

A theory of molecular organic photochemistry

Lý thuyết về sự quang hóa của các phân tử hữu cơ

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Abstract

Molecular organic photochemistry is a science that touches the matters of life. In general, interactions between a photon $h\nu$ with an organic molecule R result not only in changes in the energy and dynamic of the molecule but also its structural feature. Bond stretching, breaking, and tautomerization are among the most common alterations. This short overview intentionally presents the basic aspects of molecular organic photochemistry, including some key definitions, *i.e.* excited states, absorption, and emission (fluorescence or phosphorescence), as well as the most common pathways for photochemical reactions.

Keywords: organic photochemistry; absorption; Jablonski's diagram; excited state; ground state.

Tóm tắt

Sự quang hóa của phân tử hữu cơ là một môn khoa học liên quan đến các vấn đề của sự sống. Tương tác giữa photon $h\nu$ với phân tử hữu cơ R không chỉ dẫn đến sự thay đổi năng lượng và động lực của phân tử mà còn cả đặc điểm cấu trúc của nó. Kéo dài liên kết, cắt đứt liên kết, tautome hóa là một vài trong những thay đổi cấu trúc phổ biến nhất. Bài tổng quan này có mục đích trình bày ngắn gọn về lý thuyết quang hóa của phân tử hữu cơ, bao gồm một số định nghĩa chính, như là trạng thái kích thích, hấp thụ và phát xạ (huỳnh quang hoặc lân quang), cũng như các con đường phổ biến nhất cho các phản ứng quang hóa.

Từ khóa: quang hóa hữu cơ; hấp thụ; giản đồ Jablonski; trạng thái kích thích; trạng thái cơ bản.

1. Introduction

Molecular organic photochemistry is a broad and interdisciplinary science that studies the structural, energetic, and dynamic changes of an organic molecule when interacting with a source

of photon (light). The topic concerns with the overall process $R + h\nu \rightarrow *R \rightarrow P$, where R is an organic molecule that can absorb a photon ($h\nu$), $*R$ is an electronically excited molecule and P is the product(s) [1]. While the first half of the

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process is rather a photophysics phenomenon, the second half would be the photochemical transformation of our interest. In general, there are four fundamental primary photochemical processes to transform the $*R$ to P (see **Figure 1**). The first pathway consists of $*R \rightarrow I \rightarrow P$ where I is an intermediate such as a radical pair I(RP), a biradical I(BR) or a zwitterion I(Zw). The second pathway follows a funnel F, often a conical intersection or a surface-avoided intersection. The third pathway typically involves an electronically excited intermediate

$*I$, and the last one is an electronically excited product $*P$. The molecular structure, the transitions between the states, electron and spin configuration are studied in these research works that allow to clarify the structures as well as the energetics and dynamics aspects of the molecule. Therefore, molecular organic photochemistry may involve different physical and chemical aspects *i.e.* chemical physics, spectroscopies, synthetic chemistry, and computational chemistry.

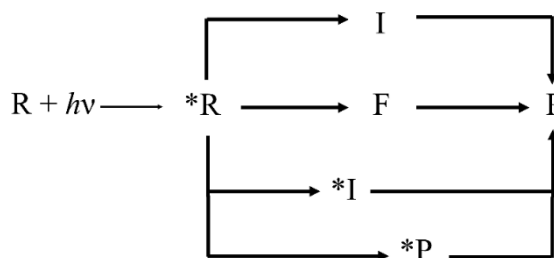


Figure 1. The overall processes of molecular organic photochemical reactions. R is the initial organic molecule, and P and $*P$ are the isolate products at the ground and excited state. I and $*I$ are intermediates at the ground and excited state. F is actually not an intermediate subject but rather a pathway, also called a funnel, *i.e.*, the conical surface intersection. (Adapted from [1]).

