1
Introduction

1.1
Photochemistry and Photophysics in Science and Technology

Photochemical and photophysical processes have been intimately related to the development of man and his environment even before his appearance on the planet. Ever since the first morning of Creation, life has not been merely a chemical process but one in which light from the Sun played a significant role: thus, photochemistry. In the first instance, simple photochemical reactions caused by the Sun's rays generated organic molecules from the constituents of the primitive atmosphere on the Earth. Subsequently, a sophisticated series of photochemical and photophysical processes, now referred to as *photosynthesis*, made it possible for simple cells to become autotrophic, provided the necessities of life, stored solar energy in the form of fossil fuels, and still supply us with practically all our food.

From the point of view of living matter, however, photochemistry is more than the means of using the energy of light. It is also a means of sensing the environment (vision), an indicator of the time of day and the season, a source of damage to cellular constituents, and a mechanism for repairing some cellular damages. Photochemistry is also heavily involved in processes that determine the composition of matter in the interstellar space, and in the formation of atmospheric pollutants. Of course, photophysical processes also occur in nature. Suffice it to say that the world would not be colored if sunlight were completely absorbed or completely reflected by the objects that surround us, and we would not be able to enjoy fireflies or other beautiful scenes without bioluminescence.

Each of these natural processes provides a sufficient reason for a scientific interest in photochemistry and photophysics. However, photochemistry and photophysics are also important from an artificial viewpoint. Their impact in the chemical, physical, biological, and medical sciences and technologies, including nanotechnology, is being felt increasing in a spectacular manner. Photochemical methods are used for producing polymeric printing plates and printed circuits, for UV (ultraviolet) curing of surface coatings and printing inks, and for laboratory and commercial synthesis of high-value chemical compounds. Photochemical and photophysical

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concepts are at the basis of important applications such as protection of dyes and plastics (and also human skin) from the damaging effect of sunlight, waste water cleaning, design of fluorescent compounds for a variety of sensing applications (wind galleries, security, optical brighteners, pollutant detectors, display devices, molecular switches and logic gates, biological markers, cellular properties, and functions), creation of photochromic materials used in sunglasses, fashion clothes and optical memories, and development of laser devices and of light-powered molecular machines. Other interesting fields concern photomedicine, multiphotonic processes, solar-powered green synthesis, molecular photovoltaics, and solar energy conversion by water photodissociation. These and other topics are dealt with in the subsequent chapters of this book.

1.2
Historical Notes

Artificial photochemical reactions have been observed as long as chemistry has been studied. Most of the earlier observations, however, were accidental and remained unexplained. The first investigation was made in 1777 by the Swedish chemist Carl W. Scheele, who observed that violet light was the most effective in darkening silver chloride. But it was only in 1817 that Theodor von Grotthuss established that *only the light absorbed is effective in producing photochemical change*. This first general principle of photochemistry passed unnoticed until 1841, when it was restated by John W. Draper and, as a consequence, is now termed the *Grotthuss–Draper law*.

Photochemistry emerged from its empirical stage when modern physics established that light is radiated in discrete quanta, called *photons*, with an energy proportional to the frequency of the light, and that absorption corresponds to the capture of a photon by an atom or a molecule. With this concept in mind, Johannes Stark and Albert Einstein between 1908 and 1913 independently formulated the photoequivalence law that essentially states that there should be a *1 : 1 equivalence between the number of molecules decomposed and the number of photons absorbed*. Experiments, however, showed that usually this 1 : 1 ratio is not observed, indicating that the Stark–Einstein law is not sufficient to characterize a photochemical process and that absorption of a photon can be followed by other processes. A distinction was thus introduced between the light-initiated reaction (*photochemical primary process*) and any subsequent chemical reactions (*photochemical secondary processes*). In some cases, such secondary reactions can proceed by a chain mechanism, which explains why one photon can decompose a great number of molecules.

