PHOTOCHEMISTRY OF ORGANIC COMPOUNDS

From Concepts to Practice

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PHOTOCHEMISTRY OF ORGANIC COMPOUNDS

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This book is dedicated to our
families, teachers and students

Contents

Special Topics

Case Studies

Foreword

This is a timely book, in several respects. First, photochemists and students of photochemistry badly need to replace the aging basic textbooks and reference books that they have been using, or at least to complement them with up-to-date material. Second, as illustrated by nearly any recent conference on photochemistry, most studies involving photochemistry are now performed by scientists whose initial training was not in photochemistry and who often do not think of themselves primarily as photochemists, but rely on light-induced transformations merely as a convenient tool. It is no wonder that these individuals ask for a comprehensive yet understandable and current introductory text. Third, like it or not, mankind is inexorably being dragged into an era in which the ability to generate energy in a sustainable manner acquires paramount importance, and this almost inevitably implies wise exploitation of solar energy. Who, if not chemists, chemical engineers, and material scientists, along with physicists and biologists, will come up with the new materials, catalysts, and processes that are needed for efficient, affordable, and environmentally benign capture of solar energy and its conversion into electricity and fuels? The numbers of researchers working in these areas will soon have to increase rapidly as nations all over the world finally begin to face reality and start to invest in solar energy research in a serious fashion. The demand for a good textbook covering photophysics and photochemistry and suitable for training increasing numbers of students is bound to grow.

The text written by Professors Klán and Wirz is masterful and well balanced. It fills the current need for a modern treatment of the subject admirably. This is not surprising, given the authors' vast experience and stature in the field. I was struck by the broad and comprehensive view of photochemistry and photophysics that they offer. I also very much appreciate their thoughtful ability to explain difficult concepts in a lucid way, accessible even to beginners. I suspect that it must have been tempting to gloss over some of the more difficult theoretical aspects of the subject, but if the authors were tempted, it does not show. They avoid glib statements of generalities and instead provide simplified yet accurate discussions, complemented with a truly impressive number of references to original literature. I like the organization, especially the inclusion of numerous case studies and special topics in a way that does not perturb the flow of the text, and I like the inclusion of problems and their selection. The graphical summary in Chapter 7 is particularly useful.

I congratulate the authors on their accomplishment and expect the book to be a tremendous success.

Josef Michl
University of Colorado at Boulder

Preface

The absorption of light by matter opens a new dimension of physical and chemical processes. Photochemistry is intrinsically an interdisciplinary field pertaining to all natural sciences and many technical disciplines. This text aims to provide a hands-on guide for scientists in all fields, inspiring and aiding them to pursue their own research dealing with desired or unwanted effects associated with light absorption, as well as for undergraduate and graduate students of chemistry. We try to face rather than evade difficult aspects, yet to provide the reader with simple concepts and guidelines, sometimes to the point of terrible simplification.

Coverage of the relevant literature is extensive, with over 1500 references being provided, but it obviously cannot be comprehensive. Both current research (up to mid-2008) and early pioneering contributions are cited and recommended reading draws attention to outstanding, more profound treatments of special topics. We have shamelessly borrowed from excellent presentations in the literature and from our teachers, but have certainly missed some essential work as a result of our predilections. The text is interlaced with 32 *Special Topics* that provide information about some special applications of photochemistry in chemistry, physics, medicine, technology and in practical life, and about important photochemical processes that occur in the human body, green plants, the atmosphere and even deep space. Moreover, 39 *Case Studies* offer a glance at particular examples, often accompanied by detailed descriptions of laboratory procedures. Solved *Problems* at the end of the chapters and in some sections are intended as a practical aid to practice and refresh the readers' preceding studies.

The essentials of a quantum mechanical treatment of the interaction of electromagnetic radiation with molecules are summarized on a descriptive basis in the introductory Chapter 1, along with a few historical remarks. The basic concepts of photophysics and photochemistry and of energy transfer as well as a classification of photoreactions are presented in Chapter 2. Laboratory proceedings and equipment are described in Chapter 3, which includes quantum yield measurements, Stern–Volmer kinetics and the global analysis of spectral data. Chapter 4 provides simple but useful models describing electronic excitation and the associated profound changes of electronic structure, which are designed to help the reader to understand and undertake to predict photochemical reactivity. Chapter 5 describes exemplary cases of mechanistic investigations and time-resolved studies of important reactive intermediates such as carbenes, radicals and enols.

