ENERGY AND INORGANIC CHEMISTRY

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Summary

World demand for energy is projected to more than double by 2050 and to more than triple by the end of the century. Finding sufficient supplies of clean energy for the future is one of society’s most important challenges. Sunlight provides by far the largest of all carbon-neutral energy sources. Solar energy conversion systems fall in three categories according to their primary energy product: solar electricity, solar fuels and solar thermal systems. Inorganic chemistry has played a fundamental role in the design of materials and molecular systems for solar energy conversion to electricity and for the production

of solar fuels.

This chapter will cover the basic principles and some of the relevant contributions of Inorganic Chemistry to the design of systems for solar energy conversion to electricity, of molecular level energy conversion devices, and of photoelectrochemical devices for hydrogen production.

1. Introduction

World demand for energy is projected to more than double by 2050 and to more than triple by the end of the century. Finding sufficient supplies of clean energy for the future is one of society's most important challenges. Sunlight provides by far the largest of all carbon-neutral energy sources. More energy from sunlight strikes the Earth in one hour $\left(4.3\times10^{20}\right)$ than all the energy consumed on the planet in a year $\left(4.1\times10^{20}\ \mathrm{J}\right)$. Yet solar electricity provides only approximately 1 millionth of the total electricity supply, and renewable biomass provides less than 0.1% of the total energy consumed. The huge gap between our present use of solar energy and its enormous undeveloped potential defines a grand challenge in energy research.

Solar energy conversion systems fall in three categories according to their primary energy product: solar electricity, solar fuels and solar thermal systems. Inorganic chemistry has played a fundamental role in the design of materials and molecular systems for solar energy conversion to electricity.

The challenge in converting sunlight to electricity via photovoltaic cells is dramatically reducing the cost/watt of delivered solar electricity. New materials to efficiently adsorb sunlight and new approaches based on nanomaterials can revolutionize the technology used to produce solar electricity. The technological development of single-crystal solar cells demonstrates the practicality of photovoltaics, while novel approaches exploiting thin films, organic semiconductors, dye sensitisation offer new opportunities for cheaper, long lasting systems.

For millennia, cheap solar fuel production from biomass has been the primary energy source on the planet; however the use of existing types of plants requires large land areas to meet a significant portion of primary energy demand. Inorganic chemistry has been involved in the design of solar fuels based on artificial, molecular-level energy conversion machines exploiting the principles of natural photosynthesis. Artificial assemblies of organic and inorganic materials replacing natural plants or algae can now use sunlight to directly produce hydrogen by splitting water. The current laboratory systems are however unstable over long periods, and too inefficient for practical applications. Basic research is needed therefore to bridge the gap between the frontier and practical technology.

Recently, considerable advances have been made in the production of hydrogen with photoelectrochemical solar cells thanks to the development of high surface area nanocrystalline semiconductors.

This chapter will cover the basic principles and some of the relevant contributions of Inorganic Chemsitry to the design of systems for solar energy conversion to electricity, of molecular level energy conversion machines, and of photoelectrochemical devices for hydrogen production.

2. General Background

2.1. Electronic Excited States

The first act of any photochemical and photophysical process is the absorption of a photon by a chemical species.

It is known from electronic spectroscopy that the probability of light absorption (and the intensity of the corresponding absorption band) is related to the characteristics of the initial and final states involved and particularly to their spin quantum number. Transitions from the ground state to excited states having the same spin quantum numbers are allowed and give rise to intense bands, whereas transitions to excited states of different spin value are forbidden (neglecting spin-orbit coupling) and can hardly be observed in the absorption spectra.

In most molecules the ground state is a singlet and the lowest excited state is a triplet that cannot be directly populated by light absorption but can be obtained from the deactivation of upper excited states. For this reason at least three states (singlet ground state and excited singlet and triplet states) are involved in photochemical processes as shown in the diagram in Figure 1.