An obvious reason for the number of decomposed molecules being smaller than the number of photons absorbed in photofragmentation reactions could be efficient recombination of primary products. It was soon realized, however, that even for other types of photoreactions, for example, photoisomerization, the number of reacted molecules can be much less than the number of absorbed photons. It was thus clear that absorption of a photon is a necessary, but not sufficient condition, to cause a photoreaction and that light energy can be used by a molecule for other purposes. It was found, indeed, that in some cases photoexcitation does not cause any reaction but leads to emission of light, that is, a *photophysical* process, and that in other cases neither a chemical change nor light emission is observed.

An important limitation to the development of photochemistry until the second decade of the twentieth century was the unavailability of adequate light sources and analytical techniques. In fact, the only light source used by the early pioneers, such as Lemoine [1] in Paris and Ciamician [2] in Bologna, was the Sun (Box 11.1).

After World War I, photochemistry became a territory of physical chemists who were particularly interested in the photolysis of small molecules in the gas phase. The notion of competition among photochemical and photophysical processes for electronically excited-state decay was gradually recognized. In the period between 1930 and 1950, the development of molecular orbital theory led to the interpretation of the electronic absorption spectra of organic molecules and the rationalization of trends in series of related molecules [3, 4]. Some years later, the main lines to interpret the absorption and emission spectra of metal complexes became available. Since 1960 the concepts to understand the reactivity of electronically excited states emerged and correlations between structure and photochemical reactivity or photoluminescence were developed, first for organic molecules [5–7] and then for metal complexes [8]. Within a few years, the tight link between photochemistry and photophysics was established [9–13]. It became clear that photochemistry (a term that commonly is taken to include photophysics) is really a distinct and separate part of chemistry because it does not concern the ground state of molecules, but concerns novel species: the electronically excited states. Focused photochemical experiments, improved spectroscopic techniques, and computational methods began to provide adequate characterization of electronically excited states of several classes of molecules. Around 1990, investigations were extended to supramolecular species [14] and photochemistry and photophysics began to play an important role in organic chemistry [15, 16], as well as in novel scientific ventures such as information processing at the molecular level [17] and creation of molecular devices and machines [18]. In recent years, the tremendous development of techniques has permitted the investigation of photochemical and photophysical properties of molecules up to time windows as short as those allowed by the uncertainty principle and at the single-molecule level (Chapter 12).

1.3
A New Dimension of Chemistry and Physics

Light excitation with a photon of suitable energy promotes a molecule from its *ground state* to an electronically *excited state* (hereafter simply called *excited state*, usually denoted by an asterisk, Figure 1.1).

As we shall see later, light excitation causes changes in the electronic structure of a molecule, so that each type of excited state has its own electronic structure, different from that of the ground state. Because the chemical and physical properties