The extensive Chapter 6 is divided into eight sections dealing with the photochemistry of the most typical organic chromophores. The information is organized according to structural categories that are common in organic chemistry, such as alkanes, alkenes, aromatic compounds and oxygen atom-containing compounds, and emphasizes a visual presentation of the material. The sections are introduced by a brief description of the photophysical properties of the corresponding chromophores and their typical photoreactions. A list of recommended review articles and selected theoretical and computational photochemistry references is also provided. The compiled information of each section is then categorized by the mechanisms of photoreactions in individual subsections. The mechanism is first discussed in general terms; a number of examples follow, in which detailed reaction schemes of the mechanism are presented and discussed. Basic information about these particular reactions, such as the multiplicity of the reactive excited species, key reaction intermediates and chemical yields, is often provided and extensively referenced to the primary and secondary literature. The last section (6.8) focuses on the reactions of auxiliary chromophores such as photosensitizers, photocatalysts and photoinitiators.

Chapter 7, on retrosynthetic photochemistry, is a graphical compilation of reaction schemes, listed according to the target structures, which can be synthesized by the photochemical reactions described in Chapter 6.

Acknowledgements

We are deeply indebted to our many colleagues who read parts of the text and drew our attention to its shortcomings by providing valued criticism: Silvia Braslavsky, Silvio Canonica, Georg Gescheidt, Richard S. Givens, Axel Griesbeck, Dominik Heger, Martin Jungen, Michael Kasha, Jaromír Literák, Ctibor Mazal, Josef Michl, Pavel Müller, Peter Šebej, Jack Saltiel, Vladimír Šindelář, Aneesh Tazhe Veetil and Andreas Zuberbühler.

Petr Klán
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1

Introduction

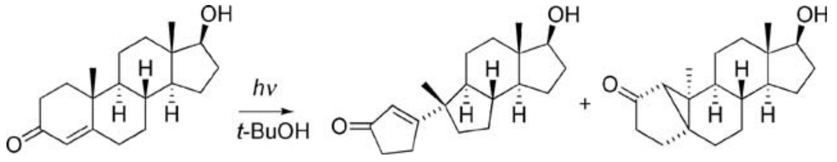
1.1 Who's Afraid of Photochemistry?

Photochemistry has become an integral part of all branches of science: chemistry, biochemistry, medicine, biophysics, materials science, analytical chemistry, signal transmission, and so on. In our daily life, we are surrounded by products that are produced with the aid of photochemistry or that exploit photochemistry or photophysics to perform their function. Examples include information technology (computer chips and communication networks, data storage, displays, circuit boards and e-paper, precise time measurement), nanotechnology, sustainable technologies (solar energy storage, waste water cleaning), security and analytical devices (holograms, sensors), cosmetics (skin protection, hair colouring, etc.) and lighting (LEDs).

The highly reactive excited states and intermediates generated by pulsed excitation can be characterized by fast spectroscopic techniques. Novel instrumentation with rising sensitivity and spatial and temporal resolution is becoming available, ultimately allowing one to detect single molecules and to follow their reactions and their motions in space. To exploit this ever-increasing wealth of information, knowledge of photochemistry's arts and pitfalls will be required of researchers in many interdisciplinary fields. The high reactivities and short lifetimes of electronically excited molecules are responsible for their utmost sensitivity to pre-association in ground-state complexes, organized media and supramolecular structures, because their reactions are likely to occur with reaction partners that are in the immediate neighbourhood when light is absorbed.

The interaction of light and matter produces astounding effects and the outcome may be hard to predict. Will light do the desired trick for you? A well-trained chemist will have a reliable notion of the reactions that might result from the addition of, say, sodium borohydride to a solution of testosterone – but would he or she dare to predict or make an educated guess about what will happen when a solution containing testosterone is irradiated (Scheme 1.1)?

Photochemistry of Organic Compounds: From Concepts to Practice Petr Klán and Jakob Wirz



Scheme 1.1

Many synthetic chemists shy away from using key photochemical reaction steps[1] that might substantially reduce the number of reaction steps required to synthesize a desired product. This is bound to change with the increasing emphasis on green chemistry. The chemical reactivity of electronically excited molecules differs fundamentally from that in the ground state. In fact, the general rules and guidelines of photoreactivity are often the *opposite* of those in ground-state chemistry (recall the Woodward–Hoffmann rules as an example). Herein lies the great potential of synthetic photochemistry: in many cases, photochemistry achieves what ground-state chemistry cannot. Light adds a new dimension to chemistry. Photochemical synthesis on a gram scale is simple and requires only relatively inexpensive equipment.

