ORGANIC PHOTO-CHEMISTRY

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Contents

Summary

Photo-chemistry is a branch of chemistry with a long history. First reactions are reported since the middle of 18th century. If one considers the light as a reagent, a photo-chemical reaction can treated as a normal chemical reaction where, in some cases, the high energy content of the excited state of a reagent can be seen as the transition state. The interaction of the matter or of a molecule with the light, i.e. a photo-physical process, is always the starting point for any other processes, chemical reactions included. The knowledge of the principal photo-physical processes and of the primary photo-chemical processes is essential for a deep comprehension of organic photo-chemistry. The principal photo-physical processes are analyzed in the first part of this work, while the principal primary photo-chemical processes, furnished with a selection of representative examples, are reported in the second part. The selection of the examples has been done with the aim of providing the reader an overview of the potential of photo-chemistry from the organic synthesis point of view.

1. Introduction

Any organic reaction needs energy to occur, which can be stored in the reagents/reactants in cases where very reactive or high energy contents species are used, or should be supplied by other means from external sources.
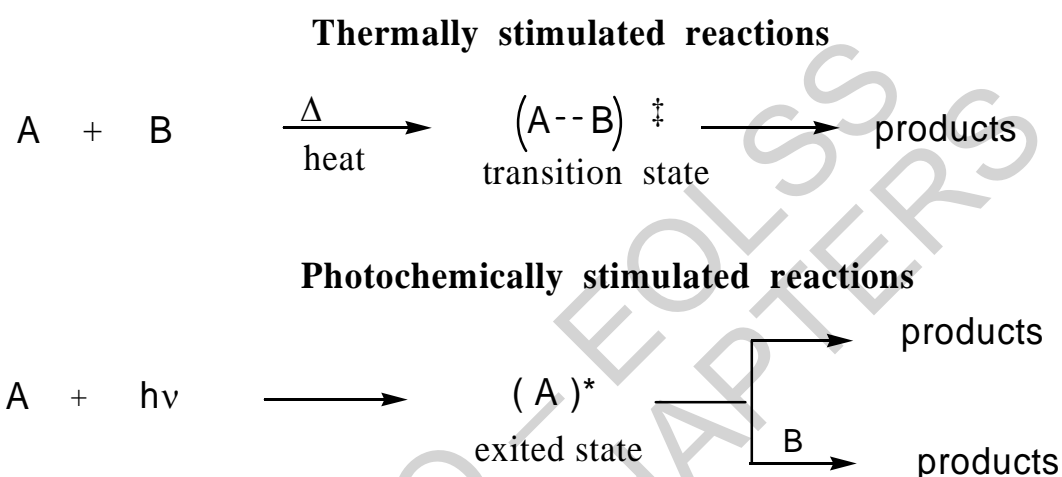
Classification of Electromagnetic spectrum	Wavelength Å	Frequency cycles/s	Wave number cm^{-1}	Energy kcal/einstein	
Far infrared	10^5 (10μm)	3×10^{13}	10^3	2.86	
Near infrared	10^4 (1μm)	3×10^{14}	10^4	28.6	
Visible light					
red	7×10^3(700nm)	4.28×10^{14}	1.43×10^4	40.8	
orange	6.2×10^3(6200nm)	4.84×10^{14}	1.61×10^4	46.1	
yellow	5.8×10^3(580nm)	5.17×10^{14}	1.72×10^4	49.3	**Photo-chemistry region**
green	5.3×10^3(500nm)	5.66×10^{14}	1.89×10^4	53.9	
blue	4.7×10^3(470nm)	6.38×10^{14}	2.13×10^4	60.8	
violet	4.2×10^3(420nm)	7.14×10^{14}	2.38×10^4	68.1	
ultraviolet					
near ultraviolet	3×10^3(300nm)	10×10^{14}	3.33×10^4	95.3	
medium ultraviolet	2×10^3(200nm)	15×10^{14}	5.00×10^4	142.9	
far and Schumann	1.5×10^3(150nm)	20×10^{14}	6.67×10^4	190.6	
X ray	$3 \times 10^2 \div 1$(30÷0.1nm)	$10^{16} \div 3 \times 10^{18}$	$3.33 \times 10^5 \div 10^8$	953÷285,910	**Radiation chemistry region**
γ-rays	10^{-2}	3×10^{20}	10^{10}	28,591,000	

Table 1: Wavelength in vacuum, Frequency and energy distribution of Electromagnetic Radiation

In usual laboratory organic chemistry, energy is supplied thermally or from microwaves or ultrasounds as more recently reported. All these sources of energy usually affect only the ground state of a molecule by increasing its translational, rotational and vibrational energy, although under special conditions electronic excited states can be reached or involved. By contrast, photo-chemistry deals with the study of chemical and physical changes (chemical reaction included) which result from the interaction of radiation from the visible and higher energy regions of the electromagnetic spectrum. Table 1 reports an approximate classification of the electromagnetic spectrum and the units commonly used in its description.

