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Organic Photochemistry

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Preface

The use of light to effect chemical change has been recognised for many years, but it is only recently that sufficient knowledge has been attained to place photochemical reactions in the realm of organic synthesis. The recent application, by Woodward and Hoffmann, of the principle of conservation of orbital symmetry to concerted reactions has made an important contribution to the understanding of many photochemical processes. This book has been written to provide an introduction to the principles and applications of organic photochemistry at a level suitable for senior undergraduate and graduate students in universities and technical institutes. It is not intended to provide an exhaustive survey of the field but rather to provide the student with an up-to-date background of the subject, on which a more detailed study can be based.

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J. M. C.
New Zealand, 1972 B. H.

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1 Introduction – excitation and the excited state

Photochemistry is the study of chemical reactions initiated by light. The interaction of electromagnetic radiation with matter covers a very wide field but it is only recently that this area of chemistry has been given serious and systematic attention. The quantum mechanical theory, developed in the late nineteen twenties, has helped in particular to rationalise the interaction of light with matter. Despite this major advance in theory, the study of organic photochemistry did not progress significantly because of the lack of suitable ultraviolet light sources and the difficulty in analysing unusual, and often complex, product mixtures. Recent improvements in analytical techniques, the development of spectroscopic methods in organic chemistry, and the availability of commercial ultraviolet light sources, have all contributed to the present rapid expansion of organic photochemistry.

1.1. The interaction of electromagnetic radiation with matter.(1–4) Electromagnetic radiation can be regarded as having a dual nature. It is propagated through space, in wave form, obeying the relationship $c = \nu\lambda$, where c is the speed of electromagnetic radiation (2.9979×10^8 m s^{-1}), ν the frequency and λ the wavelength of the radiation. At the same time, absorption or emission of radiation by matter occurs only in discrete quanta (photons) and is governed by the relationship

$$E = h\nu = hc/\lambda,$$

where E is the energy absorbed or emitted and h is the constant of proportionality or Planck's constant (6.6256×10^{-34} J s). The amount of energy absorbed or emitted is inversely proportional to the wavelength of the radiation – short wavelengths correspond to high energy absorption and long wavelengths to low energy absorption.

When a molecule absorbs energy the process is referred to as *excitation*. The molecule is raised from its *ground state* of minimum energy, to an *excited state* of higher energy. In the infrared, visible, or ultraviolet regions of the electromagnetic spectrum this may involve excitation in the rotational, vibrational or electronic energy levels. A change in the rotational levels of a molecule is characterised by low energy (long wavelength) absorption in the far infrared, while an increase in the vibrational energy of a molecule requires from 10 to 100 times more energy and occurs in the infrared region of the spectrum. An increase in molecular energy by excitation within the electronic levels requires promotion of an electron from one molecular orbital to another of higher energy, and this is an even more energetic process than vibrational excitation. In fact energy in excess of 10 times that required for vibrational excitation is required, with absorption occurring in the ultraviolet and visible regions of the spectrum. It is the last process (electronic excitation) that is of prime importance in organic photochemistry, although it is inevitably accompanied of course by some increase in vibrational and rotational energy.

Absorption by a molecule, of radiation in the ultraviolet (200–400 nm) or visible (400–800 nm) region of the spectrum can result in an excited state so high in energy that the energy absorbed is comparable in magnitude with the bond dissociation energies associated with organic molecules. For one molecule the energy of excitation $= hc/\lambda$ and for one mole the energy of excitation $= Lhc/\lambda$, where L is the Avogadro constant,

$$= \frac{6.0225 \times 10^{23} \times 6.6256 \times 10^{-34} \times 2.9979 \times 10^{8}}{\lambda(\text{nm}) \times 10^{-9}} \text{ J mol}^{-1}$$

$$= \frac{1.20 \times 10^{5}}{\lambda(\text{nm})} \text{ kJ mol}^{-1}.$$

If absorption occurs at 250 nm, then the energy associated with this transition ($E = 480$ kJ mol^{-1}) is greater than the bond dissociation energy of a carbon–carbon σ-bond ($D \sim 347$ kJ mol^{-1}). It is not surprising, therefore, that chemical reaction can be induced by excitation with ultraviolet light. The first law of photochemistry, the Grotthus–Draper law, states that only the radiation absorbed by a molecule can be effective in causing chemical change. However, not every photon ($h\nu$) absorbed by a molecule will necessarily produce a chemical change. The excitation energy can be lost by fluorescence or phosphorescence (p. 10), or by molecular collision.