Sunlight directly or indirectly (by providing food and fuel) drives most chemical transformations in biota. The spectral distribution of sunlight is close to that of a *black body* at a temperature of 5800 K (Figure 1.1, thick solid line). Outside the Earth's atmosphere, the integrated average power hitting a surface at right-angles to the propagation direction of solar irradiation (*solar constant*) is 1366 W m^{-2}. It varies by

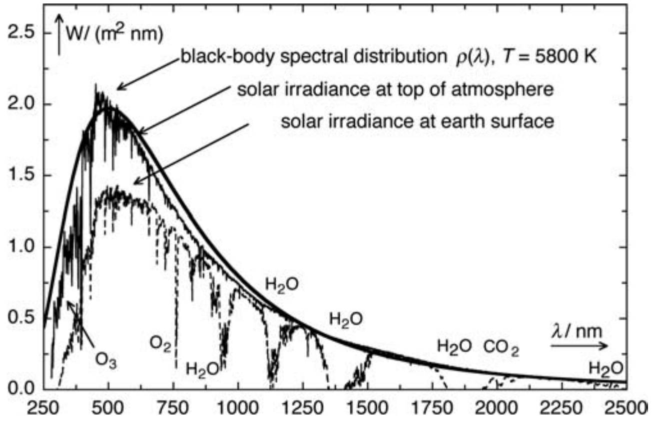


Figure 1.1 Spectra of the solar radiation outside the Earth's atmosphere (—) and at ground level (- - -) compared with the spectrum of a black body at $T = 5800$ K (**—**). The spectra are plotted using the ASTM Standard G173-03e1, Standard Tables for Reference Solar Spectral Irradiances, by permission. The broad minima in the Earth's surface spectrum are due to absorption in the Earth's atmosphere by the substances indicated. The sharp lines in both spectra at lower wavelengths (Fraunhofer lines) are due to absorption by peripheral solar gas

several percent over the year with the Earth's distance from the Sun and with the Sun's activity. The total amount of radiation received by Earth is determined by its cross-section, πR^2. The average per surface area, $4\pi R^2$, is thus one-quarter of the solar constant, 342 W m^{-2}. However, the spectrum of the solar radiation measured at the Earth's surface, also shown in Figure 1.1 (dashed line), is modified by absorption and scattering while travelling through the atmosphere. The ozone layer of the stratosphere absorbs strongly below approximately 280 nm (which is a biologically hazardous spectral region denoted UVC radiation), so that only UVB (280–315 nm), UVA (315–400 nm) and visible radiation penetrate. Water, carbon dioxide and dioxygen molecules selectively absorb in the visible and especially in the infrared region. Latitude, time of day, seasonal variations, variations in the ozone layer, clouds, fumes, haze, and so on further reduce the solar radiation received at ground level. Thus, the global average on the Earth's surface comes to about 200 W m^{-2}. For comparison, the metabolism of an adult human consumes about 9000 kJ d^{-1}, producing about 100 W as heat.

Photosynthesis (Scheme 1.2) is the source of food and fossil fuel and has played an important role in the origin of life.[a] A fully grown beech tree assimilates about 10 m^3 of CO_2 (contained in 4×10^4 m^3 of air) on a sunny day, producing the same amount of O_2 and 12 kg of carbohydrates. Globally, photosynthesis stores about 2×10^{12} t of CO_2 in biomass per year, the equivalent of 2×10^{19} kJ, most of which, however, is eventually returned to the atmosphere by reoxidation.

$$\mathrm{H_2O\ (l) + CO_2\ (g)} \xrightarrow{h\nu} \mathrm{(CH_2O)\ (s) + O_2\ (g)},\ \Delta H^{\circ}(298\ \mathrm{K}) = +467\ \mathrm{kJ\ mol^{-1}}$$

Scheme 1.2 *Photosynthesis*

Solar radiation also plays a major role in abiotic environmental photochemistry, taking place mostly in surface waters. However, the present state of knowledge about these processes is limited, because individual photosensitive substances are present at very high levels of dilution. On a cloudless summer noon, surface waters in central Europe receive approximately 1 kW m^{-2} of sunlight or about 2 mol of photons per hour between the wavelengths of 300 and 500 nm, the region of interest for photochemical reactions. About 1300 times this dose is accumulated per year.[2]

