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New Materials to Solve Energy Issues through Photochemical and Photophysical Processes: The Kinetics Involved

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Additional information is available at the end of the chapter

Abstract

Kinetic rates of energy production are extremely controlled by the competing processes that occur in systems capable of energy transfer. Besides organic and inorganic compounds already known as electronically actives, supramolecular systems can be thought to form energy transfer complexes to efficiently convert, for instance, light into electricity and the mechanisms for that can be of any kind. Photophysical and photochemical processes can simultaneously occur in such systems to provide energy conversion, by competing mechanisms or collaborative ones. Thus, to investigate the kinetic rates of each process and to understand the dynamics of the electronic excited states population and depopulation in strategically structured materials, can offer important tools to efficiently make use of this not always so evident power of supramolecular materials. In this chapter, we present the state-of-the-art of the use of photophysical processes and photochemical changes, presented by new materials and devices to provide a control of energy transfer processes and enable distinct applications, since energy conversion to sensing and imaging techniques to material characterization.

Keywords: photochemistry, photophysics, kinetics, excited states lifetime, electronic energy transfer, nanomaterials, energy conversion

1. Introduction

In nature, there are a number of processes indispensable for life maintenance that begins with light absorption. From this starting point, several chemical changes, ranked by probabilities of occurrences, are triggered to give a product. In this process, molecular photophysical and photochemical processes occur simultaneously, competing to each other for the excess energy. On the other hand, these competing processes are also collaborating to each other, since they occur through electronic excited state reactants that originate electronic excited state intermediates. Based on the structures and characteristics of these excited electronic states intermediates, new mechanisms can be proposed, yet involving dissociations, isomerization, bond cleavages, nevertheless, taking into account that these excited species present peculiar electronic distribution and, therefore, involve photophysical activation and deactivation mechanisms, that arise from their interaction with light, all governed by new and challenging kinetic laws. In this sense, the peculiar characteristic of the kinetic laws involved in molecular photophysical processes is that electronic excited species that can be reached by light absorption are considered unstable, and to achieve a more stable electronic configuration, excess energy is liberated by radiative and/or non-radiative unimolecular decays.

The photophysical processes that occur immediately following the light absorption aim to ensure the mechanisms to achieve the best energetic configuration to: (1) lead to the reactive excited intermediate, from which the photochemistry can occur or (2) achieve the faster way to release the excess energy and to retrieve the initial reactant. They can all be defined in a Jablonski diagram [1] (**Figure 1**) and their corresponding rate expressions can be obtained from there.
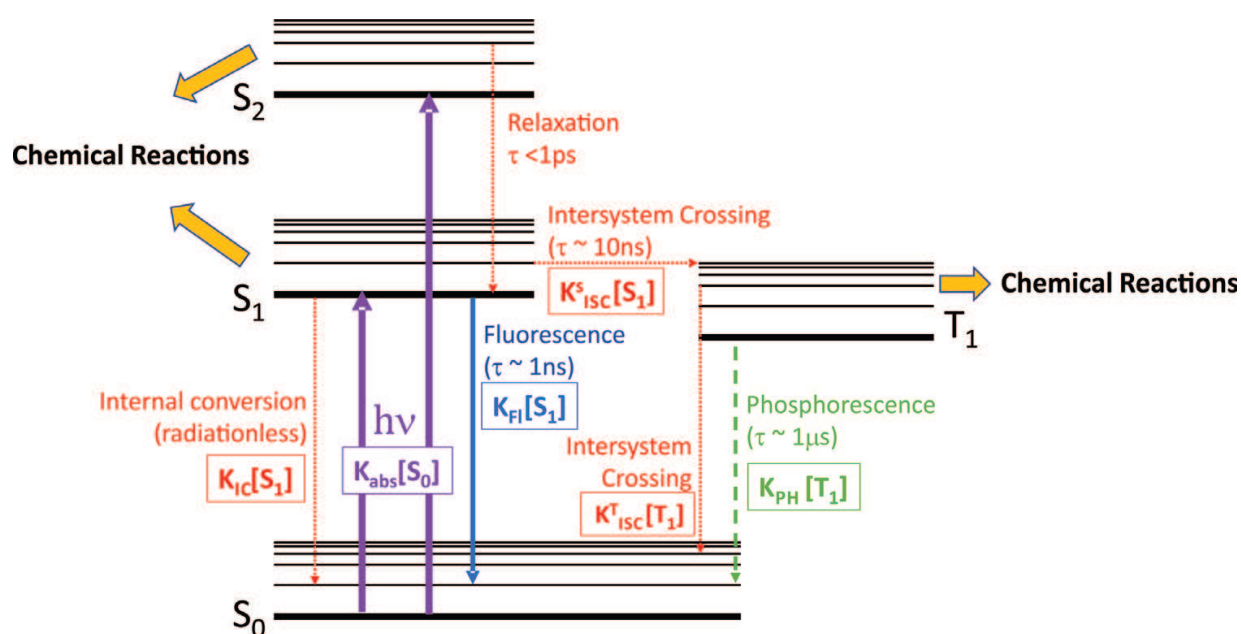

Figure 1. Jablonski diagram presenting the major radiative and non-radiative processes and their rates.

2. Photophysical processes

2.1. Absorption

The initial photophysical process that gives rise to excited states from where every photo-physical and subsequent photochemical processes occur in the radiative absorption of photons to promote an electron to a higher electronic energy state. The accessed excited state is determined by selection rules that involve symmetry and spin conservation, existence of a dipole moment and must occur to an ideal vibrational mode wavefunction in the excited state overlapped in some extent with the low energy vibrational mode of the ground electronic state, enabling some probability of transition, as predicted by the Franck-Condon principle. The magnitude of this overlap influences the moment transition in absorption and every other photophysical processes [2]. The expression that describes the transition is:

$$M = \int \psi *_{el,higher} \, \mu \psi_{el,lower} d\tau \int \psi *_{vib,higher} \, \psi_{vib,lower} d\tau \qquad (1)$$

Where the second integral is the overlap integral. From this expression, it is evident that there must be a probability of a wavefunction from a lower electronic state to absorb enough energy to be converted in another wavefunction that describes a higher electronic state and that if there is no overlap between the vibrational states expected to be involved in the transition, then the electronic transition is forbidden. It evidences the *vibronic* nature of the electronic state, in which electronic states are coupled to vibrational states. **Figure 2** presents the Franck-Condon absorption from the ground electronic state to a vibronic state of higher energy.

The absorption process populates electronic excited states from where all deactivation processes will occur. The most significant photophysical deactivation processes are:

2.2. Fluorescence

The photophysical process in which the electronic excited state is radiatively deactivated, involving singlet excited and ground states, is the fluorescence. It spontaneously occurs from the singlet excited state of lower energy, as predicted by Lewis and Kasha [3], through the emission of a photon and the energy involved in this process is similar to the absorbed energy, if no other competing process of deactivation occurs. It occurs very rapidly in a timescale that depends on the system identity but between 10^{-6} and 10^{-10} seconds for several organic compounds. If longer timescales are observed, it may evidence the occurrence of another process that results in a similar spectrum, but occurs after some other photophysical deactivation processes that populate the singlet electronic state of lower energy. This is the *delayed fluorescence* and it only can be distinguished from the fluorescence by time-resolved measurements.

