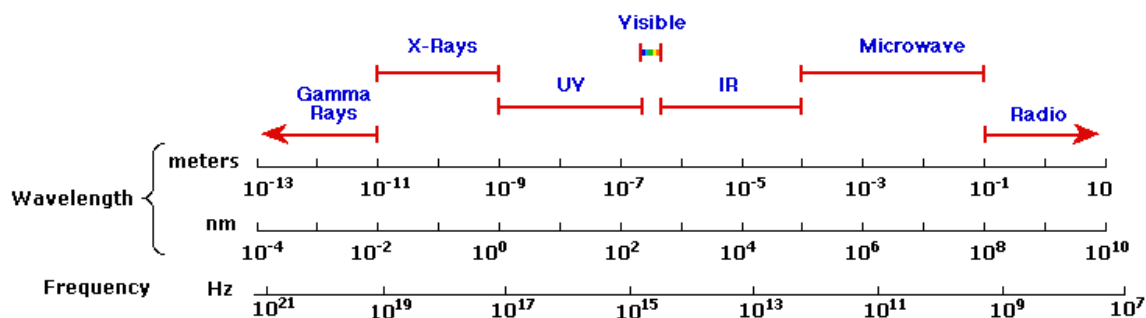


Electronic Spectroscopy

adapted by Audrey Dell Hammerich, August 24, 2013

Electronic excitation promotes a molecule from a lower electronic potential energy surface, usually the ground state, to a higher energy potential surface. This can be achieved by thermal, electrical, or optical excitation. Numerous types of processes may initiate electronic deexcitation, where the molecule loses its acquired excess energy by emitting light, including thermal (incandescence), chemical (chemiluminescence), biological (bioluminescence), and optical processes (photoluminescence). Electronic spectroscopy involves interrogating a sample by visible or ultraviolet electromagnetic radiation to change the charge distribution of electrons. This wavelength range

Figure 1. The Electromagnetic Spectrum



corresponds to energies which are sufficient to promote an electron to a higher energy electronic state.

Background

Electronic spectroscopy, as all spectroscopic methods, relies upon the interaction of the sample being examined with electromagnetic radiation, here in the ultraviolet and visible range (200-800 nm). To absorb a photon of electromagnetic radiation the sample must exhibit periodic motion whose frequency matches that of the absorbed radiation

$$\Delta E_{\text{sample}} = E_{\text{photon}} = h\nu = hc/\lambda = hc\tilde{\nu} \quad (1)$$

Once excited, if the sample loses its excess energy radiatively, the emitted photon has a frequency which matches the energy difference between the quantum electronic, vibrational, and rotational states, $-\Delta E_{\text{sample}}$. Some of the characteristics of this phenomenon will be explored.

The Born-Oppenheimer Approximation

Each electronic state is subdivided into vibrational levels which are in turn subdivided into rotational levels. While this may seem to make analysis of individual electronic transitions difficult, the Born-Oppenheimer approximation can provide guidance. The nuclei in a molecule are several thousand times more massive than the electrons and, consequently, they move far more slowly than the electrons. When an electronic transition occurs it is extremely rapid (on the order of 10^{-15} sec) and the nuclear coordinates cannot follow. This difference in time scales between the motion of nuclei and the motion of electrons leads to a separation of nuclear (vibrational and rotational) and electronic energies and a separation of their respective wavefunctions. Continuing this separation to all degrees of freedom, one can write, to a first approximation, that the total energy is additive:

$$E_{\text{total}} = E_{\text{translational}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{electronic}} + E_{\text{nuclear}} \quad (2)$$

and the total wavefunction is a product:

$$\phi_{\text{total}} = \phi_{\text{translational}} \phi_{\text{vibrational}} \phi_{\text{rotational}} \phi_{\text{electronic}} \phi_{\text{nuclear}} \quad (3)$$

We are generally interested in the internal energy of a system which excludes its translational motion so the first term in Eqs. 2 and 3 will be ignored. (Note that in the effusion lab it is just these translational energies which are important!) Our only interest in actual “nuclear” energies will be accounting for the spin of nuclei in the NMR lab and otherwise these energies will not be addressed.

Electron Angular Momentum and Electron Spin

Classically a spinning particle possesses angular momentum. An electron in an atom can be visualized classically as spinning on its axis in either a clockwise or counterclockwise direction and, consequently, has a spin angular momentum, S . This angular momentum is a true physical property intrinsic to the electron, rather than the angular momentum arising from its overall motion, and properly requires a relativistic quantum mechanical treatment. For a many-electron system the magnitude of the spin angular momentum is given in quantum mechanics by

$$\hbar[S(S+1)]^{1/2} \quad S = 0, 1/2, 1, 3/2, \dots \quad (4)$$

where \hbar is Planck's constant h divided by 2π and S is the total electron spin angular momentum quantum number. S has a quantized z -component

$$S_z = \hbar M_s \quad M_s = -S, \dots, 0, \dots, S \quad (5)$$

where M_s is the total electron spin magnetic quantum number with $2S + 1$ values. If m_s is the spin quantum number of an individual electron with values of either $+1/2$ or $-1/2$ then

$$M_s = \sum_i (m_s)_i \quad (6)$$

the sum of the values of m_s of the individual electrons. Note the parallel between the orbital angular momentum quantum number l and magnetic quantum number m_l for the electron in a hydrogen atom and the S and M_s quantum numbers here: just as there are $2(l + 1)$ values of m_l for the orbital angular momentum of the electron in a hydrogen atom there are $2(S + 1)$ values of M_s for a molecule.

An electronic state of a molecule can be characterized by the S and M_s quantum numbers. The number $2S + 1$ is known as the multiplicity of the electronic state. The lowest five multiplicities are given in Table I. To first order, quantum mechanics requires that transitions only occur between electronic states of the same multiplicity (selection rule: $\Delta S = 0$).

Table I. Some Common Multiplicities for Electronic States

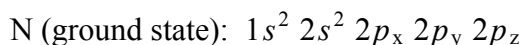
S	M_s	$2S + 1$	Multiplicity
0	0	1	singlet
$1/2$	$-1/2$ or $1/2$	2	doublet
1	-1, 0, or 1	3	triplet
$3/2$	$-3/2, -1/2, 1/2,$ or $3/2$	4	quartet
2	-2, -1, 0, 1, or 2	5	quintet

A few physical examples of different spin multiplicities:

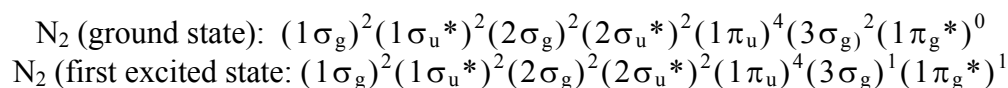
- 1) $S = 0$ – all electrons in the molecule are paired, ground state of most stable molecules
- 2) $S = 1/2$ – a single unpaired electron as in the free radical nitrogen monoxide, NO
- 3) $S = 1$ – diradicals, molecules such as oxygen with two unpaired electrons (electrons occupy different orbitals)