When the energy of the electromagnetic radiation falls in the ultraviolet (UV) or visible region (VIS) which is sufficient to promote electrons to excited states of either atoms or molecules, photo-chemical processes can be observed. In photo-chemical reactions light must be considered as a reagent which interacts or in chemical terms "reacts" directly with the electrons (σ and π electrons and lone pairs). In a classical thermally stimulated reaction, the extra energy supplied to the reagents, is necessary for reaching and overcoming the transition state at higher energy and for its evolution into the final products. Similarly, when the light (or photons in its quantum mechanics description) interacts with the electrons of a molecule or an atom, a high energy state is generally

produced which can be pictured as the transition state of a photo-chemical reaction. This high energy state or electronically excited state of the molecule is the heart of all "photo-stimulated processes" [the formation of eccimers (i.e. AA* adduct, where A* is the A molecule in a excited state) or exciplexes (i.e. A*B or (AB)* adducts should consider together with the excited A* as possible transition states for a photo-chemical reaction]. Thermal and photo-chemical stimulated processes are strongly different: in thermal processes all atoms of the molecule in its ground states are stimulated with a continue variation of the energy along the reaction coordinate; photo-chemical process deals directly with the quantum or discrete nature of the light-matter interaction (Scheme 1).

Thermally stimulated reactions

$$A \; + \; B \quad \xrightarrow[\text{heat}]{\Delta} \quad \left(A\text{--}B\right)^{\ddagger} \quad \xrightarrow{\hspace{1cm}} \quad \text{products}$$

transition state

Photochemically stimulated reactions

$$A \; + \; h\nu \quad \xrightarrow{\hspace{2cm}} \quad \left(\,A\,\right)^{*}$$

exited state

products

B products

Scheme 1: Comparison between thermally and photo-chemically stimulated reactions

2. Photo-physics: Interaction of Light with Matter and Photo-stimulated Processes
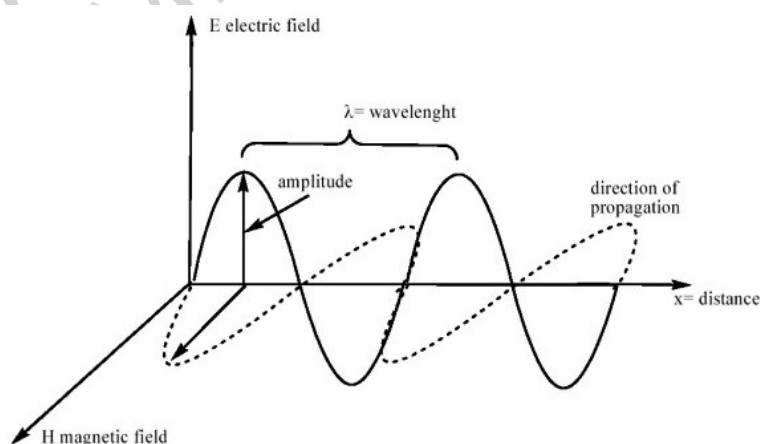
2.1. Interaction with Atoms

Figure 1: The instantaneous electric (E_y) and magnetic (H_z) strength field vectors of

light wave as a function of position along the axis of propagation (*x*)

Light is usually represented as electromagnetic radiation (described in terms of a transverse plane wave involving associated electric and magnetic fields) since this picture successfully accounts for many of the induced phenomena resulting by its interaction with the matter.(Fig.1).

The electric and magnetic components of light tend to set the electrons of a molecule or atom into oscillation from their natural motion around nuclei with a force which is proportional to the intensity of these two components: $F \propto eE + eHv/c$, where e is the electron charge, v the speed of moving electron, c speed of light in vacuum, E and H the intensity of electric and magnetic field respectively.
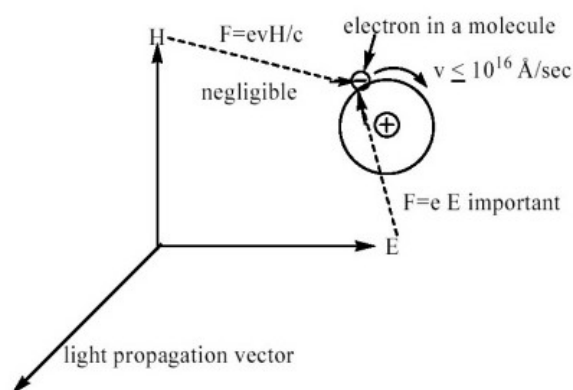

Figure 2: Interaction of electric field E and magnetic field H of an electromagnetic wave with an electron in an orbital.

