

## 11 HC11: Molecular spectroscopy and electronic transitions



### van Quantum tot Molecuul

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Molecular Spectroscopy and Electronic Transitions

Based on Atkins and de Paula, *Physical Chemistry* 10th edition, Chapter 13

In this lecture, we will study electronic transitions in *p-electron conjugate systems*, the Franck-Condon principle, the physics underlying the phenomena of *fluorescence* and *phosphorescence*, as well as the basic principles of operation of a *laser*. We will also present an application of these ideas in the medical context, namely the *photo-dynamic therapy* (PDT).

The *learning goals* of this lecture are:

- Understanding and applying  $\pi$ - $\pi^*$  electronic transitions in molecules.
- Understanding which electronic transitions can take place for either absorption or emission of a photon while the atomic nuclei are at rest (the Franck-Condon principle), including the mathematical description and implications of absorption and emission spectra.
- Understanding and applying the principles of fluorescence and phosphorescence.
- Understanding the basic principles that underlie the operation of a laser, such as the concept of population inversion.

### 11.1 Electronic transitions in molecules

In HC10 we studied the transitions between different vibrational states of a molecule. We now consider instead the *electronic transitions* that take place between different electronic states of a molecule. As opposed to vibrational transitions, which were associated to *infrared frequencies*, electronic molecular transitions take place mainly in the *visible and ultraviolet* regions of the electromagnetic spectrum, and therefore, among

## Molecular Orbitals

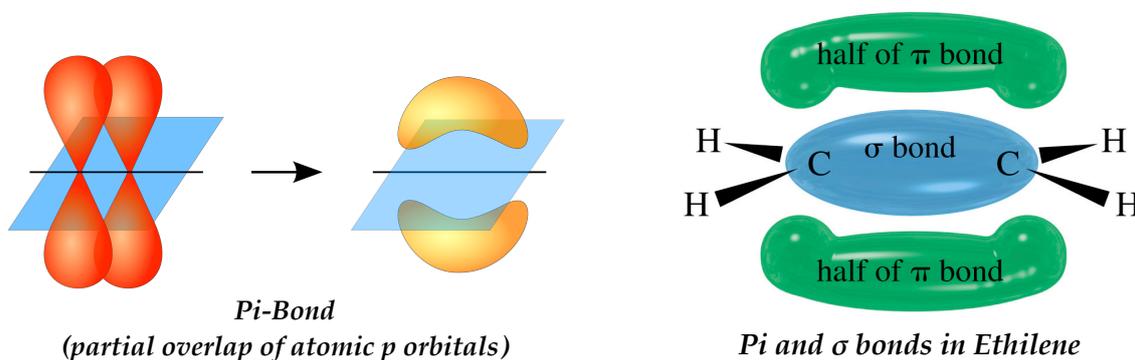


Figure 11.1: Left plot: a  $\pi$ -bond in a molecule is formed by the partial overlap between atomic  $p$ -type orbitals. Right plot: the bonding structure of ethylene,  $C_2H_4$ , showing a  $\sigma$  bond between the two  $C$  atoms (rotationally symmetric with respect to the bond axis) and the two halves of the  $\pi$  bond arising from the  $p$  atomic orbitals.

the many important properties of these transitions, they are also responsible of the *color* of materials and substances.

**Molecular orbitals** It is useful at this point to recall some important properties of *molecular orbitals*. We know that that electronic orbitals in atoms can have different principal quantum numbers:  $s$ ,  $p$ ,  $d$  and so on. In molecules, under the right circumstances, the electrons might become *de-localized* by means of the overlap between individual atomic orbitals, that is, they cannot be assigned to any of the specific components of the molecule.

The strongest type of *chemical covalent bonds* in molecules are known as  $\sigma$ -bonds, formed by a head-on overlapping between atomic orbitals leading to a molecular orbital. The key property of this bond is that the resulting orbitals are *rotationally symmetric with respect to the bond axis*. Another important type of molecular bonds are the so-called  $\pi$ -bonds, covalent chemical bonds where two lobes of one atomic orbital overlap with the two lobes of another atomic orbital, resulting in the bonding between the two atoms. In Fig. 11.1 we show how a  $\pi$ -bond in a di-atomic molecule is formed by the partial overlap between atomic  $p$ -type orbitals. In the same figure we also show the bonding structure of the ethylene molecule,  $C_2H_4$ , showing a  $\sigma$  bond between the two  $C$  atoms (rotationally symmetric with respect to the bond axis) and the two halves of the  $\pi$  bond arising from the  $p$  atomic orbitals.

In this lecture we will focus on *conjugate p-electron systems*, which denote molecules where atomic  $p$ -type orbitals are connected by means of de-localized electrons, thus giving place to  $\pi$ -type covalent bonds. These molecules are very important in organic chemistry and biology, and the wide majority of light-absorbing molecules, known as *chromophores*, that appear biology are indeed  $p$ -electron conjugate systems.

The electronic transitions within a conjugate  $p$ -electron molecular system are known as the  $\pi \rightarrow \pi^*$  transitions. This is a specific type of molecular electronic transitions, others include the  $\sigma \rightarrow \sigma^*$  and the  $n \rightarrow \sigma^*$  transitions. Here by  $\pi^*$  we indicate an *anti-bonding molecular orbital* of the  $\pi$ -type, that is, a molecular orbital that when occupied by electrons *weakens* the bond between the constituents atoms of the molecule and thus increases (rather than decreases) the energy of the molecule relative to the separated individual atoms. These  $\pi \rightarrow \pi^*$  transitions, involving de-localized  $p$ -orbitals, can be described by *Huckel theory* and are characterized by *strong light absorption*. Recall that *Huckel theory* can be used to construct