Electronic Configurations

The electronic configuration of an atom or molecule gives the number of electrons in each atomic or molecular orbital arranged according to energy. The ground state electronic configuration of a nitrogen atom is

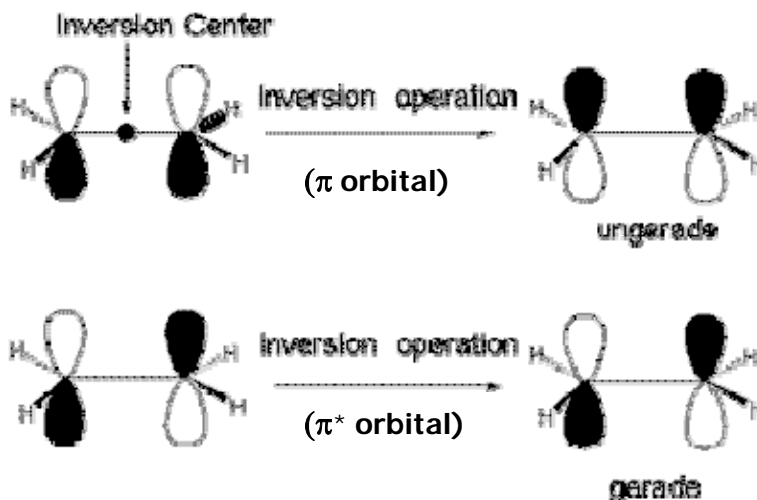


The s , p , d , f , *etc.* nomenclature is employed for atoms and their ions while diatomic molecules use the designation of σ_g and π_u for bonding molecular orbitals and σ_u^* and π_g^* for antibonding MO's. These labels give the bonding/antibonding nature of the orbital, its symmetry, and its electron density distribution. The ground state and first excited states of molecular nitrogen are given by



The g , u subscripts on the sigma and pi orbitals indicate symmetric orbitals (g , *gerade* - wavefunction does not change sign) and antisymmetric orbitals (u , *ungerade* - wavefunction becomes negative) with respect to inversion through the center of the molecule, $(x, y, z) \rightarrow (-x, -y, -z)$. Figure 2 illustrates the inversion operation on the π and π^* orbitals of ethylene to show that the respective orbitals are *ungerade* and *gerade*.

Figure 2. Symmetry of the π Bonding and π^* Antibonding Orbitals of Ethylene



It is not customary to include an unoccupied orbital such as $(1\pi_g)^0$ but it is often done when the orbital becomes occupied in an electronic state of interest.

This specification of the electronic state of a molecule does not suffice to determine its energy. Not only have the vibrational and rotational states of the molecule not been given, the distribution of the electrons in the orbitals has also been omitted. For instance, in the first excited state of N_2 given above, are the two electrons that are in different orbitals paired (antiparallel) or unpaired (parallel)? This makes a difference in the energy of the molecule. A more complete description of the electronic state of a

molecule is central to electronic spectroscopy and returns one to electron spin multiplicity.

Total Electronic Wavefunctions

For specific molecular examples take ground state molecular hydrogen, H_2 , and hydrogen in its first excited electronic state, H_2^* . The ground state electronic configuration of a hydrogen atom is $1s$. Then the molecular electronic configurations are: H_2 : $(1\sigma_g)^2(1\sigma_u^*)^0$ and H_2^* : $(1\sigma_g)^1(1\sigma_u^*)^1$. However these do not adequately specify the electronic state as we have not considered indistinguishability of the electrons and the Pauli exclusion principle: no two electrons can have the same set of quantum numbers. Then, a many-electron wavefunction must be antisymmetric (change sign) with respect to exchange of any two electrons. Writing the total electronic wavefunction as a product of an electronic wavefunction (ϕ_e) and a spin wavefunction (ϕ_s)

$$\phi_{\text{total electronic}} = \phi_e \phi_s \quad (7)$$

the antisymmetric requirement can be met if either ϕ_e or ϕ_s is antisymmetric, but not both. The spin wavefunction of an electron is designated by α if the m_s value is $+1/2$ and by β if the m_s value is $-1/2$.

Consider ground state H_2 first. Since both electrons occupy the σ_g orbital the electronic wavefunction must be $\phi_e = \sigma_g(1)\sigma_g(2)$. Since ϕ_e is symmetric (does not change sign upon exchange of the electrons) ϕ_s must be antisymmetric. The simplest antisymmetric spin wavefunction is $\alpha(1)\beta(2) - \beta(1)\alpha(2)$. It is straightforward to verify that it is antisymmetric as exchanging electrons gives $\alpha(1)\beta(2) - \beta(1)\alpha(2) = -[\alpha(2)\beta(1) - \beta(2)\alpha(1)]$. Note that $\alpha(1)\beta(2)$ is neither symmetric nor antisymmetric since $\alpha(1)\beta(2) \neq \pm \alpha(2)\beta(1)$. For the first excited state $\sigma_g(1)\sigma_u^*(2)$ is similarly neither symmetric nor antisymmetric. However the linear combination $\sigma_g(1)\sigma_u^*(2) + \sigma_u^*(1)\sigma_g(2)$ is symmetric while the combination $\sigma_g(1)\sigma_u^*(2) - \sigma_u^*(1)\sigma_g(2)$ is antisymmetric. The various symmetric and antisymmetric electronic and spin wavefunctions that are possible for two electrons are summarized in Table II.

Table II. Values of ϕ_e and ϕ_s for Two Electrons

Symmetry	ϕ_e	ϕ_s
symmetric	$\sigma_g(1)\sigma_g(2)$	$\alpha(1)\alpha(2)$
	$\sigma_g(1)\sigma_u^*(2) + \sigma_u^*(1)\sigma_g(2)$	$\beta(1)\beta(2)$
		$\alpha(1)\beta(2) + \beta(1)\alpha(2)$
antisymmetric	$\sigma_g(1)\sigma_u^*(2) - \sigma_u^*(1)\sigma_g(2)$	$\alpha(1)\beta(2) - \beta(1)\alpha(2)$

To form the total electronic wavefunction the symmetric and antisymmetric electronic wavefunctions need to be combined with the appropriate symmetric and antisymmetric spin wavefunctions (both delineated in Table II) to form an antisymmetric total electronic wavefunction. The following antisymmetric total electronic wavefunctions (ignoring normalization) result for the two molecular examples of interest:

molecule	multiplicity	wavefunction
H ₂	singlet	$\sigma_g(1)\sigma_g(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$
H ₂ *	singlet	$[\sigma_g(1)\sigma_u^*(2) + \sigma_u^*(1)\sigma_g(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$
	triplet	$[\sigma_g(1)\sigma_u^*(2) - \sigma_u^*(1)\sigma_g(2)] \alpha(1)\alpha(2)$
		$[\sigma_g(1)\sigma_u^*(2) - \sigma_u^*(1)\sigma_g(2)] \beta(1)\beta(2)$
		$[\sigma_g(1)\sigma_u^*(2) - \sigma_u^*(1)\sigma_g(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]$

The first two lines represent nondegenerate electronic states of their respective molecules. They are singlets as they are nondegenerate (have only one value of M_s and have a spin multiplicity of 1 – see Table I). The last three lines give three degenerate states for H₂* in the absence of a magnetic field. The energy of these three states is lower than the energy of the nondegenerate state of H₂* (Hund's rule: state with the maximum spin multiplicity is lowest in energy). These three states form a triplet state since they are triply degenerate (have three values of M_s and have a spin multiplicity of 3).

