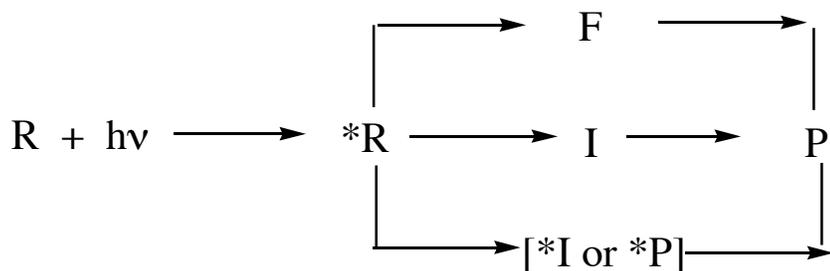


Molecular Photochemistry of Organic Compounds—An Overview

1.1 What is Molecular Photochemistry?

This text is concerned with the field of molecular photochemistry of organic compounds (or equivalently, molecular organic photochemistry), a science in which the universe of molecular structures and processes which result from the interaction of light and organic molecules. The field of molecular organic photochemistry can be conveniently classified in terms the *photophysics of organic compounds* (the interactions of light and organic molecules resulting in net physical, radiative and radiationless changes) and the *photochemistry of organic compounds* (the interactions of light and organic molecules resulting in net chemical changes).

What is *molecular organic photochemistry*? As a starting point to answering this question, consider Sch. 1.1. Molecular organic photochemistry involves the overall process $R + h\nu \rightarrow P$, where R is an organic molecule that absorbs a photon ($h\nu$) and P is an isolated product(s). In general, R will stand not only for the specific molecule, R, which absorbs the photon but also will implicitly include any other molecules that are required for production of the product P. If not stated explicitly, it will be assumed that the reaction of interest occurs in a solution of an inert solvent. A definition of molecular organic photochemistry that suits this text is: *“Molecular organic photochemistry is the science concerned with a complete mechanistic description of all of the physical and chemical steps that occur as the result of the absorption of a photon by an organic molecule R and eventuate in the formation of an isolated product P.”*



Sch. 1.1. A global paradigm for organic photochemical reactions.

The text will show that Sch. 1.1 is a remarkably simple “paradigm” which serves as a basis for analyzing all organic photochemical reactions. The paradigm of Sch. 1.1 teaches that the absorption of light causes the formation of an electronically excited state, *R , which can undergo several photophysical processes (no net chemical reaction to form P) or photochemical processes (formation of P). We shall employ the term “molecular photochemistry” to include *both* the photophysics of *R and the photochemistry of *R , since concepts and laws of photophysics and photochemistry are intimately interwoven. Indeed, it is not possible to have a proper understanding of the photochemical processes of R without a proper understanding of the photophysical processes of R. The molecular photochemistry of organic molecules is a rather broad and interdisciplinary discipline embracing the fields of chemical physics, molecular spectroscopy, physical organic chemistry, synthetic organic chemistry and supramolecular chemistry. There are three pathways which R may follow on the way to P: (1) one pathway leads to the formation of a reactive intermediate (I) which is typically a radical pair or diradical; (2) the second pathway does not involve any discrete intermediate but instead passes through a “funnel” (F) which takes R to P; and (3) the third pathway involves the formation of an electronically excited intermediate (*I) or product (*P). Of these three, pathway (1) is by far the most commonly observed.

The “molecular” part of molecular photochemistry emphasizes the use of the molecule and molecular structure and their implied dynamics and molecular substructure (electron configuration, nuclear configuration, spin configuration) as the crucial and unifying intellectual units for describing the possible, plausible and probable pathways of photochemical reactions from *cradle* (absorption of a photon by a reactant, R to form *R) to *grave* (isolation of a product, P produced by one of three pathways from *R).

1.2 Learning Molecular Organic Photochemistry: Content, Context, Cognition.

When a student is introduced to a new subject there are three intellectual pillars underlying the creation of new knowledge that provide a strategy for robust learning: the *content* of the subject, the *context* of the subject and the *cognitive* aspects of the subject. The *content* (which provides “know what” to the student) is the information that constitutes the “facts” of the subject matter. All textbooks present the content that has been compiled by a mature field of scientific inquiry. However, textbooks are usually valued by students not for their content, which is essentially the same in all textbooks, but rather because of the ability of a textbook to place the content in an appealing *context* (which provides “know how” to the student). By context of a textbook we mean the manner in which the text intellectually connects “facts” so that they provide relevant meaning and insight of the content for the student. Students also value textbooks which explicitly utilize *cognitive learning strategies and techniques* (which provide “know why” to the student) in representing the content, and place it in a context that is not only appealing to the student but also enriches, modifies and enlarges a student’s knowledge base of a subject. This text attempts to integrate content, context and cognitive learning strategies and organic photochemistry. In particular, the text takes the pedagogical position that organic chemistry has thrived because of its tradition of representing techniques into account in teaching the student the science of modern molecular structures and reaction mechanisms in a highly visual manner and of correlating structure and reactivity through a mechanistic approach which couples dynamics to structures. Molecular organic photochemistry provides a visualization and understanding of photochemical reactions through a structural and mechanistic approach. The cognitive learning strategies of the text teaches the student (1) to convert “facts” into robust knowledge, (2) to represent that knowledge through highly pictorial and visualizable representations, and (3) to organize, manage and manipulate the representations intellectually and within chosen contexts.

1.3 Why Study Molecular Organic Photochemistry?

There are many motivations for studying the molecular photochemistry of organic compounds. First, there is the pure intellectual satisfaction of creating

an understanding of how two of the most fundamental components of the universe, light ($h\nu$) and molecules (R), interact with one another to produce an electronically excited molecule ($*R$) and a product (P). In particular, there can be a special intellectual delight in learning how to integrate such fields as spectroscopy, quantum mechanics, reaction mechanisms, molecular structure and dynamics, all of which are essential for an understanding of molecular organic photochemistry. The intellectual structure of molecular organic photochemistry is inherently interdisciplinary and, therefore, requires a practitioner in the field to seek a commonality in the ideas and methods of many scientific disciplines. Molecular organic photochemistry must integrate theories from different fields. Initially these theories may appear to be based on disparate concepts and laws, such as the theory of waves and the theory of particles. We shall show that the process of achieving such an intellectual integration two initially disparate theories is not only stimulating and gratifying, but can also serve as a model for knowledge creation in any area of science or any ordinary everyday decision making.

Other motivations for studying organic molecular photochemistry are found in its importance in modern technology, biology, medicine and energy. Organic molecular photochemistry allows an understanding of the role of absorbed sunlight in important life processes such as photosynthesis, which is the fundamental means of harnessing the sun's energy to produce food and energy for our planet. Photosynthesis is initiated by a simple photoinduced electron transfer reaction. Vision, our most important sense for observing and surviving in the external world is triggered by a remarkably simple photoinduced cis-trans isomerization reaction. During the late 1900s the advent of the use of lasers which revolutionized the field of telecommunications by produced a new way of transmitting information by the use of light (through glass fibers), rather than electrons (through metal wires). New technologies, termed photonics, employ light to perform tasks that were originally relegated to the domain of electronics. Photochemistry is attaining an increasingly important role in the health sciences to cure some forms of cancers through phototherapy, to repair tissues and to perform surgery using lasers. Other

important applications of photochemistry in technology include the use of photolithography to manufacture computer chips and photopolymerization to produce protective coatings for a variety of high value materials such as optical fibers. One of the “holy grails” of photochemistry is the discovery of practical ways to convert sunlight into high grade fuels to replace fossil fuels. All of the above applications of photochemistry require an understanding of the two essential players in organic photochemistry: the photon ($h\nu$) and the molecule (R).