Solar radiation is becoming increasingly appreciated for its influence on living matter and as a source of natural energy. The current human energy consumption[3] of 4.6×10^{20} J per year or 1.4×10^{13} W amounts to about 0.015% of the solar energy reaching the Earth's surface or 2.4% of natural photosynthetic energy storage. To manage the rising problem of global warming and, at the same time, to address the gap in energy supply created by the expected decrease in carbon fuel consumption is one of the 21st century's main challenges.[4–6] Even under the optimistic assumption that the total consumption will level

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[a] Although Charles Darwin was coy about the origin of life, he famously speculated in a letter to a friend about a 'warm little pond', in which all manner of chemical substances might accumulate over time. About 100 years later, Miller and Urey shot flashes of lightning through a flask containing an 'ocean' of liquid water and an 'atmosphere' of hydrogen-rich gases, methane, ammonia and hydrogen sulfide. Light was added in later experiments. They identified all sorts of compounds in the resulting 'primordial soup', including various amino acids.

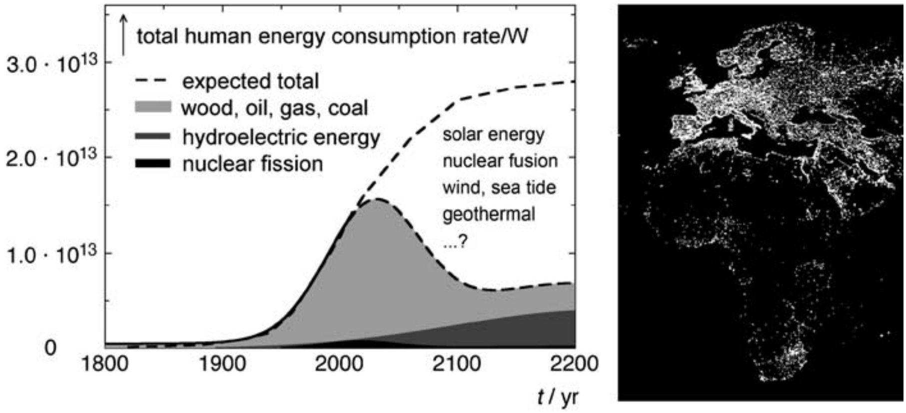

Figure 1.2 Left: human energy consumption rate. Current per capita rate ≈2300 W (EU 6000 W, USA 12 000 W). Right: night-time satellite picture of Africa and Europe showing the distribution of artificial light sources

off, as shown in Figure 1.2 (left) (notwithstanding the developing nations' expected growing energy demand; Figure 1.2, right), it is far from clear how the gap will be filled when the sources of fossil fuels are exhausted, and whether the demand that their consumption be strongly curtailed to reduce the rate of global warming can be met. Uranium ores worth exploiting are also limited, leaving few conceivable options for substantial contributions through sustainable technology, primarily solar energy storage (photovoltaics, hydrogen production), nuclear fusion, wind energy, sea tide and geothermal sources. Major efforts to increase the efficiency of all processes requiring energy and to find substitutes for energy-demanding behaviour will be needed to balance the worldwide energy demand against our non-renewable resources during this century. Light-driven processes will be a major contributor in the transformation to a low-carbon economy.[7] The production of photovoltaic cells is currently rising at a pace of about 40% per year. More dramatic increases in the exploitation of renewable energy sources will follow as soon as these techniques can compete with the rising cost of fossil fuels.

A remarkably detailed understanding of the properties and chemical behaviour of transient intermediates has been deduced from well-designed conventional methods of physical organic chemistry using standard laboratory techniques such as quenching and sensitization, trapping or radical clocks. However, working backwards from the structure of stable photoproducts and the variation of their yield as a function of various additives requires demanding preparative and analytical efforts; moreover, the lifetimes of intermediates can only be estimated from such data by making some assumptions about the rate constants of quenching or trapping (Section 3.9.6). On the other hand, flash photolysis (Section 3.7) provides absolute rate constants with little effort, but yields precious little hard information allowing the identification of the observed transients. Kinetic data obtained by optical flash photolysis alone are thus prone to false assignments and the combination of both methods is highly recommended. Once a hypothetical reaction mechanism has been advanced, the quantitative comparison of the effect of added reagents on product distributions, quantum yields and transient kinetics provides a stringent test for the assignment of the transients observed by flash photolysis (Section 3.9.8, Equation 3.38). Other time-resolved spectroscopic techniques such as MS, IR, Raman, EPR, CIDNP and X-ray diffraction provide detailed structural information permitting unambiguous assignment of transient intermediates and their chemical and physical properties can now be determined under most conditions.