Important applications have been found for molecular organic photochemistry, in particularly chemical biology [2], photosynthesis or photodecomposition [3], medicinal chemistry [4], health science (phototherapy) [5, 6], photopolymerization [7], and material science (fluorescence, sensors, organic photovoltaics), and solar energy resources [8-10]. Even when we look back at the origin of life on earth, it also involves one of the best known processes, *i.e.* the photosynthesis, where simple organisms such as cyanobacteria, to algae and plants, use sunlight energy to convert carbon dioxide and water to carbohydrate forms [11]. The biological process of vision is one of the most important photobiological transformation in humans and animals [12]. The photoreceptors, which are composed of small organic chromophore molecules embedded in a protein matrix, are

readily present in the eyes. Upon absorption of a photon, the chromophore molecules jump to the excited states and induce structural changes in the protein scaffold. Subsequent signals are then translated into biological information. In organic synthesis, the α -cleavage of ketones, also called the Norrish reaction (**Figure 2**) is the most well-known photochemistry reaction [13]. In the type I Norrish reaction, the excited molecule undergoes a cleavage of the α -carbon bond of the C=O function to produce a radical pair intermediate I(RP), while in the type II Norrish reaction, the excited molecule undergoes an intramolecular abstraction of the γ -hydrogen to produce a 1,4-biradical intermediate I(BR). Thus, the absorption and different photochemical pathways of photochemistry involve a large number of organic, inorganic and hybrid chromophores (carbonyl, ethylene and conjugated polyenes, enones, benzene and

aromatic chromophore) as well as their metal complexes.

A photochemistry process can be either a radiative or radiationless process. In this summary of molecular photochemistry, we only discuss the radiative ones. Other radiationless processes such as vibrational relaxation (energy

dissipated to the surroundings), internal conversion (IC, coupling of an electronically excited state to a vibrational state that belongs to a lower electronic state), or intersystem crossing (ISC, transition to a state with different spin multiplicity) are not detailed here.

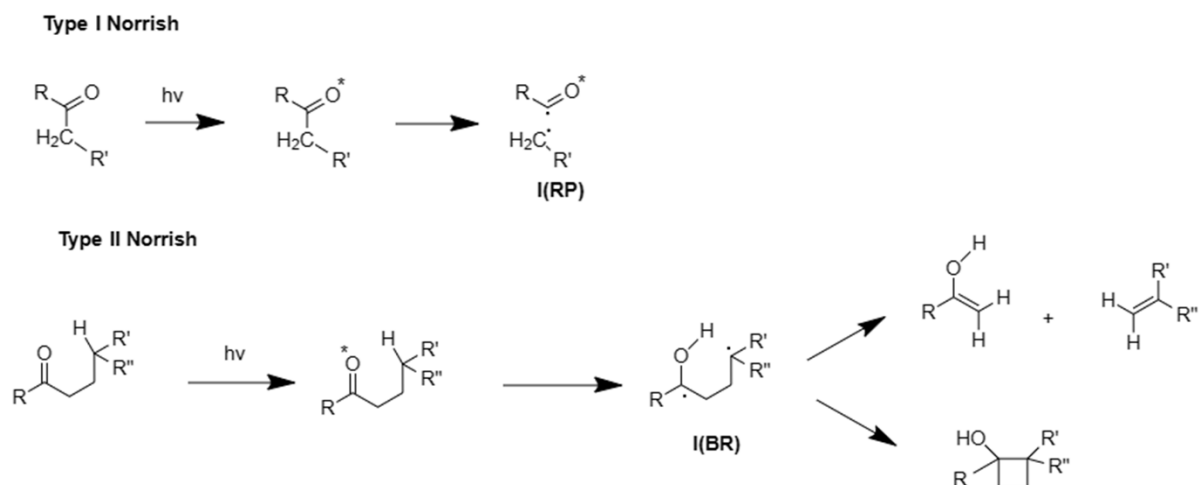


Figure 2. The type I and type II Norrish reactions, or the α -cleavage of ketones, occurs *via* radical pair intermediate I(RP) and 1,4-biradical intermediate I(BR), respectively.