The antisymmetric total electronic wavefunction (electronic and spin) for an N electron system consisting of electronic wavefunction ϕ_a, \dots, ϕ_z and spin wavefunctions α, β can be easily constructed from the Slater determinant

$$\phi_{\text{electronic}}^{\text{total}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1)\alpha(1) & \phi_a(2)\alpha(2) & \dots & \phi_a(N)\alpha(N) \\ \phi_a(1)\beta(1) & \phi_a(2)\beta(2) & \dots & \phi_a(N)\beta(N) \\ \vdots & \vdots & & \vdots \\ \phi_z(1)\alpha(1) & \phi_z(2)\alpha(2) & \dots & \phi_z(N)\alpha(N) \\ \phi_z(1)\beta(1) & \phi_z(2)\beta(2) & \dots & \phi_z(N)\beta(N) \end{vmatrix} \quad (8)$$

where the N factor is for normalization.

Boltzmann Statistics

The different electronic states have different energies. At thermal equilibrium, these states will also have different populations, their ratio given by the Boltzmann distribution law

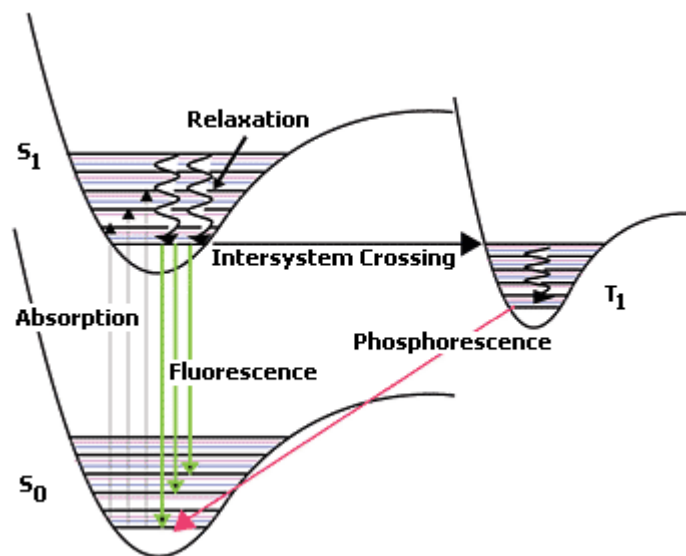
$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = e^{-\Delta E/kT} = \frac{1}{e^{\Delta E/kT}} \quad (9)$$

with N_{upper} and N_{lower} the respective populations of the upper and lower electronic states, $\Delta E = E_{\text{upper}} - E_{\text{lower}}$ the energy difference between the two states, k the Boltzmann constant, and T the absolute temperature. Taking an electronic state separation in the middle of the UV/VIS range (500 nm or $20,000 \text{ cm}^{-1}$ – the order of magnitude typical of electronic transitions), evaluation of the Boltzmann distribution shows that a molecule will basically only reside on the ground state electronic surface. The electronic energy gap is simply too large compared with the thermal energy, kT . Furthermore, evaluation of the distribution for vibrational populations shows that for all, save molecules with the lowest vibrational frequencies (*e.g.*, heavy diatomics such as Br_2 or I_2), the population of any level beyond the ground level is vanishingly small. The FTIR lab shows that the population of rotational levels is another matter altogether. The greater the energy difference ΔE between the electronic states or vibrational levels the more excess population exists in the lower energy one. One can therefore assume that an electronic transition starts from the ground vibrational level of the ground electronic state.

Electronic Transitions

Absorption and emission of light occurs very rapidly (approximately 10^{-15} sec, the time it takes for the photon to travel a single wavelength) in discrete quanta due to interaction of the oscillating electric field vector of the light wave with electrons in the molecule. This time is for the actual process of absorbing or generating a photon. The slower range of times for fluorescence and phosphorescence is the average time it takes before spontaneous emission occurs. Since at room temperature the vast majority of molecules are in the lowest vibrational level of the ground singlet electronic state, absorption of a photon of sufficient energy will excite the molecule from the ground state (S_0) to an excited state (S_1 , S_2 , *etc.*). Generally, the excitation will be to a higher vibra-

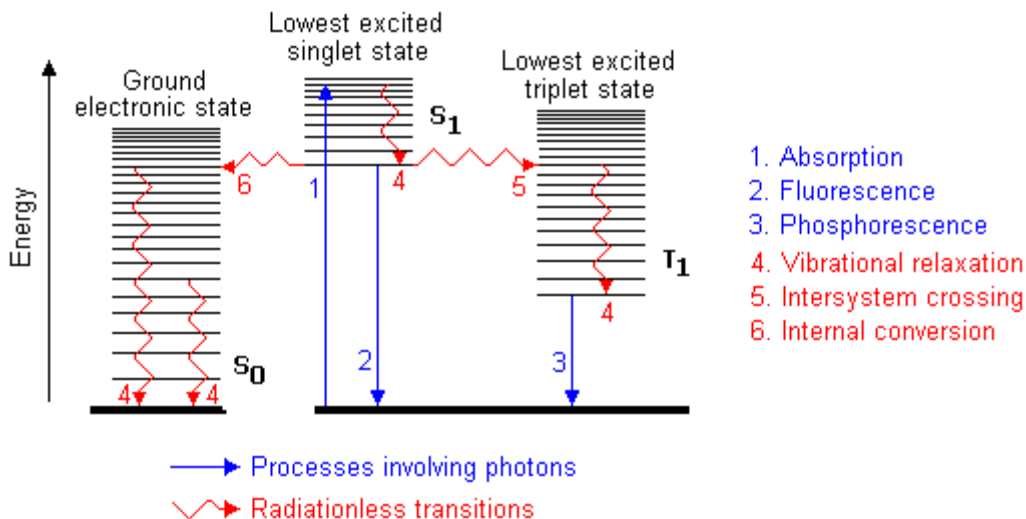
Figure 3. Simplified Luminescence Processes Following Photon Absorption



tional level of the excited state. Below is a simplified portrayal of the luminescence events. However, if one is focused on the fluorescence and phosphorescence pathways, the presence of the r -dependence of the potential surfaces and the rotational levels displayed in Fig. 3 are unnecessary complexities. Consequently Jablonski diagrams are often used which allows one to explain both the spectra and kinetics of fluorescence and phosphorescence in a rather straightforward manner.