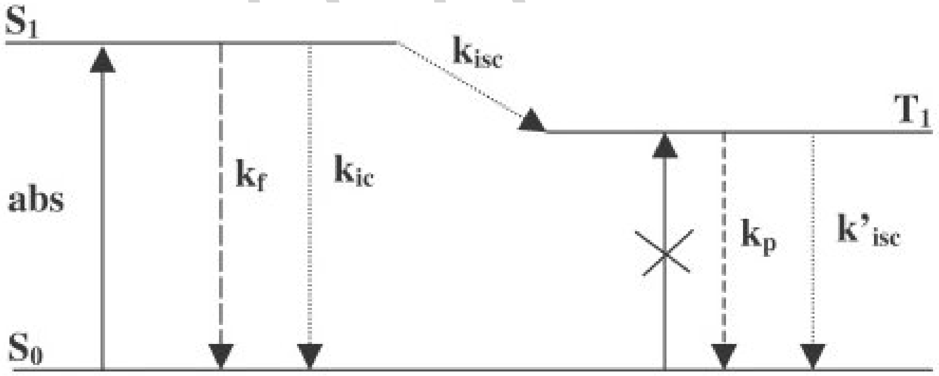

Figure1. Jablonski diagram showing the formation and the photophysical deactivation processes of excited states. k_f , k_{ic} , k_{isc} , k_p and k'_{isc} are the unimolecular rate constants for fluorescence, internal conversion, S_1-T_1 intersystem crossing, phosphorence, T_1-S_0 intersystem crossing respectively.

The excited state that is formed following light absorption is a high energy unstable species which may undergo to different possible deactivations. Photophysical excited state deactivations can occur via emission of light (luminescence) or degradation of the excess energy into heat (radiationless deactivation).

Luminescence is called fluorescence or phosphorence depending on whether the excited state has the same or different spin compared to the ground state. In the same way radiationless deactivation is called internal conversion when it occurs between states of the same spin and intersystem crossing when it occurs between states of different spin. Each intramolecular decay step is characterized by a rate constant (Figure 1) and each excited state by its lifetime given by,

$$\tau = \frac{1}{\sum_i k_i} \tag{1}$$

where k_i is the first order rate constant for a generic unimolecular process that causes the disappearance of the excited state.

For each process it can be defined the quantum yield, given by the ratio between the number of chemical species (molecules, photons, etc.) produced and the number or photons absorbed per unit of time. A particularly important quantity when dealing with coordination compounds is the quantum yield of emission from the lowest spin forbidden excited state (phosphorescence quantum yield Φ_p) given by the following relation (referring to Figure 1)

$$\Phi_\mathrm{p} = \eta_\mathrm{p} k_\mathrm{p} \tau_{T_1} \tag{2}$$

η_isc is the efficiency of population of the emitting excited state from the state populated by light absorption and τ_{T_1} is the lifetime of the emitting excited state given by

$$\tau_{T_1} = \frac{1}{k_\mathrm{p} + k_\mathrm{isc}} \tag{3}$$

When the intramolecular deactivation steps are not too fast, i.e. when the lifetime of the excited state of a species A is sufficiently long, the excited molecule may have a chance to give rise to bimolecular processes involving a second species B which can encounter A freely diffusing in solution or be linked to A via a variety of chemical interactions. Usually for transition metal complexes only the lowest spin forbidden excited state satisfies this requirement.