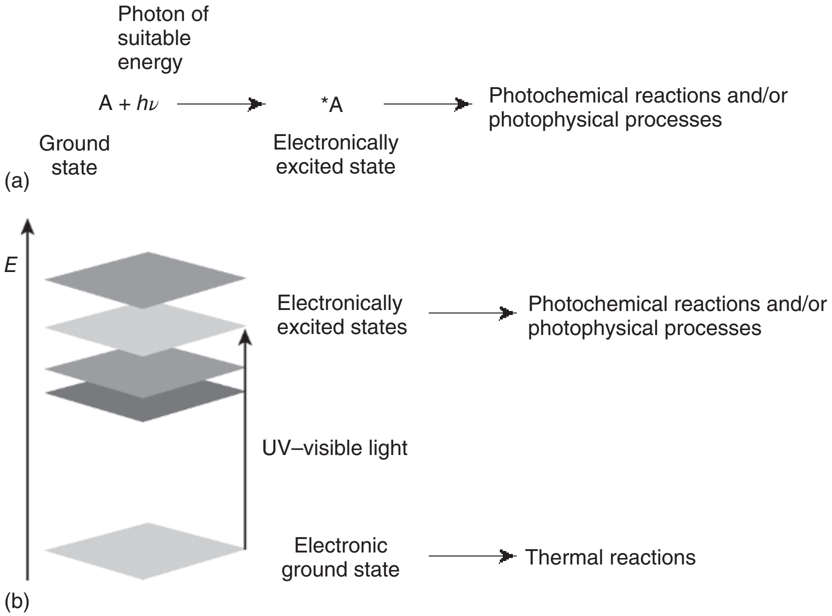

Figure 1.1 (a) Light excitation with a photon of suitable energy promotes a molecule from its *ground state* to an electronically *excited state*, a new chemical species with its own chemical and physical properties; the excited state then undergoes deactivation by chemical reactions and/or by radiative or nonradiative photophysical processes. (b) Because each molecule has only one ground state and many different excited states, light excitation opens new dimensions to chemistry and physics.

of a molecule depend on its electronic structure, each excited state has its own chemical and physical properties. A wealth of experimental data and theoretical studies demonstrated that this is indeed the case (Table 1.1).

The ground state of a molecule is involved in the conventional chemical reactions, sometimes called *thermal reactions,* because they need heat to occur; the ground state is also responsible for the absorption spectrum, that is, for the color. The excited states are responsible for deactivation processes that can be chemical in nature (photochemical reactions) or involve energy loss processes, either radiative (luminescence) or nonradiative. Therefore, light excitation opens new dimensions to chemistry and physics. To chemistry, because excited states can react in different ways, both qualitatively and quantitatively, compared with the ground state. To physics, because each excited state not only exhibits its own absorption spectrum (color) but can also be deactivated by its own photophysical processes, including light emission. The interaction between light and matter entwines photochemistry (chemical reactions caused by light) and photophysics (excitation and deactivation processes, with or without light emission). The excited state viewed as a new molecule is further discussed in Section 4.1. Before going any further in discussing photochemical and photophysical events, it is worthwhile to examine first the nature of light.

Table 1.1 Comparison between some ground- and excited-state properties for a few selected molecules.

	Ground state	Excited state
HCN[a]		
H–C bond distance (pm)	106	114
C–N bond distance (pm)	116	130
Bond angle (°)	180	125
Formaldehyde[b]		
Geometry	Planar	Pyramidal
4-Amino-4′-nitro-*p*-diphenyl[c]		
Dipole moment (D)	5	16
Phenol[c]		
pK_a	10	4
$[Ru(bpy)_3]^{2+}$[b]		
Reduction potential (V, vs SCE)	−1.28	+0.84
1-Nitro-3,4-dimethoxybenzene[c]		
Nucleophilic attack (OH^-)	4 position	3 position
***trans*-$[Cr(NH_3)_4Cl_2]^+$**[c]		
Ligand substitution product (H_2O)	*trans*-$[Cr(NH_3)_4(H_2O)Cl]^{2+}$	*cis*-$[Cr(NH_3)_3(H_2O)Cl_2]^+$

[a] $^1A''$ excited state.
[b] Lowest energy, spin-forbidden excited state.
[c] Lowest energy, spin-allowed excited state.

1.4
The Nature of Light

In the wave model, electromagnetic radiation is characterized by a wavelength, λ, a frequency, ν, and a velocity, c. The three quantities are related by the relationship

$$\lambda\nu = c \tag{1.1}$$

The value of c is constant ($2.998 \times 10^8\ m\,s^{-1}$ in vacuum), whereas λ (and ν) may cover a wide range of values (Figure 1.2). The SI units for λ and ν are the meter (m) and the hertz (Hz), respectively. In some cases, the *wavenumber* $\bar{\nu}$ (defined as the number of waves per centimeter) is also used to characterize electromagnetic radiation. The electromagnetic spectrum encompasses a variety of types of radiation from γ-rays to radiowaves, distinguished by their wavelengths (or frequencies, or wavenumbers). When dealing with photochemistry and photophysics, that is, with electronically excited states, the expression "light" is used to mean electromagnetic radiation capable of causing electronic excitation or involved in electronic deactivation of molecules, which means the portion of the electromagnetic spectrum ranging from 200 to 1000 nm (1.5×10^{15} to 3×10^{14} Hz or 5×10^4 to $1 \times 10^4\ cm^{-1}$), which includes the near-UV, visible, and near infrared regions (Figure 1.2).