Since the speed of electrons is at least two orders of magnitude lower than the speed of light, the magnetic contribution to the total force exerted is negligible (Fig.2).

Two principal phenomena arise from this interaction in relation to the energy of light.

i) The energy of light does not match with the difference in energy between occupied and unoccupied atomic orbitals or occupied bonding and unoccupied antibonding molecular orbitals, *i.e.* there is no absorption of light by the matter. The light is reflected or refracted by the matter and these phenomena are governed by the laws of classic optical physics.

ii) The energy of light matches with the energy gap between bonding and antibonding molecular orbital or atomic orbitals. In this case the energy is called resonant with the frequencies at which electrons oscillate in bonds and around nuclei. For atoms, typically these frequencies fall in the range of 10^{15}-10^{16} s^{-1} *i.e.* 200-700 nm (visible and ultraviolet region). The interaction in such a case forces the electron to oscillate resonantly with the electromagnetic radiation and its motion describes an orbital at higher energy. This process is pictured for a hydrogen atom for a transition of an electron from a 1*s* orbital to a 2*p* orbital, which occurs at 121.6 nm (Fig. 3).

After 10^{-7} o 10^{-8} s., the excited atom relaxes to ground state 1s emitting a photon of the same energy (121.6 nm). All atoms in the vapor phase show practically coincident absorption and emission bands.
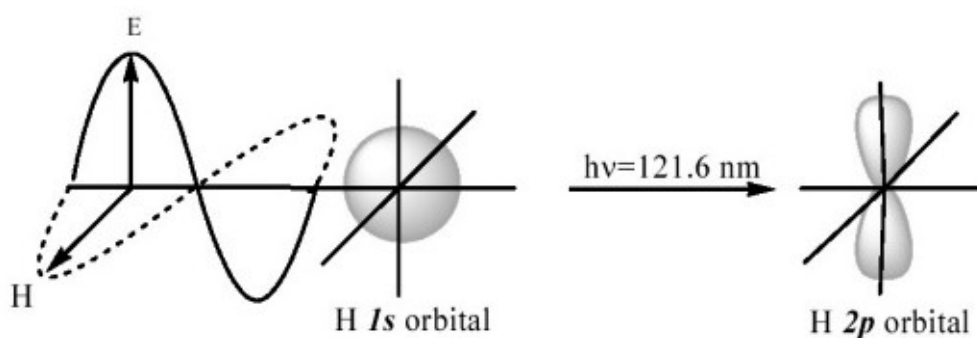
Figure 3: Pictorial visualization of the interaction of electric field with an electron in a hydrogen atom the corresponding to the 1*s* to 2*p* transition at 121.6 nm
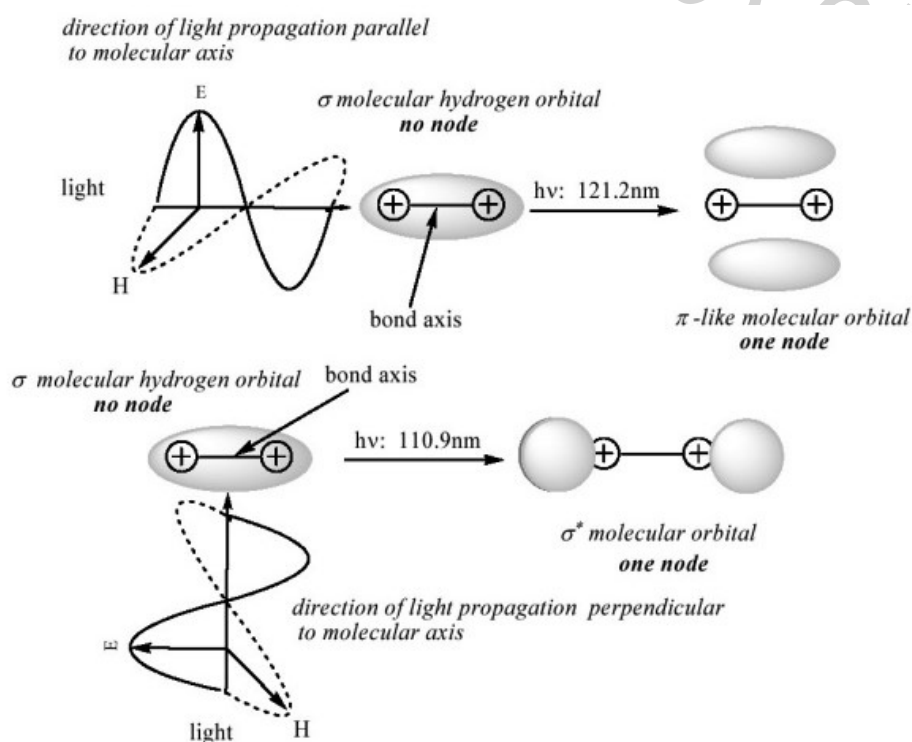
2.2. Interaction with Molecules