The most important bimolecular processes are energy transfer and electron transfer.

$$*\mathrm{A} + \mathrm{B} \xrightarrow{k_\mathrm{en}} *\mathrm{A} + \mathrm{B} \quad \text{energy transfer} \tag{4}$$

$$*\mathrm{A} + \mathrm{B} \xrightarrow{k_\mathrm{et,red}} \mathrm{A}^+ + \mathrm{B}^- \quad \text{oxidative electron transfer} \tag{5}$$

$$*\mathrm{A} + \mathrm{B} \xrightarrow{k_\mathrm{et,ox}} \mathrm{A}^- + \mathrm{B}^+ \quad \text{reductive electron transfer} \tag{6}$$

Electron transfer may involve either the oxidation or the reduction of the excited state. The ability of an excited state to intervene in energy transfer process is related to its zero-zero spectroscopic energy, E^{0-0}, while for the electron transfer the relevant thermodynamic parameters are the oxidation (5) and reduction (6) potentials of the $\mathrm{A}^{+}/\mathrm{A}^{*}$ and $\mathrm{A}^{*}/\mathrm{A}^{-}$ couples. Because of its higher energy content an excited state is both a stronger reductant and a stronger oxidant than the corresponding ground state. To a first approximation the redox potentials for the excited state couples may be calculated from the potentials of the ground state couples and the zero-zero excitation energy E^{0-0}:

$$E\left(\mathrm{A}^{+}/\mathrm{A}^{*}\right) = E\left(\mathrm{A}^{+}/\mathrm{A}\right) - E^{0-0} \qquad (7)$$

$$E\left(\mathrm{A}^{*}/\mathrm{A}^{-}\right) = E\left(\mathrm{A}^{*}/\mathrm{A}^{-}\right) - E^{0-0} \qquad (8)$$

2.1.1. Classification of Excited States in Coordination Complexes

Great attention is currently paid to transition metal complexes for their photochemical, photophysical and electrochemical properties. This interest is stimulated in particular by attempts to design and construct systems capable of performing useful light or redox induced functions.

Transition metal complexes are made of metal ions and ligands which can also exist separately from each other. The metal ligand interaction is often weak enough to allow the manifestation of intrinsic properties of the metal and ligands (e.g. ligand centered and metal centered absorption bands and redox waves) but strong enough to cause the appearance of new properties characteristic of the whole compound (e.g. metal-to-ligand or ligand-to-metal charge transfer bands).

For this reason the spectroscopic, redox and kinetic properties of transition metal complexes are usually discussed with the assumption that the ground state, the excited state and the redox species can be described in a sufficiently approximate way by localized molecular orbital (MO) configurations, therefore it is possible to make a classification of the various electronic transitions according to the localization of the molecular orbitals involved. Specifically three fundamental types of electronic transitions are identified:

- Transitions between MOs predominantly localized on the central metal are called metal centered, ligand field (LF) or d-d transitions;
- Transitions on the ligands are usually called ligand-centered (LL*) or intraligand transitions;
- Transitions involving MOs of different localization, which cause the displacement of electronic charge from the ligands to the metal or viceversa. These transitions are divided in metal- to-ligand-charge-transfer (MLCT) and ligand-to-metal-charge-transfer (LMCT) transitions.

For sake of clarity Figure 2 reports a simplified qualitative MO diagram for Ru(II) polypyridine complexes, an extensively studied class of compounds because of their useful excited state properties.

Ru^{2+} is a d^6 metal ion and the polypyridine ligands possess σ donor orbitals localized on the nitrogen atoms and π^* acceptor orbitals delocalized on the aromatic rings.

According to a single configuration one electron description of the excited state in an octahedral geometry the excitation of an electron from a filled metal centered dπ orbital to the π^* orbital of the ligands give rise to an MLCT excited state, whereas promotion of an electron from the $d\pi$ to the $d\sigma$ orbital results in a ligand field (LF) excited state. Ligand centered excited states are obtained by promoting an electron from π_L to π_L^*. All these excited state may have singlet or triplet multiplicity although spin orbit coupling mixes the multiplicity in MLCT and MC excited states.

The high energy excited states of transition metal complexes undergo fast radiationless deactivation and only the lowest excited state and the upper states populated on the basis of the Boltzmann equilibrium law may play a role in photon emission and in energy and/or electron transfer.

