HANDBOOK OF PHOTOCHEMISTRY

THIRD EDITION

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Luca Prodi
M. Teresa Gandolfi

with introductory sections by Josef Michl and Vincenzo Balzani

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Foreword

Photochemists are always looking for information of all sorts. There is often an urgent demand for certain information that seemingly should be, but for some reason is not, conveniently available. All of us have a special reference book or two that we treasure that serve as portals to information that we need right away. Maybe it's a book with some good one liners for a speech we have to deliver or a thesaurus with the *mot juste* that we need to convince our colleagues of the beauty of our science in a lecture. Or maybe it's a reference book of prayers that we go to in desperation when experiments are not working. For a photochemist an ideal reference book provides rapid access to that rate constant, that quantum yield, that triplet energy, that fluorescence spectrum, that actinometer, etc. that suddenly is important in making an argument or checking a hypothesis. Where to find such data conveniently and authoritatively and quickly?

The Handbook of Photochemistry has been a very special reference book for photochemists since the first edition appeared in 1973. The collection of data complied in this edition was judiciously selected and presented in a user friendly manner such that it was easy to find the pertinent information. At that time important photochemical parameters such as excited state energies, rate constants, spectral information were not conveniently gathered. "The Handbook" was a break through in that regard and presented data with a high level of scholarship. The second edition, which appeared in 1993 built on the excellent scholarship of the first edition.

The third edition (2005) follows in the fine tradition of excellent, user-friendly scholarship, with some additional features. The new edition starts Chapter 1, an overview of the photophysics of organic molecules in solution by Josef Michl, followed by Chapter 2, an overview of the photophysics of transition metal complexes by Vincenzo Balzani. These are welcome essays, well worth reading by students and experts alike. Chapter 3 and the following chapter launch into the "meat" of the Handbook, large tables of data with references on the photophysical properties of organic and inorganic molecules.

The photochemical community will certainly be pleased to see the new updated arrival of The Handbook. Faculty should obtain a copy and put within easy reach of their students. When students ask where can I find….just point them to The Handbook. The sooner they become accustomed to using it as an information resource, the better off their research and understanding of photochemistry will be.

Enjoy.

Nicholas J. Turro
Columbia University (NY)

Preface to the third edition

In our everyday research and teaching activity as photochemists, the Handbook of Photochemistry has always been an invaluable reference. Therefore, needless to say, we embarked in the preparation of this revised and expanded edition of the Handbook with the greatest enthusiasm.

In the last thirteen years, since the release of the second edition of this Handbook, photochemical sciences have continued their vigorous expansion, as witnessed by the ever-increasing number of scientific papers dealing with photochemistry. Many spectroscopic and photochemical techniques that used to be prerogative of specialist research groups are now available in a wide range of laboratories. It has also become evident that chemistry as a whole has evolved rapidly. In many instances the traditional fields of chemistry – organic, inorganic, physical, analytical, biological – tend to overlap and merge together, giving rise to disciplines, such as those related to nanosciences. Light-induced processes play, indeed, an important role in these emerging fields of science. In such a context, we felt that times were ripe for a third edition of the Handbook of Photochemisty.

As for the previous editions, the goal of the third one is to provide a quick and simple access to the majority of the chemical and physical data that are crucial to photochemical investigations – from the planning and set up of experiments to the interpretation of the results. For the preparation of this Handbook, we could profit from an excellent starting material, that is, the second edition by S. L. Murov, I. Carmichael and G. L. Hug, published in 1993. We decided to maintain the format of most of the existing tables of data, not only because they were quite well organized, but also because many scientists got used to them during the years. By taking advantage of modern literature databases and related powerful search engines, we updated and expanded such tables with data on hundreds of new compounds. In particular, the section dealing with reduction potential values (Chapter 7), in the light of the importance of electron-transfer processes in photochemistry, was considerably enriched. In preparing the tabular and graphical material, we devoted a great effort to improve the readability and reach a style uniformity throughout the book.

The most relevant new entries of this third edition are indeed the tables gathering together the photophysical (Chapter 5), quenching (Section 6d) and reduction potential (Section 7b) data on metal complexes and organometallic compounds. Moreover, we found appropriate to expand and update, on the basis of our experience, some of the "technical" sections, and specifically light sources and filters (Chapter 11) and chemical actinometry (Chapter 12). We also introduced a section (Chapter 10) which describes the problems that are most frequently encountered in photoluminescence measurements, and illustrates a simple correction method to take into account the related effects. These sections will hopefully provide preliminary information at a glance, but are not intended to replace the many excellent books on photochemical methods and techniques that are available on the market and cited in the references.