1.4 The Structure of Scientific Theories. The Value of Pictorial Representations and Visualization of Scientific Concepts

Molecular photochemistry involves a number of theories or representations which are integrated to describe the interaction of light and organic molecules to produce electronically excited states (Sch. 1.1, $R + h\nu \rightarrow {}^*R$) and to describe the pathways from electronically excited states to products (Sch. 1.1, ${}^*R \rightarrow P$). Organic chemists are accustomed analyzing ground state thermally induced reactions of R in terms of molecular structure and molecular dynamics. We shall employ the molecular structural theory of organic chemistry as both a familiar and effective approach for understanding mechanistic organic photochemistry, although some important modifications will be made as we proceed. We shall be in less familiar ground as we develop a theory of light and of the interaction of light with molecules where the usual structural theory is replaced by a theory of interacting waves. As a result we shall see to understand paradigms of wave and quantum mechanics, which have evolved as authoritative and effective platforms for understanding all aspects of molecular organic photochemistry.

Indeed, the concepts of atoms, molecules, electrons, nuclear configurations, periodicity and chemical bonding in terms of molecular orbitals are most precisely represented in terms of the mathematics of wave and quantum mechanics. In order to understand molecular organic photochemistry, in addition to familiar chemical representations involving molecular structure

and molecular dynamics, we must develop an understanding of the perhaps less familiar concepts of electron spins, electromagnetic radiation, photons, wave mechanics and quantum mechanics. Fortunately, we shall show that there are classical representations which are readily visualizable and which capture the essence of most of the features of wave and quantum mechanics. These classical representations will provide “quantum intuition” for an understanding of the details of the pathways given in Sch. 1.1.

A mature scientific theory serves as a working model for a community of practitioners if it repeatedly is able to make predictions and provide a platform for an understanding of laboratory observations. The predictive attributes of a theory are especially admired, valued and important. Theories may make quantitative or qualitative predictions which serve as a tool for designing and conducting experimental research. In this sense the intellectual structure of a theory serves the experimentalist as a guiding tool for conducting research in a manner analogous to the way scientific equipment provides a tool for recording observations. The use of many scientific theories in everyday science is often limited if the theory is cast in a mathematical framework that is obscure to the student and is beyond the reach of the typical organic chemist. Thus, for an organic chemist an important feature of a good, everyday, working scientific theory is the ability to create a system of *qualitative structural representations* that are abstracted from direct experimental observations and can be expressed *pictorially* and *geometrically* and therefore can be readily *visualized*.

Geometric representations of natural phenomena are “pictures” that can be extremely useful to the working researcher, because they provide an everyday language in which observations can be organized, described, arranged, interpreted and understood. Using geometry, the scientist can develop qualitative *intuitive theories*. The latter provide the tremendous value of being able to provide a common language for the logical arrangement and discussion of past observations and prediction of future observations that are easily understood by all practitioners of a field. As required, these “pictures” can be translated into more rigorous mathematical frameworks.

In this text we shall employ pictorial representations of the concepts and rules and laws of wave and quantum mechanics to describe photochemical and photophysical processes of organic molecules. Many of the important concepts in quantum mechanics involve “matrix elements” (mathematical computation of the prediction of the value of an experimental quantity). Among the important quantities of interest in organic photochemistry are the matrix elements for energy of electronic, vibrational and spin states, energy differences between states, dipole moments, selection rules for transitions, orbital correlation diagrams, oscillator strengths, spin-orbit couplings, etc. The authors note at the outset that although quantum mechanics has a deep mathematical structure and that the quantitative aspects of quantum mechanics have an inescapable mathematical framework. *However, this text attempts to demystify all of the important quantum mechanical concepts by expressing them in terms of qualitative, pictorial analogies and structural models.* This approach is justified if the student is not after mathematical precision but is seeking to be guided by broad outlines provided by visualizable models of the photochemical systems of interest. This approach is effective if we are capable of selecting pictorial representations which capture the “heart” of the system under analysis and thereby obtain a physical rather than a mathematical understanding of the system. The pictures can provide a physical and quantum “intuition” of processes at the microscopic level.

For those who plan to proceed more deeply into the mathematics of quantum mechanics, we hope that the pictorial representations will provide useful tools as a framework for the more quantitative aspects. Of course, the interested and able student can proceed to other textbooks and references which are provide to delve as deeply into the mathematical aspects as desired.

1.5 The Paradigms of Molecular Organic Photochemistry

In performing everyday, “normal science and research”, the scientist to the understanding seeks answers to questions such as the following: What legitimate concepts and tools should be employed to analyze, organize,

understand and predict observations of interest and importance to the project at hand? What are the legitimate methods of computation, measurement or instruments that should be used in defining and quantifying an observation? Which observations are the most important to make initially? How does one determine whether an unexpected observation is an extraordinary result or a trivial artifact or an embarrassing error? To what authority does a scientist appeal in making decisions on which theory or method to employ to answer such questions?

It may seem that there would be many subjective opinions concerning how to answer the above questions. One might therefore suspect that the performance of everyday science would be a matter of constant controversy among scientists so that it would be difficult to obtain a consensus on how to design, execute, interpret and understand laboratory observations. However, clearly this is not the case in mature “hard” sciences such as Physics and Chemistry. Consensus occurs among scientists when *authoritative scientific paradigms* exist that make it easy for scientists to agree on how to deal with the important questions listed above. Indeed, authoritative scientific paradigms allow the practicing scientist to perform everyday research and for a student to be readily initiated into a mature field of science by studying, learning and mastering the paradigms of the field. The development of a *scientific paradigm for molecular photochemistry of organic molecules* is a critical objective of this text and provides a context for the pedagogical structure of the content described in the text. Let us examine the concept of scientific paradigms and how it relates to the development of a paradigm for molecular organic photochemistry.