Special Topic 1.1: Historical remarks

Many of the above considerations regarding the impact of photochemistry on the future of mankind were expressed 100 years ago in prophetic statements by Giacomo Luigi Ciamician (1857–1922).[8,9] The first attempts to relate the colour of organic compounds to their molecular structure date back to the mid-19th century, when synthetic dyes became one of the chemical industry's most important products. In 1876, Witt introduced the terms *chromophore* (a molecular group that carries the potential for generating colour) and *auxochrome* (polar substituents that increase the depth of colour). Dilthey, Witzinger and others further developed the basic model. Such colour theories had to remain empirical and rather mystical until the advent of molecular quantum mechanics after 1930, and it took another 20 years until simple molecular orbital theories such as Platt's free electron model (FEMO), Hückel molecular orbital theory (HMO) and Pariser, Parr and Pople's configuration interaction model (PPP SCF CI) provided lucid and satisfactory models for the interpretation of electronic spectra of conjugated molecules. Such models were also successful in rationalizing trends in series of related molecules and in describing the electronic structure and reactivity of excited states.

More sophisticated *ab initio* methods can and will increasingly provide accurate predictions of excited-state energies, transition moments and excited-state potential energy surfaces of fairly large organic molecules. However, these methods are less amenable to generalization, intuitive insight or prediction of substituent effects. The translation of quantitative *ab initio* results into the language of simple and lucid MO theories will remain a necessity.

General lines of thought on how to understand the reactivity of electronically excited molecules emerged only after 1950. T. Förster, M. Kasha, G. Porter, E. Havinga, G. Hammond, H. Zimmerman, J. Michl, N. Turro and L. Salem were among the intellectual leaders who developed the basic concepts for structure–reactivity correlations in photochemistry (Section 4.1). Spectroscopic techniques together with computational methods began to provide adequate characterization of excited states and their electronic structure. Simple models such as correlation diagrams were used for the qualitative prediction of potential energy surfaces. Matrix isolation at cryogenic temperatures permitted the unambiguous identification of reactive intermediates.

The rapid development of commercially available lasers and electronic equipment allowed for the real-time detection of primary transient intermediates by flash photolysis. Photochemistry thus emerged as the principal science for the study of organic reaction mechanisms in general, because it can be employed to generate the intermediates that are postulated to intervene in chemical reactions of the ground state. Cutting edge research provides unprecedented spatial and temporal resolution to monitor structural dynamics with atomic-scale resolution, to detect single enzyme or DNA molecules at work and to construct light-driven molecular devices.