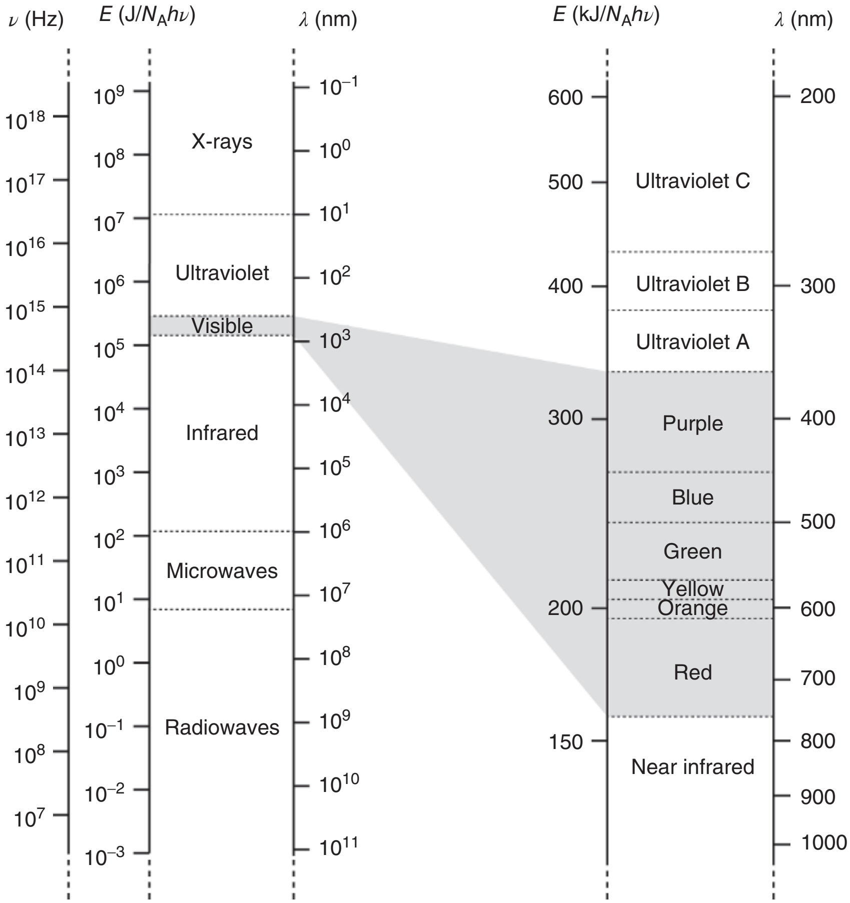

Figure 1.2 Electromagnetic spectrum.

In the quantum model, a beam of radiation is regarded as a stream of *photons*, or *quanta*. A photon has a specific energy, E, related to the frequency of the radiation, ν:

$$E = h\nu \tag{1.2}$$

where h is the Planck's constant (6.63×10^{-34} J s). This picture of light as made up of individual photons is essential to photochemistry and photophysics. Photons are at the same time *energy quanta* and *information bits*. Living examples of this double-faced nature of light are provided by the two most important photochemical processes taking place in the biological world: photosynthesis and vision. All the natural phenomena related to the interaction between light and matter and the great number of applications of photochemistry and photophysics can ultimately be traced back to these two aspects of photons.