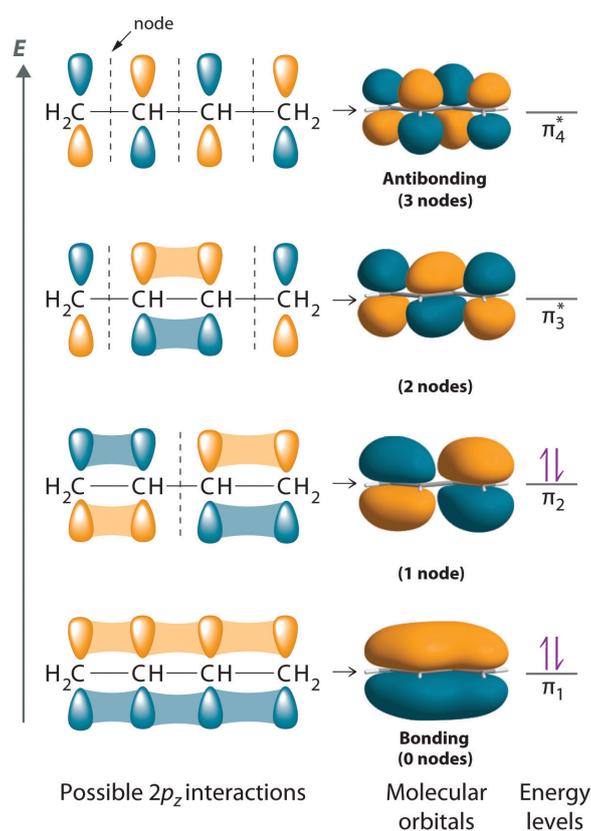


Figure 11.2: Schematic representation of the molecular orbitals of the butadiene molecule, C<sub>4</sub>H<sub>8</sub>. The two bottom orbitals are *bonding* π molecular orbitals, while the top two ones are instead *anti-bonding* π\* molecular orbitals. The highest occupied molecular orbital (HOMO) is here π<sub>2</sub>, while the lowest unoccupied molecular orbital (LUMO) is instead π<sub>3</sub>\*. Note that in the HOMO the two electrons are paired (opposite spins).

linear combinations of atomic orbitals (LCAO) into molecular orbitals to determine the energies of π electrons in general conjugated molecules.

For molecular orbitals, we often make the distinction between *HOMO*, the *highest occupied molecular orbital* and *LUMO*, the *lowest unoccupied molecular orbital*. Let us consider the representative case of the butadiene molecule C<sub>4</sub>H<sub>6</sub>. In Fig. 11.2 we show a schematic representation of the molecular orbitals of butadiene. The two bottom orbitals are *bonding* π molecular orbitals, while the top two are instead *anti-bonding* π\* molecular orbitals. The highest occupied molecular orbital (HOMO) is here π<sub>2</sub>, while the lowest unoccupied molecular orbital (LUMO) is instead π<sub>3</sub>\*. Note that in the HOMO the two electrons are paired, that is, they have opposite spins.

**Allowed molecular transitions** In order to determine which electronic molecular transitions are possible, we need to take into account the corresponding *selection rules*. In the case of individual atoms and of vibrational transitions in molecules, these selection rules have been reviewed in HC10. Similarly as in the case of the selection rules for electronic transitions in individual atoms, also for electronic transitions in molecules, only if the dipole moment matrix element satisfies  $\mu_{fi} \neq 0$  a given transition will be allowed.

Therefore, in the case of electronic transitions between the molecular orbitals of butadiene represented in Fig. 11.2, only those that are characterized by a non-zero electric dipole matrix element,  $\mu_{fi} \neq 0$ , will be

physically allowed. Using the wave function for the molecular orbitals of butadiene, it can be shown that

$$\int \Psi_{\pi_3}^* \hat{\mu} \Psi_{\pi_2} d\tau \neq 0, \quad (11.1)$$

and therefore a transition between the HOMO and LUMO levels, that is, a  $\pi \rightarrow \pi^*$  transition, is allowed. This transition will have associated the absorption of visible light by the butadiene molecule. It can also be shown that if  $x$  is the molecular bonding axis, only  $\mu_{x,fi} \neq 0$ , while instead  $\mu_{y,fi} = \mu_{z,fi} = 0$ . This has the consequence that the optical transition  $\pi_2 \rightarrow \pi_3^*$  will only be possible for *light polarized along the  $x$  axis*. On the other hand, the absorption of a photon by the HOMO-1 level, that is, the electronic state immediately below HOMO, labeled  $\pi_1$  in Fig. 11.2, resulting into a transition to the LUMO level  $\pi_3^*$  turns out not to be allowed by the selection rules, since all the possible dipole moment matrix element vanish,

$$\int \Psi_{\pi_3}^* \hat{\mu} \Psi_{\pi_1} d\tau = 0. \quad (11.2)$$

By computing the energy of allowed electronic molecular transitions, it can be shown that often organic molecules actually absorb light in the *ultraviolet range*, for instance ethylene absorbs at  $\lambda = 163$  nm while butadiene at  $\lambda = 220$  nm.

**More about electronic molecular transitions** We can now present some additional facts that are important for the understanding of the physics underlying electronic transitions between molecular orbitals:

- In molecular orbitals, the *conjugation length* is defined as the length of the orbital resulting from the partial overlap of atomic  $p$ -orbitals. The more  $p$ -orbitals that contribute to a molecular orbital, the larger its conjugation length will be. This means that an electron that belongs to this orbital will be *more de-localized* the larger the conjugating length of that orbital, since it will be able to *hop* between more atoms that compose the molecule. As a general rule, the greater the conjugation length of a molecular orbital, and thus the greater the amount of de-localization of the electrons that belong to this orbital, the smaller its energy, or in other words, the *stronger its contribution to the molecular bonding*.

Recall that a similar behaviour was observed when studying the particle in a box system using the Schroedinger equation in HC3. There we saw that the energy of the allowed quantum states of the particle scaled with the length of the box  $L$  as  $E \sim L^{-2}$ , in other words, the greater the box (and thus the de-localization) the smaller the energy of the particle, qualitatively the same behaviour as for molecular orbitals.

- Another important type of electronic molecular transitions are the  $n \rightarrow \pi^*$  optical transitions. Recall that by  $n$  we denote the molecular orbital of an *auxochrome*, a functional group of atoms with free (unbounded) electron pairs that when attached to a *chromophore* (that is, a light-absorbing molecule) modifies both the wavelength and intensity of absorption. In some circumstances, an electron might transition between a  $n$  orbital of an *auxochrome* to the  $\pi^*$  orbital of a *chromophore*. In this transitions, the larger the conjugation length, the larger the *extinction coefficient* that determines how strongly this specific molecule will absorb light of a given wavelength.
- It can be shown that there is a direct connection between the value of the dipole moment transition

matrix element  $\mu_{fi}$  and the extinction coefficient  $\epsilon(\nu)$  for light of a given frequency, that determines how strongly this molecule does absorb light of this specific frequency. Intuitively, one could expect that the greater the value of the electric dipole moment transition matrix element  $\mu_{fi}$ , the stronger the absorption of light with wavelengths corresponding to this specific electronic transition. And indeed, the integral over all frequencies of  $\epsilon(\nu)$  is proportional to the square of  $\mu_{fi}$ , in other words

$$\int \epsilon(\nu) d\nu \propto |\mu_{fi}|^2. \quad (11.3)$$

Therefore, for very *narrow* transitions, the extinction coefficient  $\epsilon$  is simply proportional to  $|\mu_{fi}|^2$ .