Figure 4 depicts a Jablonski diagram which gives physical processes that may occur following absorption of a photon by a molecule. The energy diagram illustrates a singlet ground electronic state (the horizontal parallel bars labeled S_0), a lowest excited singlet (S_1 , upper set of parallel bars), and a lowest triplet (T_1). At each energy level, molecules can exist in a number of vibrational energy levels, which are represented by the multiple lines in each electronic state. Transitions between states are depicted by a vertical line connecting the ground and excited state. Generally straight lines are reserved for radiative transitions and wavy lines for nonradiative transitions. The lowest

Figure 4. Jablonski Energy Diagram: Processes Following Photon Absorption



energy absorption is the HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) transition.

Molecular Orbitals Involved in Electronic Transitions

Ground state electrons are classified as bonding, in sigma (σ) or pi (π) bonds, or as nonbonding (n), in lone pairs. Electronically excited electrons occupy antibonding molecular orbitals, sigma antibonding (σ^*) or pi antibonding (π^*) MO's. Figure 5 gives the excitation processes possible between the σ , π , and n ground states and the antibonding σ^* and π^* states though symmetry may preclude the actual transition from taking place in a particular molecule (the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions). This no-

menclature is strictly correct only for diatomics. However, it is extended to chromophores – the structural entity within a molecule which is absorbing or emitting the photon. In the 200 – 800 nm region accessible via our instrumentation, the transitions which are probed are the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in Fig. 5.

Figure 5. Possible Modes of Electronic Excitation for a Molecule

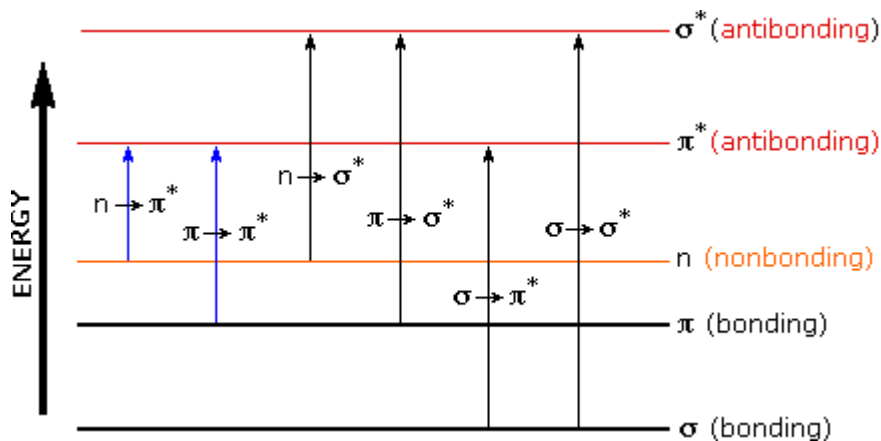


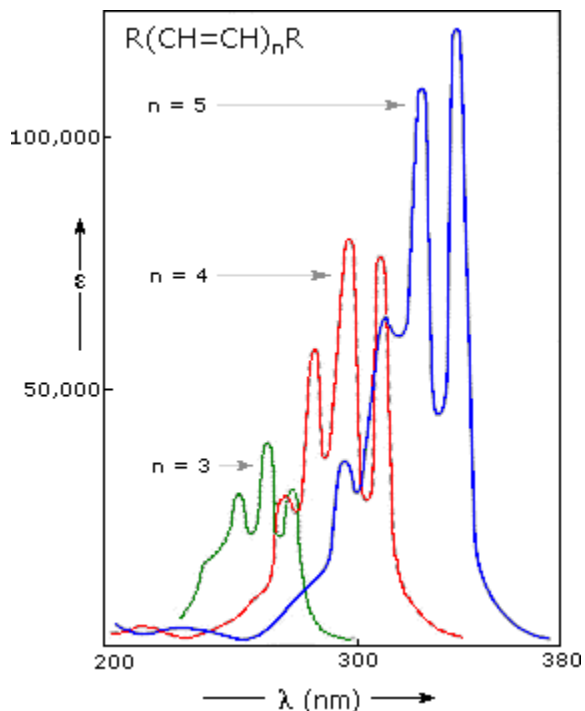
Table III gives the wavelength (λ) and extinction coefficient (ϵ) (molar absorptivity) for some chromophores absorbing in the UV/VIS region. At a given wavelength, absorbance (A) is related to the concentration (c) and pathlength (l) by $A = \epsilon cl$.

Table III. Some Typical Chromophores Absorbing in the UV/VIS

Chromophore	Example	Excitation	λ_{\max} , nm	ϵ	
C = C	ethylene	$\pi \rightarrow \pi^*$	171	15,000	
C \equiv C	acetylene	$\pi \rightarrow \pi^*$	180	10,000	
C = O	formaldehyde	$n \rightarrow \pi^*$	290	15	
		$\pi \rightarrow \pi^*$	180	10,000	
N = O	nitromethane	$n \rightarrow \pi^*$	275	17	
		$\pi \rightarrow \pi^*$	200	5,000	
C – X	X = Br	$n \rightarrow \sigma^*$	205	200	
	X = I	$n \rightarrow \sigma^*$	255	360	
C ₆ H ₅ – (C = C) _n – C ₆ H ₅	conjugated polyenes	$\pi \rightarrow \pi^*$	$n = 2$	328	56,000
			$n = 3$	358	75,000
			$n = 4$	384	86,000
			$n = 5$	403	94,000
			$n = 6$	420	113,000

The wavelength region in which a transition occurs is typical for the chromophore, irrespective of the molecular environment. Of note in Table III is the increasing ϵ and increasing wavelength of the $\pi \rightarrow \pi^*$ absorbance maximum with increasing conjugation. This effect is seen in the UV spectra given in Fig. 6.

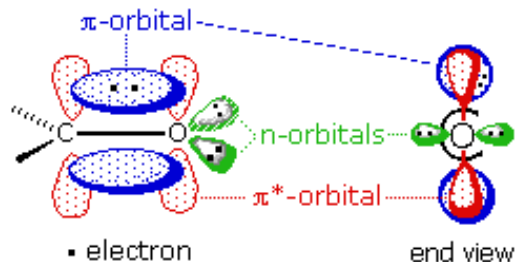
Figure 6. Effect of Conjugation on UV Spectra of Polyenes