2. Some definitions of excited states: singlet states, triplet states, diradicals, and zwitterions

First, in terms of energy, photophysical and photochemical processes are always simultaneously described in the Jablonski diagram (**Figure 3**). The promotion of a molecule at the singlet ground state (S_0) to the excited states by absorption of photons occurs *via* the spin allowed singlet-singlet absorption (to S_1 state) or spin-forbidden singlet-triplet absorption (to T_1 state). The extinction coefficient ϵ (or oscillator strength) is characterized for the absorption process. Typically, an allowed electronic transition (singlet-singlet) corresponds to high oscillator strength, while for a forbidden transition, a very low (near zero) oscillator strength is normally expected. After being excited to a (sub)level of the S_1 or T_1 excited states, the molecule can

return to the ground state *via* a radiative or a non-radiative decay path. The former one can be either fluorescence (spin-allowed singlet-singlet emission), or phosphorescence (spin-forbidden triplet-singlet emission). These processes are dynamically characterized by a rate constant of fluorescence k_F or a rate constant of phosphorescence k_P , respectively. For the latter, non-radiative decay processes such as internal conversion and intersystem crossing are amongst them but are not discussed here because they rather refer to photophysical processes.

Secondly, the electronic transition during the photochemistry processes is very much in-line with the electronic configuration of the molecular orbitals. The electronic configuration of the ground state (S_0) of a normal organic molecule can be described as $(HO)^2(LU)^0$, meaning that two electrons must be paired ($\uparrow\downarrow$) and are localized in the HOMO orbital. At the

excited state, the electronic configuration of *R is not restricted by the Pauli principle, and so the two electrons of the half-filled orbital $(HO)^1(LU)^1$ can be either spin paired ($\uparrow\downarrow$) or unpaired ($\uparrow\uparrow$). The first case corresponds to the singlet excited state (S_1) while the second one to the triplet excited state (T_1). Similarly, for the intermediate I, $^1I(D)$ and $^3I(D)$ represent the singlet and triplet diradical intermediates with

two electrons localized in the two half-filled orbitals. When two electrons are both located in one of the two non-bonding orbitals, *i.e.* $I(NB)^2(NB)^0$, the specie is considered as a zwitterion $I(Zw)$. Zw species always involved in the late steps $^1R \rightarrow ^1I(Zw)$ and $^1R \rightarrow F$ of the photochemical reaction while D species always involved in the $^3R \rightarrow ^3I(D)$ step of the photochemical reaction that initiated in 3R .

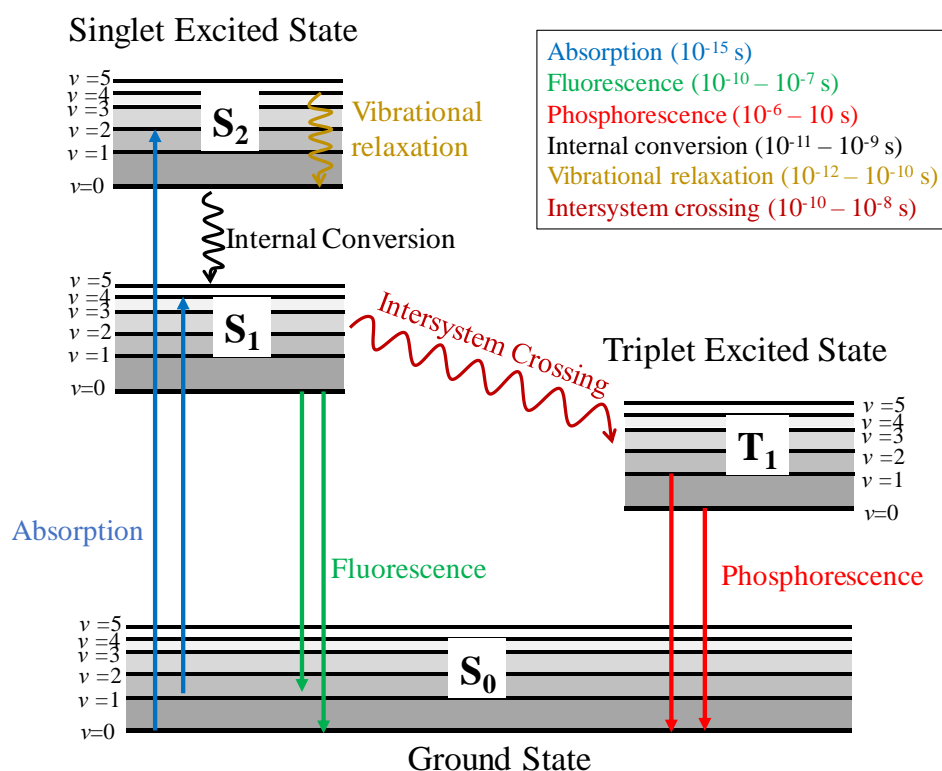


Figure 3. Simplified Jablonski diagram for processes in molecular organic photochemistry. Absorption (blue arrow), fluorescence (green arrow), and phosphorescence (red arrow) correspond to radiative processes while internal conversion (black wave), vibrational relaxation (golden wave), and intersystem crossing (dark red wave) are non-radiative ones. The typical rate of each process is also given in the inset.