In his famous book [1] on the “Structure of Scientific Revolutions”, Thomas Kuhn, a philosopher of science, defined a *scientific paradigm* as a complex set of intellectual and experimental structures consisting of assumptions, concepts, strategies, methods and techniques that provide a framework for performing scientific research in a field and for interpreting the observable phenomena of the universe in a systematic and reproducible manner. According to Kuhn, the *accepted paradigms of a field are the authority to which scientists appeal in deciding on the course of everyday, normal scientific activities and in*

recognizing exceptional results and likely errors or artifacts. Scientists readily accept and employ the authority of the reigning paradigms because the latter have been repeatedly demonstrated to be powerful tools for providing rules for rapidly and efficiently performing the normal science of everyday research, which consists of solving “scientific puzzles” related to natural phenomena of interest. The power of the paradigm as an authority derives from its ability to consistently and successfully direct scientific inquiry into formulating and solving scientific puzzles. The paradigm sets the expectations and coordinates the standards for what a scientific community considers legitimate concepts, laws, theories and research within the field over which the paradigm governs. In effect, a scientific community is defined by the paradigm that directs the everyday research efforts of the practitioners. *This text is concerned with the description and development of the paradigms of modern molecular organic photochemistry.*

The authority of the paradigm prevents practitioners in a field from wasting time quibbling over fundamentals or irrelevancies or errors or artifacts; because they share the same paradigm, practitioners can proceed rapidly to advanced levels of inquiry without arguing over fundamental issues. For example, the paradigm of atomic and molecular structure is so authoritative that no modern chemist or physicist argues whether molecules can be usefully represented by three dimensional models of atoms connected by bonds that result from the interactions of electrons and nuclei. Photochemists do not argue about whether electronically excited states, *R , are involved in photochemical reactions. A modern photochemist *always starts with the assumption that the global paradigm of Sch. 1.1 is a good starting point for the investigation of any organic photochemical reaction.* However, a little over 100 years ago the paradigm of describing molecular structures in terms of three dimensional geometry was hotly debated {2} by the scientific community and before 1955 years ago there were no authoritative paradigms which governed the description of organic photochemical reactions. Yet today we are convinced that all observable chemical phenomena, no matter how complex, can be understood

and investigated based on the paradigm of molecular structure and dynamics and that organic photochemistry is no exception!

1.6 Exemplars as Cognitive Tools and Guides to Experimental Study

Typically, a textbook will implicitly employ paradigms that constitute the assumptions, concepts, strategies, methods and techniques of the field of interest. An important cognitive tool in learning a field's paradigms is the explicit consideration of specific exemplary examples called *exemplars*. The latter provide an excellent pedagogical tool to introduce students to new fields of science. An exemplar can be loosely defined as a universally recognized scientific accomplishment or study that for a time provides a theoretical and experimental map for the scientist on how to investigate a new system. The exemplar informs the scientist of the entities that exist in nature and that do not exist in nature and the ways that entities that exist behave. The use of exemplars is the one which is used widely in this text.

The field of *molecular organic photochemistry* may be considered as being governed by an integrated set of paradigms that have been demonstrated to be effective for solving scientific puzzles in the mature fields of *photochemistry, spectroscopy, chemical physics and organic chemistry*. The integration of this set of paradigms serves as the backdrop for the design of experiments, for the investigation of organic photochemical reactions, and for the theoretical computation, interpretation and prediction of those reactions. In this text we shall explicitly use Kuhn's concepts of paradigms and appropriate exemplars to assist the student in understanding organic photochemical reactions from the initial act of light absorption by an organic molecule ($R + h\nu \rightarrow {}^*R$) to the isolation of a product (P). The application of the paradigm of Sch. 1.1 represents a "cradle to grave" *mechanistic approach* to molecular organic photochemistry for understanding the overall $R + h\nu \rightarrow P$ reaction.

In closing this section on paradigms, the student must be warned that the ruling paradigms are by no means permanent, but are always subject to change. This is because of the tentative nature of theories, the incompleteness of

experimental information and the inevitable possibilities of completely unanticipated results which may be observed in the future. The history of science over the past two centuries has shown that paradigms that were considered absolutely unshakable, were not only shakable, but completely replaced by new governing paradigms. For example the classical paradigm of light as a classical electromagnetic wave has been replaced by the quantum mechanical paradigm in which light is viewed as a quantized entity possessing both wave and particle characteristics. The electron, considered as a classical particle at the turn of the 19th century is now considered as a quantized entity with both wave and particle characteristics (both paradigm shifts will be described in Sections 4.2-4.5).

1.7 The Paradigms of Molecular Organic Photochemistry

Molecular organic photochemistry integrates the global paradigms of organic chemistry with the paradigms describing the interaction of electromagnetic radiation (photons) with matter (organic molecules). The paradigm of organic chemistry employs the structure of the molecule (with its implied electronic, nuclear and spins configurations) as the key organizing concepts; the paradigm of electromagnetic radiation employs photons or oscillating electromagnetic waves as the key organizing concept. Thus, *the field of molecular photochemistry is concerned with interactions of light (represented by photons or oscillating electromagnetic waves) and matter (represented by molecules) that lead to the formation of *R and its eventual conversion to P.*

The successes of molecular organic chemistry over the past 150 years is mainly due to the authoritative paradigm of molecular structure and the adoption of molecular structure as the key intellectual unit to describe the reactions of organic molecules. Since the text assumes that the effectiveness of the molecular structural approach employed by organic chemists is the most powerful way to approach molecular organic photochemistry, a brief review of the fundamental meaning of structure is useful at this point. A “structure” may

be defined in an abstract mathematical manner in terms of the following properties: (1) composition; (2) constitution; (3) local 3D configuration; (4) global spatial architecture. Note that these are the same terms that organic chemists employ to describe molecular structure, but the terms derive from very fundamental mathematical ideas of topological and Euclidean geometry [3]. Composition refers to the number and kinds of entities or “fundamental elements” which make up a structure. For organic molecules we think of composition as referring to the molecular formula, that is, the number and kinds of atoms in a molecule. Constitution refers to the way that the entities of a geometric structure are connected to one another. For molecules we think of the “constitutional formula” or Lewis structure which is intended to display the way atoms are connected to generate a molecular constitution and its associated molecular structure. It is important to note that this level of structure is non-metric (no implied bond lengths or angles), and considers only the qualitative feature of connections and does not consider any stereochemical aspects. Configuration refers to the representation of a constitution as a three dimensional geometric object for which bond lengths and bond angles have specific, measurable values. For an organic molecule the term configuration refers specifically to the disposition of each of the bonded atoms in 3 D space about a central atom such as carbon, nitrogen or oxygen. Finally, the global spatial architecture refers to the specific instantaneous or average overall 3 D geometry of a geometric object. For an organic molecule the term refers to the shapes or conformations produced by rotations about single bonds, such as carbon-carbon bonds, carbon-nitrogen bonds or carbon-oxygen bonds.

In this text we shall use molecular structures as the intellectual units for visualizing the pathways indicated in Sch. 1.1. By visualizing complex structures (electron configuration, nuclear configurations, spin configurations) and the transitions between structures (changes in one or more of the configurations) we shall produce a powerful structural paradigm for understanding organic the $R + h\nu \rightarrow P$ processes from “cradle to grave”.

It is important for the student to recognize that a global paradigm, such as Sch. 1.1, possesses an authority in a scientific field which determines the

fundamental structures which the practitioners believe can and cannot exist. Therefore, the global paradigm defines the structures that are considered for observation, characterization, investigation and used in interpretation of the $R + h\nu \rightarrow P$ process. For example, the paradigm determines which transitions are “allowed” between structures and which are “forbidden”. The paradigm teaches how to predict what is possible, what is plausible, what is probable and how to prove which is which. The text will teach how the photochemist uses the paradigms of molecular photochemistry of organic molecules to define a complete list of possible structures which are assumed to exist, and how to predict which of these structures are the most plausible under a certain set of conditions. The text also teaches how to determine which transitions between structures are “allowed” and which are “forbidden” in a global manner and how to modify the notions of “allowed” and “forbidden” with variations in experimental conditions. With these paradigms in hand, the practicing photochemist does not waste time with experiments that attempt to characterize structures that cannot exist or to measure the rates of transitions between structures which are impossible or implausible!