When the lowest state is LF it undergoes fast radiationless deactivation to the ground state and/or ligand dissociation reactions. As a consequence at room temperature the excited state has a very short lifetime, no luminescence can be observed and no bimolecular processes usually take place. On the other hand LL* and MLCT excited states are usually not strongly displaced compared to the ground state geometry and luminescence can be observed.

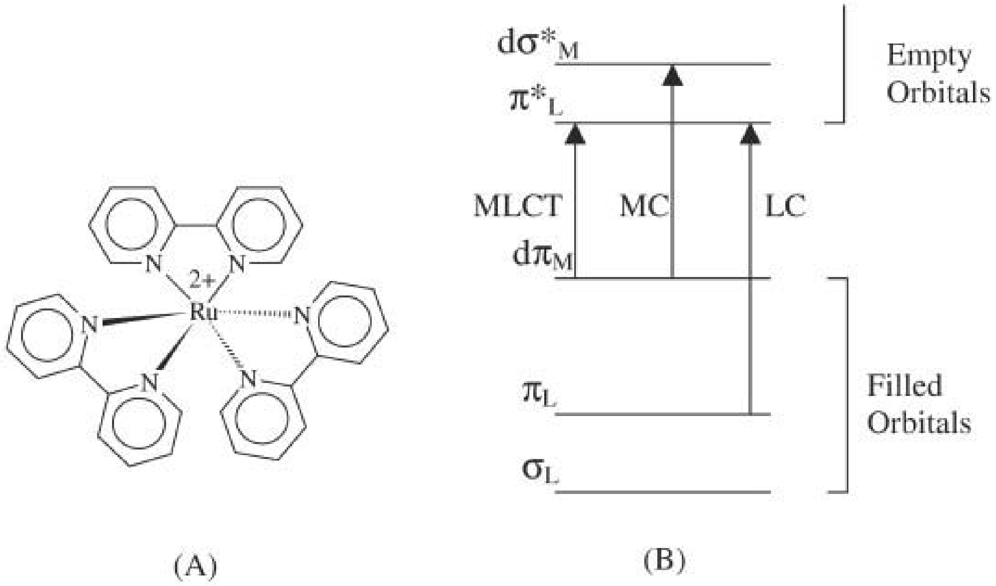

Figure 2: (A) Structure of $Ru(bpy)_3^{2+}$ and (B) Simplified molecular orbital diagram for $Ru(bpy)_3^{2+}$ complex showing the types of transitions occurring in the UV-Visible region.

The energy positions of the LF, MLCT and LL* states depend on the ligand field strength, the redox properties of metal and ligands and the intrinsic properties of the ligands. As a consequence in a series of complexes of the same metal ion the energy ordering of the various excited states can be controlled by a rational choice of the ligands. In this way it is possible to design complexes having, at least to a certain degree, the desired properties. For most Ru(II) polypyridine complexes, the lowest excited state is ^{3}MLCT which undergoes relatively slow radiationless transitions and thus exhibits long lifetime and intense luminescence emission.

2.2. Electron Transfer Processes

Many coordination compounds and notably Ru(II) polypyridine complexes are extensively studied in energy and electron transfer processes. Electron transfer kinetics are particularly important because they are the initiating event of many of the energy conversion reactions that will be treated in detail in the following sections.

Electron transfer regardless of the ground or excited state nature of the reactants can be treated with the same formalism.

The electron transfer reaction can be schematized as

$$*\mathrm{A} + \mathrm{B} \rightarrow \mathrm{A}^+ + \mathrm{B}^-$$

where an excited donor $(*\mathrm{A})$ transfers an electron to an acceptor B becoming an oxidized species B^+ at the ground state.

The general equation expressing the rate constant of a reaction is the Eyring equation

$$k_{\mathrm{et}} = k\nu \exp\left(\frac{-\Delta G^*}{KT}\right) \tag{9}$$

Where ΔG^* is the activation energy of the process, K ant T are the Boltzmann constant and the absolute temperature respectively, ν is the nuclear frequency factor and k is the transmission coefficient, a parameter which expresses the probability of the system to evolve from the reactant configuration to the product one once it has been reached the crossing of the potential energy curves along the reaction coordinate (Figure 3).