UV Transitions of the Carbonyl Group: Formaldehyde

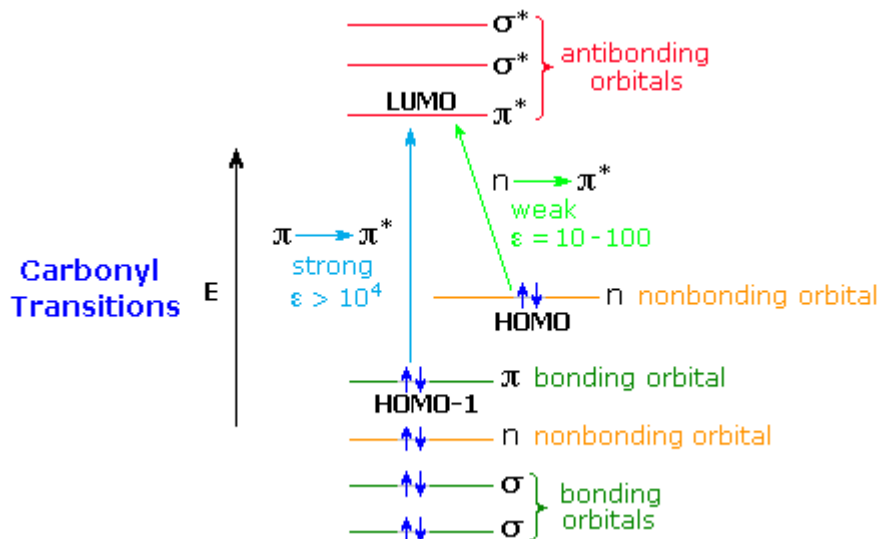
From Table III one would expect two distinct absorptions in the UV region for a molecule containing a carbonyl group (Fig. 7). The two common transitions of an isolated carbonyl group are the $n \rightarrow \pi^*$ transition (lower in energy, $\lambda_{\max} = 290$ nm), and the $\pi \rightarrow \pi^*$ transition ($\lambda_{\max} = 180$ nm). The group has 10 valence electrons ($4 + 6$) and

Figure 7. Orbitals of an Isolated Carbonyl Group



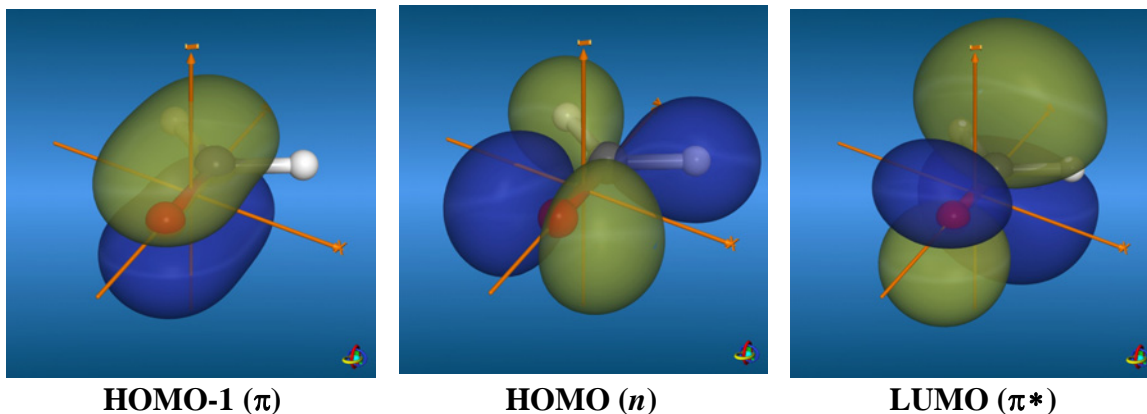
has the energy level diagram given in Fig. 8.

Figure 8. Energy Level Diagram for the Carbonyl Molecular Orbitals



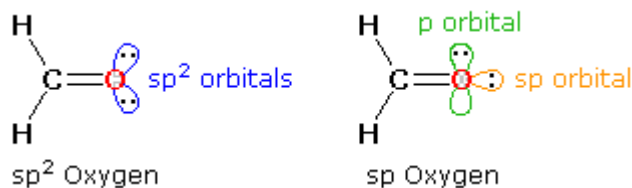
A specific molecular example can illustrate why the $n \rightarrow \pi^*$ absorption is weaker (smaller ϵ) than the $\pi \rightarrow \pi^*$ transition. Formaldehyde (CH_2O) is the simplest molecule containing a carbonyl group. There are 16 electrons ($6 + 2 \times 1 + 8 = 16$) and eight occupied orbitals. Figure 9 gives the MO's for the highest two occupied orbitals and the lowest unoccupied orbital. The weak nature of the $n \rightarrow \pi^*$ transition is attributable to the poor overlap of the p -orbital containing the higher energy electron pair (middle panel) with the π^* orbital (right panel). They are essentially orthogonal. The transition is formally “forbidden”. In contrast, π (left panel) and π^* orbitals overlap almost completely, so the probability of a $\pi \rightarrow \pi^*$ excitation is high (the probability is

Figure 9. HOMO-1, HOMO, and LUMO Molecular Orbitals of Formaldehyde



proportional to the square of the overlap integral of the π and π^* orbitals). The fact that the two lone pairs on oxygen are not equivalent may seem surprising. The energy diagram of Fig. 8 as well as the quantum calculations yielding the HOMO in Fig. 9 indicate that, contrary to the expected sp^2 hybridization for the oxygen atom given in the left side of Fig. 10, the actual hybridization of O must include a substantial contribution

Figure 10. Lewis Structures for Formaldehyde

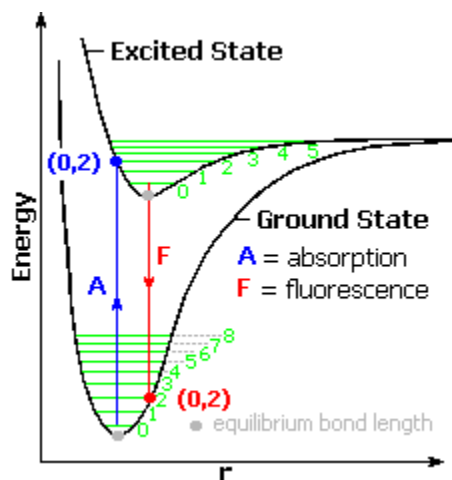


from the sp hybrid on the right. The structure given on the right has a higher energy lone pair in a p -orbital and a lower energy lone pair in an sp hybrid orbital.

Radiative Transitions: The Franck-Condon Principle and the Stokes Shift

Classically, the Franck–Condon principle states that an electronic transition is most likely to occur when the positions and velocities of the nuclei remain essentially unchanged during the transition. This approximation is founded upon the very rapid (~ 1 fs) nature of the absorption and fluorescence processes. If the nuclei do not move, their kinetic energy is zero. The electronic transition begins from the equilibrium position of the initial potential surface, shown as the two grey dots in Fig. 11. In order to make the transition, without any change in kinetic energy, the system must move to the classical turning point of the destination electronic state potential (indicated by the large blue dot)

Figure 11. Radiative Transitions between Two Electronic States



for absorption and the red dot for fluorescence). It is at the classical turning points that the motion of the system reverses and the kinetic energy is momentarily zero. The “vertical” nature of the transitions is portrayed by the straight lines *A* and *F* in the figure.