In molecular photochemistry the most fundamental structures are molecules (and their component atoms, electrons, nuclei) and photons (or an oscillating electromagnetic radiation). The molecular photochemist is convinced that all phenomena involving the interaction of light and matter can be studied and understood in terms of these structures and the transitions between these structures.

1.8 A Global Paradigm for Molecular Organic Photochemistry.

It is now time to be more specific and to discuss the global paradigm (Sch. 1.1) that will be the authority for learning the science of molecular organic photochemistry. Sch. 1.1 is a compact global paradigm that schematically represents the “mechanistic pathway” of the overwhelming majority of known organic photochemical reactions, from cradle to grave, i.e., $R + h\nu \rightarrow P$. The paradigm shows three pathways that will be considered:

(a) The absorption of light to produce an electronically excited state ($R + h\nu \rightarrow {}^*R$). This step will be described in detail in Chapter 4 as the resonant interaction between a photon or oscillating electromagnetic field and the electrons of an organic molecule.

(b) A pathway from ${}^*R \rightarrow F \rightarrow P$ which does not involve the occurrence of reactive intermediate between *R and P . Although an intermediate is not involved in the conversion of *R to P , there is a specific molecular structure termed F (for “funnel”) which takes the excited molecule into the final product. Funnel on excited energy surfaces and will be discussed in detail in Chapter 6.

(c) A pathway, and by far the most commonly observed ${}^*R \rightarrow I \rightarrow P$. For this pathway *R is transformed by a primary photochemical process (${}^*R \rightarrow I$) into a reactive intermediate, I , which then proceeds through secondary thermal reactions ($I \rightarrow P$) to form P . In Chapter 6 we shall learn that there are only a very small number of primary photochemical reactions which are required to understand the majority of photochemical reactions of organic molecules. Furthermore, these photochemical primary processes may all be understood in terms of the principles of orbitals, vibrations and spins presented in Chapters 2 and 3.

(d) A pathway in which *R is converted to another electronically excited state on the way to P , i.e., (${}^*R \rightarrow {}^*P \rightarrow P$) or (${}^*R \rightarrow {}^*I \rightarrow P$). The formation of electronically excited complexes, called exciplexes, are the most common example of this pathway and will be discussed in Chapter 4.

This paradigm of Sch. 1.1 implies that, in general, organic photochemical reactions which convert a reactant(s) R to a product(s), P , can be understood in terms of the structures of reactant molecules (R), photons ($h\nu$), electronically excited molecules (*R), reactive intermediates (I) produced from electronically excited molecules and funnels (F) which occur on electronically excited energy surfaces. By a “global paradigm” we mean that the concepts expressed in Sch. 1.1 are independent of the specific molecular structures of interest. The paradigm of Sch. 1.1. has been observed to successfully explain the pathways of organic

photochemical reactions repeatedly in the past, and therefore is a plausible and useful initial paradigm to explain pathways of any organic photochemical reaction without specifying the detailed structures of R, hv, *R, I, F or P.

1.9 From the Possible to the Plausible to the Probable

Let us now consider what we mean by the concepts possible, plausible, probable and proven in the context of the paradigm of the global molecular photochemistry. For a pathway to be *possible*, molecules (and their nuclear and spin substructures) must obey the four great conservation laws of all chemical reactions: (1) conservation of energy; (2) conservation of momentum (orbital and spin); (3) conservation of mass (or atoms); and (4) conservation of charge. As we shall see, these conservation laws place considerable restrictions on the number of *a priori possible* structures (*R, I, *I, P, *P, F) and pathways (Sch. 1.1) that a photochemical reaction can follow. ***Only the set of structures and pathways that obeys the conservation laws is considered possible and all others are ruled out, absolutely, no exceptions!***

However, even when the great conservation laws are fully met, the paradigm constrains the actual number of *possible* pathways of a photochemical reaction through consideration of the details of molecular structure and implied energies associated with structures, by consideration of available interactions which couple structures and by consideration of the available mechanisms of momentum and energy exchange. ***These considerations lead to a set of "selection rules" that indicate the plausible (at some assumed level of approximation) reactions from the initial set of possible reactions.***

Next, one considers specific details of structure and the available interactions and reorganization energy and time scales available to the structure. These considerations determine the *kinetics or rates* of the steps in Sch. 1.1. After taking these kinetic considerations into account, the remaining, much smaller set of plausible pathways which occur at the fastest rates, is considered to be the most *probable*, i.e., those processes which proceed at the fastest rates. The text will teach how to employ structures and interactions which cause transitions

between structures to decide on whether a pathway is possible, plausible or probable. It will also teach the methods (Chapter 8) available to the photochemists to experimentally *prove* which of the probable pathways is actually the one that occurs under a given set of conditions.

The task, therefore, in understanding an overall photochemical transformation, $R + h\nu \rightarrow P$, is first to be able to list *all of the plausible pathways* that are available to *R (formation of I, passage through a funnel F, formation of *I or *P) after the absorption of a photon by R and then to predict the rates of the pathway(s) to P compared to the rate of all other plausible pathways available to *R which do not lead to P. Prediction of an observed or most probable pathway of a photochemical reaction under a given set of conditions requires the ability to use the paradigm of molecular organic photochemistry to make judgments based on knowledge of known, measured rates, exemplars, or theoretically estimated rates based on structure, interactions, energy and dynamics for a given set of conditions. The paradigm of molecular organic photochemistry teaches us that, in order to understand molecular organic photochemical reactions, we must first use the conservation laws, structure and energy to deduce plausible pathways and then use exemplar paradigms, experimental measurements or theory to deduce the probable pathways. The beauty of a mature paradigm is that it assures us that *if we follow the rules given by the global and exemplar paradigms, we can, in principle, understand all known molecular organic photochemistry, and experimentally determine the most important unknown aspects.* The goal of this text is to teach, and for the student to learn, the global and exemplar paradigms which relate, from cradle to grave, to the structural, energetic and dynamic of molecules and photons to photochemical transformations such as $R + h\nu \rightarrow P$.

1.10 Examination of the Global Paradigm of Molecular Organic Photochemistry

Let us now consider the most common example of global paradigm given in Sch. 1.1 the $*R \rightarrow I \rightarrow P$ sequence, which involves the following steps:

- (1) *absorption of a photon of light*, $h\nu$, by a reactant molecule, R to produce an electronically excited state, $*R$;
- (2) *primary photochemical reaction* of an electronically excited state, $*R$, to produce a thermally equilibrated ground state reactive intermediate, I;
- (3) *thermally induced reaction* of I to produce the observed product(s), P.