## 11.2 The Franck-Condon principle

We now turn to discuss the *Franck-Condon principle*, which describes the transitions in which a *simultaneous* change in the vibrational and electronic states of a molecule takes place, due to the emission or absorption of a photon of the appropriate energy. This principle is important to explain the *vibrational fine structure* in the optical absorption spectrum. Recall that vibrational transitions (in the *infrared* range of the EM spectrum) have associated much smaller energies than optical transitions (in the *visible* range), and thus appear in the optical absorption spectrum as small splittings of the main absorption lines. In general, we denote as a *vibronic transition* a transition that involves simultaneous modifications in the vibrational and electronic energy states of a given molecule.

The Franck-Condon (FC) principle states that since nuclei are so much more massive than electrons,  $m_e \ll m_N$ , *electronic transitions* between different quantum states take place at much shorter time-scales than those for which the nuclei can respond, therefore the *vibrational transitions* take place at slower rates. In other words, the probability of an *electronic molecular transition* is the highest where the *relative separation between two atomic nuclei* is unchanged. This phenomenon is thus also known as a *vertical transition*, since in a  $(r, E)$  plane the transition takes place vertically along the  $y$  axis, as shown in Fig. 11.3. As in general in quantum mechanics, the transition probability will be proportional to the overlap between vibrational wave functions in the ground electronic and in an excited electronic states, and it can be shown that this overlap is maximal when the relative separation between nuclei  $r$  is unchanged.

The physical interpretation of the Franck-Condon principle is summarized in Fig. 11.3, where we show a schematic representation of the molecular potential energies for the ground and the excited electronic states in a molecule. This molecular potential energy is nothing by the Morse potential that we discussed in HC10, Eq. (10.21). According to the Franck-Condon principle, the most intense vibronic transitions take place between the ground vibrational state in the electronic ground state to the vibrational state *lying immediately above it* in the electronic excited state. Transitions to other vibrational states also occur, but with lower intensities.

In the quantum mechanical description of the FC principle, the molecule undergoes a transition to the upper vibrational state that most closely resembles the vibrational wave-function of the vibrational ground state of the lower electronic state. The two wave functions shown here exhibit the greatest overlap and hence the matrix element for the transition probability among them is the highest.

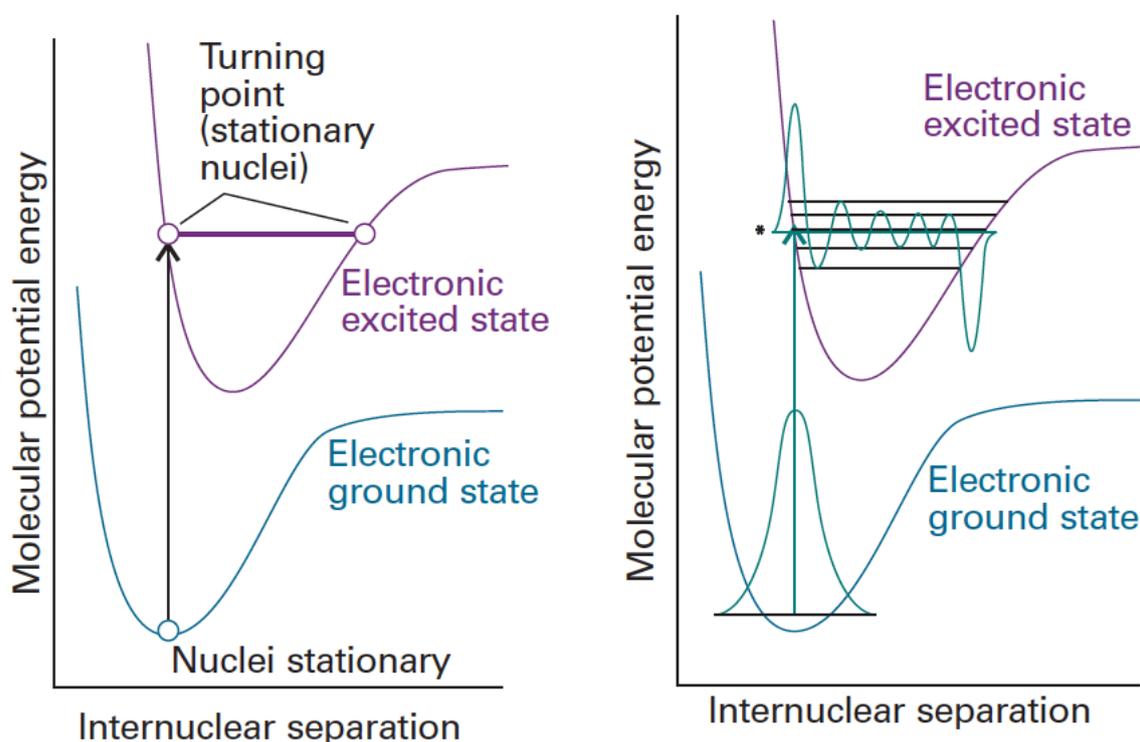


Figure 11.3: Schematic representation of the molecular potential energy (Morse potential Eq. (10.21)) for the ground and the excited electronic states in a molecule. Left plot: according to the Franck-Condon principle, the most intense vibronic transitions takes place between the ground vibrational state in the electronic ground state to the vibrational state lying immediately above it in the electronic excited state, in a way that the *inter-nuclei separation* is kept constant. Transitions to other vibrational states also occur, but this lower intensities. Right plot: in the quantum mechanical description of the FC principle, the molecule undergoes a transition to the upper vibrational state that most closely resembles the vibrational wave-function of the vibrational ground state of the lower electronic state. The two wave functions shown here exhibit the greatest overlap, and hence the matrix element for the transition probability among them is the highest, corresponding to a transition with fixed inter-nuclear separation.

