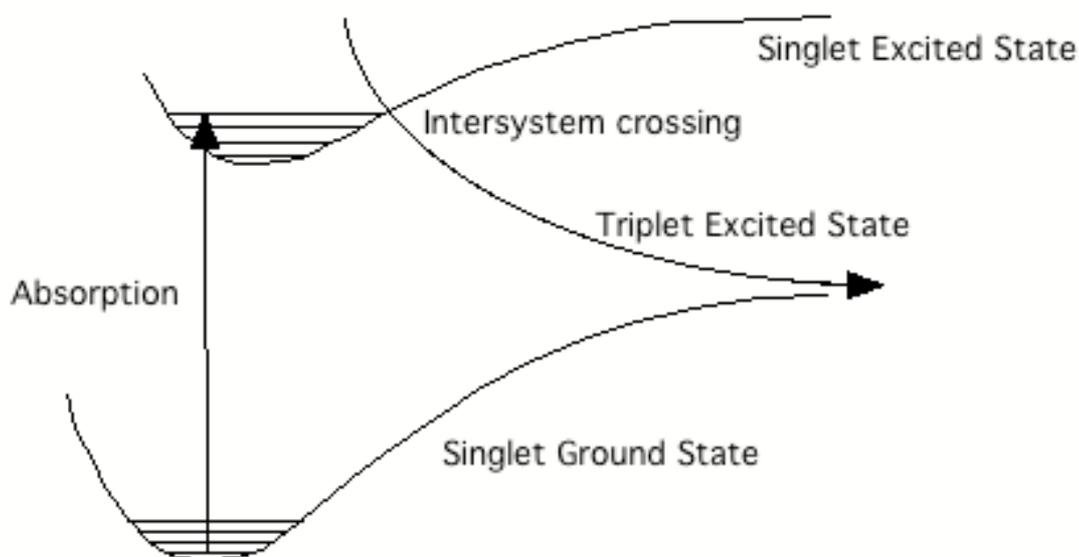
Fig 3.3 Phosphorescence

Fig 3.4 A photochemical reaction (dissociation)

Fig. 3.4 shows an example of a photochemical reaction, in this case a dissociation. As in the previous cases the process starts with the excitation to a singlet excited state. As in phosphorescence, there is an intersystem crossing. However, in this case the triplet excited state is repulsive. Therefore the molecule will dissociate after reaching the triplet state. The excess energy is transformed into (relative) kinetic energy of the dissociation products.