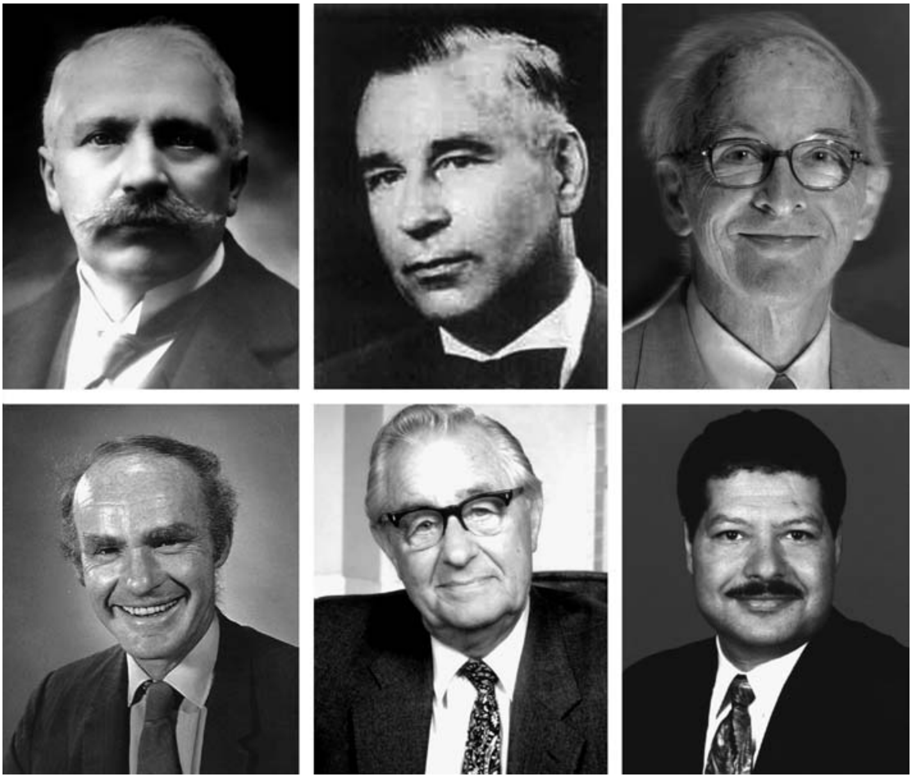

Figure 1.3 Some of photochemistry's icons. Top (from left to right): Giacomo Ciamician (1857–1922), Theodor Förster (1910–1974), Michael Kasha (1920–). Bottom: George Hammond (1921–2005), George Porter (1920–2002), Ahmed Zewail (1946–). Photographs reproduced by permission of the Scientists (M. K., A. Z.), or of successors at their former institutions

Special Topic 1.2: Quantity calculus

By convention, physical quantities are organized in the International System (SI) of quantities and units, which is built upon seven *base quantities* (Table 1.1), each of which is regarded as having its own *dimension*. The current definitions of the corresponding *base units* are given in the IUPAC Green Book, *Quantities, Units and Symbols in Physical Chemistry*.[10] A clear distinction should be drawn between the names of units and their symbols, e.g. mole and mol, respectively.

Table 1.1 *The SI base quantities*

Base quantity			SI unit	
Name	Symbol for quantity	Symbol for dimension	Name	Symbol
Length	l	L	metre	m
Mass	m	M	kilogram	kg
Time	t	T	second	s
Electric current	I	I	ampere	A
Thermodynamic temperature	T	Θ	kelvin	K
Amount of substance	n	N	mole	mol
Luminous intensity	I_V	J	candela	cd

A *measurement* amounts to the comparison of an object with a reference quantity of the same *dimension* (e.g. by holding a metre stick to an object). The value of a *physical quantity Q* can be expressed as the product of a *numerical value* or *measure*, $\{Q\}$, and the associated *unit* $[Q]$, Equation 1.1.

$$Q = \{Q\}[Q],\ e.g.,\ h = 6.626 \times 10^{-34}\ \mathrm{J\,s}$$

Equation 1.1

The symbols used to denote units are printed in roman font; those denoting physical quantities or mathematical variables are printed in italics and should generally be single letters that may be further specified by subscripts and superscripts, if required. The unit of any physical quantity can be expressed as a product of the SI base units, the exponents of which are integer numbers, e.g. $[E] = \mathrm{m^2\,kg\,s^{-2}}$. Dimensionless physical quantities, more properly called quantities of dimension one, are purely numerical physical quantities such as the refractive index n of a solvent. A physical quantity being the product of a number and a unit, the unit of a dimensionless quantity is also one, because the neutral element of multiplication is one, not zero.

Quantity calculus, the manipulation of numerical values, physical quantities and units, obeys the ordinary rules of algebra.[11] Combined units are separated by a space, e.g. $\mathrm{J\,K^{-1}\,mol^{-1}}$. The ratio of a physical quantity and its unit, $Q/[Q]$, is a pure number. Functions of physical quantities must be expressed as functions of pure numbers, e.g. $\log(k/s^{-1})$ or $\sin(\omega t)$. The *scaled quantities* $Q/[Q]$ are particularly useful for headings in tables and axis labels in graphs, where pure numbers appear in the table entries or on the axes of the graph. We will also make extensive use of scaled quantities $Q/[Q]$ in practical 'engineering' equations. Such equations are very convenient for repeated use and it is immediately clear, which units must be used in applying them. For example, a practical form of the ideal gas equation is shown in Equation 1.2.

$$p = 8.3145 \frac{n}{\mathrm{mol}} \frac{T}{K} \left(\frac{V}{\mathrm{m^3}}\right)^{-1} \mathrm{Pa}$$

Equation 1.2

If the pressure is required in psi units, the equation can be multiplied by the conversion factor 1.4504×10^{-4} psi/Pa = 1 to give Equation 1.3.

$$p = 1.206 \times 10^{-3} \frac{n}{\mathrm{mol}} \frac{T}{\mathrm{K}} \left(\frac{V}{\mathrm{m}^3} \right)^{-1} \mathrm{psi}$$

Equation 1.3

In this text, the symbols H^+ and e^- generally used by chemists are adopted as symbols for the *proton* and *electron*, rather than p and e, respectively, as recommended by IUPAC. The symbol *e* represents the elementary charge; the charge of the electron is –*e*, that of the proton is *e*. In chemical schemes these charges will be represented by $\ominus$ and $\oplus$, respectively. Some fundamental physical quantities and energy conversion factors are given in Tables 8.1 and 8.2.