3. Absorption, emission and Frank-Condon principle

Absorption ($R + h\nu \rightarrow ^*R$) is the triggering process that brings the molecule from ground state R (of energy level E) to the electronically excited state *R (of higher energy level *E), as in **Figure 3**. The process occurs almost instantaneously, with a very high rate constant of about 10^{-15} s. The state energy diagram can be constructed from both absorptions to singlet (spin-allow) and triplet states (spin-forbidden),

$S_0 + h\nu \rightarrow S_1$ and $S_0 + h\nu \rightarrow T_1$, respectively. In general, the most important parameters to determine the state energy diagram as well as the rate constant of the pathways to S_1 and T_1 are the structures, energies, electronic configuration, quantum yield, and lifetimes of the excited species *R .

The shape of absorption spectra: The energy that is required for a molecule going to the excited states is $\Delta E = (^*E - E) = h\nu$, where E and *E are the energy of the ground state R and

excited state $*R$, and ν the frequency of the absorption. For atomic absorption spectra, we can define exactly each absorption as a sharp line that corresponds to a given frequency ν . However, the same cannot be expected for molecular absorption spectra. Generally, in molecular absorption, the sharpness of absorption band depends a lot on the coupling between the electronic and the vibrational states. Even at low temperature in the gas phase, the absorption of a molecule may involve many vibrational transitions over a range of energies, which can lead to a poor resolution spectrum. The situation can be even worse in solvent, when a large number of solvent molecules surrounding the chromophore can form different supramolecular configurations. The experimental absorption spectra in those cases can be largely broadened, in some cases to the extent of a featureless band.

Frank-Condon (FC) principle: The FC principle states that at the instant of the electronic transition, the most probable electronic transitions are those that possess the

most similar vibrational wave functions in the initial- and the final-state (**Figure 4**) [14]. The similarity of vibrational wave functions in the two states corresponds to a net positive overlap FC integral $\langle \chi_1 | \chi_2 \rangle$. The square of that vibrational overlap integral ($\langle \chi_1 | \chi_2 \rangle^2$), called the FC factor, determines the matrix element of the electronic transition. The FC principle can be simply interpreted as the high probability for electronic transition occurs with the molecule possessing similar nuclear configurations and momentum for initial and final states in some region of space. For example, in **Figure 4a**, the overlap FC integral is maximized for the transition from $\nu=0$ (GS) to $\nu=2$ (ES), corresponding to the most probable FC transition (highest intensity) in the absorption spectra. Based on the FC principle, the solvation of the broad absorption band could be resolved. The vibrationally resolved (**Figure 4b**) and non-resolved absorption spectra (**Figure 4c**) are also displayed for comparison. FC principle is applied not only for absorption but also for the emission process, *i.e.* fluorescence.