Last but not least, the Handbook now features two introductory chapters written by two world leaders in photochemical sciences. Chapter 1, by Josef Michl, deals with the photophysics of organic molecules in solution. Chapter 2, by Vincenzo Balzani, describes the photophysical properties of transition metal complexes. Again, these sections cannot certainly be adopted in substitution of photochemistry textbooks; however, we felt that a concise overview of the most important light-induced processes that take place in organic and inorganic molecules would have been of help for students and for researchers that wish to get closer to the wonderful world of photochemistry.

In the preparation of this edition we benefited from the contribution of many people. First, we are grateful to all the members of our research group in Bologna, not only for fruitful discussions, but also for their friendship and support. We are particularly indebted to Vincenzo Balzani, Luca Moggi, Alberto Juris, Margherita Venturi of the Department of Chemistry of the University of Bologna, and to Roberto Ballardini of the ISOF Institute of CNR in Bologna. Mara Monari, Serena Silvi, Paolo Passaniti and Alberto Di Fabio gave us invaluable help for typing and checking several parts of the manuscript. Special thanks to Josef Michl for his contribution and Nick Turro for his fine foreword, and all the colleagues around the world that kindly sent us reprints and preprints of their papers or just simple, but precious information.

No book, of course, is free of errors and imperfections. We attempted to keep mistakes at a minimum by careful and repeated checks, and we apologize in advance for those that we could not avoid. We sincerely hope that readers will enjoy this new edition and that it will continue to be "The Handbook" of the photochemical community.

Photochemistry has come a long way since the pioneering work of Giacomo Ciamician, to whom our Department is named after. However, the ideas expressed by Ciamician in his visionary speech of 1912, entitled "The photochemistry of the future" are still the most appropriate to conclude this preface. The following sentence, quoted in the first two editions of the Handbook of Photochemistry, is worth repeating:

"On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is."

G. Ciamician, *Science*, **1912**, *36*, 385-394.

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Bologna, May 2005

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By Josef Michl, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215, U.S.A.

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1a INTRODUCTION

The following is a short overview of the principles of photophysics. We start by providing a brief survey of electronic excited states in Section 1b. This material can be found in textbooks of quantum chemistry but we have directed it to the specific needs of those wishing to learn the fundamentals of photophysics. We then proceed to the description of radiative (Section 1c) and non-radiative (Section 1d) transitions between electronic states. Strictly speaking, the material of Section 1c belongs to the discipline of electronic spectroscopy at least as much as it belongs to photophysics, but it was felt that it would be useful to outline the basics here instead of referring the reader elsewhere. Section 1e deals with the procedures that are in common use for the analysis of photophysical and photochemical kinetic data.

1b ELECTRONIC STATES

1b-1 Electronic Wave Functions

Because of their substantially smaller mass, electrons have much less inertia than nuclei and under most circumstances are able to adjust their positions and motion nearly instantaneously to any change in nuclear positions. It is therefore almost always acceptable to separate the problem of molecular structure into two parts, and to write the molecular wave function as a product of an electronic part, parametrically dependent on the nuclear geometry, and a nuclear part, different in each electronic state. The electronic wave function carries information about the motion of electrons within the molecule. Because of their light mass, electrons must be treated by quantum mechanics. The nuclear wave function contains information about molecular vibrational motion. Although strictly speaking nuclear motion must also be treated quantum mechanically, at times it is useful to approximate it by classical mechanics. The separation of electronic and nuclear motion is known as the *Born-Oppenheimer approximation*. The translation of a molecule as a whole is treated separately, almost always by classical mechanics, and need not concern us. Free rotation of an isolated molecule needs to be treated by quantum mechanics, but since we deal only with solutions, where it is severely hindered, we will be able to treat it classically if we need to consider it at all.

Electronic wave functions and their energies are found by solving the electronic Schrödinger equation, assuming stationary nuclear positions. In principle, an infinite number of solutions exists for any chosen geometry. Those at lower energies are quantized and their energy differences are on the order of tens of thousands of cm^{-1}. At higher energies, the energy differences decrease to thousands of cm^{-1} and less, and above the ionization potential, a solution exists at any energy. In the continuum regime, one or more electrons are unbound and the

molecule is ionized (oxidized). For molecules with positive electron affinity, it is also possible to add an electron (reduction).