**Dipole matrix element for vibronic transitions** In order to compute the matrix element for the electric dipole moment of such a vibronic transition, we need to take into account the sum of electronic and of nuclear contributions to the total molecular dipole moment operator, that is

$$\hat{\vec{\mu}} = -e \sum_j \vec{r}_j + e \sum_I Z_I \vec{R}_I, \quad (11.4)$$

where  $j$  runs over the electrons and  $I$  over the nuclei in our molecule, and  $Z_I$  is the total positive charge of the nucleus  $I$ . In order to compute the dipole transition matrix element, for both the initial and final states we separate the wave function into its electronic  $\Psi_e$  and vibrational  $\Psi_\nu$  components. This way the dipole matrix element for a given vibronic transition between an initial  $\Psi_i = \Psi_{\epsilon_i} \Psi_{\nu_i}$  and final  $\Psi_f = \Psi_{\epsilon_f} \Psi_{\nu_f}$  final state, will be given by

$$\vec{\mu}_{fi} = \int \Psi_{\epsilon_f}^* \Psi_{\nu_f}^* \left[ -e \sum_j \vec{r}_j + e \sum_I Z_I \vec{R}_I \right] \Psi_{\epsilon_i} \Psi_{\nu_i} d\tau, \quad (11.5)$$

which can be rearranged as follows:

$$\vec{\mu}_{fi} = -e \sum_j \int \Psi_{\epsilon_f}^* \vec{r}_j \Psi_{\epsilon_i} d\tau_\epsilon \int \Psi_{\nu_f}^* \Psi_{\nu_i} d\tau_\nu + e \sum_I Z_I \int \Psi_{\epsilon_f}^* \Psi_{\epsilon_i} d\tau_\epsilon \int \Psi_{\nu_f}^* \vec{R}_I \Psi_{\nu_i} d\tau_\nu, \quad (11.6)$$

where we have used that the vibrational wave functions  $\Psi_\nu$  depend only on the inter-nuclei separation  $\vec{R}_I$  while the electronic wave functions  $\Psi_{\epsilon_i}$  depend only on the position of the electrons  $\vec{r}_i$ .

The second term in Eq. (11.6) vanishes since the electronic wave functions are *orthogonal among them*,

$$\int \Psi_{\epsilon_f}^* \Psi_{\epsilon_i} d\tau_\epsilon = 0 \quad \text{for } i \neq f, \quad (11.7)$$

but note that this does not apply to the *vibrational wave functions* necessarily, they correspond to different electronic states so they do not need to be orthogonal among them. Taking this property into account, we find that the dipole matrix element can be written as

$$\vec{\mu}_{fi} = -e \sum_j \int \Psi_{\epsilon_f}^* \vec{r}_j \Psi_{\epsilon_i} d\tau_\epsilon \int \Psi_{\nu_f}^* \Psi_{\nu_i} d\tau_\nu \equiv \mu_{\epsilon_f \epsilon_i} S(\nu_f, \nu_i), \quad (11.8)$$

where we have introduced the following definitions:

$$\mu_{\epsilon_f \epsilon_i} \equiv -e \sum_j \int \Psi_{\epsilon_f}^* \vec{r}_j \Psi_{\epsilon_i} d\tau_\epsilon. \quad (11.9)$$

$$S(\nu_f, \nu_i) \equiv \int \Psi_{\nu_f}^* \Psi_{\nu_i} d\tau_\nu. \quad (11.10)$$

The first of these expressions,  $\mu_{\epsilon_f \epsilon_i}$ , corresponds to the *electronic dipole transition matrix element* between two molecular electronic states. The second of these expressions,  $S(\nu_f, \nu_i)$ , corresponds instead to the *overlap between the vibrational wave functions in the ground and in the excited states*. Therefore, the rate for a vibronic transition that involves simultaneously the change in the electronic and vibrational states of a molecule will be proportional to the *Franck-Condon factor*,

$$|S(\nu_f, \nu_i)|^2, \quad (11.11)$$

which states quantitatively what was qualitatively illustrated in Fig. 11.3, namely that the rate for vibronic transitions is maximal when the vibrational wave functions in the ground and excited electronic states resemble the most.

### 11.3 Fluorescence and phosphorescence

We now describe to important phenomena related to light emission by molecules:

- *Phosphorescence* is the *slow emission of light* in molecules, taking place in an interval of *microseconds or more*.
- *Fluorescence* is the *fast emission of light* in molecules, taking place within a time interval of *nanoseconds or less*.

Therefore, these two phenomena related to light emission in molecules have time scales that differ by several orders of magnitude, and now we explain the reason for this behaviour.

**Fluorescence** Let us start by discussing the phenomenon of *fluorescence*. From our discussion of HC10, we can recall a number of important properties of the electronic transitions within the two-level system, represented in Figs. 10.1 and 10.2, in particular we found that:

- The Einstein coefficient for stimulated absorption  $B_{fi}$  was proportional to the integral of the extinction coefficient over the relevant absorption band. It is therefore an intrinsic property of a given molecule.
- The Einstein coefficients for stimulated absorption and emission are identical,  $B_{fi} = B_{if} \equiv B$ .
- The Einstein coefficient for spontaneous emission  $A$  was proportional to both  $B$  and  $\nu^3$ , with  $\nu$  being the frequency of the emitted light:

$$A = \left( \frac{8\pi h\nu^3}{c^3} \right) B, \quad (11.12)$$

implying that spontaneous emission become relevant only at relatively high frequencies.

With these properties, we can compute rate of variation in time of the population of molecules in in the excited electronic state  $f$  due to emission an absorption as follows

$$\frac{dN_f}{dt} = -N_f A - N_f B_{if} \rho(\nu) + N_i B_{fi} \rho(\nu). \quad (11.13)$$

In normal circumstances  $\rho(\nu)$ , the density of states of the EM field is small (unless a very powerful illumination is used) and can be neglected. This leaves a simple differential equation which depends only on the probability of spontaneous emission  $A$ ,

$$\frac{dN_f}{dt} = -N_f A \quad \rightarrow \quad N_f(t) = N_0 e^{-At} = N_0 e^{-t/\tau_R}, \quad (11.14)$$

where  $\tau_R = 1/A$  is the *radiative lifetime* of this specific electronic state of the molecule. The higher the rate for spontaneous emission, the smaller the radiative lifetime of the molecule will be. In the absence of other processes that decrease the population of the state  $f$ , the radiative lifetime  $\tau_R$  is equal to the total lifetime of the excited state.