1.2. Excitation.$^{(1-4)}$ Interaction of matter with electromagnetic radiation results in excitation of the matter to a higher energy level. With electronic excitation the transition that the electron undergoes can be classified according to the orbitals involved.

The Schrödinger wave equation describes the electron distribution in the hydrogen atom by the atomic orbitals s, p, d and f and these orbitals can be used for all other atoms. Molecular orbitals are formed by a combination of the atomic orbitals, the most common being a *linear combination of atomic orbitals* (LCAO). A given number of atomic orbitals always gives rise to the same number of molecular orbitals. Combination of two atomic orbitals, on different atoms, by overlap along the internuclear axis results in the formation of two molecular orbitals, a bonding orbital (either σ or π), and an antibonding orbital (σ^* or π^*). The overlap of spherical s-orbitals always results in the formation of the molecular orbitals σ and σ^*, whereas the molecular orbitals formed by the linear combination of two p-orbitals will depend on their relative orientation. End-on overlap, along the internuclear axis, leads to σ- and σ^*-molecular orbitals (fig. 1.1(*a*)) while side-on overlap results in a bonding π- and an antibonding π^*-molecular orbital (fig. 1.1(*b*)). The wave function used to describe an atomic p-orbital shows one lobe of the orbital to be positive and one to be negative. A bonding combination of atomic orbitals requires the overlap of orbitals of like sign and is characterised by a concentration of electron density between

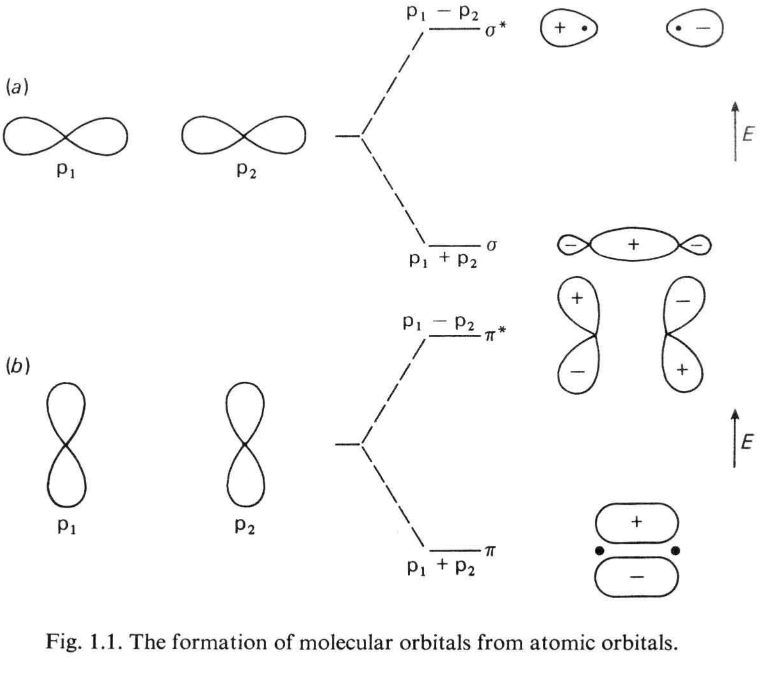

Fig. 1.1. The formation of molecular orbitals from atomic orbitals.

the bonding atoms. Overlap of orbitals of unlike sign leads to an antibonding molecular orbital characterised by a depletion of electron density between the bonding atoms (fig. 1.1). Orbitals not involved in the LCAO process are described as non-bonding n-orbitals, the energies of which are generally between that of the highest bonding and lowest antibonding molecular orbital.