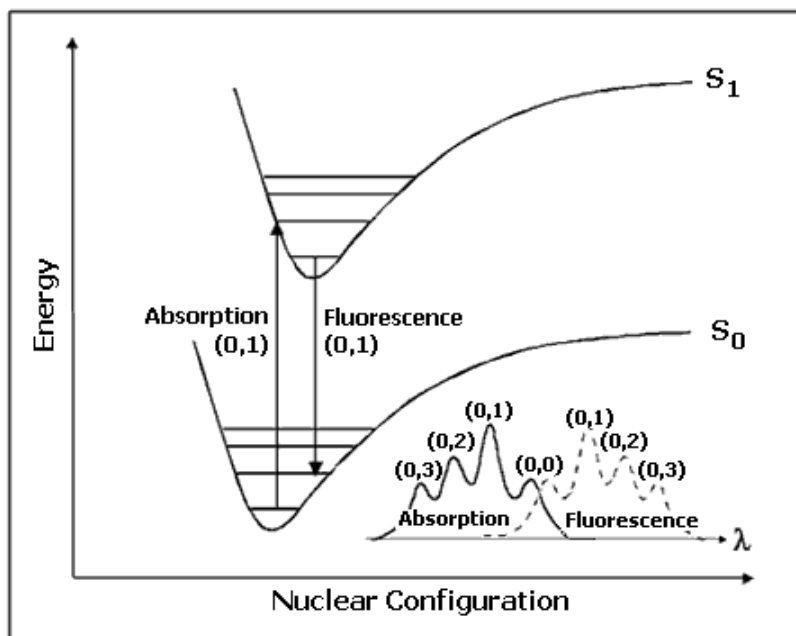
The figure plots the energy of the ground and excited states as a function of nuclear configuration (for a diatomic this is the nuclear separation). The excited state is usually shifted to the right with respect to the ground state because the molecule generally expands in the excited state (bond order decreases). During absorption, there is insufficient time for displacement of the nuclei giving rise to the vertical arrow *A* transition in the figure. The transition goes to a higher level vibrational state in which the nuclear displacements are sufficiently large to encompass the nuclear configuration of the ground initial state. After excitation, the molecule will quickly relax to the lowest vibrational level of the excited electronic state, but now under the influence of the new equilibrium position of the excited surface. The relaxation time is short compared with the lifetime of the electronic excited state. Again the Franck-Condon principle may be invoked for the fluorescence transition to the ground state. This vertical transition is given by arrow *F* and ends in a higher vibrational level of the ground state where the nuclear configuration is sufficiently expanded to match the configuration of the excited state. The quantum mechanical formulation of the Franck-Condon principle states that the intensity of a vibronic transition (its probability) is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states involved in the transition.

The Stokes shift describes the experimental observation that the fluorescence wavelength is longer than the excitation wavelength. The fluorescence absorption spectrum and, due to the rapid relaxation of the promoted state in the excited potential surface, the emission spectrum both originate from the lowest vibrational level. Energetically, then, these processes – transitions to higher vibrational levels followed by vibrational relaxation – result in the emission wavelength being redshifted (occurs at longer wavelengths or lower energies) relative to the absorption wavelength. To a first approximation there is only one transition which both have in common, the transition to and from the lowest vibrational level, the 0-0 transition. The 0-0 bands do not precisely coincide as, immediately after absorption, an excited state is produced which has the same nuclear configuration as the ground state and before emission the nuclei rearrange to accommodate the excited state electron distribution (*i.e.*, the equilibrium bond length increases as seen in Fig. 11). There can be cases of substantial overlap of the absorption and emission spectra and in resonance fluorescence there is no relaxation so the absorption and emission wavelengths are coincident.

The absorption and emission spectra reflect the vibrational level structures in the ground and the excited electronic states, respectively. Often, for fluorescing chromophores, these level structures are rather similar on both electronic surfaces since electronic excitation does not significantly alter the geometry of the molecule. Furthermore the Franck-Condon principle predicts that, for the transitions which are most probable in absorption, their inverse transitions will be most probable in emission. The

similarity of the potential surfaces and the “vertical” nature of the transitions yield absorption and emission spectra which are mirror images of each other as seen in Fig. 12.

Figure 12. Absorption and Emission Spectra: Stokes Shift and Mirror Image Rule



The Electronic Excited State

The absorption of a photon of energy by a chromophore is an all or nothing process and can only occur with specific quanta of incident light of specific wavelengths. If the absorbed photon contains more energy than is necessary for an electronic transition, the excess energy is generally converted into vibrational and rotational energy. On the other hand, if a collision were to occur between a molecule and a photon having insufficient energy to promote a transition, no absorption occurs. For solutions, the absorption band is broadened rather than consisting of sharp peaks due to the closely spaced vibrational energy levels in addition to thermal motion that admits a range of photon energies which match a particular transition.

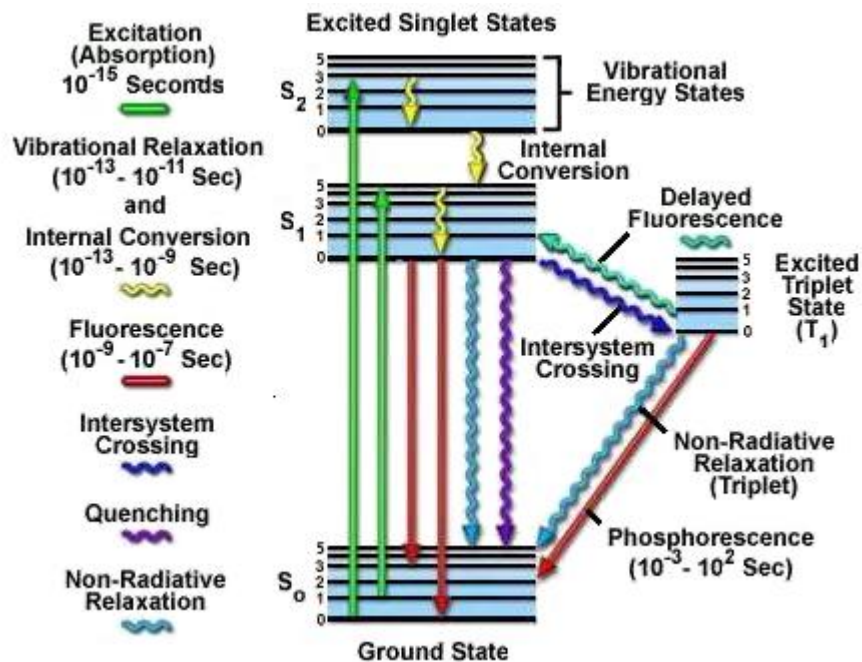
Optical transitions excite molecules from the lowest vibrational level of the electronic ground state to an accessible vibrational level in an electronic excited state in ~ 1 fs. Since the ground electronic state is a singlet state, the destination electronic state is also a singlet because excitation of a molecule by absorption normally occurs without a change in electron spin-pairing. All internuclear distances and angles (including those involving the solvating environment or different conformations) are therefore preserved in the excited state. Consequently, the energies of vibrational and rotational transitions do not change during the optical transition. They will do so only after the optical transition has occurred.