In general however there are other contributions to this process that need to be taken into account. Indeed, the total life time of an excited state  $f$  will receive contributions from various mechanisms, in addition to spontaneous emission. The most important ones are:

- The internal conversion (IC) from an excited vibrational state to the vibrational ground state of a given electronic level, with constant rate  $k_{IC}$ .
- An inter-system crossing (ISC) from a singlet to a triplet state, with constant rate  $k_{ISC}$
- Other processes such as *electron transfer*, with constant rate  $k_Q$ .

To study these electronic transitions within molecules, in general it is useful to use a special type of diagrams known as *Jablonski diagram*, which schematically indicates the transitions that can take place starting from an excited state. In Fig. 11.4 we show the schematic representation of the fluorescence and

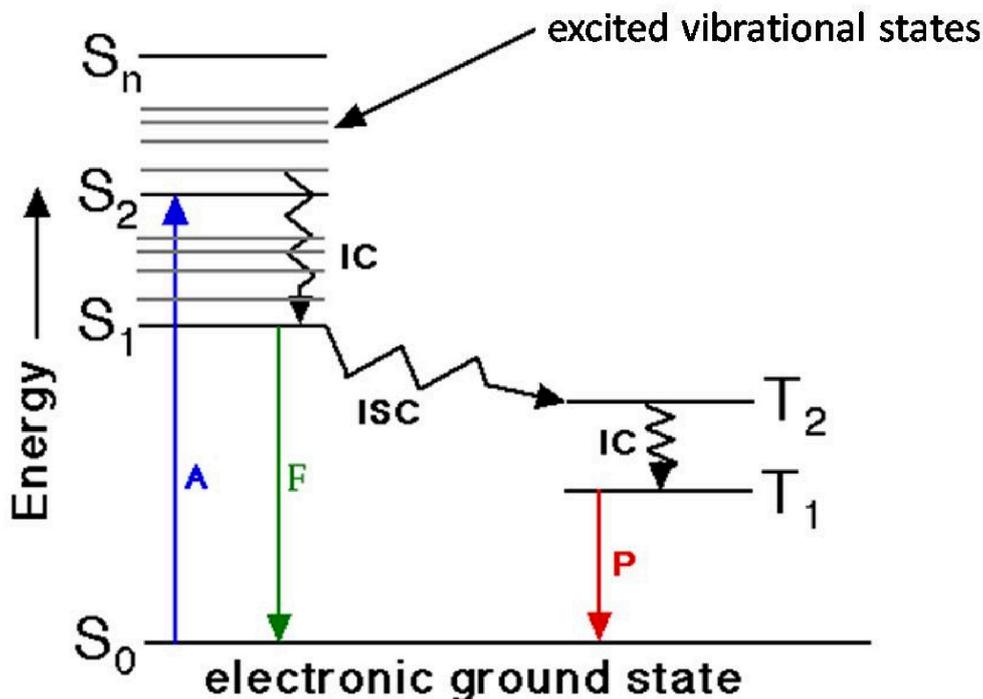


Figure 11.4: Schematic representation of the fluorescence and phosphorescence phenomena by means of the *Jablonski diagram*. In this diagram, *A* indicates the absorption of a photon, *F* and *P* represent the fluorescence and phosphorescence transitions respectively, *S* and *T* denote singlet and triplet states, and finally *IC* and *ISC* label the internal conversion and the inter-system crossing respectively.

phosphorescence phenomena by means of a Jablonski diagram. In this diagram, *A* indicates the absorption of a photon, *F* and *P* represent the fluorescence and phosphorescence transitions respectively, *S* and *T* denote singlet and triplet states, and finally *IC* and *ISC* label the internal conversion and the inter-system crossing respectively.

Let us discuss the Jablonski diagram of Fig. 11.4. First of all, an electron in the electronic ground state absorbs an incoming photon and is promoted to an excited electronic state, as well as to an excited vibrational state. From the internal conversion (*IC*) process, this electron loses energy via non-radiative (vibrational) transitions until it is found in the ground vibrational state of the first excited electronic state  $S_1$ . From there on, two things can happen: either decay to the electronic ground state (*fluorescence*) or a inter-system crossing (*ISC*) to a triplet state, which eventually gives rise to a much slower light emission (*phosphoresce*) since the triplet to singlet transition is suppressed. We therefore see that an important component of the fluorescence process involves the molecule relaxing from an excited vibrational state to the lowest vibrational state via non-radiative transitions.

As a result of the competition between the various processes that de-populate the excited state  $f$ , its total lifetime  $\tau$  will be in general shorter than the radiation lifetime  $\tau_R$ . The *total lifetime of the excited state* is called the *fluorescence lifetime*  $\tau_F$ . Therefore, in general the radiative lifetime will be different (larger) from the fluorescence lifetime. Let us make this statement more quantitative. In the presence of these additional

processes, the *occupancy number* of the electronic state  $f$ ,  $N_f$ , will vary with time as follows:

$$\frac{dN_f}{dt} = -N_f(A + k_{IC} + k_{ISC} + k_Q) \quad \rightarrow \quad N_f(t) = N_0 e^{-(A+k_{IC}+k_{ISC}+k_Q)t}, \quad (11.15)$$

from where we readily see that the fluorescence lifetime  $\tau_F$  will be determined by the sum of the rates of all processes that de-populate  $f$ , namely,

$$1/\tau_F = A + k_{IC} + k_{ISC} + k_Q, \quad (11.16)$$

In the fluorescence process, one usually introduces the *quantum yield*  $\Phi_F$  defined as the number of emitted photons divided by the number of absorbed photons

$$\Phi_F \equiv \frac{\# \text{ Emitted Photons}}{\# \text{ Absorbed Photons}} = \frac{A}{A + k_{IC} + k_{ISC} + k_Q}, \quad (11.17)$$

Let us now take a look at the rates for these various processes in a representative molecule, in this case *chlorofyll*. In this molecule, the rates for the various processes that de-populate the quantum state  $f$  are

$$\begin{aligned} k_R = A &= 0.5 \times 10^8 \text{ s}^{-1} &\rightarrow &\tau_R = 20 \text{ ns} \\ k_{ISC} &= 1.0 \times 10^8 \text{ s}^{-1} &\rightarrow &\tau_{ISC} = 10 \text{ ns} \\ k_{IC} &= 1.5 \times 10^8 \text{ s}^{-1} &\rightarrow &\tau_{IC} = 16.6 \text{ ns} \end{aligned} \quad (11.18)$$

from where the fluorescence lifetime is  $\tau_F = 3.3$  ns, and the fluorescence quantum yield  $\Phi_F = 0.166$ , meaning that for each 100 absorbed photons by the molecule, there will be 16 emitted photons.