Two electrons are assigned to each molecular orbital such that their spins are paired and, in general, a molecule in its ground state has all of its electrons spin-paired in the bonding (and non-bonding) orbitals. Electronic excitation of a molecule results in the promotion of an electron from one molecular orbital to another of higher energy, e.g., $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. In simple molecules excitation of an electron from the σ- to the σ*-orbital requires the greatest energy (fig. 1.2) and the wavelength of the absorption associated with this transition is generally below 150 nm in the far ultraviolet (10–200 nm), a region of the electromagnetic spectrum not readily accessible to conventional irradiation apparatus. This transition is therefore of limited significance to the organic photochemist and this is also true of the $n \rightarrow \sigma^*$ transition, requiring wavelengths of excitation of *c.* 200 nm. It is the alternative excitation processes ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) that are responsible for the bulk of organic photochemical reactions. The wavelength of light associated with these two excitations is observed in accessible regions of the ultraviolet and visible part of the electromagnetic spectrum.

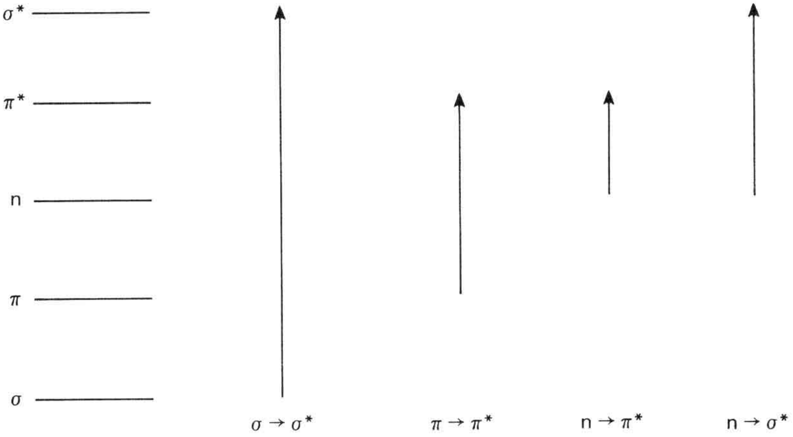

Fig. 1.2. Electronic excitation processes.

The absorption wavelength for any particular transition is dependent on the structure of the molecule. For ethylene the $\pi \rightarrow \pi^*$ transition occurs at 171 nm with an associated energy of 700 kJ mol^{-1}, while for butadiene the lowest $\pi \rightarrow \pi^*$ transition is observed at 214 nm with an associated energy of only 560 kJ mol^{-1}. As conjugation is increased, the energy required for $\pi \rightarrow \pi^*$ excitation decreases and the transition occurs at longer wavelength. The $n \rightarrow \pi^*$ excitation of saturated carbonyl compounds occurs at *c.* 280 nm and corresponds to an energy of *c.* 430 kJ mol^{-1}.

The $\pi \rightarrow \pi^*$ excitation process (fig. 1.3) can result in two possible electron arrangements. The arrangement with the electron spins paired is termed the *singlet state*, and designated S_1, and that with the electron spins parallel is termed the *triplet state*, and designated T_1. This nomenclature follows from the multiplicity (M) observed in atomic absorption and emission spectra. M is defined as $2S + 1$, where S is the total spin of the system. Thus with a spin-paired system, $S = 0$ and $M = 1$ (singlet), and for a spin-parallel system, $S = 1$ and $M = 3$ (triplet). The subscript 1 after S and T defines the excited states as the first excited singlet and triplet respectively. The ground state with the electron spins paired is consequently a singlet and designated S_0. Of the excited states S_1 and T_1, the triplet is of lower energy in accord with Hund's rule, which states that the most stable arrangement of electrons in atoms (or molecules) is that with maximum multiplicity. In addition to this, the triplet will have a longer lifetime than the singlet state since a spin inversion must accompany any deactivation of the triplet. The $n \rightarrow \pi^*$ excitation of a