When only non-relativistic electrostatic energy terms are included in the potential energy part of the Hamiltonian operator contained in the Schrödinger equation, the resulting state wave functions are eigenfunctions of the total spin angular momentum operator and can be classified as singlets, triplets, etc., if the molecule contains an even number of electrons, or doublets, quartets, etc., if the number of electrons is odd. In organic molecules, only singlets and triplets are ordinarily of interest. Among the additional small terms normally neglected in the absence of atoms of high atomic number, spin-orbit coupling and electron spin-spin dipolar coupling are the most important, in that they cause the pure spin multiplet states to mix to a small degree. Also the hyperfine interaction term, which describes the coupling of electron and nuclear spin, can play this role. We shall return to these terms in Sections 1b-7, 1c-2, and 1d-3.

Often, we are only interested in the wave function of the lowest energy, which describes the ground electronic state. In ordinary organic molecules, this is the lowest singlet state (S_0). This wave function is the easiest one to solve for, but even it can only be found very approximately for molecules of any complexity. Most simply, the approximate solutions are expressed in the form of a spin symmetry adapted antisymmetrized product of one-electron wave functions, called an electron configuration state function (Fig. 1b-1). The antisymmetrization is needed to satisfy the Pauli principle, and is achieved by arranging the product of one-electron wave functions into a determinant (the Slater determinant). The one-electron wave functions used are referred to as occupied molecular spinorbitals, and those that could have been used, but were not, are known as virtual or unoccupied molecular spinorbitals, whose number is infinite. The best possible choice of molecular spinorbitals, defined as the one that gives the lowest ground-state energy, carries the name *Hartree-Fock* or *self-consistent spinorbitals*. Physically, a wave function approximated by a single configuration describes the motion of electrons in the field of stationary nuclei and the time-averaged field of the electrons.

Molecular spinorbitals are normally written as a product of an electron spin function (α, spin up, or β, spin down) and a space function, referred to as a molecular orbital. In a closed-shell configuration, each occupied molecular orbital is used twice, once with each choice of spin (Fig. 1b-1). Molecular orbital energies are related to reduction-oxidation properties of ground states of molecules. In an approximation developed by Koopmans, the energy of an occupied Hartree-Fock orbital is equal to minus the energy needed to remove an electron from that orbital to infinity (the ionization potential), and the energy of an unoccupied Hartree-Fock orbital is equal to minus the energy gained when an electron is brought from infinity and added to that orbital (electron affinity).

Molecular orbitals are ordinarily approximated as a linear combination of atomic orbitals centered at the atomic nuclei. These atomic orbitals are known as the basis set. Years of experience have revealed the basis set size and type that are

needed to achieve a desired level of accuracy. Orbitals composed primarily from inner shell atomic orbitals are occupied in all low-energy states. Roughly half of the orbitals derived from atomic orbitals of the atomic valence shell are occupied and the other half are empty. Together, these orbitals span the so-called valence space. Rydberg orbitals are high-energy diffuse orbitals best expressed as combinations of atomic orbitals of higher principal quantum numbers.

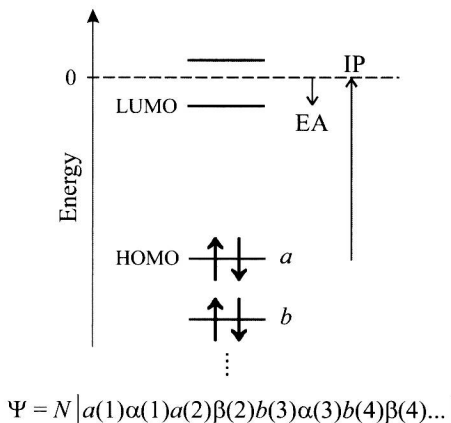$$\Psi = N \left| a(1)\alpha(1)a(2)\beta(2)b(3)\alpha(3)b(4)\beta(4)... \right|$$

Fig. 1b-1. A symbolic representation of a closed-shell electronic wave function.

It is always better, but especially important at biradicaloid geometries (those with only two electrons in two approximately non-bonding orbitals in low-energy states), not to ignore the instantaneous as opposed to the time-averaged field of the other electrons. The energy lowering associated with this improvement is called electron correlation energy. The most common way to write a correlated wave function is to use a linear combination of many configurations instead of a single one. Depending on the details, this computationally much more demanding procedure is then called configuration interaction, coupled clusters, etc.