2.3. Phosphorescence

Phosphorescence is a radiative deactivation process characterized by a red-shift of the emission spectrum. It is a process that occur from an electronic excited state with less energy than that from where fluorescence occurs. In fact, it occurs from a triplet electronic state with less energy
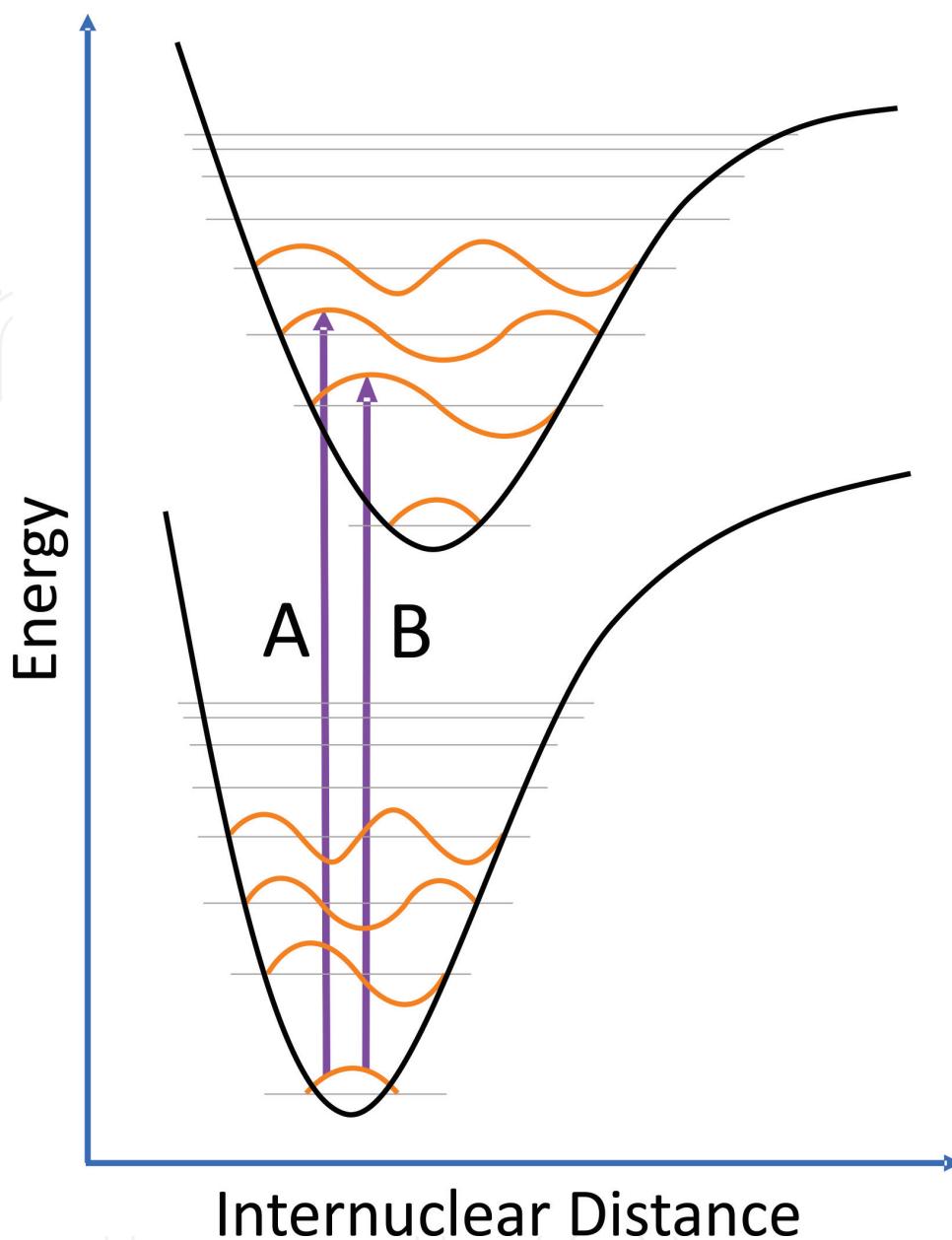
Figure 2. Franck-Condon vibronic absorption from the electronic ground state to an excited state: From the lowest vibrational state (v_0) in the ground state to A) the lowest vibrational state (v_0) in the excited electronic state and B) to a higher vibrational state (V_4) in the excited electronic state.

than the singlet electronic excited state of lower energy. Since spin changes are forbidden in electronic transitions, this is a process that occurs only if relaxation in the spin selection rule occurs, provided by spin-orbit coupling derived from the coupling of the electron spin motion with its orbital motion. Due to that prohibition, this is a very slow process, taking from 10^{-6} seconds to minutes or even hours to occur [2].

2.4. Vibrational relaxation

The process of releasing the energy given by the absorption of a photon as kinetic energy is the vibrational relaxation. It involves the conversion of a vibrational mode within an electronic

state to another vibrational mode within the same electronic state. This process is very fast, taking around 10^{-14}–10^{-11} seconds. It usually takes place immediately following absorbance and, since it occurs between vibrational levels, generally it does not result in electronic level changes [1, 2].

2.5. Internal conversion

A non-radiative process that promotes the conversion of a singlet electronic excited state of higher energy into another singlet electronic state of lower energy is the internal conversion. It can involve any two singlet states and, when occurring between the singlet electronic excited state of lower energy and the singlet ground state, it competes with fluorescence, being one reason for a decrease in fluorescence quantum yield. It occurs rapidly with release of kinetic energy [1, 2].

2.6. Intersystem crossing

The non-radiative process of conversion of an electronic excited singlet state into a triplet one through an isoenergetic process is the intersystem crossing. This is a very slow process, because it is forbidden by spin multiplicity selection rules and it only takes places if an effective spin-orbit coupling occurs [1, 2].

These radiative and non-radiative processes are unimolecular, involving only the electronic states of a single molecule. Nevertheless, there are several other bimolecular processes, characterizing energy transfer processes or even chemical reactions.