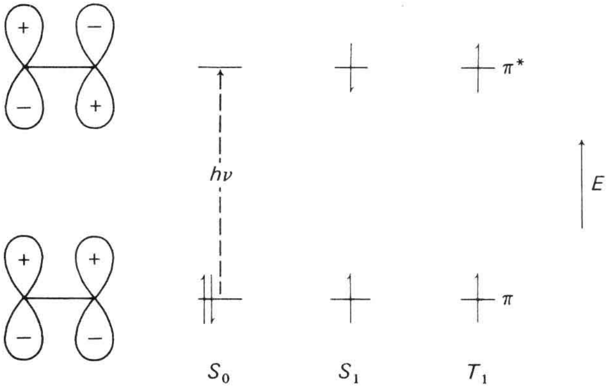

Fig. 1.3. $\pi \rightarrow \pi^*$ excitation of ethylene.

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carbonyl group is depicted in fig. 1.4, and again singlet and triplet excited states are possible. The n → π* excitation is energetically more favoured than π → π* excitation of the carbonyl group and, although the latter process is observed at *c.* 170 nm, it is the former excitation process that is responsible for the majority of the photochemical reactions of ketones.

Electronic transitions occur very rapidly (*c.* 10^{-15} s), more rapidly than the time required for a molecular vibration (*c.* 10^{-13} s), and consequently the geometry of the excited state produced will be initially the same as that of the ground state from which the electron promotion occurred. The Frank–Condon principle states that the relative nuclear positions are unaltered in electronic excitation and corresponds to the vertical transition shown on the potential energy diagram (fig. 1.5). The equilibrium internuclear distance of the excited state will be greater than that of the ground state, a consequence of excitation from a bonding molecular orbital to an antibonding molecular orbital. A molecule in the ground state will exist in one of its lowest vibrational levels (represented by the horizontal lines in fig. 1.5) and excitation obeying the Frank–Condon principle will afford the first excited singlet of the molecule high in vibrational energy. The excess vibrational energy of the excited state will be rapidly lost by molecular collisions and dissipated as heat. Electronic transitions can occur from any vibrational level of the ground state to any vibrational level of the excited state. Thus the energy required to effect an electronic transition will vary within a limited range and give rise to a broad absorption band.

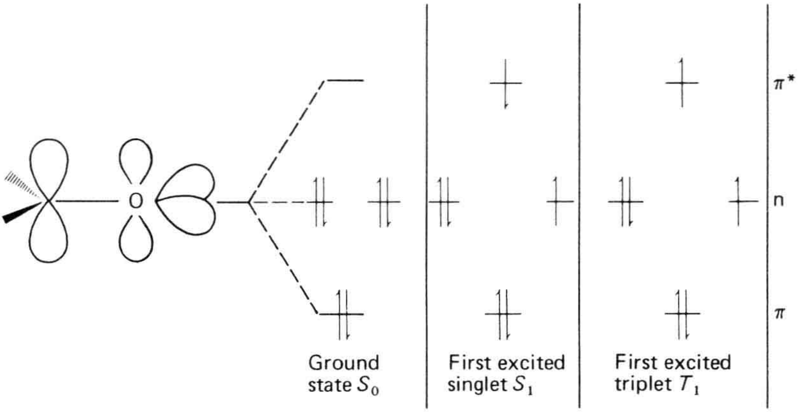


Fig. 1.4. n → π* excitation of the carbonyl group.