1.2 Electromagnetic Radiation

We are dealing with the interactions of light and matter. The expression 'light' is used here somewhat loosely to include the near-ultraviolet (UV, $\lambda = 200$–400 nm) and visible regions (VIS, $\lambda = 400$–700 nm) of the entire electromagnetic spectrum (Figure 1.4), which spans over 20 orders of magnitude.

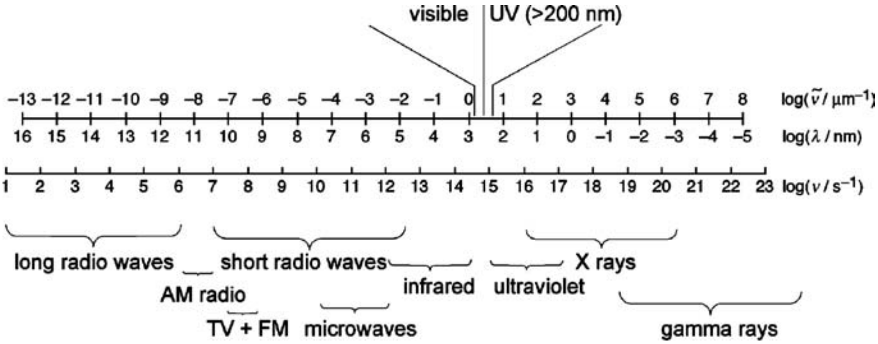

Figure 1.4 Electromagnetic spectrum

The first law of photochemistry (Grothus, 1817; Draper, 1843) states that only absorbed light is effective in photochemical transformation.

The second law of photochemistry (Einstein, 1905) states that light absorption is a quantum process. Usually, one photon is absorbed by a single molecule.

The particle nature of light was postulated in 1905 by Einstein to explain the *photoelectric effect*. When light is incident on a metal surface in an evacuated tube, electrons may be ejected from the metal. This is the operational basis of photomultipliers and image intensifiers, which transform light to an amplified electric signal (see Section 3.1).

The kinetic energy of these electrons is independent of the light intensity. This surprising result was not understood until Einstein proposed that light energy is quantized in small packets called *photons*. The photon is the quantum of electromagnetic energy, the smallest possible amount of light at a given frequency ν. A photon's energy is given by the *Einstein equation* (Equation 1.4), where $h = 6.626 \times 10^{-34}$ J s is Planck's constant.[b]

$$E_\mathrm{p} = h\nu$$

Equation 1.4

Einstein made the bold prediction that photons with an energy below that needed to remove an electron from a particular metal would not be able to eject an electron, so that light of a frequency below a certain threshold ν_th would not give rise to a photoelectric effect, no matter how high the light intensity. Moreover, he predicted that a plot of the photoelectrons' maximum kinetic energy, E_max, against the frequency of light ν should be a straight line with a slope of h (Figure 1.5). R. A. Millikan verified this 10 years later.[12]

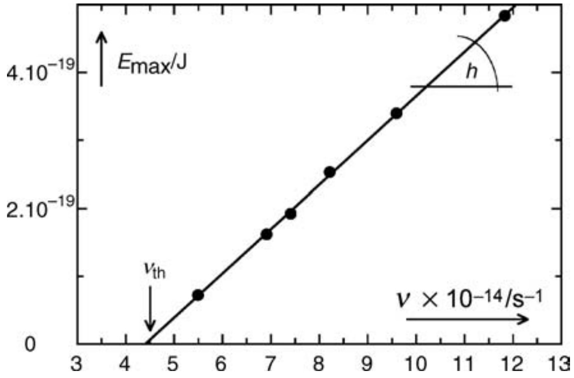

Figure 1.5 Maximum kinetic photoelectron energy E_max ejected from sodium metal as a function of light frequency. Adapted from ref. 12

The frequency ν of light is inversely proportional to its wavelength λ, $\nu = c/\lambda$, where $c = 2.998 \times 10^8\,\mathrm{m\,s^{-1}}$ is the speed of light; it is often replaced by the wavenumber, $\tilde{\nu} = \nu/c = 1/\lambda$, which corresponds to the number of waves per unit length. The SI base units are $[\nu] = s^{-1}$ and $[\tilde{\nu}] = m^{-1}$. We will generally use the derived units $\mathrm{cm^{-1}}$ ($= 100\,\mathrm{m^{-1}}$) for wavenumbers of vibrational transitions and $\mu\mathrm{m}^{-1}$ ($= 10\,000\,\mathrm{cm^{-1}}$) for wavenumbers of electronic transitions.