3. Energy transfer processes

Energy transfer can occur between similar molecules or distinct compounds and the way they interact will define the more appropriate transfer mechanism for each case. Depending on the mechanism and the energetic characteristics of the energy transferred, the transfer can be classified as [1]:

1. Hole transfer: When a positively charged molecule interacts with another molecule to achieve its energetic equilibrium and resulting in the second molecule to present the positive charge.

$$D^+ \; + \; A \; \rightarrow \; D \; + \; A^+ \; \textbf{hole transfer} \tag{2}$$

2. Electron transfer: Similarly, if a negatively charged molecule interacts in some way with another neutral molecule to result in the second molecule now as negatively charged.

$$D^- \; + \; A \; \rightarrow \; D \; + \; A^- \; \textbf{electron transfer} \tag{3}$$

3. Energy transfer: When the interaction between molecules, one of them in the electronic excited state and the other occupying the electronic ground state results in the second

molecule occupying the excited state and the initially excited molecule in the electronic ground state.

$$D^* \quad + \quad A \quad \rightarrow \quad D \ + \ A^* \quad \textbf{energy transfer} \tag{4}$$

The energy transfer mechanisms involve an entity which presents the excess energy, defined as donor (D) and an entity that can receive this excess energy, defined as acceptor (A). They are classified as radiative or a non-radiative process, depending on the occurrence of the luminescent emission from the donor.

3.1. Radiative energy transfer

The donor in the electronic excited state relaxes to radiatively release its excess energy. Thus, fluorescence (or phosphorescence) needs to occur to promote the energy transfer through the absorption of the fluorescence of the donor by the acceptor [4]. It is known as the trivial energy transfer mechanism and it is enabled by the overlap between the absorption spectrum of the acceptor with the luminescence spectrum of the donor. It does not require that donor and acceptor be in the same environment and it is independent of the luminescence lifetime of the donor and depends on the concentration of the acceptor ([A]), the quantum yield of the donor (φ_{eD}) and the molar extinction coefficient of the acceptor (ε_A).

$$Rate = k_{fl}^D P_{abs}^A [D^*] \quad \text{with} \qquad P_{abs}^A \propto [A] l \int_0^\infty F_D(v)\varepsilon_A(v)dv \tag{5}$$

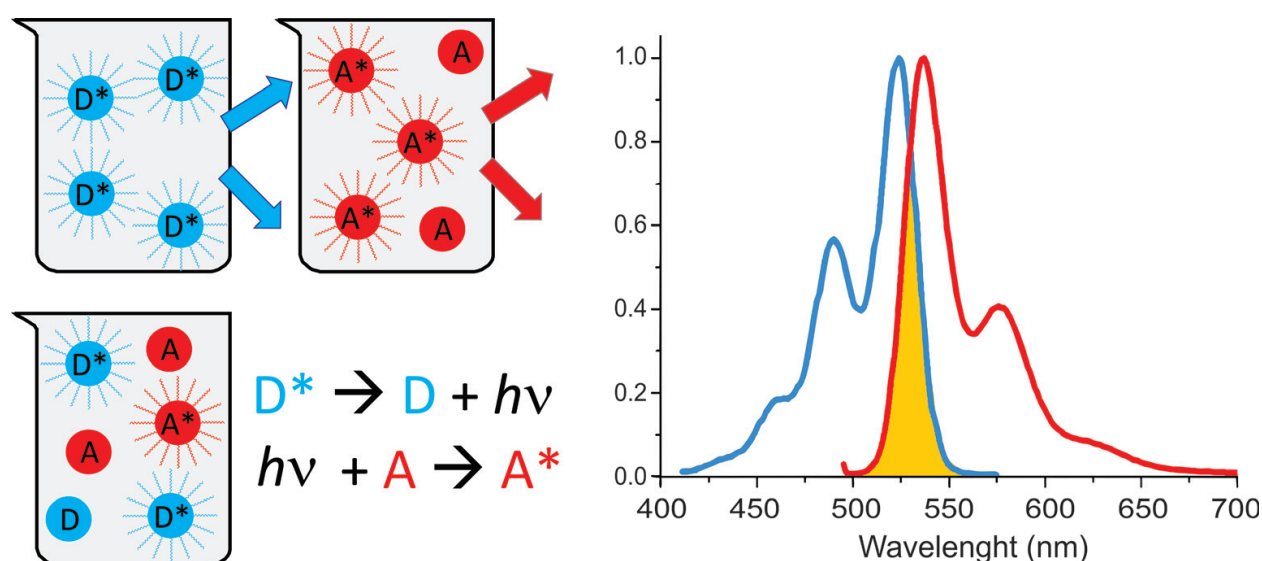Scheme in **Figure 3** presents the trivial mechanism of energy transfer.

Figure 3. Scheme of the trivial mechanism of energy transfer.

3.2. Non-radiative energy transfer

Inversely to the trivial mechanism, non-radiative energy transfer mechanisms are strictly dependent on the luminescence lifetime of the donor, since it only occurs while the donor is in its electronic excited state. It needs the formation of a collision complex between the donor and the acceptor and the energy transfer occurs with the right molecular distance:

$$A + D* \rightarrow [AD*] \rightarrow [A*D] \rightarrow A* + D \tag{6}$$
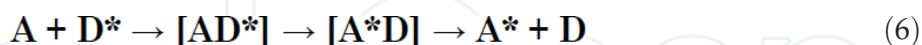
Its rate is given by the magnitude of the transition moment between the electronic wavefunction that describes the collision complex before and after the transfer from the donor to the acceptor:

$$k = \frac{2\pi}{\hbar} \left| \int \Psi^*_{A*D} H' \Psi_{AD*} \right|^2 \rho(E) \tag{7}$$

Where $\Psi_{AD*} = \Psi_A \Psi_{D*}$ is the complex wavefunction before the energy transfer and $\Psi_{A*D} = \Psi_{A*} \Psi_D$ is the wavefunction that describes the complex after the energy transfer.

Depending on the nature of the energy transfer, the intermolecular distance and the similarity of excited state energies, they can occur by a resonant mechanism called Forster resonance energy transfer (FRET) or based on the electron exchange called Dexter energy transfer.

3.3. Forster resonant energy transfer

Energy transfer that occur in a rate similar to the donor fluorescence lifetime initially involves a Coulombic interaction between the electronic excited state of the donor and the electronic ground state of the acceptor that evolves to interaction of the acceptor electronic excited state with the donor ground state. These Coulombic interactions are only possible due to the energy proximity of the emission of the donor and the absorption of the acceptor, enabling a virtual energy transfer, in which absorption and emission of the energy occur simultaneously. Because the Coulombic interactions between the electronic states of both donor and acceptor occur during the donor fluorescence lifetime and they are predominant and represent the influence of the dipole-dipole interaction, they are dependent on the inter-species distance by a factor of r^{-3}. The probability of occurrence of the energy transfer, then, is proportional to the square of the distance, hence r^{-6}. The rate of the energy transfer is given by the Forster expression [4]:

$$k_{DA} = \frac{9000k^2 \ln 10}{128\pi^5 n^4 N_A \tau_{DA} r^6} \int \frac{F_D(\tilde{v})\varepsilon_A(\tilde{v})}{\tilde{v}^4} d\tilde{v} \tag{8}$$

Where k^2 is the relative orientation of the dipole of the donor and the acceptor, F_D is the intensity of fluorescence of the donor, ε_A is the acceptor coefficient of extinction, τ_{DA} is the donor fluorescence lifetime in the presence of the acceptor and r is the distance between donor and acceptor.