The exemplar paradigm of Sch. 1.1 reminds the photochemist to always ask and to attempt to answer a number of standard questions (puzzles) concerning the details of a photochemical reaction. For example,

- (1) How does a photon interact with R to be **absorbed** and to produce $*R$?
- (2) What are the possible and plausible **structures, energetics and dynamics** available to $*R$ and I which occur along the reaction pathway (the reaction coordinate) from $*R \rightarrow P$?
- (3) What are the possible and plausible **primary photochemical processes** corresponding to the $*R \rightarrow I$ process?
- (4) What are the legitimate **theoretical approaches, experimental design strategies, experimental techniques and computational strategies** for experimentally "observing" the species $*R$ and I that are postulated to occur along the reaction pathway from $R \rightarrow P$?
- (6) What are the competing **kinetic** pathways for photophysics and photochemistry of $*R$ along the pathway $*R \rightarrow P$ which compete with the formation of I?
- (7) What sorts of **structures** correspond to $*R$ and I in typical organic photoreactions?

Questions such as these, which are implicitly posed by the paradigm of Sch. 1.1 are handled through the establishment of a working paradigm and by reference to exemplar investigations.

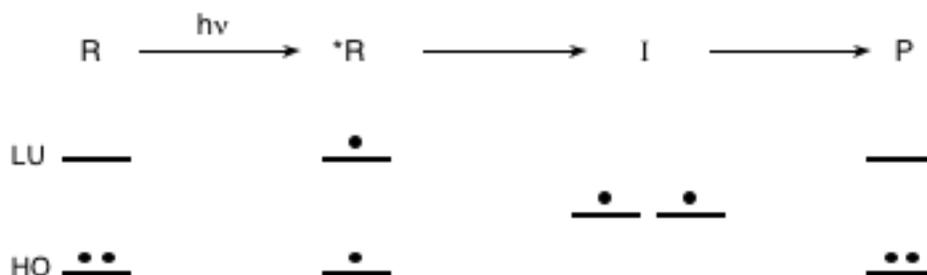
1.11 From the Global to the Everyday Working Paradigm.

In solving normal everyday scientific puzzles, a great deal of time is saved by employing an "everyday working paradigm" that applies to many common situations and, based on considerable experience and precedent, is found to be generally applicable. This shortcut of using a working paradigm is a sort of mechanistic "Occam's razor", relieving the photochemist from examining a large number of hypothetically plausible, but historically improbable situations, each time a photochemical reaction is analyzed or an experiment is designed or a theoretical point is being discussed. We shall always start with Sch. 1.1 as an a global paradigm of molecular organic photochemistry and see how we can continuously refine it into an evermore specific everyday working paradigm for molecular organic photochemistry. A very effective method for refining Sch.1.1 is the appeal to exemplars (Section 1.6).

The student of organic chemistry is familiar with the effectiveness of the exemplar approach though the study of *functional groups*, an atom or group of atoms that possess qualitatively similar reactivities, spectroscopic and physical properties independent of the molecule in which the group is found. Coupling the functional group approach with the exemplars from molecular orbital theory provides a powerful means of predicting chemical reactivity at a qualitative level and will be used in the text for an understanding of the photochemistry of exemplar systems.

For an understanding of the photochemistry of the common functional groups of organic chemistry (e.g., ketones, alkenes, enones, aromatic compounds, etc.), the working paradigm will only consider (1) the electron configurations of the two molecular orbitals (the highest occupied orbital, the "HOMO" (abbreviated as HO) and lowest unoccupied orbital, the "LUMO" (abbreviated as LU) and (2) the spin configurations of the electrons in the HO and LU for the structures (R, *R, I and P) shown in Sch. 1.1. Let us consider Sch. 1.2 as a "working" paradigm for the examination of molecular organic photochemical reactions. The Scheme displays qualitatively the energy of the HO and LU orbitals and at this level, electron spin is not explicitly considered. The energies of the HO and LU for R, *R and P are assumed to be far apart in energy (typically > 40 kcal/mole) whereas the energies of the Mos for I are

assumed to be very similar in energy (so the idea of a HO and LU may no longer be appropriate). It is assumed in the working paradigm of Sch. 1.2 that all of the remaining electrons that are not shown in the Scheme are spin paired in orbitals of lower energy and are of secondary importance in determining the course of the photochemical and photophysical processes. For R, *R and P, the starting point for analysis of a photophysical or photochemical process will be the assignment of the



Sch. 1.2 The global paradigm of organic photochemical reactions displaying orbital configurations of R, *R, I and P.

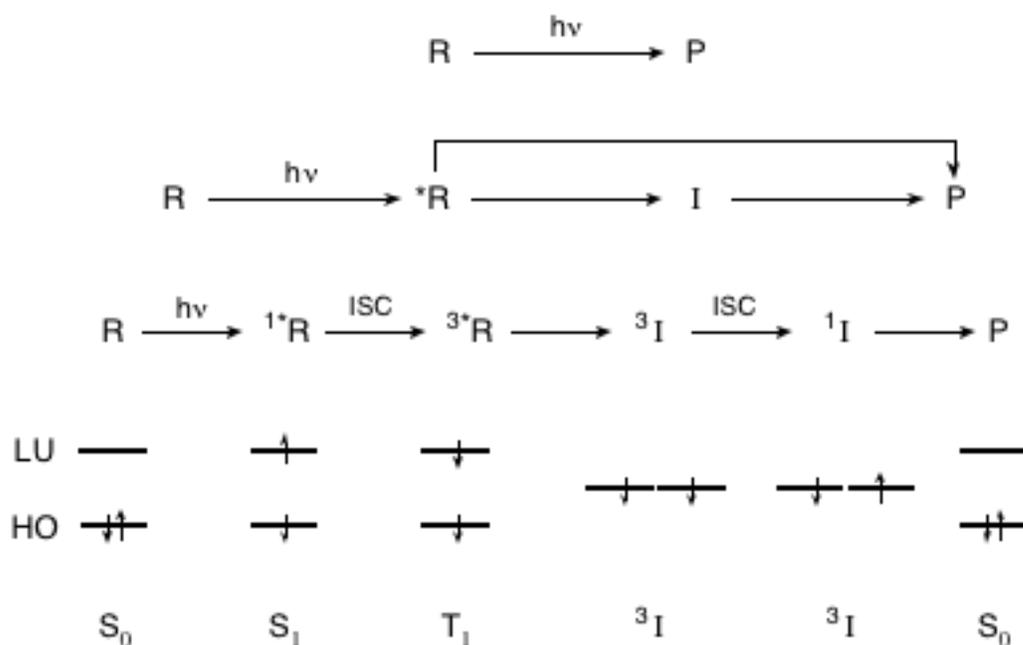
electronic nature of highest occupied orbital (HO) and the lowest unoccupied orbital (LU), where the orbitals are ranked in energy from highest to lowest. This amounts to assigning an electron configuration to R, *R and P. The reactive intermediate(s) I is classified according to the occupancy of two electrons in two orbitals of similar energy, as in a radical pair or diradical (the term biradical and diradical are used interchangeably in the photochemical literature). In all cases the orbitals assigned to the HO and LU will be simple one electron orbitals that are familiar to the student from courses in organic chemistry and physical chemistry.

The working paradigm suggests a number of questions that need to be answered in studying or analyzing any organic photochemical reaction:

- What is the absorption spectrum of R which leads to *R?
- What is the electronic configuration of *R (orbital occupancy of HO and LU).
- What are the plausible primary photochemical processes typical of *R?
- What is the electronic nature of I?