Figure 4: Pictorial representation of light absorption by a hydrogen molecule positive ion. The light wave and 1σ orbital have two possible resonances: one interaction of electric field (upper drawing) drives the electron into oscillations perpendicularly to the bond axis; the other (lower drawing) drives the electron into oscillation along the bond axis

The same considerations seen for atoms are also valid for molecules. In this case the involved electrons are those of molecular orbitals of cylindrical σ or plane symmetric π orbitals. The absorption or emission of light occurs from transitions involving two molecular orbitals of different energy. Furthermore, interaction of electromagnetic radiation with the electrons can occur along different directions with respect to the axis of the ground state molecular orbital and in such cases the corresponding oscillation of the electrons from their equilibrium position can describe different molecular orbitals

with different energies. In Figure 4, this aspect is analyzed for molecular hydrogen (H_2). When the electric field of the incident light is directed along the molecular axis a π orbital is produced (absorption at 121.2 nm) whereas for light polarized perpendicularly to the molecular axis a σ antibonding orbital is described (absorption at 110.9 nm). In other words, in the first case the transition may occur from a σ bond to π-like orbital, while in the second case the transition may occur from σ bond to antibonding σ orbital.

2.3. Photo-physical Processes

As shown in Table 1, organic molecules can undergo photo-chemical processes by absorbing light in the visible and ultraviolet region. Excluding radicals (*e.g.* molecules with unpaired electrons) which are paramagnetic, all organic compounds are diamagnetic in the ground state, with paired (antiparallel) electron spins in the bonding molecular orbitals (singlet state indicated as S_0). The absorbed energy causes the excitation or promotion of an electron from an initially occupied low energy orbital to a higher energy unoccupied orbital giving rise to one of two possible coupled spin states: either an electronic excited singlet state S_1 with paired antiparallel electron spins ($s=1/2$ with the magnitude of the total combined spin $S = 0$) or an electronic excited triplet state T_1 with electron spins pointing in the same direction or unpaired electrons ($S = 1$). The term singlet arises from the fact that paired spin electrons with combined spin $S = 0$ have only a single component of the angular momentum in a vector model of coupled momenta. For example, under the influence of an external magnetic field an electronic state is split into $2S+1$ quantized states along the direction of the field. Hence, three states are possible for an excited state with two unpaired electrons whereby the electron spins can be both aligned with the external magnetic field in the + and – z direction or their components along the z direction point in opposite directions giving a zero resultant. For an organic molecule many different singlet or triplet excited states S_n and T_n are possible; T_n electronic states are referred to as spin electronic isomers since they have the same situation of unpaired electrons and are different from spin isomers of S_n electronic states where no unpaired electrons are present. For symmetry reasons, quantum mechanics selection rules state that electrons can "jump" only within spin electronic isomers or in other words, transitions between T_n and S_n spin isomers are forbidden. Excited molecules after a certain time recover to the ground state by releasing the absorbed energy by different ways via photo-physical/photo-chemical processes. A photo-physical process is a transition that exchanges an excited state with another or an excited state with the ground state and always occurs before any chemical transformation. Physical processes are also classified as *radiative* (i.e. absorption or emission of light occurs during this process) and *radiationless* processes (i.e. processes where light is not involved).

Common radiative physical processes are:

1) "Allowed" or singlet-singlet absorption ($S_0 + h\nu \rightarrow S_1$ or S_n) (S_0 + h$\nu \rightarrow S_1$ or S_n). This absorption is experimentally characterized by the extinction coefficient ε_s (subscript s means singlet-singlet transition)

2) "Forbidden" singlet-triplet absorption ($S_0 + h\nu \rightarrow T_1$ or T_n) characterized by the extinction coefficient ε_t (subscript t means singlet- triplet transition).

3) "Allowed" or singlet-singlet emission $(S_1$ or $S_n \rightarrow S_0 + h\nu)$ called *fluorescence* and characterized by the radiative rate constant k_F.

4) "Forbidden" triplet-singlet emission $(T_1$ or $T_n \rightarrow S_0 + h\nu)$ called *phosphorescence* characterized by the radiative rate constant k_P

Common *radiationless* photo-physical processes are:

5) "Allowed" transition between state of the same spin (singlet or triplet). These transitions, termed *internal conversion (IC)*, occur by absorption or production of heat. They are commonly encountered in relaxing processes from high to low energy state (e.g., $S_n \rightarrow S_{n\text{-}1}$ or $T_n \rightarrow T_{n\text{-}1} + heat$) and are characterized by the rate constant k_{IC}.