It is also possible to avoid molecular orbitals altogether and to construct the molecular electronic wave function directly from hybridized atomic orbitals (linear combinations of atomic orbitals located at the same nucleus). This so-called valence-bond method introduces correlation energy from the outset, but suffers from other difficulties. It has the intuitively appealing feature that the various contributions to the electronic wave function map readily onto the familiar Lewis structures of molecules. Carried to completion within a given starting atomic basis set, the molecular orbital and the valence-bond methods converge to the same result, known as the full configuration interaction wave function. Within the limits dictated by the use of a finite basis set, this is the exact solution of the Schrödinger equation, but present-day computer technology only permits its computation for

very small molecules and limited basis sets, and this is not likely to change in the foreseeable future.

An altogether different approach is to give up the search for the molecular electronic wave function, which is a function of the space and spin coordinates of all electrons present in the molecule and contains far more information than is actually needed for any practical purpose, and to search for the total electron density function instead. Electron density within a molecule only depends on the three spatial variables, and is in principle sufficient for the evaluation of observable quantities. It is evaluated from the so-called Kohn-Sham determinant, built from Kohn-Sham orbitals. Although this determinant is analogous to the Slater determinant of wave function theories, it is not a wave function of the molecule under consideration, but only a construct used to make sure that the search for the optimal density is constrained to those densities for which an antisymmetric wave function in principle exists (it represents a wave function of a fictional molecule whose electrons do not mutually interact, and is chosen so as to produce the best total electron density in the variational sense). The various versions of this so called density functional method differ from each other in the functional used, i.e., in the assumptions they make in evaluating the total energy from electron density distribution in space. This relation is exact in principle and includes contributions from electron correlation energy, but the true form of the requisite functional is not known. The most popular functionals are semiempirical in that their general form agrees with first principles but the details have been adjusted empirically to yield optimal agreement with various experimental results.

Usually, the energy calculation is repeated for many stationary nuclear geometries and the one that yields the minimum total energy for the molecule is referred to as the optimized geometry of the ground state. The single-configuration approximation has the best chance of being adequate at geometries close to this optimized geometry, whereas at biradicaloid geometries the use of one of the methods that include electron correlation is mandatory. At these geometries, density functional methods usually have difficulties.

In photophysics and photochemistry, several of the lowest energy wave functions and their energies are normally needed. With the exception of the wave function of the lowest triplet state, and sometimes also one of the low-energy singlet states, it is only rarely possible to use the single-configuration approximation for excited states, and for accurate results, methods based on linear combinations of configuration state functions are always used. Optimization of geometries in excited states is possible, but again with the exception of the lowest triplet state, much more difficult than in the ground state. In density functional methods, electronic state energy differences are calculated directly from the ground state electron density. In the vicinity of ground state equilibrium geometries, these so called time-dependent density functional methods perform quite well.

The observable properties of a molecule in a particular electronic state, such as its permanent dipole moment, are obtained as the expectation value of the appropriate operator, such as the dipole moment operator M, over its electronic wave

function, evaluated at the equilibrium geometry. They can change quite dramatically as a function of the electronic state. More properly, the calculation is repeated for many geometries in the vicinity of the equilibrium geometry and averaged over the molecular vibrational wave function, discussed below. Since the variation of molecular properties over a small range of geometries is usually small, this is rarely necessary unless the observable value vanishes by symmetry at equilibrium.

1b-2 Potential Energy Surfaces

The nuclear geometry of a molecule with N nuclei is specified by the values of $3N-6$ internal coordinates, since three of the total of $3N$ degrees of freedom are needed to describe the location of the center of mass and three to describe rotations relative to a laboratory frame. Only the geometry of a diatomic molecule, which is always linear and therefore has only two axes of rotation, is described by $3N-5$ internal coordinates, i.e., by the bond length alone.

A collection of $3N-6$ internal coordinates at a particular geometry represents a point in a $3N-6$ dimensional mathematical space. A surface produced in a $3N-5$ dimensional graph in which the total molecular electronic energy of the ground state is plotted against the geometry is known as the ground state potential energy surface. In spite of its name, the total electronic energy contains not only the kinetic and potential energy of the electrons, but also the potential energy of the nuclei. It is not easy to visualize multidimensional potential energy surfaces, and it is customary, albeit frequently misleading, to show limited portions of a surface in two-dimensional (Fig. 1b-2) or three-dimensional (Fig. 1b-3) cuts through the $3N-5$ dimensional plot.
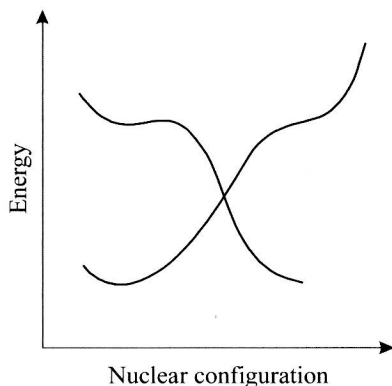

Fig. 1b-2. Two-dimensional cut through potential energy surfaces (schematic).