When the probability of occurrence of non-radiative energy transfer is 50%, a critical distance, called Forster radius, is reached and it is defined as the distance in which the transfer rate, k_{DA}, is equivalent to the donor fluorescence lifetime, when in the absence of the acceptor, τ_D^{-1}:

$$k_{DA} = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6 \tag{9}$$

The critical distance is much longer than the bond distances and the energy transfer is said to be a long-distance energy transfer.

3.4. Dexter energy transfer

The mechanism of electronic energy transfer that involves the electron transfer between the electronic excited state of the donor to the unoccupied excited state of the acceptor, simultaneously to the transfer of an electron of the electronic ground state of the acceptor to the poorly occupied electronic ground state of the donor, characterizing an electron exchange mechanism is the Dexter energy transfer. Since it is an exchange interaction, it needs an overlap between the wavefunctions of the donor and the acceptor to occur.

The rate of the electron exchange is proportional to the ratio between the donor-acceptor distance and the sum of their Van der Waals radii.

$$k_{T\ (exchange)} \propto \exp(\ 2r_{DA}\ /\ L) \tag{10}$$

The donor-acceptor distance, in this case, is short, corresponding to distances of a complex formation. These mechanisms are illustrated in **Figure 4**.
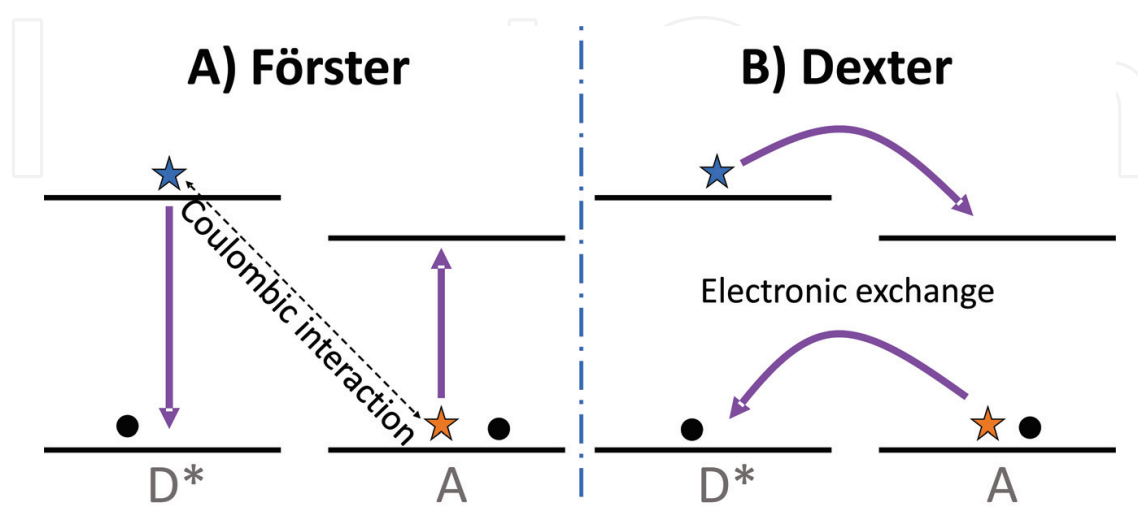

Figure 4. Diagrams illustrating the (A) Forster resonant energy transfer and (B) Dexter energy transfer mechanisms.

4. Energy transfer complexes

Non-radiative energy transfer mechanisms involve the formation of energy transfer complexes. In most cases, these complexes are formed by collision; thus, their kinetics of formation is governed by diffusion rates and is dependent on the molecule-environment interactions. Its
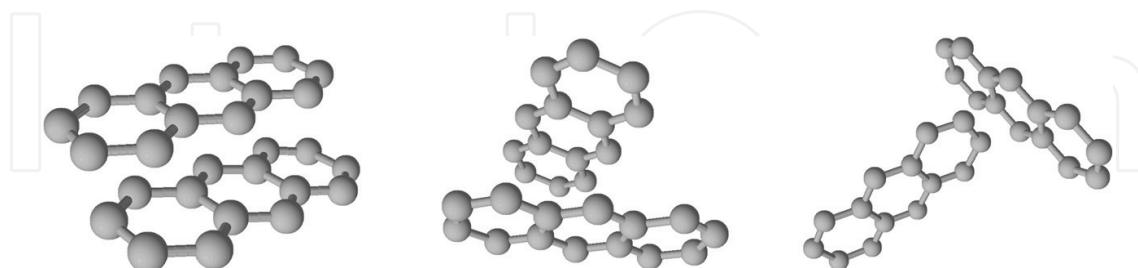

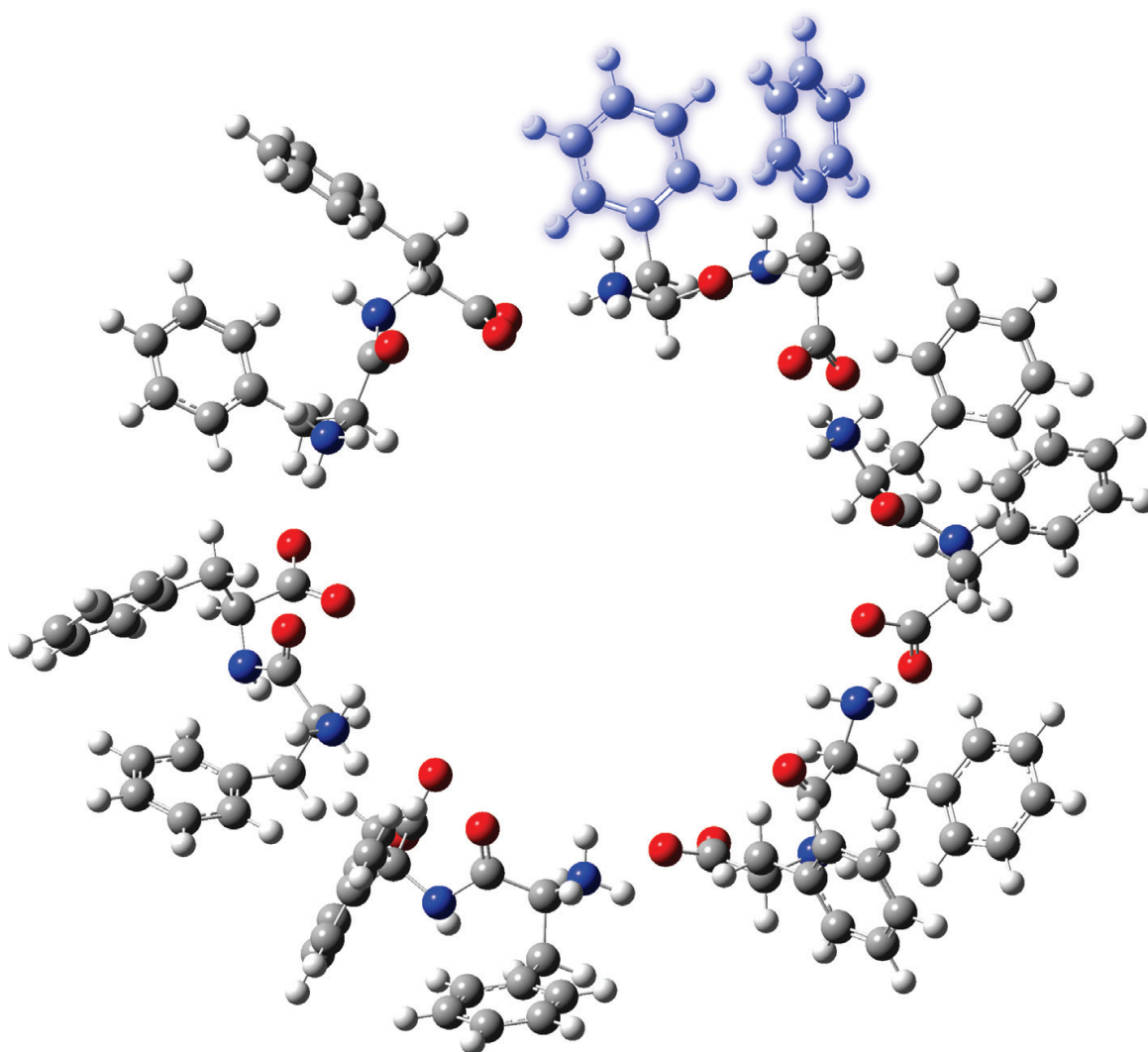**Figure 5.** Excimer configurations.