The interaction of light with molecular systems is generally an interaction between *one* molecule and *one* photon[1] that, as already shown in Figure 1.1a, can be schematically written in the very general form as follows:

$$A + h\nu \rightarrow {}^{*}A \tag{1.3}$$

where A denotes the ground-state molecule, $h\nu$ the absorbed photon, and *A the molecule in an electronically excited state. As the equation implies, the excited molecule *A is the molecule A with an extra energy $h\nu$. From Equations 1.1 and 1.2, it follows that the photon energy is 9.95×10^{-19} and 1.99×10^{-19} J, respectively, for light of 200 and 1000 nm. To better appreciate the size of the photon energy, we must compare it with the energies of the chemical bonds, which are normally expressed in kilojoules or kilocalories per mole. A mole is an Avogadro's number, 6.02×10^{23}, of objects. We may extend the concept of mole to photons, defining an *einstein* as one mole of photons. When *one mole* of molecules absorbs *one einstein* of photons, it is equivalent to one photon absorbed by one molecule (Equation 1.3). The energy of one einstein of photons at 200 nm is 599 kJ (143 kcal), and that of one einstein of photons at 1000 nm is 119.8 kJ (28.6 kcal). These energy values are of the same order of magnitude of those required to break chemical bonds (e.g., 190 kJ mol^{-1} for the Br-Br bond of Br_2; 416 kJ mol^{-1} for the C-H bond of CH_4). The energy that a molecule obtains when it absorbs a photon of light is therefore not at all negligible. For example, absorption of a 300 nm photon by naphthalene corresponds to an energy of 400 kJ mol^{-1}, comparable with the energy that would be taken up by naphthalene ($C_{p,m}(g) = 136\ \mathrm{JK^{-1}\ mol^{-1}}$) if it were immersed in a heat bath at 3000 K (p. 10 in Ref. [16]). The availability of such an extra amount of energy is the reason *an excited molecule has to be considered as a new chemical species* that has its own chemical and physical properties, often quite different from the properties of the ground-state molecule. Whether light absorption causes bond breaking as would be expected on the basis of the energy argument is another story. As we will see later, it depends on the competition among various deactivating processes (Section 1.6).

1.5
Absorption of Light

Because *only the light absorbed is effective* (generalization of the Grotthuss–Draper law, Section 1.2), the measurement of the light absorbed by the investigated system is of primary importance.

The absorption of a monochromatic beam of light by a substance dissolved in a transparent medium is described by the Beer–Lambert law,

$$I = I_0 \times 10^{-\varepsilon bc} \tag{1.4}$$

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[1] In particular experimental conditions, multiphotonic processes can occur (Box 3.1), which extend the simplest photochemical paradigm involving one photon, one absorber, one excited state, and one outcome.

where I is the intensity of the transmitted light, I_0 the intensity of the incident light, ε the molar absorption coefficient (in $\mathrm{M^{-1}\,cm^{-1}}$), b the optical path (in cm), and c is the solution molar concentration. Note that natural logarithms are sometimes used.

The quantity that is usually measured with spectrophotometers is the *absorbance*,

$$\mathrm{A} = \log(I_0/I) = \varepsilon bc \tag{1.5}$$

The molar absorption coefficient ε represents the ability of the substance to absorb light and depends on the wavelength of the incident light.

1.6
Quantum Yield, Efficiencies, and Excited-State Reactivity

The only significant measure of the ground-state reactivity of a molecule, with respect to a given reaction, is the rate constant or specific rate of the reaction. The same is true for the excited molecule except that, in such a case, there is usually a competition among several processes and the rate constants can only be obtained indirectly from the measurement of related quantities.

The quantitative aspects of the consequences of light excitation can be easily discussed within the simplest and most common paradigm of Equation 1.3 (one molecule absorbs one photon) and the assumption that excited-state deactivation occurs by competing unimolecular chemical (rate constant k_p) and radiative (k_r) and nonadiative (k_nr) physical processes (Figure 1.3). In the interaction between light and matter, photochemistry (the chemical reactions caused by light) and photophysics (light excitation and radiative and nonradiative deactivation processes) are intertwined.