In case of electron transfer reaction it has been proposed a modification of (9) due to R. Marcus[7]

$$k_{\mathrm{et}} = k\nu \exp\left(\frac{-(\Delta G^0 + \lambda)^2}{4\lambda KT}\right) \tag{10}$$

where the activation energy ΔG^* is expressed as

$$\Delta G^* = \left(\frac{\left(\Delta G^0 + \lambda\right)^2}{4\lambda} \right) \quad (11)$$

ΔG^0 is the free energy variation which accompanies the process, while λ is the total reorganizational energy and represents the vertical energy necessary to transform the nuclear configurations of the reactant and of the solvent to those of the product state (Figure 3). It is the sum of inner λ_i and outer λ_o components: λ_i is due to the vibrational rearrangement consequent to the electron transfer, while λ_o is comprehensive of the reorganization of the solvation sphere (repolarization).Electron transfer reactions have been also treated from the quantum mechanical point of view in formal analogy to radiationless transitions, considering the weakly interacting states of a supermolecule AB: the probability (rate constant) of the electron transfer is given by a "golden rule" expression of the type ,

$$k_\text{et} = \frac{4\pi^2}{h}\left(H_{AB}{}^\text{el}\right)^2 FCWD \quad (12)$$

Where $H_{AB}{}^\text{el}$ is the electronic coupling factor between the two electronic states involved in the process and $FCWD$ is the Franck-Condon factor (nuclear factor) weighted for the Boltzmann population of the energy levels. It can be shown that in the high temperature limit (when $h\nu < kT$ for the relevant nuclear vibrational frequencies, an approximation not too inaccurate for many cases at room temperature) the nuclear factor takes the form,

$$FCWD = \left(1/4\pi\lambda kBT\right)^{1/2} \exp\left[-\left(\Delta G^0 + \lambda\right)^2 \Big/ 4\lambda kBT\right] \quad (13)$$

The exponential term of Eq. (13) is the same as that predicted by the classical Marcus model based on parabolic (free) energy curves for reactants and products such as those of Figure 3, where the activation free energy is that required to go from the equilibrium geometry of the reactants to the crossing point of the curves. Both the classical and quantum results in equations (10) and (13) contain an important prediction, namely, that three typical kinetic regimes exist, depending on the driving force of the electron transfer reaction: (i) a "normal" regime for small driving forces $\left(-\lambda < \Delta G^0 < 0\right)$ where the process is thermally activated and is favored by an increase in driving force; (ii) an "activationless" regime $\left(-\lambda = \Delta G^0\right)$ where no gain in rate can be obtained by changing the driving force; (iii) an "inverted" regime for strongly exergonic reactions $\left(-\lambda > \Delta G^0\right)$ where the process slows down with increasing driving force. Increasing λ slows down the process in the normal regime, but accelerates it in the inverted regime. The three kinetic regimes are schematically shown, in terms of classical Marcus' parabolas, in Figure 4.