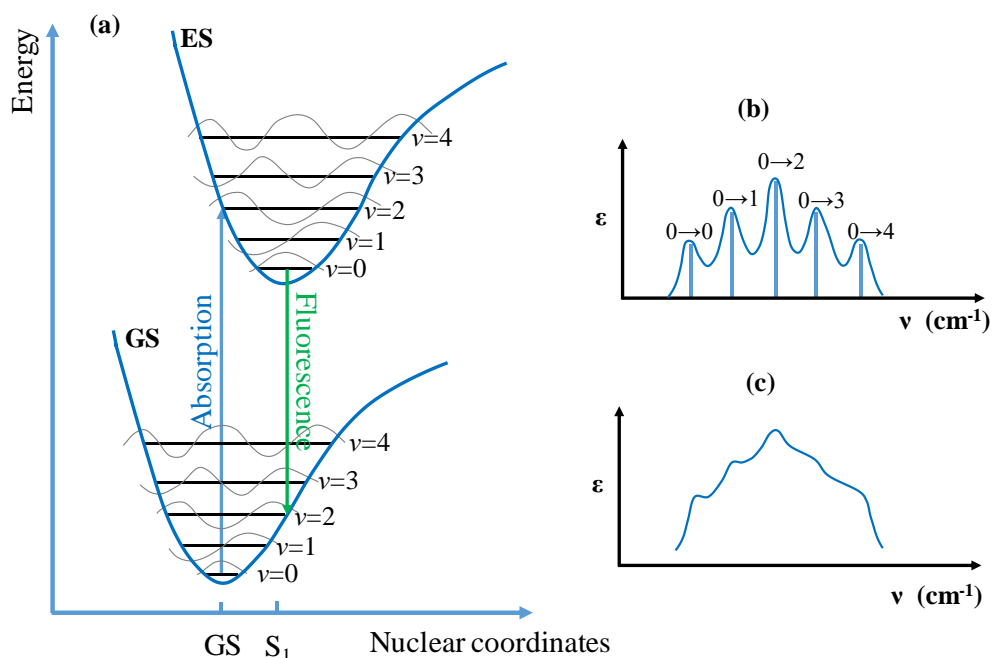


Figure 4. (a) Franck Condon effect in absorption and emission with vibrational resolution for $\nu=0-4$ in which highest overlap FC integral are $\nu=0$ (GS) to $\nu=2$ (ES) for absorption, and $\nu=0$ (ES) to $\nu=2$ (GS) for fluorescence; (b) Vibrationally resolved absorption spectra; (c) Non-resolved absorption spectra.

Emission is a radiative decay process that brings the molecule from the electronically excited state *R (*E , higher energy) back to the ground state R/P (E , lower energy), accompanying by the emission of a photon of energy $\Delta E = (^*E - E) = h\nu$. Fluorescence (spin-allowed singlet-to-singlet emission) and phosphorescence (spin-allowed triplet-to-singlet emission) are two radiative processes which are characterized by the rate constants k_F and k_P . A similar FC principle is identified for emission, leading to the most probable transition corresponding to the most conserved configuration of nuclear geometry in the excited state to the ground state.

4. Plausible pathways from ES to GS and their fundamental surface topologies

4.1. Definition of PE curves and PE surfaces

A potential energy (PE) curve displays the relative energy of the molecule vs. the varying molecular structure of the system along one reaction coordinate. In the molecular photochemistry processes, the reaction coordinate is normally the nuclear geometry that changes due to the absorption or emission process, e.g. a σ -bond stretching or breaking, and a π -bond twisting. In reality, the excitation of a molecule may happen with simultaneous geometrical changes of several molecular coordinate parameters, i.e. stretching and breaking of sigma bonds (C-C, C-O...), and/or twisting of the C=C bond, and tautomerization. In those cases, the PE surface proves a better approximation to accurately describe the energy of the molecule vs. the molecular structure change, with the description of at least two reaction coordinates. However, as the PE surface is a 3D object and difficult to visualize, many research still rely on the PE curve. It is believed to describe the energy changes of the states along the reaction coordinate with a much more

reasonable cost in most cases of photochemistry reaction [15].

4.2. Fundamental topologies of the funnel of PE curves/surfaces from ES to GS

When studying the transformation of a molecule from *R to P , one must consider its jump from a representative point on the excited state surface to the representative point on the ground state. There are several critical points that allow us to study the photochemical reaction pathway: (i) the molecular geometry at the critical point r_c on the excited state surface, from which the molecule jumps to the ground state surface, (ii) the energy barriers that separate *R from the funnel leading to the ground state surface, (iii) the molecular geometry along the reaction coordinate that follows the fastest overall pathway from *R to P , (iv) the deactivation coordinates which determine the most probable ground state structure, and (v) the barriers that separate *R to I . It is noteworthy that the recent development of quantum chemistry assisted by computational methods has made important progress in clarifying the nature of the transformation and following the PE surfaces of the photochemical reaction that are difficult to access by conventional experimental methods [16, 17].

If r_c is the critical point for both structural and energetic change, then we can distinguish five fundamental topologies of pathways leading a molecule from the electronically excited state to the ground state as seen in **Figure 5**.