6) "Forbidden" transition between excited states of different spin, called *intersystem crossing* (*ISC*), are essentially encountered in relaxing processes with heat production (e.g., $S_n \rightarrow T_n$ or $T_n \rightarrow S_{n\text{-}1} + heat$) and characterized by the rate constant k_{ST} or k_{TS}.

7) From both singlet and triplet excited states chemical processes, characterized by their reaction rate constant k_R^S and k_R^T can occur.
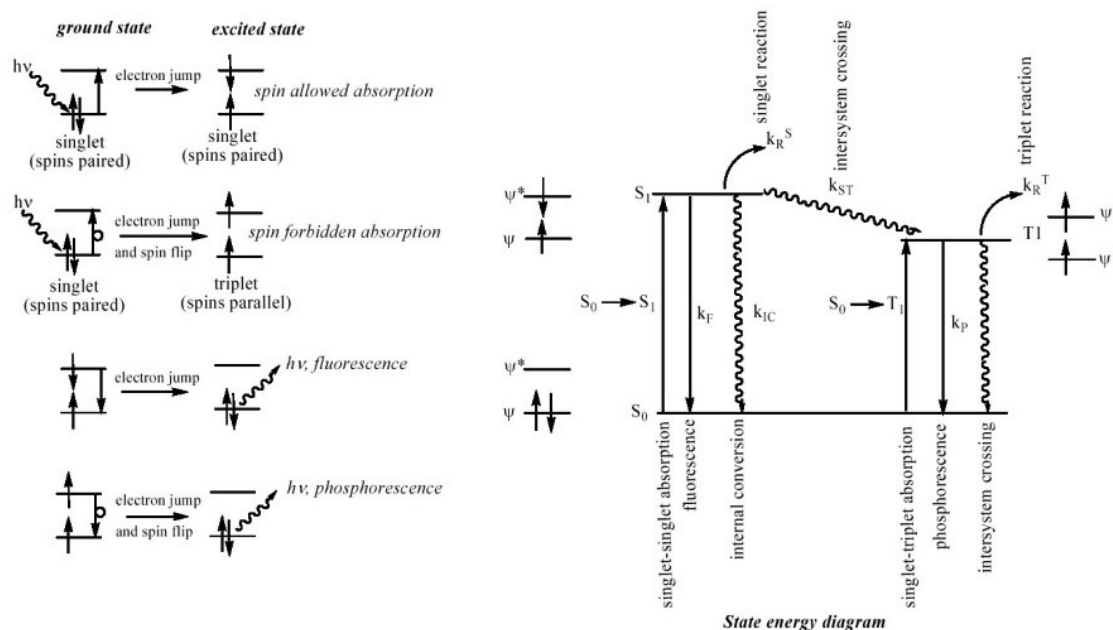

Figure 5: Energy level description and state energy diagram of absorption and emission. The arrows indicate photons and the spin orientation; wavy arrows indicate photons.

It is obvious that only photo-chemical processes whose rate constants k_R^S and k_R^T are higher than a quenching *radiative* (fluorescence lifetime $k_F 10^{-15} \div 10^{-6}$ sec.; phosphorescence $10^{-6} \div 30$ s.) or *radiationless* (relaxation to the ground state by internal conversion from singlet excited or intersystem crossing from triplet excited state) photo-physical processes can be observed. Thus a good comprehension of the photo-physical

properties of a molecule is essential in order to discriminate between the various photo-chemical decay processes. All these processes are schematized by an energy state diagram shown in Figure 5.

In contrast to atoms, where the electronic transition between two allowed electronic states occur exchanging the same energy (i.e. absorption and emission of light of the same energy), in molecules these processes are complicated by their vibrational and rotational degrees of freedom. Each electronic state (ground singlet or excited singlet or triplet) described by the Lennard-Jones potential energy function, is divided into quantized vibrational and rotational levels, each one characterized by a quantum number and a wave function solutions of the complete Schrödinger equation (Fig. 6).