According to Figure 1.3, the excited-state decays with overall first-order kinetics; its *lifetime* $\tau(^*\mathrm{A})$ is given by Equation 1.6,

$$\tau(^*\mathrm{A}) = \frac{1}{k_\mathrm{p} + k_\mathrm{r} + k_\mathrm{nr}} = \frac{1}{\sum_j k_j} \tag{1.6}$$

The probability of each deactivation process is related to its relative rate. For each process of the *A excited state, an *efficiency* $\eta_i(^*\mathrm{A})$ can then be defined as follows:

$$\eta_i(^*\mathrm{A}) = \frac{k_i}{\sum_j k_j} = k_i\tau(^*\mathrm{A}) \tag{1.7}$$

Each process starting with the absorption of a photon and ending with the disappearance of the molecule or its deactivation to the ground state (Figure 1.3) is called a *primary process*. The *quantum yield* (Φ_i) of a primary process is defined as

$$\Phi_i = \frac{\text{Number of molecules undergoing that process}}{\text{Number of photons absorbed by the reactant}} \tag{1.8}$$

with both quantities referring to the same time interval. On the assumption that the concentration of the excited state reaches a stationary value on continuous

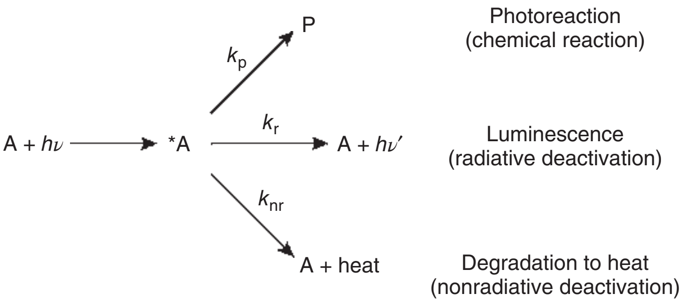

Figure 1.3 Essential steps of the light–matter interaction. For more details, see text.

irradiation, for the system illustrated in Figure 1.3 we then have

$$\frac{d[{}^*A]}{dt} = I_m - k_p[{}^*A] - k_r[{}^*A] - k_{nr}[{}^*A] = 0 \tag{1.9}$$

where I_m is the average number of einsteins absorbed by the reactant in unit volume and unit time.

$$I_m = (k_p + k_r + k_{nr})[{}^*A] \tag{1.10}$$

$$\Phi_p = \frac{k_p[{}^*A]}{I_m} = \frac{k_p}{k_p + k_r + k_{nr}} \tag{1.11}$$

More generally, if the excited state *A directly reached by irradiation gives rise to *n* primary processes, the quantum yield of a specific process *i* is given by the ratio of the rate constant (i.e., the reactivity) of that process to the sum of the rates of all the *n* processes that deactivate the excited state:

$$\Phi_i = \frac{k_i}{\sum_j k_j} \tag{1.12}$$

From Equations 1.11 and 1.12, it follows that

$$\Phi_i = k_i \tau({}^*A) = \eta_i({}^*A) \tag{1.13}$$

Therefore, the quantum yield coincides numerically with the efficiency of the process and thus its value must range from zero to unity. Equation 1.13 also shows that the rate constant of process *i* can be obtained from the experimentally measured quantum yield and excited-state lifetime:

$$k_i = \frac{\Phi_i}{\tau({}^*A)} \tag{1.14}$$

From Equation 1.14 it is clear that if a series of photoreactions have similar quantum yields, there is no guarantee that the corresponding excited states have the same rate constant.

When the products of the primary chemical process are radicals or other unstable compounds, they may undergo secondary thermal reactions. In these cases, the experimentally measured quantum yield (overall quantum yield) may be either higher (owing to chain reactions) or lower (owing to a cage effect or other back reactions) than the primary quantum yield.

The lifetime, which represents the time required to reduce the number of molecules that populate the excited state to $1/e$ of its initial value, can be experimentally determined following the decay of some quantity proportional to the number of molecules that populate the excited state (Section 12.3.2).

The determination of quantum yields requires the measurements of two quantities (Equation 1.8), namely, the change in the concentration of the reactant (or products, P or $h\nu'$ in Figure 1.3) and the number of photons absorbed by the reactant. It should be pointed out that, because of the wavelength dependence of light absorption and the peculiar properties of the different excited states of a molecule, monochromatic (or at least nearly monochromatic) light should be used in order to obtain reliable quantum yield values.

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