The excited state can undergo numerous processes. Some include structural changes such as dissociation, predissociation, or initiation of a photo-induced chemical reaction. These are not the emphasis here. Upon promotion to an excited electronic state the excess energy can be eliminated and the molecule returned to its ground state by a number of radiative and nonradiative processes.

Radiative and Nonradiative Decay Pathways (What Goes Up Must Come Down)

Radiative decay describes molecular deexcitation processes which are accompanied by photon emission, most notably fluorescence and phosphorescence. Molecules in excited electronic states can also relax by nonradiative pathways where excitation energy is not converted into photons but is dissipated by thermal processes such as vibrational relaxation and collisional quenching. In addition, there are the isoenergetic processes of internal conversion and intersystem crossing which enable transitions between different electronic states with the same or different spin multiplicities, respectively. The Jablonski diagram in Fig. 13 offers a convenient representation of the excited state structure and the relevant transitions.

Figure 13. Jablonski Diagram: Overview of Luminescence



Initially Created Excited Electronic State on S₁ and S_n

With ultraviolet or visible light, common fluorophores (molecules which fluoresce and/or phosphoresce) are usually excited to higher vibrational levels of the first (S₁) or second (S₂) singlet electronic energy state as they, too, are generally singlets in

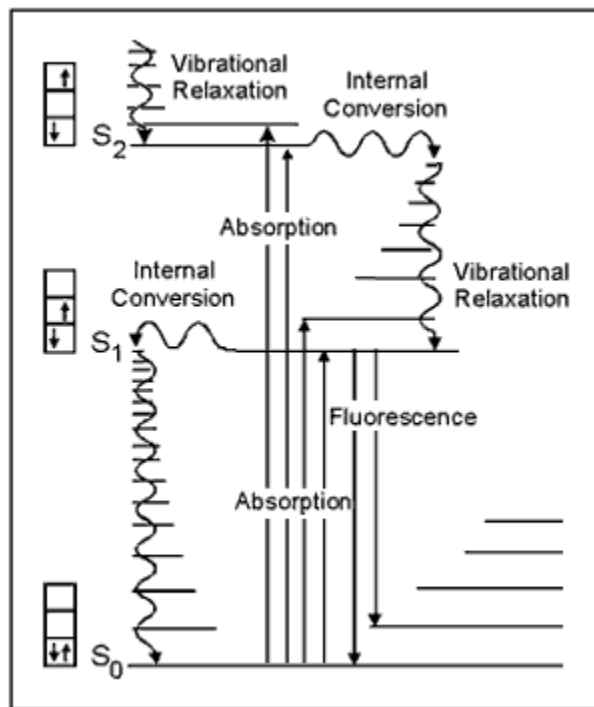
their ground state. One of the absorption (or excitation) transitions, shown by the left-hand vertical arrow, occurs from the lowest vibrational energy level of the ground electronic state to the third vibrational level in the second excited state. Another transition is depicted from the second vibrational level of the ground state to the highest vibrational level in the first excited state ($S_0, \nu = 2$ to $S_1, \nu = 5$). Irradiation with a wide spectrum of wavelengths generates an entire range of transitions that populate the various vibrational energy levels of the excited states. These transitions have varying degrees of probability and, when combined, comprise the absorption spectrum of the molecule.

Vibrational Relaxation and Internal Conversion on S_1 and S_n

Immediately following absorption of a photon, an electronically, vibrationally, and rotationally excited molecule will most likely relax to the lowest vibrational energy level of the first excited state (small wavy vertical arrow in Fig. 13 connecting the $\nu = 5$ with the $\nu = 0$ vibrational levels of S_1). This process of vibrational relaxation occurs in less than a picosecond. The excess vibrational energy is converted into heat, which is absorbed by neighboring molecules upon colliding with the excited state fluorophore. Other relaxation processes are at least four orders of magnitude slower than vibrational relaxation. Consequently, molecules virtually always completely relax to their ground vibrational level during their excited lifetimes. Furthermore, the molecule has sufficient time to achieve a thermally equilibrated lowest-energy excited state. Take a typical C – H bond whose stretching frequency is 10^{14} Hz: in 10^{-9} s (a nanosecond – typical lifetime of an excited molecule on S_1) the bond will have completed 100,000 cycles of vibration!

If the molecule were promoted to an electronically excited state higher than S_1 another mode of relaxation, internal conversion, becomes available. Internal conversion is the isoenergetic transfer of electronic energy into vibrational energy of the fluorophore itself by a radiationless transition to a higher vibrational level of a lower electronic surface of the same multiplicity. It is the spontaneous relaxation of an electron to a lower energy state, accompanied by a simultaneous increase in vibrational energy of the molecule. It is shown in Fig. 13 by the wavy vertical arrow connecting S_2 with S_1 . Higher singlet states decay so rapidly by internal conversion ($\sim 10^{-13}$ to 10^{-11} sec) that other processes from these states, such as fluorescence, cannot compete. However, vibrational relaxation still cools the molecule to its lowest vibrational level even in highly excited electronic states as it is a faster process (energy gap between adjacent vibrational levels is smaller than the gap between electronic states). Internal conversion is even possible from S_1 to the ground state as Fig. 14 indicates, though the larger energy difference between S_1 and S_0 than between the more highly excited electronic states makes the process slower ($\sim 10^{-11}$ to 10^{-9} sec). As internal conversion to the ground state is a slower process, other relaxation mechanisms become more important. Note that in Fig. 13 internal conversion appears to be an energy “loss” process as the arrow representing it is pointing straight down and S_2 is “above” S_1 . The y-axis in Fig. 13 should not be interpreted as an accurate indication of energy. More appropriate descriptions in a Jablonski diagram are given by Figs. 4 and 14 in which internal conversion is properly shown as a “horizontal” transition.

Figure 14. Vibrational Relaxation and Internal Conversion



Fluorescence from S_1

An excited molecule typically resides in the lowest excited singlet state (S_1) for periods on the order of 10^{-8} sec before finally relaxing to the ground state. If relaxation from this long-lived state is accompanied by emission of a photon, the process is known as fluorescence. The lifetime of an excited singlet state is approximately 10^{-9} to 10^{-7} sec and therefore the decay time of fluorescence is of the same order of magnitude. If unperturbed by competing processes, the lifetime of fluorescence is the intrinsic lifetime of the excited singlet state. The closely spaced vibrational energy levels of the ground state, coupled with normal thermal motion, produce a wide range of photon energies during emission. As a result, fluorescence is normally observed as emission intensity over a band of wavelengths rather than a sharp line. Even though a quantum of radiation is emitted in fluorescence this quantum is, on average, lower in energy than the quantum absorbed by the molecule due to vibrational relaxation (both after absorption and after emission). This shifts the fluorescence spectrum to longer wavelength, relative to the absorption spectrum, the Stokes Shift.