As can be seen from the Jablonski diagram in Fig. 11.4, in general fluorescence radiation will correspond to longer wavelengths (that is, smaller energies) than the absorbed light, since the electrons undergo internal transitions losing energy before a photon is radiated. This difference is as known as the *Stokes shift*: the difference, either in wavelength or in wave number, between the absorption and fluorescence emission maxima.

**Phosphorescence** In the *phosphorescence* radiation phenomenon, the molecule goes from a *singlet* excited state to a *triplet* excited state, via the so-called inter-system crossing, as illustrated in Fig. 11.4 (see also the left plot of Fig. 11.7). The resulting triplet states are long-lived, with lifetimes that can range from microseconds to seconds, since a transition to the ground state is forbidden by the selection rules (Pauli exclusion principle). Recall that a *singlet to triplet conversion* is a transition from paired spin to unpaired spin in a given molecular electronic state.

Therefore, as shown in Fig. 11.5, the origin of a *phosphorescence* transition is a transition from a ground singlet state (with paired spins) to the excited LUMO state where the electron spin remains the same. From there, a transition from the excited singlet state to the excluded triplet state via inter-system crossing will take place, since the latter has lower energy due to Hund's rule. This inter-system crossing is enhanced by the spin-orbit coupling, and thus mostly occurs when heavy nuclei are nearby, such as S, Fe or Mg. The longevity of the *phosphorescence* radiation is then explained since the relaxation of a triplet to a singlet ground state is spin-forbidden.

The key property of phosphorescence is that, following light absorption, the subsequent re-emission takes

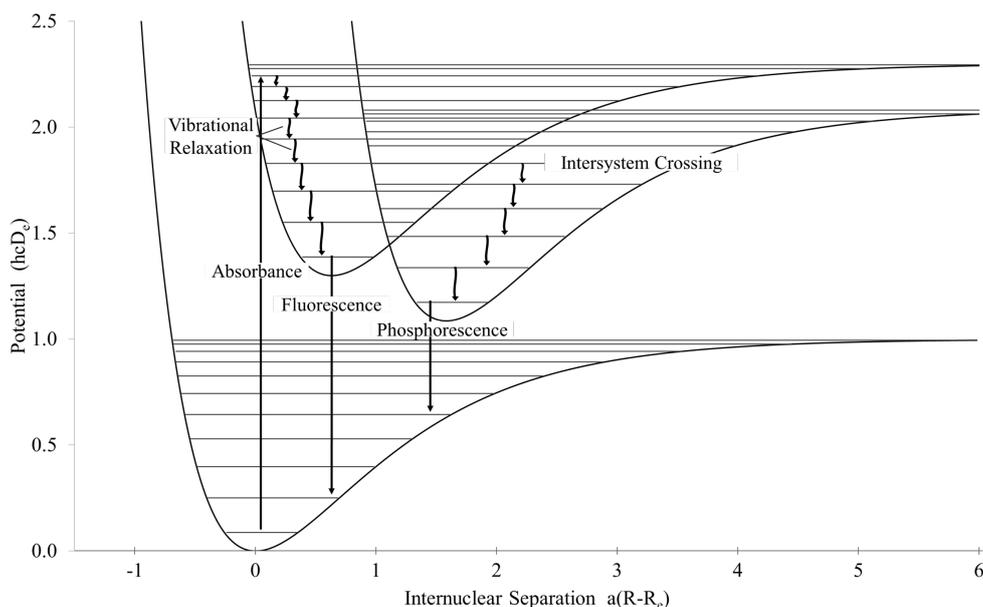


Figure 11.5: In *phosphorescence transitions*, the molecule undergoes an inter-system crossing from a singlet to a triplet state, and the resulting state has a very long lifetime since the relaxation from the excited triplet to the singlet ground state is not allowed by Pauli's exclusion principle.

place at a lower intensity for up to several hours after the original excitation. It is thus a very slow transition.

## 11.4 Lasers

The use of lasers is ubiquitous in spectroscopy, as well as in many forms of microscopy and in a wealth of medical applications. Therefore, it is important to understand how a laser works. The name *laser* was originally an acronym of *Light Amplification by Stimulated Emission of Radiation*, since it is a device that *amplifies the intensity* of the incident electromagnetic radiation. Let us now show how this is possible.

To illustrate how a laser works, we consider first of all the usual two-level system, such as the one depicted in Fig. 10.1. Since the Einstein coefficient for stimulated emission is  $B_{if}$ , the rate of  $f \rightarrow i$  transitions leading to light *stimulated emission* will be given by  $N_f B_{if} \rho(\nu)$ , as we have demonstrated in HC10. Now, a necessary condition for *lasing* is achieving *population inversion* in the system, that is, a situation such that in thermal equilibrium the population of excited states is higher than the population of lower energy states. Only under this condition it will be possible to achieve more stimulated emission than stimulated absorption, and this achieve amplification of the incident radiation intensity. Otherwise, given that the Einstein coefficients for stimulated absorption and emission are the same,  $B_{fi} = B_{if}$ , and that in thermal equilibrium the ratio of populations of the ground state and the excited state are given by the Boltzmann distribution

$$\frac{N_f}{N_i} = \exp\left(-\frac{E_f - E_i}{k_B T}\right), \quad (11.19)$$

it would be impossible to achieve more emission than absorption.