(a) *Spectroscopic minima*: this is the case where an equilibrated excited state surface minimum of *R occurs close to the geometry of the ground state minimum R (at r_c). In general, there is no significant changes in the molecular bonding of the R and *R states. This topology is expected for the π , π^* states of rigid aromatic compounds with no readily available distortional motion. For the spectroscopic

minima funnel, it happens in both radiative and non-radiative photophysical processes, depending on the difference in energy between two surfaces.

(b) *Extended surface touching*: an excited state surface touches a ground state surface at a critical point r_c , followed by an isoenergetic level of energy between R and *R although there are extended geometry changes after r_c . In this case the transition from *R to R is smooth and continuous (adiabatic). This surface topology normally corresponds to a σ -bond stretching that eventually leads to bond breaking, *i.e.* the H abstraction reaction and α -cleavage of ketones (Norrish reaction).

(c) *Extended surface matching*: the excited-state and the ground-state surface are well separated so that there is no interaction between the two surfaces along the reaction coordinate before and after the critical point r_c . The primary photochemical product can be either the excited state of the intermediate *I or of the product *P. There is no funnel from ES (from *R, *I or *P) to GS so the reaction is adiabatic photoreaction. Exciplexes, eximers, twisted internal charge transfer state, [18] and excited-state proton transfer [19] are amongst the typical mechanisms from *R to *I(*P).

(d) *Surface crossing*: the excited-state and ground-state surfaces cross one another at a critical geometry r_c . In the 3D form, this cross section is the conical intersection (CI). The rate of surface crossing belongs to the ultrafast photochemical and photophysical transition, as being as high as 10^{-12} – 10^{-13} s $^{-1}$. The CI is considered one of the most effective pathways to take a molecule from an excited state to a ground state, towards different products (P_1 or P_2) or even back to R. The rate of a reaction passing through CI only depends on the rate that the molecule passes from R* to CI. If there exists any barrier between *R and CI, the rate of passing over this barrier is the one that determines the rate of the surface crossing [20, 21].

(e) *Excited-state surface minimum*: an equilibrated excited-state surface minimum occurs close to a geometry r_c above a ground-state maximum that serves as a funnel to the ground-state surface. This usually leads to a strong avoid surface crossing (ASC). This topology is typical for pericyclic reactions or twisting about double bonds in the excited singlet state.

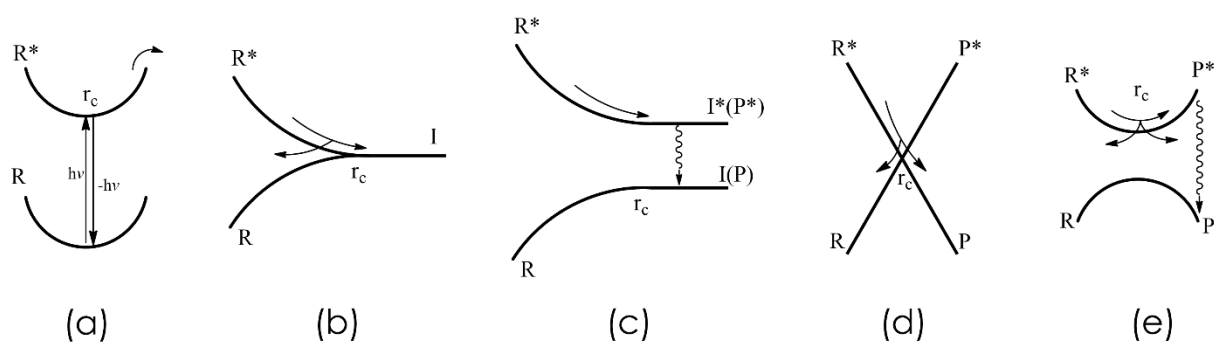


Figure 5. Illustration of PE curves of five popular topologies of funnel leading a molecule R from ES to GS. (a) Spectroscopic minima or FC minima, (b) Surface touching, (c) Surface matching, (d) Surface Crossing or Conical Intersection (CI), (e) Excited-State Surface Minima or Avoid Surface Crossing (ASC). (Adapted from [1])

5. Conclusions

In conclusion, this short communication has brought several key definitions and processes in the molecular organic photochemistry. It will be of use to students and teachers, as well as researchers who are interested in studying the different states of a matter, or a molecule under the absorption of photon (light), with its door opened to many possible applications.

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