Figure 6. Supramolecular diphenylalanine hexagonal crown forming an energy transfer complex upon absorption of the phenyl groups of a single peptide.

mandatory exigence is to have one of the molecules involved in the complex formation in the electronic excited state. The success of collisions will give the number of intermediates in the excited states that present the ideal characteristics for energy transfer. These excited state complexes are classified depending on the identity of their components [2–4]:

1. *Excimers* are the excited state complexes that are formed by two similar compounds. They present the same absorption electronic spectra as the isolated molecules, but emission spectra broader and red-shifted than the emission expected for the isolated molecule. The emission spectrum is the result of the emission of a new compound, the complex, formed during the excited state of the molecule that absorbed the electromagnetic radiation and is formed by collision. Excimers present several distinct orientations, from the totally overlapped orientation, called sandwich excimer, to some partially overlapped and the t-shaped excimer. **Figure 5** presents these configurations.

2. *Exciplexes* are the complexes formed by distinct compounds, with one of them being at the electronic excited state. They are also governed by diffusion rates, but in a very specific manner, since it depends on efficient simultaneous collisions. Their absorption spectra are similar to that observed for the isolated absorber, but the emissions are very difficult to predict, since several competing pathways of deactivation, with kinetics influenced by the environment and the interaction forces acting to keep the exciplex together, during the excited state of the complex. This is the case of exciplexes involved in supramolecular photochemical reactions, as exemplifies in **Figure 6**.

5. From photophysical to photochemical processes

All these photophysical processes modulate the energy and the characteristics of the interme-diates prior to the occurrence of photochemical modifications. They occur in typical amounts of time; thus, light absorption is the determining step and it takes femtoseconds (10^{-15} sec-onds) to occur. The radiative deactivation of the lowest excited state to reach the ground state is the fluorescence, which occurs in nanoseconds (10^{-9} seconds) timescale; its occurrence informs about the electronic excited state lifetime and, therefore, about its stability. If it is long enough, several processes can occur and the radiative deactivation is not observed or its yield is diminished. From there, reactive intermediates can be formed in the excited state and, if funnels or interconversion situations are avoided by, for instance, guaranteeing that the energy barrier is too high to be superposed, then the final product, result of all photophysical and photochemical processes that occur during the lifetime of the electronic excited state, is the excited product. The ground state product is obtained when the excess energy is released as radiative emission [3].

Nevertheless, if the energy barrier is superposed and funnels are formed, the reactive excited state intermediate cannot be formed and the chemical reaction occurs in the ground state. These events can be summarized in **Figure 7**.

The rate constants and the probabilities of these processes determine which path can lead to the product formation. To describe the excited states and the changes that occur to yield the
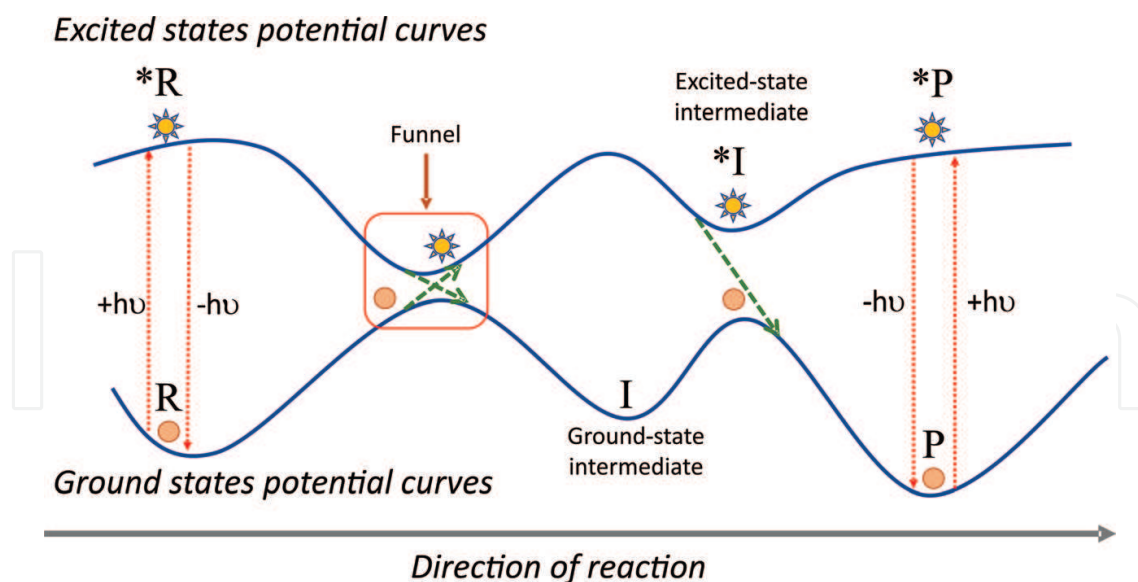
Figure 7. Potential curves of ground and electronic excited states of a photochemical reaction. (R) is the ground state reactant, (*R) is the excited reactant, (I) is the ground state intermediate of a reaction, (*I) is the excited state intermediate, (*P) is the excited state product and (P) is the final product of the overall process.

product is the key to perform any kind of reaction control and to choose all the experimental conditions that satisfy the reaction requirements. The rate constants, the intermediate formation and structures, the reasons for interconversions, energy migrations and excited states deactivation are crucial to exert any sort of reaction control. For that, the kinetic laws of excited state intermediate formation, the characteristics of funnels and the difference between thermal and photo-activated chemical reactions and the kinetics involved in energy transfer processes must be scrutinized. As showed by Soboleva et al. [5], to describe the electronic excited states lifetimes is very important to even propose mechanisms for charge transfer in supramolecular systems. In their work, they showed that electron transfer kinetics can be monitored by time-resolved luminescence quenching measurements of a chromophore in the presence of a quencher to describe the electron-transfer reactivity in sodium dodecyl sulfate (SDS) micellar systems. They observed that the mobility of the quencher is faster than the electron-transfer rate, which resulted in the conclusion that, in the cases where electron transfer between donor and acceptor is slower than the diffusion rate, the transfer is then controlled by reaction kinetics instead of by diffusion.