(e) What are the secondary thermal reactions of I that lead to P?

The working paradigm of Sch. 1.2 requires one more level of elaboration to become an everyday working paradigm. This final level includes not only the electronic configurations of *R and I, but also the spin configurations of *R and I, as shown in Sch. 1.3. The electronic configurations of R and P will always be described as having two electrons in the HO and none in the LU.



Sch. 1.3 Exemplar paradigm for an organic photochemical reaction that proceeds through a triplet state.

The electronic configuration of *R and I, both of which typically possess one electron in each of two orbitals, can have the electrons either paired ($\uparrow\downarrow$) or unpaired ($\uparrow\uparrow$). When *R or I possess two orbitally unpaired electrons and the electron spins are antiparallel (spin paired, $\uparrow\downarrow$), the structure is termed a *singlet* state and labeled S_x , where the subscript x is a label for ranking the energy of the singlet state (the subscript 0 being reserved for the lowest energy electronic ground state). In general, R and P will be singlet states ground states (whose electronic structure will be discussed in detail in Chapter 2) and therefore are labeled S_0 . If the electrons are spin paired ($\uparrow\downarrow$) in *R , we term this a singlet *excited* state and label it S_1 where the subscript indicates that the state is the *first excited*

singlet state (i.e., $^*R(S_1)$ in Sch. 1.2). If the electrons spins are parallel ($\uparrow\uparrow$) in *R , we term this a *triplet* excited state and label it T_1 where the subscript indicates that the state is the *first* triplet excited state (i.e., $^*R(T_1)$ in Sch. 1.2). Likewise, the reactive intermediate I may either be a singlet ($\uparrow\downarrow$) or a triplet ($\uparrow\uparrow$). If I is a singlet state its electronic configuration may be that of a diradical, D (one electron in each orbital), or a zwitterions Z (two electrons in one orbital, none in the other). In this case we use a superscript where 1 indicates a singlet state and 3 indicates a triplet state, i.e., $^1I(\uparrow\downarrow)$ and $^3I(\uparrow\uparrow)$.

In summary, Sch. 1.3 represents a “zero order” working paradigm for many photochemical reactions of organic molecules that proceed through a triplet excited state. For any given reaction we can replace R with a ketone, a polyene, an enone, an aromatic compound, etc. We then need to know the nature of the HO and MO of each of these structures which will allow us to deduce the electronic configuration of *R and to use this information to generate “selection rules” for the plausible reactions that will produce I. Predicting and understanding photochemical reactions will require a knowledge of the structures of the entities, $R(S_0)$, $^*R(S_1)$, $^*R(T_1)$, 3I , 1I , and $P(S_0)$. and of the probabilities of the transitions between the structures connected by the pathways shown in the paradigm.

Sch. 1.3 provides a useful *exemplar paradigm* for the reactions of ketones. This exemplar indicates that the photochemistry of ketones mainly occurs from T_1 . We shall see in Chapter 6 that application when T_1 has the electronic configuration $HO = n$ orbital and $LU = \pi^*$ orbital, there are only a small set of primary photochemical processes which are plausible to produce triplet intermediates, 3I . The latter must be converted to a singlet intermediate, 1I before the final product $P(S_0)$, which is a singlet state, can be formed. The exemplar paradigm opens an interesting and important new question that need to be answered in studying or analyzing any organic photochemical reaction:

How do the processes $^*R(S_0) \rightarrow ^*R(T_1)$ and $^3I \rightarrow ^1I$, which require a change in electron spin occur? We shall describe answers to this interesting question in Chapter 3.

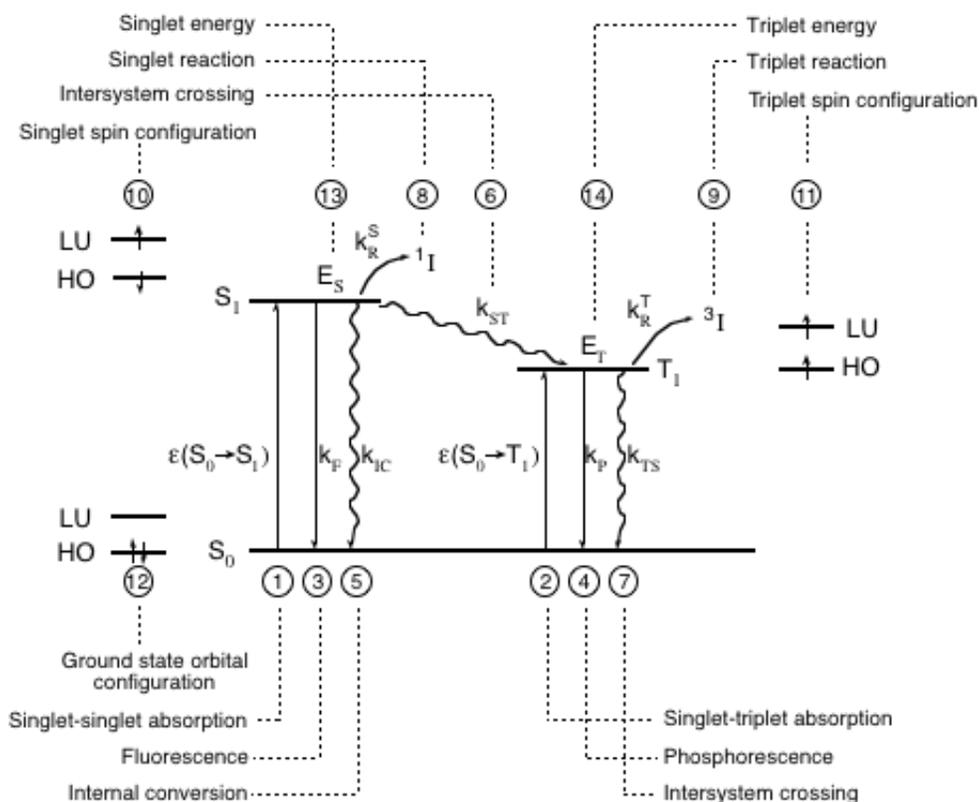
Now that we have introduced the important global, working and exemplar paradigms for analyzing organic photochemical reactions, we need to develop an important paradigm, the *state energy diagram*, which allows the ready use and manipulation of the working and exemplar paradigms.

1.12 State Energy Diagrams: Electronic and Spin Isomers

Our working paradigm of organic photochemistry has teaches that the three molecular states (S_0 , S_1 and T_1) are the most important to consider when analyzing a photochemical reaction. A *state energy diagram* (Sch. 1.4) is an important compact structure displaying the relative energies of the ground state, S_0 , the lowest energy excited singlet state, S_1 , and the lowest energy triplet state, T_1 , of a molecule. Higher energy singlet states (S_2 , S_3 , etc) and higher energy triplet states (T_2 , T_3 , etc) need not be explicitly included in the working state diagram, because experience has shown that excitation of these higher energy excited state generally results in deactivation to S_1 and T_1 faster than any other measurable process (Kasha's Rule, Chapter 4). In a state energy diagram, the y (vertical coordinate) represents the potential energy of the system and the x (horizontal) coordinate has no physical meaning. Thus, the information contained by a state energy diagram is the ranking of the energies of the S_0 , T_1 and S_1 states.