The intensity of an absorption band follows two empirical laws: Lambert's law, which states that the fraction of radiation absorbed is independent of the source intensity, and Beer's law, which states that the radiation absorbed will be directly proportional to the solution concentration. While this latter law does not hold over a wide concentration range, in dilute solutions the deviations are small. The following equation, known as the Beer–Lambert law, is a mathematical expression of these laws:

$$\log_{10}\frac{I_0}{I} = A = \varepsilon c l \qquad \text{(Beer–Lambert law).}$$

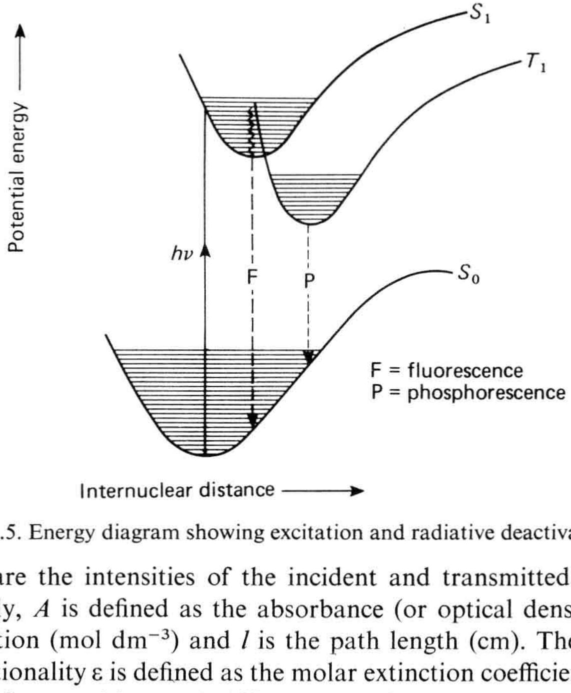


Fig. 1.5. Energy diagram showing excitation and radiative deactivation.

I_0 and I are the intensities of the incident and transmitted radiation respectively, A is defined as the absorbance (or optical density), c the concentration (mol dm^{-3}) and l is the path length (cm). The constant of proportionality ε is defined as the molar extinction coefficient and is a measure of a transition probability. For a singlet $\pi \rightarrow \pi^*$ excitation, ε normally has a value in the range 10^2–10^4 m^2 mol^{-1}, indicating a high probability of excitation, while for a singlet $n \rightarrow \pi^*$ process ε is usually in the range 1–5 m^2 mol^{-1}. For singlet to triplet excitation processes, the extinction coefficients are very small and less than unity, indicating the low probability of these transitions.

The application of quantum mechanical theory to electronic excitation processes has led to a set of *selection rules* by which transitions can be classified as allowed or forbidden. All excitation processes involving conservation of spin (or multiplicity) are allowed, e.g. $S_0 \rightarrow S_1$, $T_1 \rightarrow T_2$, while those involving a change in spin are *spin-forbidden*, e.g. $S_0 \rightarrow T_1$. Excitation processes between states with the same symmetry are allowed, e.g. $\pi \rightarrow \pi^*$ singlet excitation of ethylene, while transitions between states of different symmetry are *symmetry-forbidden*, e.g. $n \rightarrow \pi^*$. Although $S_0 \rightarrow T_1$ excitation is a spin-forbidden process, it is, in fact, often observed owing to a breakdown in the selection rules. The selection rules result from calculations based on the electronic states being 'pure'. In practice the true nature of a given state, singlet or triplet, will include some mixing with other states, which is due to an interaction between the electron spin vector and the orbital angular momentum vector. This is known as spin orbit coupling. Thus a first excited triplet state is more accurately described as largely T_1 with small components due to S_0, S_1, T_2 and perhaps other excited states. Mixing of states is enhanced by magnetic fields, unpaired electrons, and heavy atoms. For example, 9,10-dibromoanthracene has a more intense $S_0 \rightarrow T_1$ absorption than has anthracene itself. The low intensity of $S_0 \rightarrow T_1$ transitions preclude these from being an effective method of populating the triplet excited state. The symmetry-forbidden $n \rightarrow \pi^*$ singlet excitation is usually observed with an extinction coefficient between 1 and 5 $m^2\ mol^{-1}$ which is of sufficient magnitude to obtain a significant excited singlet state population. Failure of the selection rules to hold rigorously for symmetry-forbidden transitions results from a modification of the ground (or excited) state symmetry by vibrational motion of the molecule. A vibrational mode has characteristic symmetry; it may differ from that of the stationary chromophore and when this is so any description of the ground (or excited) state symmetry must include the vibrational components. A transition can occur when any of the symmetry components are common to both the ground and excited states.