All these phenomena occur in a system of competition vs. cooperation, through intermediates and governed by probabilities of occurrence and rate constants, as they direct the mechanisms that are employed in a great number of applications. Examples are probing in imaging diagnosis, energy conversion and storage, data storage, photodynamic therapy, among several others.

6. State-of-the-art

Nowadays, photophysical and photochemical processes are perceptively and actively being applied in several areas of science and technology to promote a rapid and sustainable way to

better everyone's life worldwide. Examples are the several uses of photochemistry kinetics in distinct processes and its application to new materials development, in special those for energy conversion and energy harvesting [6–11].

Recently, research into optoelectronic organic materials is being developed to describe new options with potential for applications in emissive devices, sensors and solar cells [7]. Although these materials have been successfully tested as part of these devices, they are numerous and a serious difficulty has been to determine which characteristics are determinant for a material to present a specific property and how to replicate that in others. The answer invariably has been found in determining the kinetics of deactivation of the electronic excited states and, therefore, of the photophysical properties and photochemical processes. The efficiency of a device containing organic electroluminescent compounds is strictly related to the efficiency of the exciton formation and, thus, it depends on the conjugation lengths [7], which determine the mechanisms of energy transfer among the material [12]. For instance, in their work, Arkan and Izadyar studied the mechanism of charge transfer and the rate of exciton formation and dissociation in dye-sensitized solar cells based on TiO_2/Si/porphyrins. They observed the rate of exciton formation/dissociation in metal-porphyrins, revealing the occurrence of an efficient charge transport in these systems.

Indeed, it is expected that efficient solar cells present great ability of exciton formation, efficient exciton transport and charge transport from the donor to the acceptor [13] to minimize the influence of the competitive processes such as exciton recombination that reduces the energy conversion efficiency [14].

Exciton formation is a driving force of the solar cell efficiency, which causes the exciton recombination to be an event that needs to be controlled. In several devices, recombination must be understood to be avoided to guarantee the highest efficiency. Many solar cells have been based on perovskite due to their ability of delivering efficiencies as high as 22% [15]. In their work, Dar et al. characterized the charge carrier recombination process that occurs in a bromide-based perovskite by measuring the transient absorption kinetics are several excitation intensities (5–100 μJ cm^{-2}). For that, they assumed that the carrier dynamics is mainly governed by bimolecular recombination, being expressed and decay kinetics:

$$dn/dt = \gamma(t)n^2 \tag{11}$$

Where, in disordered systems, the time-dependent recombination is approximately to [16]:

$$\gamma(t) = \gamma_0 t^{-\alpha} \tag{12}$$

That gives the carrier concentration kinetics: $1/n = -1/n_0 = \gamma_0 \, t^{1-\alpha}/(1-\alpha)$, independent of the initial carrier density and, thus, independent of the excitation intensity.

Through this treatment, they identified the time-dependent recombination as a function of the morphology of the perovskite. They found that the polycrystalline perovskite structure presents grain boundaries that are physical obstacles for the carrier motion, which results in a

decrease of the recombination rate. They were able to determine that the recombination rate constant is a consequence of the perovskite morphological inhomogeneity.

Recombination is an important mechanism of depopulation of the excited state, from which energy is generated. Controlling the exciton recombination has been a strategy for enhancing the solar cell efficiency, but it needs an accurate characterization of the kinetics of all competing processes of deactivation and, sometimes, it can lead to a poorly effective control of the recombination. Other strategies have been developed, focusing on enhancing the exciton formation, other than avoiding recombination. Many studies have demonstrated that processes such as multiple exciton generation in quantum dots and singlet exciton fission in molecular chromophores have greatly contributed to enhance the power conversion efficiency of devices such as solar cells and fuels cells. To carefully characterize, both processes had proven to consist of an embracing strategy to promote higher efficiencies. Beard et al. [17] studied the characteristics of the mechanisms multiple exciton generation [18] and singlet exciton fission [19, 20], searching for their similarities, in order to give enough information on how to improve the exciton formation in such devices, independently of the device configuration. They found that the two mechanisms are different, because in multiple exciton generation, two excitons are created in a single quantum dot whereas in singlet exciton fission, two species are electronically coupled to give rise to an overall singlet excited state that allows a transition from the singlet excited state to two coupled triplet excited states. In the former, there is spin conservation, in the latter, two triplets are created, each one presenting half the energy of the prime singlet excited state. Also different are their dynamics. Exciton multiplication, in both mechanisms, occurs very fast, nevertheless, the difference lies on lifetimes of the newly generated excitons. In exciton singlet fission mechanism, the new excited triplet states present lifetimes of microseconds, originated from singlet states with lifetimes of nanoseconds [19], whereas in multiple exciton generation, the excitons present lifetimes of picoseconds [21]. Despite these differences, they concluded that in solar cells, the enhancement in the efficiencies calculated considering both mechanisms are similar. They informed that there is still much work to be done regarding the solar cell structures to minimize non-radiative recombination and provide more efficiency to them, but solar cells with power conversion efficiency of over 30% can be easily obtained by multi-exciton generation. Also, Thompson et al. [22] showed that it is possible to achieve more efficient solar cells exploiting the singlet exciton fission mechanism, and Semonin et al. [23] achieved an increase in the external photocurrent efficiency of quantum dot solar cells exploiting the multiple exciton generation mechanism.

The photophysical processes that are responsible for the population of electronic excited states after the fast absorption of light by the absorber can be exploited for several imaginable applications. An example is the work of Wu et al. [24], where photolysis kinetics, quantum yield and bioavailability of a ketone (acetylacetone) during UV irradiation were investigated. They found that, after the absorption of UV light by the ketone, a series of photophysical processes overcame the photochemical reactions of decomposition. Interestingly, they observed that the energy transfer mechanisms that occur after the absorption of sunlight guarantee the high efficiency of the photochemical changes. Since the degradation products of the ketone after the photochemical reactions were similar to the metabolic products in biofermentation, they argue that the acetylacetone may be used in water treatment at the pre-treatment stage and

may give some important information on the photochemical characteristics of several other β-diketones in water.