The concept of population inversion in the simple case of a two-level system is illustrated in Fig. 11.6: starting from a system in thermal equilibrium, obeying Boltzmann statistics and thus where the population

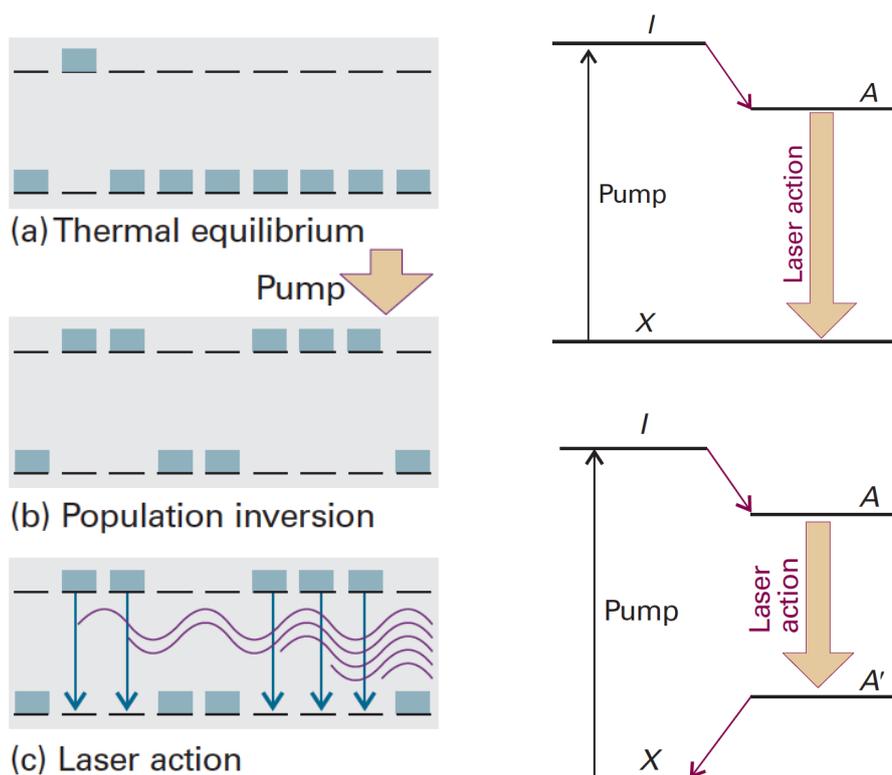


Figure 11.6: Left plot: the operation of a laser is based on the principle of *population inversion*: starting from a system in thermal equilibrium, obeying Boltzmann statistics and thus where the population of the excited state is smaller than that of the ground state, a *pumping system* increases the population of the excited state until it becomes larger than that of the ground state. In these conditions, stimulated emission will dominate over absorption and this the laser will indeed enhance light intensity. Right plot: The schematic operation of a three-level (upper diagram) and four-level (lower diagram) laser, where we indicate the specific transition that is responsible for the lasing.

of the excited state is smaller than that of the ground state,  $N_f < N_i$ , a *pumping system* increases the population of the excited state until it becomes larger than that of the ground state. Under these conditions, the overall rates for stimulated emission will be higher than those of the stimulated absorption, and lasing (light amplification) will take place. The crucial point for the laser operation is therefore how to best implement this pumping to achieve population inversion.

It is easy to realize is that actually *lasing is impossible in a two level system*. To see this, note that due to the equality of the Einstein coefficients,  $B_{if} = B_{fi}$ , the population of  $N_f$  can only be as large as 50% of the total population of the system,  $N_T = N_i + N_f$ , no matter how hard we pump. To implement the lasing concept one needs at least a system with three quantum states or even four. In Fig. 11.6 we show the schematic operation of a three-level and four-level laser, where we indicate the specific transition that is responsible for the lasing. Of all the possible transitions in the system, the one that is responsible for the lasing effect (and that requires population inversion) is  $A \rightarrow X$  for the three-level laser and  $A \rightarrow A'$  for the four-level laser, and therefore the pumping should be such that in equilibrium  $N_A \geq N_X$  ( $N_A \geq N_{A'}$ ) for the three (four) level laser. The best molecules to be used for lasing are thus for which the rates of inter-system transitions are those that facilitate the most achieving population inversion.

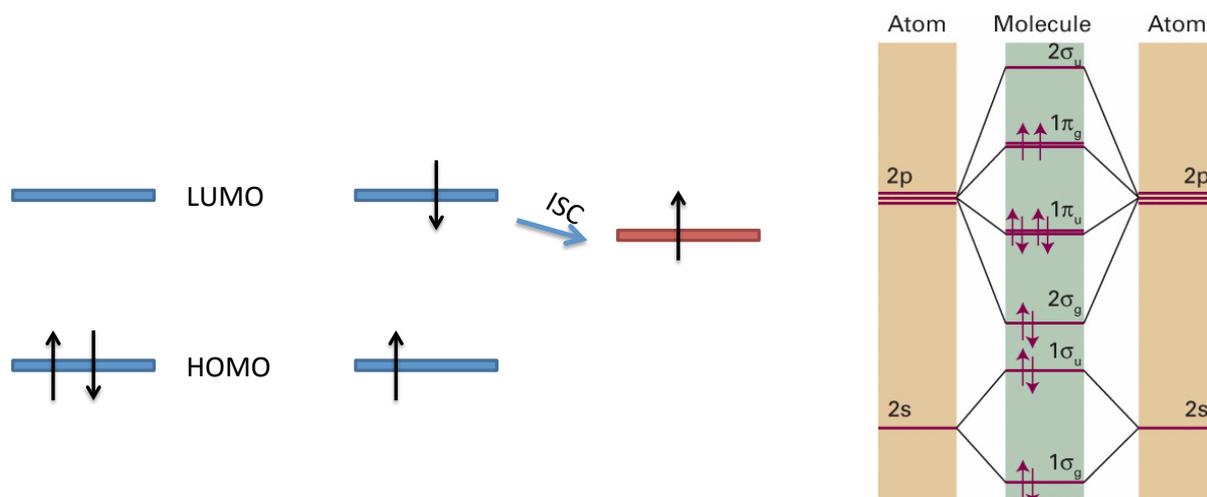


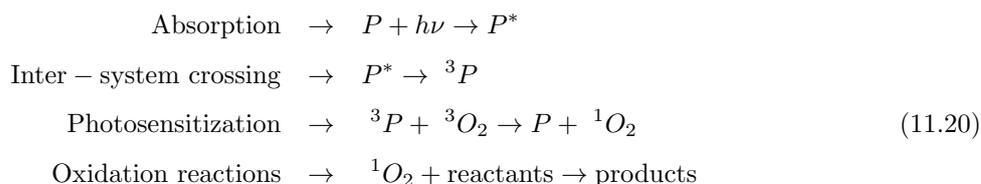
Figure 11.7: Left plot: the basic molecular electronic transition in *Photodynamic Therapy* is the one from a singlet state with paired electrons to a triplet state where the two electrons have unpaired spin via an inter-system crossing. Right plot: schematic representation of the molecular orbitals in the  $O_2$  molecule, where the  $2s$  orbitals form two  $\sigma$ -bonds and the  $2p$  orbitals form two  $\sigma$  and two  $\pi$  bonds.