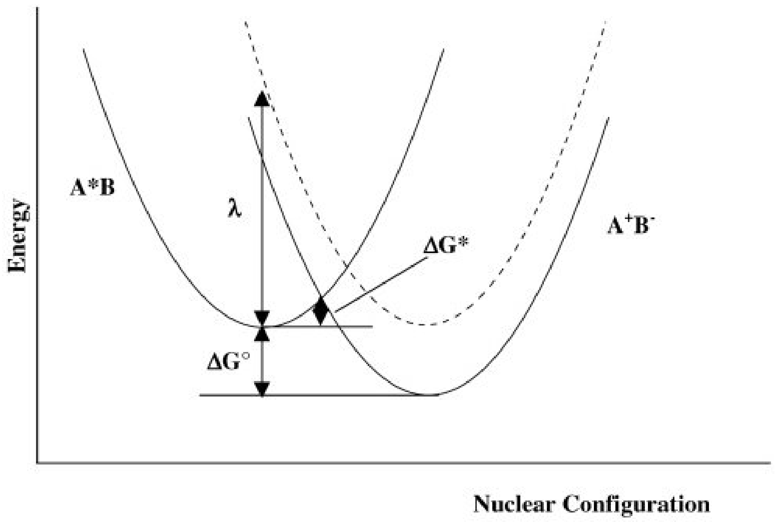

Figure 3: Free energy curves and kinetic parameters for an electron transfer process

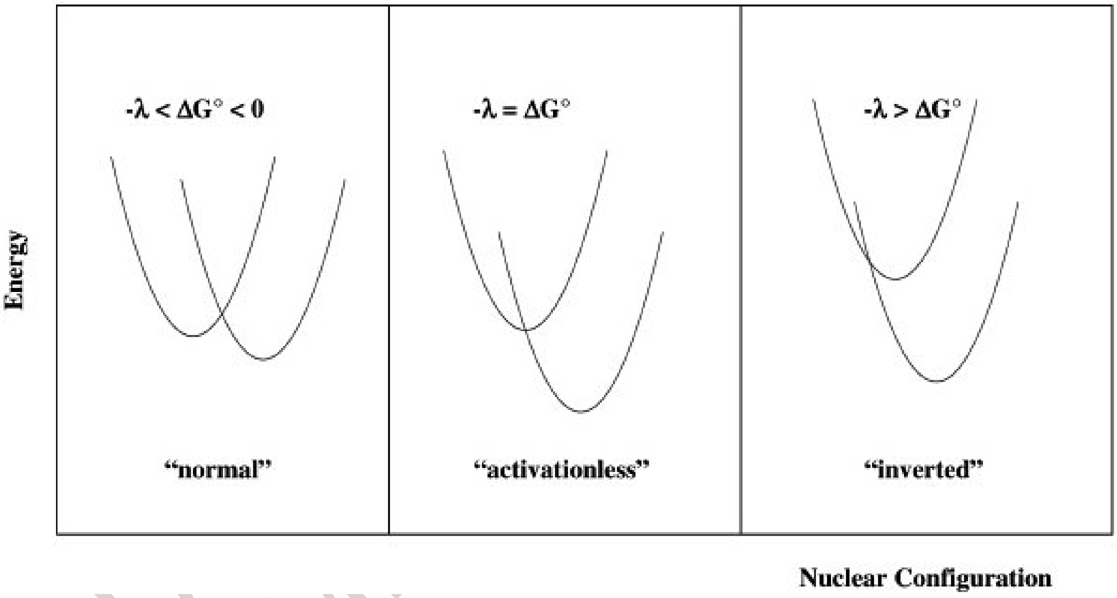

Figure 4: Free energy curves for reactant and product states of an electron transfer process in the energy ranges of the Marcus model

The inverted region was initially predicted by Marcus and the decrease in the electron transfer rate constant with $-\Delta G^0$ has been observed experimentally many times. This is an important and remarkable result both for natural and artificial photosynthesis and energy conversion: it predicts that, following electron transfer quenching of the excited $A^*\text{-}B$, the back electron transfer in the inverted region for the charge separated state $A^+\text{-}B^-$ becomes slower as the energy stored increases.

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Professor Bignozzi's research is concerned with experimental investigations in photoinduced energy and electron transfer processes in inorganic coordination compounds, in extended solids and in functional nanomaterials. The overall goal of the research is to develop a molecular level understanding of chemical reactivity and excited state reactivity in homogeneous and heterogeneous environments important to material science and photochemistry. Practical applications of this research include solar energy conversion, chemical sensing, photocatalysis, design of nanomaterials for environmental decontamination, photochromic and electrochromic devices. He is the author of over 140 papers and review articles on international journals and of 10 patents.