Another version of the energy state diagram, known as Jablonski diagram, where both vibrational and rotational level are taken into account is shown in Fig. 7. Absorption occurs from the lowest vibrational level v_0 of the S_0 electronic level (this vibrational level is practically the only populated one at room temperature) to the v_n vibrational level and r_n rotational level of the S_n excited level. In the *radiationless* (internal conversion) processes, the absorbed energy is dissipated over all allowed vibrational or rotational states otherwise radiative processes can take place (fluorescence or phosphorescence). The probability of these transitions are regulated by the *Frank-Condon factor* or overlap integral, which states that a transition occurs between vibrational levels where a net positive overlap of the vibrational wave function v_0 of the ground state S_0 with the v_n of the excited state S_n exists; the degree of this overlap accounts for the intensity of the absorption and emission bands related to the transition (Fig.6).
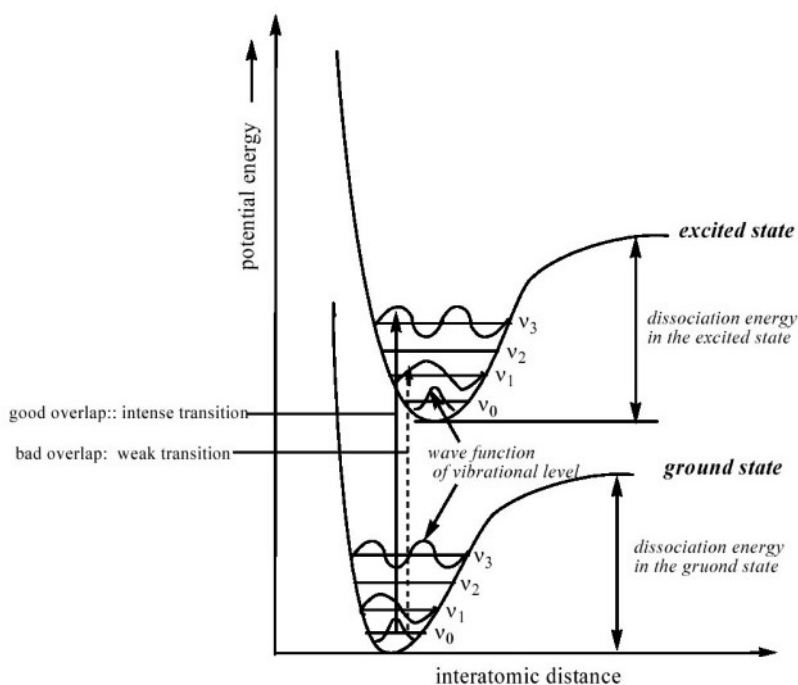

Figure 6: Lennard-Jones potential energy diagram in relation to interatomic distance for the ground state and the first singlet excited state of a molecule. Quantized vibration levels are shown with the corresponding wave function. Intense transitions are observed

when a good overlap between the wave function of the ground ν_0 vibrational level and ν_n of the excited state.

During the transition (excitation process), only electrons are reorganized; the heavier nuclei remain in their ground state geometry. This condition is referred to as the *Franck-Condon principle*.

The emission in molecules occurs always from the lowest vibrational and rotational level of the excited state (*Kasha rule*) and, as a consequence, the maximum of emission is found at lower energy than that of absorption (Figs. 7,8).
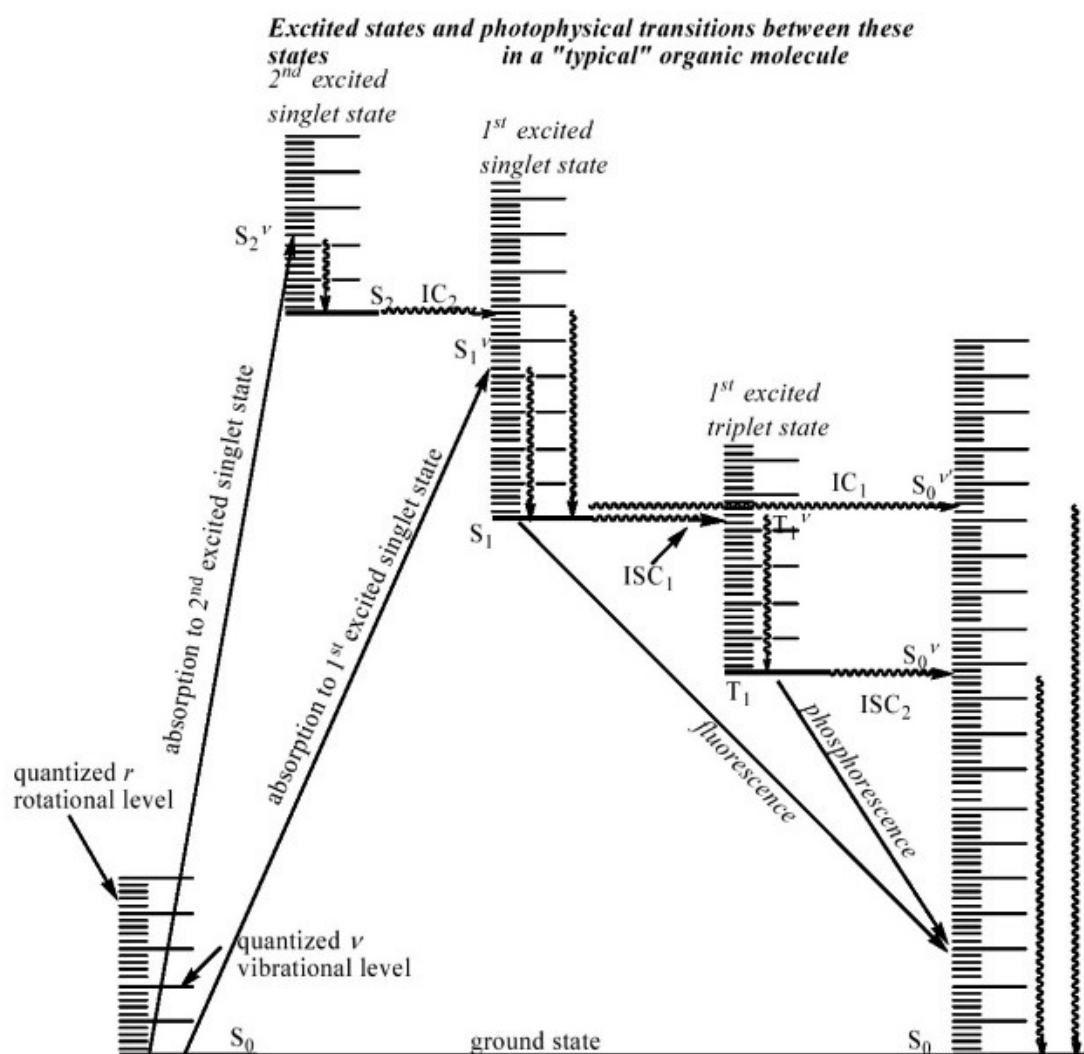