It is generally assumed that the nuclear geometries of all states displayed in a state diagram are not very different from the equilibrium nuclear geometry of the ground state, S_0 . Since all of the structures in the state energy diagram have the same composition (numbers and kinds of atoms) and the same constitution (atom connectivity) as S_0 , but are chemically different from S_0 , all of the states in the state diagram (S_0 , S_1 and T_1) evidently are isomers of each other! What is the basis of the isomerism? The isomerization is brought about by the differences in the *electronic configurations* (*electronic isomers*) or in the *spin configurations* (*spin isomers*) between the displayed states. Thus, the S_n states are electronic isomers of each other, and the T_n states are electronic isomers of each other. The differences are due to differences in the orbital configurations (HO

and LU) of each state. The S_n and T_n states are related to each other as *spin-electronic isomers*, i.e, singlet spin configuration ($\uparrow\downarrow$) or triplet spin configuration ($\uparrow\uparrow$). In addition to the spin-electronic isomerization the states in the state energy diagram may be stereoisomers of one another (same constitutions, same spin-electronic configurations, different spatial arrangements of the atoms).



Sch. 1.4. The State Energy Diagram. A fundamental paradigm of modern molecular photochemistry.

As an everyday working paradigm, the state energy diagram indicates the relative energetic ordering of the ground state (S_0), the lowest excited singlet state (S_1), and the lowest triplet state (T_1). The state energy diagram also presents a handy way to organize and systematize *all plausible* photophysical processes as those representing transitions between any two electronic states in the diagram. The *probability* of a transition between any two states, however, requires knowledge of specific molecular structures and reaction conditions,

which can be varied at will by the experimenter. The photophysical processes (defined as transitions in the energy diagram that interconvert excited states with each other or excited states with the ground state) from S_1 and T_1 must always be considered in a photochemical analysis, since photophysical processes will, in principle, be competitive with the photochemical processes. If the photophysical processes are too fast, the competing photochemical processes will be inefficient.

As a paradigm, the state diagram defines the *plausible* photophysical radiative processes, which involve the absorption or emission of a photon, as those shown in Sch. 1.4:

1. "Spin allowed" singlet-singlet absorption ($S_0 + h\nu \rightarrow S_1$), characterized experimentally by an extinction coefficient $\epsilon(S_0 \rightarrow S_1)$;
2. "Spin forbidden" singlet-triplet absorption ($S_0 + h\nu \rightarrow T_1$), characterized experimentally by an extinction coefficient $\epsilon(S_0 \rightarrow T_1)$;
3. "Spin allowed" singlet-singlet emission, called *fluorescence* ($S_1 \rightarrow S_0 + h\nu$), characterized by a rate constant, k_F ;
4. "Spin forbidden" triplet-singlet emission, called *phosphorescence* ($T_1 \rightarrow S_0 + h\nu$), characterized by rate constant, k_P .

The state energy diagram defines the *plausible* photophysical *radiationless* processes as those shown in Sch. 1.4:

5. "Spin allowed" transitions between states of the same spin, called *internal conversion* (e.g., $S_1 \rightarrow S_0 + \text{heat}$), characterized by a rate constant, k_{IC} ;
6. "Spin forbidden" transitions between excited states of different spin, called *intersystem crossing* (e.g., $S_1 \rightarrow T_1 + \text{heat}$), characterized by a rate constant, k_{ST} ;
7. "Spin forbidden" transitions between triplet states and the ground state - also called intersystem crossing (e.g., $T_1 \rightarrow S_0 + \text{heat}$) - and characterized by a rate constant, k_{TS} .

As a useful extension of the state energy diagram, *primary photochemical processes* can be defined as transitions from an electronically excited state $^*R(S_1 \text{ or } T_1)$ that yield molecular structures of different constitution

or configuration from that of S_0 . These chemically different molecular structures are the reactive intermediates, I, of Sch. 1.1, 1.2 and 1.3 and are produced by

8. Photochemical reaction from S_1 to produce a reactive intermediate, 1I , called *primary photochemical reaction* $S_1 \rightarrow ^1I$ whose rate constant is k_R^S .

9. Photochemical reaction from T_1 to produce a reactive intermediate, 3I , called *primary photochemical reaction* $T_1 \rightarrow ^3I$ whose rate constant is k_R^T .

The theory of organic photoreactions (Chapter 6) will provide us with the selection rules for deciding on the *plausible* primary photochemical processes for common electronic configurations of S_1 and T_1 . Again, this working paradigm is not complete, since for simplicity at this stage it does not explicitly consider the processes $^*R \rightarrow F \rightarrow P$ or $^*R \rightarrow (^*I, ^*P) \rightarrow P$.

The *thermal* reactions ($I \rightarrow P$ in Sch. 1.2) that transform I (which may be a diradical or a zwitterion) into the product(s) P are not explicitly included in the state energy diagram which refers only to structures whose geometries are similar to those of S_0 . The $I \rightarrow P$ reactions, are called *secondary thermal reactions* and are considered to occur in exactly the same reactions as when I is produced by a thermolysis. An understanding of the $I \rightarrow P$ processes is, however, crucial for a complete description of the overall process $R + h\nu \rightarrow P$. A more complete description is provided by the working paradigm of a potential energy surface, which will be described in the next sections and in detail in Chapter 6.

In order to determine which of the *plausible* processes are *probable* from S_1 or T_1 , we need information on the relative rates of all of the plausible photochemical and photophysical processes that compete for deactivation of these states. These relative rates will depend on a number of structural and energetic factors that will be discussed in Chapters 2-6.

1.13 An Energy Surface Description of Molecular Photochemistry

In proceeding from the state energy diagram (fixed nuclear geometry of S_0) to a complete analysis of a photochemical reaction (changed nuclear geometry) it is necessary to keep track of a number of structures, energy and

dynamics of transitions. This complicated energetic, structural and dynamic bookkeeping is nicely handled by the paradigms associated with *potential energy curves and surfaces* (which will be discussed in detail in Chapters 3 and 6). For now we shall present a preview of how this paradigm of energy surfaces handles the problem of simultaneously integrating the structure, energetics and transition dynamics involved in photochemical processes. Strictly speaking, potential energy surfaces are multidimensional mathematical object and are therefore difficult to visualize. However, as a reasonable “zero order” approximation to an energy surface we shall employ an approximation that uses two-dimensional “potential energy curves”; however, for simplicity we will use the term surface to describe these curves.