The basic mechanism of light amplification in a laser arises from the *snowball effect* applied to stimulated emission: each time that a stimulated emission takes place, additional photons with the correct energy are produced, inducing yet further additional simulated emissions, with an exponential grow of the intensity of the incident electromagnetic radiation.

## 11.5 Photodynamic Therapy (PDT)

*Photodynamic therapy*, or PDT for short, is a representative example of a medical application which is based on the optical transitions between different molecular electronic states. PDT, also known as *photochemotherapy*, is a form of photo-therapy involving light and a photosensitizing chemical substance, which in conjunction with molecular oxygen can eliminate cancerous tissue.

PDT works as follows. We start from a molecular singlet state, with two paired electrons (opposite spin) in the same electronic quantum level. This level will be the HOMO, the Higher Occupied Molecular Orbital, as illustrated in Fig. 11.7. Using laser radiation, an electron is excited to first the LUMO orbital and then via an inter-system crossing it ends up in its first excited triplet state  $^3P$ . The resulting state photosensitizes the formation of an excited singlet state of  $O_2$ ,  $^1O_2$ , which are extremely reactive and destroy cellular components. Therefore, the photochemical cycle that leads to the shrinkage of diseased tissue is the following:



Note that the energy in the triplet state is lower than that of the singlet state due to Hund's rule, as

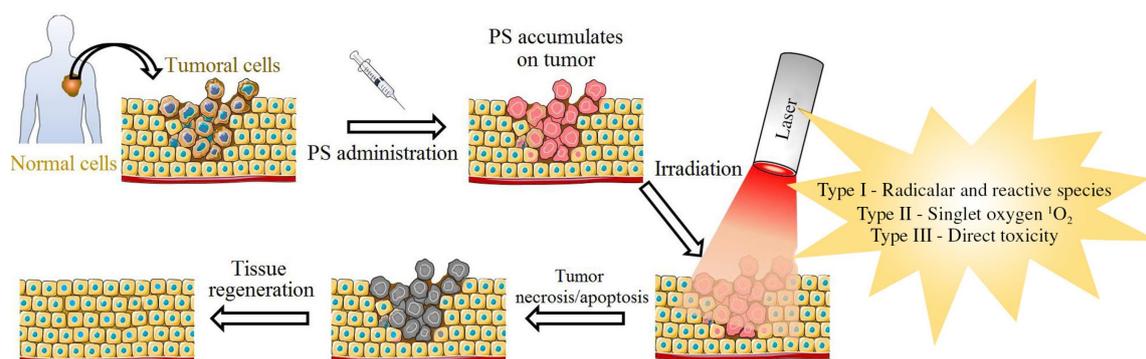


Figure 11.8: In photo-dynamic therapy, a photo-sensitive (PS) molecule is injected on the patient and accumulates on tumor. The subsequent irradiation activates a chemical reaction which creates reactive oxygen molecules  $^1O_2$  which destroy the cancerous tissue.

illustrated in Fig. 11.7. In the right plot of Fig. 11.7 we show a schematic representation of the molecular orbitals in the  $O_2$  molecule, where the  $2s$  orbitals form two  $\sigma$ -bonds and the  $2p$  orbitals form two  $\sigma$  and two  $\pi$  bonds. As we mentioned above, an inter-system crossing transition is enhanced by large spin-orbit couplings, and therefore occurs mostly where heavy nuclei such as S, Fe and Mg are nearby. Since the relaxation from the triplet state to the singlet ground state is forbidden by Pauli exclusion system (which forbids two electrons with the same spin in the same quantum state), the electronic configuration displayed in Fig. 11.7 has a remarkable longevity, which facilitates the photosensitization of a large number oxygen molecules. This is the same mechanism that explained the very long lifetime of phosphorescence.

Therefore, PDT is based on the photosensitization of  $O_2$  molecules to turn them into extremely reactive and destroy cancerous tissue. In this technique, first of all the patient is injected with a photosensitive molecule, and one waits until this substance accumulates in the tumor. Then the tumor is illuminated with laser light, induces the singlet to triplet transition in the molecule and which leads to the selective formation of reactive  $^1O_2$  and the restriction of cancerous tissue. This technique is mostly used for cancer present in body cavities such as mouth, throat or bladder. A summary of the PDT mechanism is shown in Fig. 11.5.

## 11.6 Summary and outlook

Some of the important lessons that we have learned in this lecture are the following:

- The absorption of light (visible and UV) in biological molecules takes place predominantly by means of  $\pi \rightarrow \pi^*$  transitions in  $p$ -conjugated electron systems.
- A larger  $p$ -electron conjugation length leads to absorption at longer wavelengths, that is, at smaller photon energies. This is explained by the reduced electron confinement for large conjugation lengths.
- Symmetry considerations are important when determining whether or not an given optical transition is possible within a specific molecule.
- The Franck-Condon principle explains the transitions in which a *simultaneous* change in the vibrational and electronic states of a molecule takes place, the so-called *vibronic transitions*.

- The Einstein coefficient for spontaneous emission determines the radiation lifetime of a molecule  $\tau_R$ , which in general is different (larger) than its total lifetime.
- The fluorescence lifetime  $\tau_F$  is usually shorter than the radiative lifetime  $\tau_R$  due to competing processes that de-populate the excited states.
- The phosphorescence phenomenon is explained by the long-lived emissions from a triplet excited state to a singlet ground state.
- The light amplification achieved in a laser is based on the concept of *population inversion*.
- The Photodynamic Therapy is an representative example of a medical application based on optical transitions in biomolecules.