The ground state potential energy surface contains minima that correspond to the geometries and energies of more or less stable molecules and can be associated with their chemical (Lewis) structures. The minima are separated by barriers, and the lowest cols between minima correspond to transition states of chemical reactions. The height of a col above the minimum is the activation energy, and the width of the col is related to the activation entropy.

Connecting the set of points representing the next higher energy solutions yields the potential energy surface for the first excited state, and one can continue to define potential energy surfaces for as many states as needed (Fig. 1b-2). The excited surfaces also have minima and barriers separating them. Excited state minima located in the geometrical vicinity of a ground state minimum are called spectroscopic since their existence and shape can ordinarily be deduced from molecular electronic spectra. There usually are additional excited state minima and funnels at other geometries, particularly biradicaloid ones. Funnels are conical intersections, $(3N–8)$-dimensional subspaces in which one potential energy surface touches another, i.e., an electronic state has the same energy as the one just below or just above it. If the two touching states have equal multiplicity, their touching is avoided in the remaining two dimensions. Plotted in these two dimensions, the potential energy surfaces of the two states have the appearance of two conical funnels touching at a single point, the lower upside down and the upper right side up (Fig. 1b-3). Plotted along a single coordinate that passes through a touching point, they look like two crossing lines (Fig. 1b-2). If they have different multiplicity, potential energy surfaces cross freely. The minima and conical intersections in a potential energy surface are often separated by barriers with cols. Minima and funnels located at geometries far from any ground state minima can be referred to as reactive (see below).
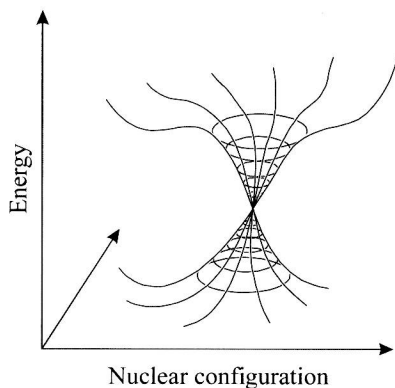

Fig. 1b-3. Three-dimensional cut through potential energy surfaces (perspective view, schematic).

1b-3 Vibrational Wave Functions

The total internal energy of a molecule is obtained by adding the internal nuclear kinetic energy to the electronic energy described by the potential energy surface. At any one time, the molecular geometry is represented by a point in the $3N–6$ dimensional nuclear configuration space, and thus by a point on the potential energy surface. The total energy is represented by a point located vertically above the latter, by an amount corresponding to the nuclear kinetic energy. In a molecule that is not exchanging energy with its environment, the total energy is constant, and the point representing the total energy moves in a horizontal plane, directly above the point that represents the electronic energy, which is located on the potential energy surface (Fig. 1b-4).
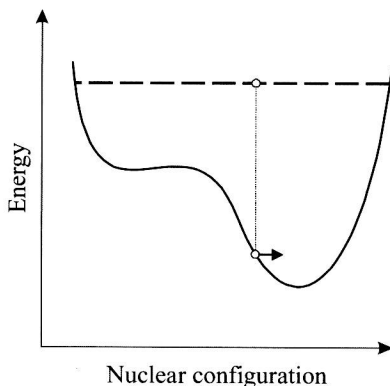

Fig. 1b-4. A schematic representation of the force vector acting on nuclei at a particular choice of nuclear configuration.

In contemplating nuclear dynamics one can invoke an analogy to a balloon soaring at a constant height above a mountainous landscape containing sharp peaks reaching almost to infinity at geometries in which two or more nuclei come very close together. The lateral force acting on the balloon above any one point is given by minus the gradient of the potential energy surface at that point. In completely flat regions of the surface, at its minima, cols, and other points where the gradient of the surface is zero, the force vanishes, and at other points, the force pushes the balloon away from peaks in the general direction of valleys leading toward a nearby minimum. When ground is far below, the balloon moves fast, and when it is close, the balloon slows down.

In the classical limit, and in an appropriately chosen coordinate system, the molecule behaves as if the shadow of the balloon, with the sun at zenith, were to follow the path of a ball that rolls on the surface without friction. In the quantum mechanical description, solutions of the Schrödinger equation for nuclear motion