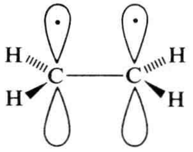
1.3. The excited state.(1–7) The shorter lifetime and higher energy of the singlet compared with the triplet excited state may be attributed to a difference in electron spin. The longer lifetime of an excited triplet species reflects the need for a spin inversion to accompany any deactivation. In general, singlet excited states have lifetimes in the range 10^{-9} to 10^{-5} seconds while triplets are much longer lived and have lifetimes in the range 10^{-5} to 10^{-3} seconds. An estimate of the singlet excited state lifetime τ, is obtained from the following expression

$$\tau \sim \frac{10^{-5}}{\varepsilon_{\max}} \text{ seconds}$$

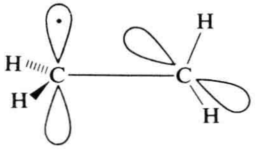
where ε_{max} is the molar extinction coefficient at the wavelength corresponding to maximum absorption. For example, the $\pi \rightarrow \pi^*$ singlet excitation of ethylene has a maximum of 171 nm with an extinction coefficient of 1553 $m^2\ mol^{-1}$ resulting in an estimated singlet lifetime of 6.4×10^{-9} seconds, while the singlet $n \rightarrow \pi^*$ excitation of acetone has a maximum at 279 nm with an extinction coefficient of 1.5 $m^2\ mol^{-1}$ resulting in an estimated singlet lifetime of 6.7×10^{-6} seconds.†

The difference in spin between excited singlet and triplet species gives rise to different properties. The singlet spin-paired state is diamagnetic while the triplet state, with two unpaired spin-parallel electrons, is paramagnetic. For any reaction to proceed from the triplet state, paramagnetic quenchers and free radical scavengers, such as molecular oxygen, must be excluded. The most powerful diagnostic tool for characterisation of a triplet state species is electron paramagnetic resonance spectroscopy (e.p.r.).⁽⁵⁾ E.p.r. is similar to nuclear magnetic resonance but is a consequence of *electron* spin rather than *nuclear* spin. Since all singlet states are spin-paired ($S = 0$), this method is not applicable to their detection. A triplet state, with a total spin $S = 1$, consists of a set of three sublevels arising from the magnetic quantum numbers, $M_S = 0, \pm 1$. In an external magnetic field these sublevels are of different energy and it is possible, by using the e.p.r. technique, to observe electron transitions between them. Initially applied to an examination of the naphthalene triplet, the e.p.r. technique has become increasingly important in both diagnosis and examination of the triplet state. From these observations the lifetime of the triplet species can be obtained.

The simple energy diagram (fig. 1.5) shows different equilibrium internuclear distances for the ground, excited singlet and triplet states. The singlet and triplet state energies resulting from $\pi \rightarrow \pi^*$ excitation are a function of the angle of twist about the carbon–carbon σ-bond. The excited states tend to stabilise themselves by distortion from the



S_0



T_1, E_{min}

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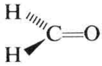
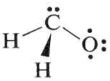
† The wavelength of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations are solvent-dependent. On increasing the solvent polarity, the $\pi \rightarrow \pi^*$ absorption generally moves to longer wavelength (a bathochromic shift) whereas the $n \rightarrow \pi^*$ band usually moves to shorter wavelength (a hypsochromic shift).

ground state geometry. For ethylene the lowest energy of the excited triplet corresponds to the orbitals being orthogonal. In terms of the Frank–Condon principle excitation produces the excited state with planar geometry and any distortion must occur after the excitation step. The geometric changes produced in n → π* excitation of simple carbonyl compounds are quite pronounced. In the ground state the carbon–oxygen bond distance of formaldehyde is 0.121 nm whereas in the excited singlet state this is increased to 0.132 nm and the molecular geometry changes from planar to pyramidal with an out-of-plane angle of *c.* 25°. In the first excited triplet state the out-of-plane angle is further increased to *c.* 35° although the carbon–oxygen bond distance is not significantly affected.