The energy transferred to a molecule by the absorption of a photon is $\Delta E = h\nu = hc\tilde{\nu}$. The energy of 1 mol of photons (1 einstein), $\lambda \approx 300$ nm, amounts to $N_\mathrm{A}E_\mathrm{p} = N_\mathrm{A}hc\tilde{\nu} \approx 400\,\mathrm{kJ\,mol^{-1}}$ and is sufficient for the homolytic cleavage of just about any single bond in organic molecules. For example, a similar amount of energy would be taken up by

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[b] The constant h was introduced in 1899 by Max Planck to derive a formula reproducing the intensity distribution of a *black-body radiator* (Section 2.1.3). To this end, Planck had to assume that a hot body emits light in quanta of energy $h\nu$, but he considered this assumption to be an amazing mathematical trick rather than a fundamental property of nature.

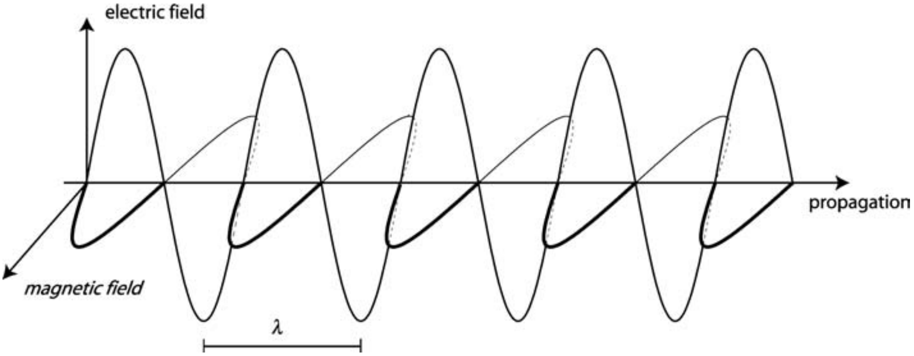

Figure 1.6 Electromagnetic wave along a propagation axis *x*. Note the scaling parameter λ. For $\lambda = 300$ nm, a full wave spans a length that is more than two orders of magnitude larger than that of an average molecule. The propagation axis could be replaced by time *t* to indicate the electromagnetic wave's oscillations at a given point in space. For a light wave of $\lambda = 300$ nm, the scale shown would then represent a time span of 10^{-15} s

naphthalene [$C_{p,\mathrm{m}}(\mathrm{g}) = 136\,\mathrm{J\,K^{-1}\,mol^{-1}}$] if it were immersed in a heat bath at 3000 K. This might suggest that organic molecules are indiscriminately destroyed by irradiation with UV light. Fortunately, this is not the case and we shall see why. The physical description of light is mind-boggling. Classical optics can be fully 'understood' by mathematically treating light beams as electromagnetic waves (Figure 1.6).

Other phenomena are best described in terms of light's particle nature (Equation 1.4). These seemingly contradictory properties are inseparable parts of the dual nature of light. Both must be taken into account when considering a simple process such as the absorption of light by matter. The above statements will surprise few readers because they have heard them many times before. But consider the experiment depicted in Figure 1.7.

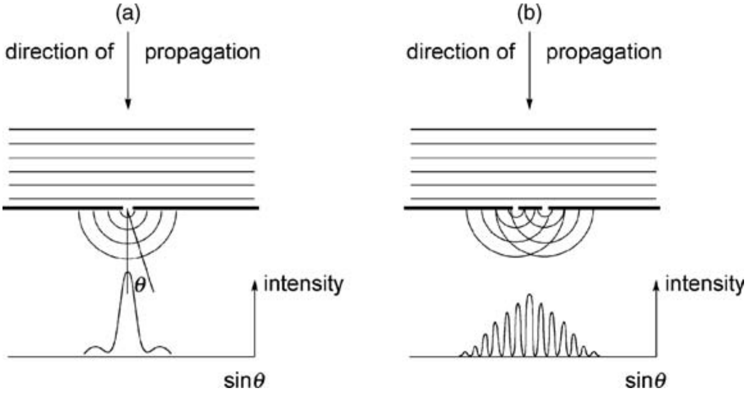

Figure 1.7 Parallel waves (representing either light or water waves in a ripple tank) encountering a barrier with (a) one small slit producing diffraction and (b) two small slits whose separation is equal to 10 times their width, producing an interference–diffraction pattern