Figure 7: Jablonski diagram: solid lines are radiative transition; wave lines are radiationless processes: vertical are vibrational and rotational relaxation processes; horizontal IC: internal conversion, ISC: intersystem crossing.

In relation to the density of vibrational levels, the absorption or the emission spectrum appears as a structured band with visible vibrational structure (case b Fig.8) or as a broad band (case c Fig. 8).
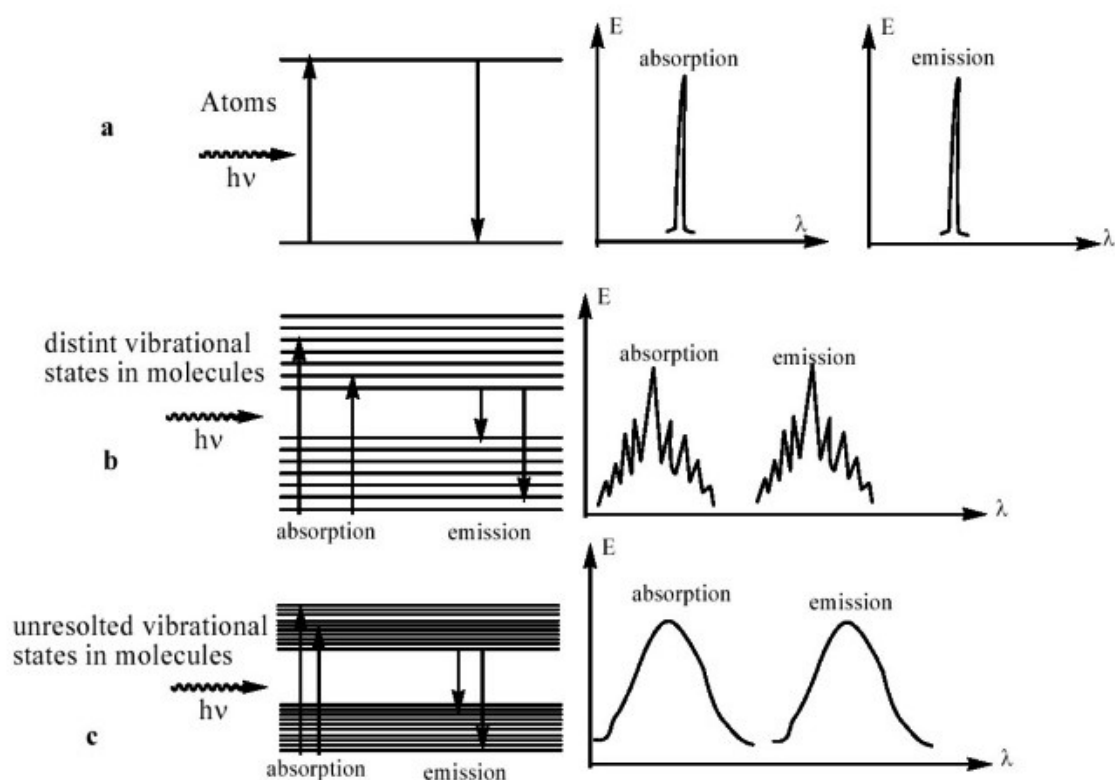
Figure 8: a: sharp line absorption and emission typical of atoms at low pressure vapor phase;
b: broad-band absorption and emission spectrum typical of certain rigid molecules at low vapor phase with resolved vibrational bands.
c: broad-band absorption and emission spectrum typical of molecules in solution with unresolved vibrational bands