S_0 planar



$S_1(T_1)$ pyramidal

Once formed, the excited singlet and triplet states will either undergo chemical reaction or lose their excitation energy by a radiative or non-radiative process (fig. 1.6). There are two types of radiative deactivation, *fluorescence* and *phosphorescence.* Fluorescence is the emission of radiation accompanying the deactivation of an excited species to a lower state of the same multiplicity, e.g. $S_1 \rightarrow S_0$, $T_2 \rightarrow T_1$, and is a spin-allowed process. Phosphorescence is the emission of radiation accompanying the deactivation of an excited species to a lower state of different multiplicity, e.g. $T_1 \rightarrow S_0$, and is a spin-forbidden process. Excitation results in the occupation of excited states high in vibrational energy. This energy is rapidly lost (*c.* 10^{-10} seconds) by collisional transfer, a process referred to as *vibrational cascade*, and radiative deactivation normally occurs from the lowest vibrational level of the excited state. As a consequence it is usual for less energy to be emitted than is absorbed and the emission spectrum will be shifted to longer wavelength compared with the absorption spectrum (Stokes' law). Occasionally the excited state will gain thermal energy and move to a higher vibrational level prior to deactivation and the emission spectrum will be moved to a shorter wavelength than the absorption spectrum. This is termed anti-Stokes behaviour.

The non-radiative processes are of two general types, namely *internal conversion* (IC) and *intersystem crossing* (ISC). Internal conversion involves the transition from one state to another of the same multiplicity without loss of energy. This is demonstrated by the $S_1 \rightarrow S_0$ process (fig. 1.6) where the ground state is initially formed in a high vibrational level and subsequently undergoes rapid vibrational cascade to its lowest energy level. Intersystem crossing is the conversion of one state to another of different multiplicity without loss of energy and provides the most favourable route to the triplet state. At the point in the energy diagram (fig. 1.5) where the excited singlet and triplet cross, the potential and kinetic energies of both states are the same and intersystem crossing from the singlet to the triplet state can occur. Clearly ISC is most efficient when the singlet and triplet excited states are of comparable energy. The triplet so produced will be high in vibrational energy and vibrational cascade will rapidly follow. The reverse process of intersystem crossing, $T_1 \rightarrow S_1$, is highly unlikely since the most stable form of the triplet is lower in energy than the singlet state. The ease and efficiency of intersystem crossing varies from compound to compound, being dependent on the structural environment of the chromophore. In general the longer lived an excited singlet, the more liable it is to undergo intersystem crossing. Carbonyl compounds give a high triplet state population by this route.

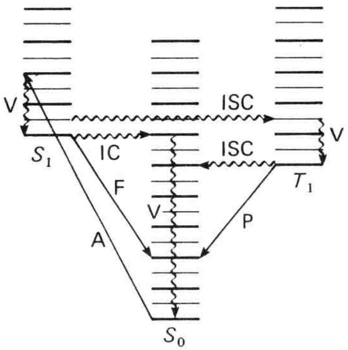


Fig. 1.6. A Jablonski diagram showing excitation and deactivation routes.
A = absorption ($\sim 10^{-15}$ s)
F = fluorescence (10^{-9}–10^{-5} s)
P = phosphorescence (10^{-5}–10^{-3} s)
V = vibrational cascade ($\sim 10^{-10}$ s)
IC = internal conversion ($\sim 10^{-10}$ s)
ISC = intersystem crossing ($\sim 10^{-6}$ s)

Irradiation of a molecule normally results in the absorption of a single photon with subsequent competition between radiative and non-radiative deactivation, and chemical reaction. Not every photon absorbed will necessarily be effective in bringing about chemical change

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