The energy transfer in organic systems can also be used to monitor distinct environments by enabling several mechanisms of tracking the changes in the electronic excited states involved in the photophysical or photochemical processes. Sensing and imaging are, therefore, ways to collect information on distinct environments.

In our research group [25], we have focused on the proposal of new materials that are able to efficiently form energy transfer complexes and give rise to new photophysical characteristics that are very sensitive to specific environmental changes. An example is a new material based on supramolecular structures of a dipeptide, diphenylalanine, composing an exciplex with a chromophore, coumarin. In distinct proportions, this system was able to modulate the coumarin sensibility to $O_{2(g)}$ dissolved in water, presenting distinct fluorescence spectra from that expected for coumarin, which was a result of the energy transfer complex formation and the new electronic excited states that resulted from the interactions between the components. Wang et al. [8], on the other hand, developed a method for monitoring photochemical reaction kinetics, presenting spatial resolution, the laser-excited muon pump-probe spin spectroscopy (photo-μSR). With this, they expected to monitor the dynamic of excitations and to explore the mechanism of photophysical and photochemical processes. Using pentacene as subject, they temporally and spatially mapped these processes at the single-carbon level and observed that the photochemical reactivity of a specific carbon atom is modified in the presence of a specific excited state.

Energy conversion can also be based on hole transfers or proton transfers and can involve photophysical processes, photochemical reactions or both processes in a collaborative way. Elbin and Bazan [7] proposed a new electron-deficient compound based on three-coordinate boryl substituents adjacent to highly conjugated distyrylbenzene derivative (DSB) or poly (aryleneethynylene)s (PAE). In these materials, boron atom provides a vacant p_z-orbital that confers them a strong electron acceptor character, enabling a significant delocalization. They showed that due to the distinct photophysical characteristics of the constituents, the excited state migration by FRET is modulated and, depending on the substituent, light of distinct colors are emitted from these systems. Based on that, they believed that these materials can find application in displays.

Also based on hole transfer to promote energy conversion is the electrochemical energy conversion in a system called fuel cell. It consists of an additional way for chemical energy conversion, without photocatalytic effect. It is an electrochemical system which converts chemical energy into electricity through the oxidation of a fuel [26, 27], which takes place in the anode of the cell, and the reduction of the oxygen from atmosphere in the cathode. Some of these fuel cells are classified by temperature operation [28], especially, Proton Exchange Membrane Fuel Cells (PEMFCs) work at low temperatures (from room to 100°C) [29] with a Nafion® membrane electrolyte. Low temperatures requires a very active catalyst in the electrodes, usually being platinum (Pt) [30]. A direct ethanol fuel cell (DEFC) is a very attractive electrochemical energy converter [31], and its unitary fuel cell scheme is shown in **Figure 8**. The fuel is supplied into the anode side and the air (or pure O_2(g)) is supplied into the cathode. The electrolyte carries protons from the anode to the cathode and the electrons are availed at an external electrical circuit to produce work.
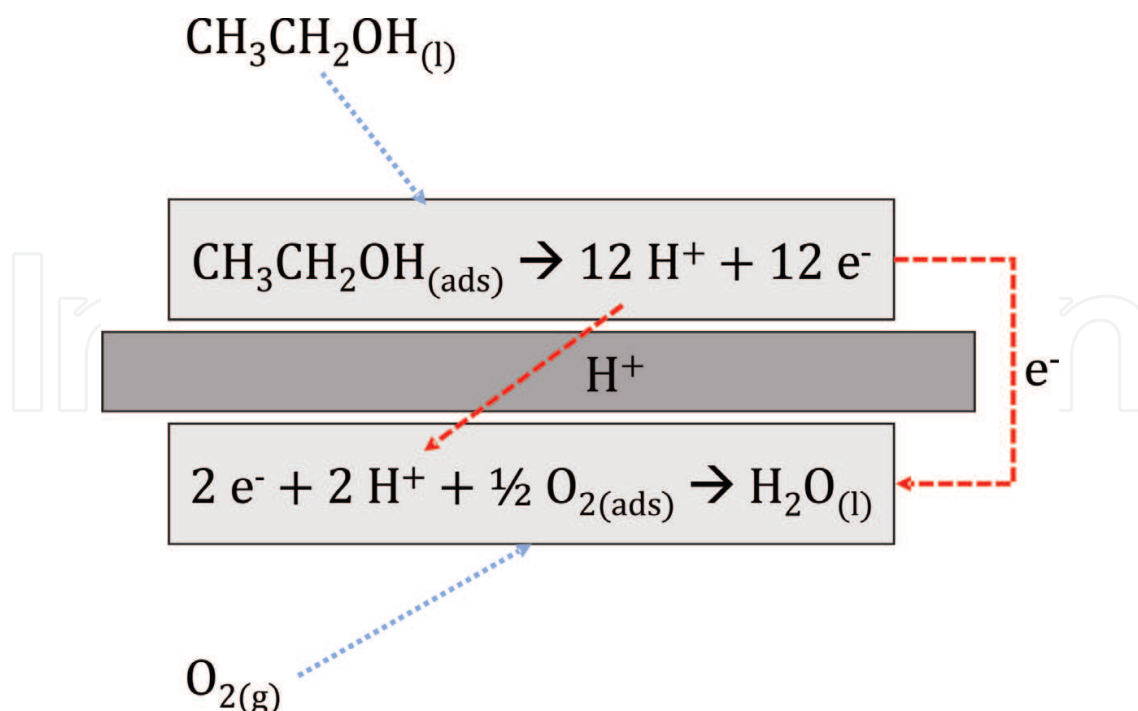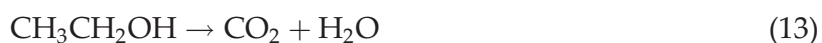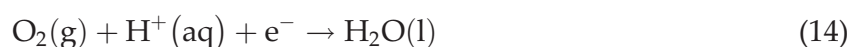
$$CH_3CH_2OH_{(l)}$$

$$CH_3CH_2OH_{(ads)} \rightarrow 12\ H^+ + 12\ e^-$$

$$H^+$$

$$e^-$$

$$2\ e^- + 2\ H^+ + \tfrac{1}{2}\ O_{2(ads)} \rightarrow H_2O_{(l)}$$

$$O_{2(g)}$$

Figure 8. Scheme of direct ethanol fuel cell.

Ethanol is inserted into the fuel cell, adsorbs at electrode surface and is oxidized as shown in **Figure 8**.

$$CH_3CH_2OH \rightarrow CO_2 + H_2O \tag{13}$$

While oxygen from air is reduced:

$$O_2(g) + H^+ (aq) + e^- \rightarrow H_2O(l) \tag{14}$$

Which gives the overall reaction of the direct ethanol fuel cell (admitting complete ethanol oxidation reaction):

$$CH_3CH_2OH(l) + O_2(g) \rightarrow H_2O(l) + CO_2(g) + energy \tag{15}$$

With the energy being mostly electrical work and heat. The electric work is dependent on the potential difference between cathode and anode: the larger the difference, the bigger the electrical work. Redox kinetics, thus, influences this amount of energy conversions, by inducing the number of electrons that are injected into the electrical circuit, resulting in electrical current.