The energy involved in photo-stimulated processes spans from 38Kcal/einstein or 38Kcal/mole (i.e. 750nm, red-infrared region) up to 250 Kcal/einstein (120nm near ultraviolet region). These energies are above or in the range of standard bond energies of organic compounds. The energy of vibration spans from 10 to 1 Kcal/mole and rotational energies 0.1 Kcal/mole i.e. between one and two orders of magnitude less than electronic energies. In Figure 9, a Scheme of these energetics is reported along with the energy levels of singlet and triplet states of some organic molecules, compared with the spectrum of the sun or UV lamps.

The previous energy considerations underline how high is the energy transferred to a single molecule when it absorbs a photon compared to thermal heat transfer. Normally it is impossible to transfer the equivalent energy via thermal means without destroying the molecular integrity.
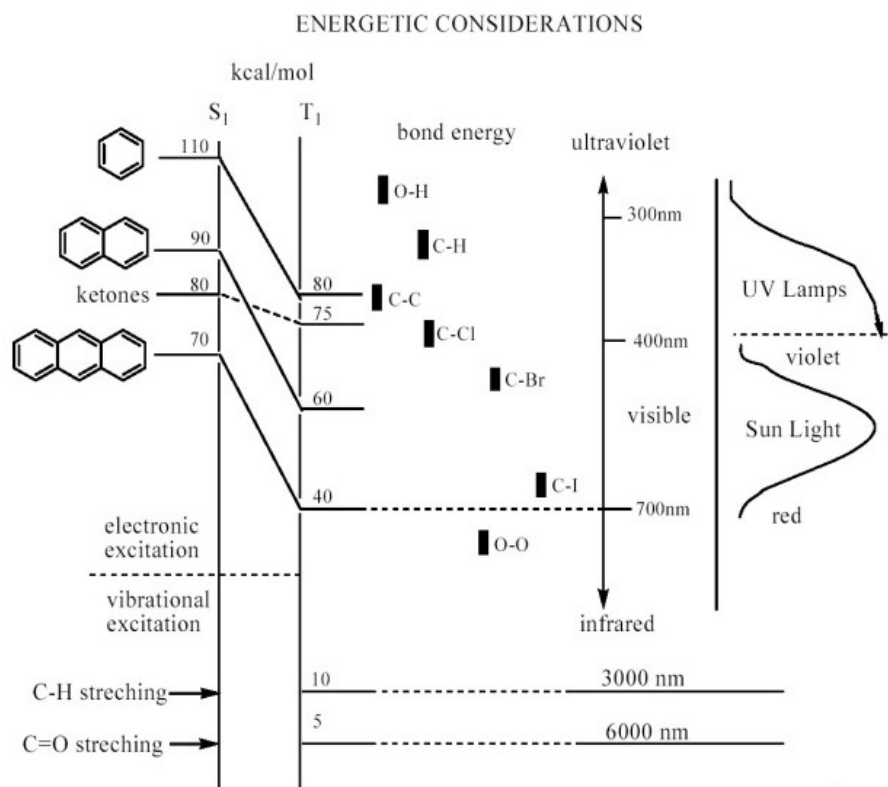
Figure 9: The energy of photo-chemical processes compared with the sun spectrum and that supplied by UV lamps. Vibrational energy are reported for comparison

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Biographical Sketch

Antonio, Papagni born in Bisceglie (Ba) in 1954, graduated in Chemistry from the University of Milan in 1981. Researcher at the Zambeletti Pharmaceutical Company from 1981 to 1983. Ph. D. student from 1983 to 1986, receiving Ph D in Chemistry (Mentor prof. S. Maiorana). Consultant and researcher at Mediolanum Pharmaceutical Company from 1987 to 1990. He joined the Organic Chemistry Department of the University of Milan in December 1990 as Researcher in Organic Chemistry. In 1998 he moved to the University of Milano-Bicocca as Associate Professor in Organic Chemistry. Co-author of a university textbook in Practical Organic Chemistry, of more than 80 papers in international scientific journals including 1 international patents and ca 50 oral and poster communications at national and international meetings. Member of the Scientific Board of CMG (University of Milano Bicocca - Sapio Industrie network); application reviewer for national and international funding agencies (I-MIUR). Reviewer for Wiley-VCH and other journals. Local research team coordinator in many national research projects. Current scientific interests involve design, synthesis and characterization of organic, organometallic and/or fluorinated compounds with biological activity, semiconducting and/or opto-electronic properties.