Quenching of Fluorescence

A number of important solutes, such as oxygen and halide ions, are efficient fluorescence quenchers, reducing the fluorescence intensity. Upon collision, the fluorophore is deexcited nonradiatively in a nonradiative energy transfer process called

collisional or dynamic quenching. Ground state molecular oxygen reacts with excited singlet as well as triplet states of many potential fluorophores. It promotes intersystem crossing of S_1 to T_1 thereby quenching fluorescence. In static quenching the quencher forms a nonfluorescent complex with the ground state of the fluorophore.

Intersystem Crossing and Other Relaxation Processes Competing with Fluorescence

Several other relaxation pathways that have varying degrees of probability can precede or compete with the fluorescence emission process. The excited state can dissipate its excess energy nonradiatively as heat (illustrated by the left-most vertical wavy arrow in Fig. 13), the excited fluorophore can collide with another molecule to transfer energy in a nonradiative process (*e.g.*, collisional quenching, as indicated by the right-most vertical wavy arrow), or the molecule can transfer to the lowest excited triplet state (T_1) in a phenomenon known as intersystem crossing (the lower diagonal wavy arrow in the figure). The latter process is relatively rare, but ultimately results either in emission of a photon through phosphorescence or a transition back to the excited singlet state before returning to the ground state as delayed fluorescence.

Intersystem crossing is a spin-dependent internal conversion, an isoenergetic transfer of electronic energy (horizontal transition) into vibrational energy of the fluorophore by a radiationless transition to a higher vibrational level of a lower electronic surface. As opposed to internal conversion, the lower electronic potential energy surface has a different electron spin multiplicity. The low probability of intersystem crossing arises from the fact that molecules must first undergo spin conversion (quantum mechanically this is spin orbit coupling) to produce unpaired electrons, an unfavorable, “forbidden” process.

Energy transfer, in the form of vibrations and rotations, is enhanced by physical contact of the excited molecule with other particles with which heat can be transferred. In practice most excited state molecules never emit any energy because other molecules are present with which the excited molecule can collide and transfer its energy before a radiative event can occur. The lifetime of a triplet state is much longer than that of an excited singlet state (about 10^{-4} to 10 sec) and therefore loss of excitation energy by collisional transfer is generally enhanced.

Phosphorescence from T_1

A radiative transition from the triplet excited state to the singlet ground state requires another change of spin multiplicity. Transitions between triplet states and singlet states are forbidden (actually have a very low probability of occurrence) so the time scale for phosphorescence emission is several orders of magnitude larger than that for fluorescence. Emission from the triplet state occurs with lower energy relative to fluorescence (T_1 is lower in energy than S_1) and the emitted photons have longer wavelengths.

Summary of Major Processes

Absorption ($\sim 10^{-15}$ s) – At room temperature, the vast majority of molecules are in the lowest vibrational level of the ground electronic state (generally a singlet). Absorption of a photon promotes the molecule from the ground state (S_0) to an excited electronic state of the same multiplicity (S_1 , S_2 , etc.). Most often, the excitation is to a vibrationally excited level of the upper state.

Vibrational relaxation ($\sim 10^{-13}$ to 10^{-11} s) – This process occurs within a given electronic state. When a molecule accesses a vibrationally excited level of an electronic state, it will quickly relax to the lowest vibrational level of that state. The energy is released as heat to the surroundings through collisions with other molecules.

Internal conversion ($\sim 10^{-13}$ to 10^{-9} s) – This is a radiationless transition between two electronic states having the same spin multiplicity (i.e. $S \rightarrow S$ or $T \rightarrow T$). It is an isoenergetic process (horizontal transition) in which the excess electronic energy of the upper state is deposited into higher vibrational levels of the lower state. The large variability in the time scales results from the faster conversions between highly excited states ($\sim 10^{-13}$ to 10^{-11} s) compared with the slower internal conversion process between S_1 and S_0 (10^{-11} to 10^{-9} s).

External conversion: This is a radiationless transition between two electronic states having the same spin multiplicity (i.e. $S \rightarrow S$ or $T \rightarrow T$) where the transition to the lower state is induced by collisions. The collisional deactivation eventually converts the electronic energy into heat. Term often used interchangeably for collisional quenching.

Fluorescence ($\sim 10^{-9}$ to 10^{-7} s) – This is a radiative transition which generally occurs from the lowest vibrational level of the first excited state (S_1) to a higher vibrational level of the ground state (S_0).

Intersystem crossing ($\sim 10^{-10}$ to 10^{-4} s) – This is a radiationless transition between two electronic states of different spin multiplicity (i.e. $S \rightarrow T$ or $T \rightarrow S$). It is an isoenergetic process (horizontal transition) in which the excess electronic energy of the upper state is deposited into higher vibrational levels of the lower state. As the lower electronic state has a different spin multiplicity, this pathway requires a reversal of electron spin which is a forbidden process. The low probability of spin reversal accounts for the large variation in times.

Phosphorescence ($\sim 10^{-6}$ to 10^2 s) – A radiative transition which requires an interaction leading to a change of electronic spin. This can be achieved through interactions with other molecules or through spin-orbit coupling within the molecule. For isolated or shielded molecules, it can lead to phosphorescence emission. For non-protected molecules in solution, it generally leads to nonradiative deexcitation because phosphorescence is a very slow process, leaving many opportunities for nonradiative decay.

Web References

1. Michael K. Dent, University of Guelph:
http://131.104.156.23/Lectures/CHEM_207/uv-vis.htm
2. Brian Herman, Joseph R. Lakowicz, Douglas B. Murphy, Thomas J. Fellers and Michael W. Davidson; Universities of Texas, Maryland, John Hopkins, Florida State
<http://www.olympusfluoview.com/theory/fluoroexciteemit.html>
3. Stefan Immel, Technical University of Darmstadt
<http://csi.chemie.tu-darmstadt.de/ak/immel/tutorials/orbitals/molecular/formaldehyde.html>
4. Ian D. Johnson, Michael W. Davidson; Florida State University (**excellent tutorial**)
<http://www.olympusmicro.com/primer/java/jablonski/jabintro/index.html>
5. William Reusch, Michigan State University:
<http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/spectrum.htm#uv1>
<http://www.cem.msu.edu/~reusch/VirtualText/photchem.htm>
6. Michael A.J. Rogers, Bowling Green State University
[http://www.bgsu.edu/departments/chem/faculty/rogers/701/AAPOWERPOINT_PRESENTATION2\(15\).ppt](http://www.bgsu.edu/departments/chem/faculty/rogers/701/AAPOWERPOINT_PRESENTATION2(15).ppt)
7. Kendric C. Smith, Stanford University
<http://www.photobiology.info/Photochem.html>
8. Yufeng Wei, Rockefeller University
http://www.rockefeller.edu/spectroscopy/flouresence2_pop.php
9. <http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/lumin1.htm>