At the anode, the ethanol adsorbs on electrode and the oxidation is characterized by the dehydrogenation. Some studies with Fourier transformed infra-red (FTIR) in situ [32], differential electrochemical mass spectroscopy (DEMS) [33, 34] show that the main products from electrochemical ethanol oxidation reaction, on Pt-based catalysts, are acetic acid and formaldehyde [35]. The electric work produced by direct ethanol fuel cell depends on the number of electrons that circulate at electrical circuit and the number of electrons generated by the redox reaction. Thus, the kinetic of ethanol oxidation reaction limits fuel cell performance.

Rightmire et al. [36] studied the ethanol oxidation reaction on Pt in acidic media and showed the determining step of the reaction is formaldehyde formation. Moreover, Hitmi et al. [37] showed that the rate of formation of acetaldehyde is larger than acetic acid formation from ethanol oxidation reaction. The formation of acetic acid from acetaldehyde depends on the adsorption of acetaldehyde on electrode surface, as proposed by Podlovchenko et al. [38].

$$CH_3CH_2OH_{sol} \rightarrow CH_3CH_2OH_{ads} \rightarrow CH_3CHO_{ads} \rightleftharpoons CH_3CHO_{sol} \quad (16)$$
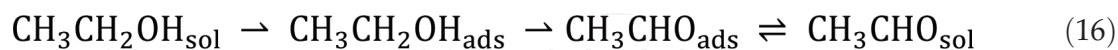
The main problem of the catalysts is the poisoning effect by carbonaceous products from ethanol oxidation reaction strongly adsorbed on Pt. Nowadays, research is focused on the development of new catalytics presenting higher chemical stability and electrochemical kinetic rates. There are several works reporting Sn-modified Pt electrocatalyst as a more active material for ethanol oxidation reaction [39]. There are many other interesting materials, such as PtRh [40], PtMo [41] and PtPd [42], but better performances of DEFC were observed employing PtSn at the anode, which effects the kinetic of ethanol oxidation [43, 44].

Figure 9 shows the linear sweep voltammetry obtained for the ethanol oxidation on Pt electrocatalysts. FTIR were collected *in situ* with electrode polarization in ethanol solution. Pt
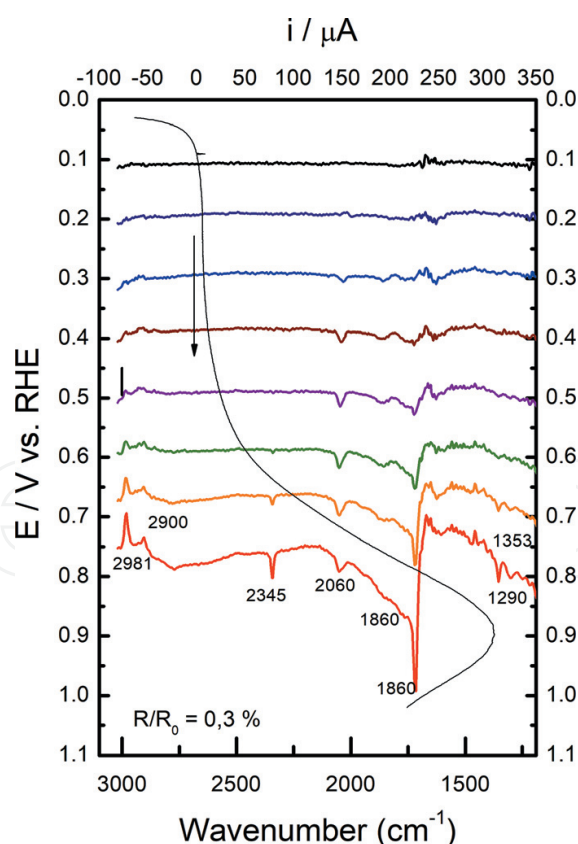

Figure 9. Linear sweep voltammetry and FTIR registered on Pt catalysts in 0.5 mol L^{-1} H$_2$SO$_4$ and 0.5 mol L^{-1} CH$_3$CH$_2$OH, at room temperature, v(lsv) = 1 mV^{-1} and FTIR measurements carried out in a mixture of 0.1 HClO$_4$ (mol L^{-1}) and CH$_3$CH$_2$OH (0.1 mol L^{-1}).

was polarized at 0.05 V vs. Reversible hydrogen electrode (RHE) and potential scan was set to 1.0 V at 1 mV s^{-1}, and the current in μA at top axis. The FTIR were collected at distinct electrode polarizations on steps of 0.1 V. The negative bands correspond to the formation of chemical species and positive bands correspond to consumption of adsorbed chemical species. The band at 2345 cm^{-1} refers to CO_2 formation [45] and it is observed only above 0.6 V vs. Reversible Hydrogen Electrode (RHE). The peak at 1860 cm^{-1} corresponds to COOH deflection [45] observed at 0.2 V, which suggests the fast formation of acetic acid on Pt, in acid solution and a difficulty to generate CO_2, which indicates complete ethanol oxidation. Peaks at 2981 and 2900 cm^{-1} correspond to CH_2 and CH_3 stretching, resulting from ethanol consumption. The peaks at 1715, 1353 and 1290 cm^{-1} correspond to the formation of aldehydes and carboxylic acids, such as acetaldehyde and acetic acid [32, 37].

Thus, the conversion of chemical energy into electrical energy depends on the potential and the kinetics of the reactions; the development of new materials for a better exploitation of fuel is, then, limited by the characteristics of the electrochemical reactions kinetics.

7. Conclusion

To understand the kinetic rates and laws of the dynamic processes of the energy transfers that involve the interaction between compounds, through the electronic excited states and the characteristics of the excited states is crucial to determine the applications, specially in energy conversion. Also, photochemical processes can be greatly exploited to cause the modifications in the materials that enable their ability of energy transfer. Regarding to this, the rate constants of the photochemical reactions determine the paths that yield products and they are strictly related to the electronic excited states involved in the photochemical processes. If rate constants, intermediate structures and their mechanisms of formation and the energetic balance involved in each change, it is possible to achieve the desired reaction control through experimental conditions control. New materials, capable of distinct electronic processes that can influence photophysical and photochemical processes, are of great interest, nowadays. They become more and more specific and selective, aiming higher efficiencies of energy conversion, as well as faster and sustainable ways to promote degradation of pollutants. Also, as energy conversion in fuel cells, depends on the kinetic rates of electron generation, the development of material for complete oxidation reaction of ethanol would disseminate its usage. This means that there are no limits to develop new materials with properties suitable for the needs of the modern society and those that promote changes using the abundant initiator of sunlight to trigger the changes are the most prominent candidates.

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