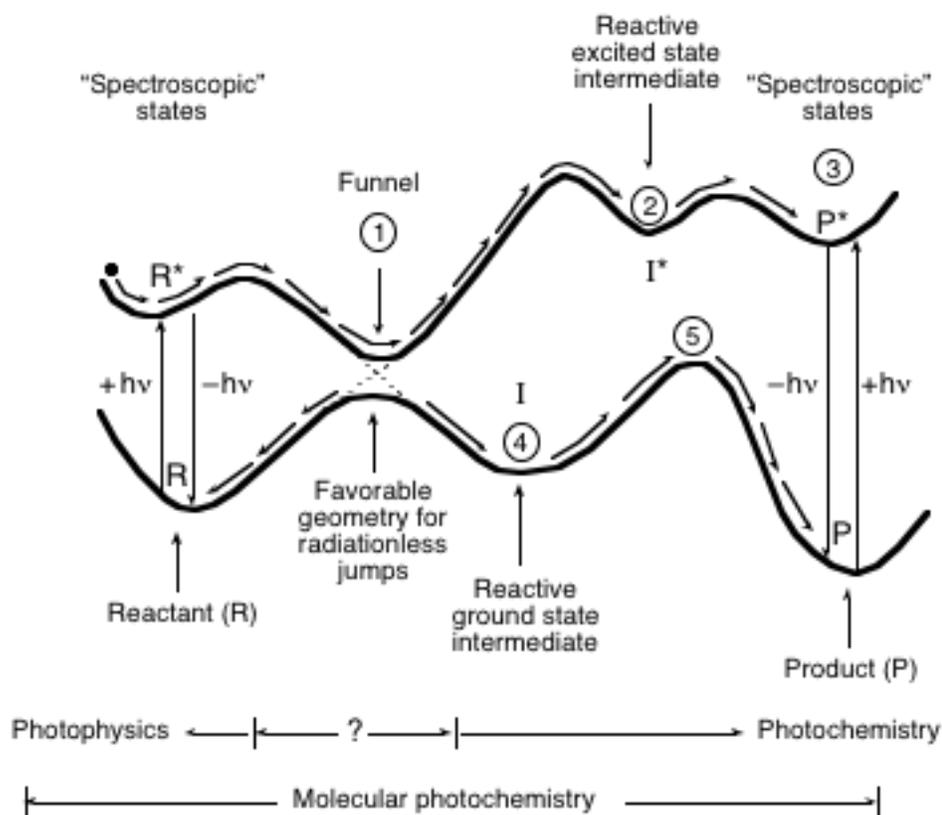
A potential energy surface is a natural extension of the concept of a state energy diagram as the nuclear geometry of *R changes from one that is similar to that of R and begins to resemble that of the possible structures (e.g., I) involved in the photochemical transformation of $^*R \rightarrow I \rightarrow P$. Consider the hypothetical example of the energy surfaces of the ground and excited states shown in Sch. 1.5. Whereas in the state energy diagram a nuclear geometry similar to that of the ground state is assumed for all of the structures considered, each point on the potential energy curve represents a different nuclear geometry (specified on the x-axis) and a specific potential energy (specified on the y-axis). For a given nuclear configuration, the energy of a molecule is determined mainly by its electronic orbital configuration and its spin configuration. The energy surface shown is the one corresponding to the lowest energy for a specific change of nuclear geometry corresponding to the *reaction coordinate* (y-axis).

In Sch. 1.5 hypothetical surfaces are shown for the overall reaction $R \rightarrow P$ for two different starting electronic configurations, a ground state R and an excited state *R . The lower energy surface is termed the *ground state electronic surface* and the higher energy surface is termed the *excited state electronic surface* (in this hypothetical example for simplicity we assume both the ground and excited surfaces are *singlet* surfaces). Both surfaces correspond to the same overall $R \rightarrow P$ transformation (reaction coordinate) in terms of changes in nuclear configuration. We can term any point of interest on either surface as a

representative point. We can envision photophysical and photochemical processes in terms of the motion of a "representative point" on a potential energy curve with each point corresponding to a specific nuclear configuration. Starting from R we can track the representative point from R to the excited surface and imagine the trajectory of the representative point along the excited surface or along the ground surface. The representative point of the system must be on one surface or the other on the way from R \rightarrow P. To the extent that these hypothetical surfaces are valid, they allow a visualization or "map" of *all plausible pathways* for the R \rightarrow P transformation. Let us consider some of the *a priori* plausible pathways for the electronically excited state *R based on the nuclear geometry changes that are "mapped out" by the two curves of Sch. 1.5.

The potential energy surface is assumed to completely control nuclear motion of molecules expected for regions of the surface that come close to one another. When two surfaces come close together, each surface may compete for control of the motion of the representative point and, therefore, the control of the nuclear motion of the reacting system.

For example, one possible pathway after the $R + h\nu \rightarrow ^*R$ process occurs, is for *R to proceed along the excited surface to region (1), which happens to be a minimum or funnel that leads to the ground surface for a certain nuclear geometry. Such a situation is very favorable for a "jump" from the excited surface to the ground surface and *vice versa* (we shall see why in Chapter 3 and 6). Some electronically excited molecules may thus "jump" to the ground surface and "spill" into the R minimum (resulting in a net "photophysical" cycle, $R + h\nu \rightarrow ^*R \rightarrow F \rightarrow R$).



Sch. 1.5. Schematic representation of a ground state (R) and an excited state (*R) energy surface. The arrows on the surface indicate the motion of a point representing a molecule whose nuclear geometry is moving along the reaction coordinate from left to right.

Other molecules *R moving on the excited surface may be able to gather sufficient thermal energy to overcome the energy barrier on the excited surface and proceed to region (2) to produce an *electronically excited reactive intermediate*, *I, and to eventually reach region (3), which corresponds to *P, an excited state of the product, P. When *I is formed, a true photoreaction has occurred, since a reactive intermediate I and its excited state *I will possess a nuclear geometry that is quite distinct from that of R.

It is also possible for some molecules approaching region (1) to jump in another direction from the minimum of region (1) to the ground surface and arrive at (4), which is a geometry corresponding to a minimum on the lower surface. This minimum corresponds to a new molecular structure, the reactive intermediate, I; when the structure I is achieved, a photochemical reaction has occurred. Since I is a reactive intermediate, it may live long enough to gather

thermal activation and proceed over barrier (5) to yield the product, P. For the pathway $R^* \rightarrow (1) \rightarrow (4) \rightarrow (5) \rightarrow P$ the nuclear motion was controlled by the excited-state surface for part of the reaction, $*R \rightarrow (1)$, and by the ground-state surface, $(4) \rightarrow (5) \rightarrow (6)$, for another part of the reaction. Indeed, such a situation appears to be typical of many photoreactions as we shall see in Chapter 6.

As a rule, the absorption and emission of light occur near minima corresponding to the nuclear geometry of the reactants and products (this rule is called the Franck-Condon Principle and will be discussed in Chapter 4). Thus, there is both a radiative ($*R \rightarrow R + h\nu$) and a radiationless ($*R \rightarrow F \rightarrow R$) pathway for $*R$ to return to R. These pathways which return the system back to R after the absorption of light are termed *photophysical* pathways and are of great importance, because they will generally compete with the *photochemical* pathways that carry $*R$ to I and eventually to P. Of course, it is also possible that $*R$ may proceed to an electronically excited $*I$ and $*P$, although this pathway is rarely found.

Although Sch. 1.4 represents an arbitrary and hypothetical photochemical reaction $R + h\nu \rightarrow P$, the pathways and processes shown represent examples of most of the important photochemical and photophysical processes and allow for some generalizations based on considerable theoretical and experimental experience: (a) absorption ($R + h\nu \rightarrow *R$) and emission ($*R \rightarrow R + h\nu$ and $*P \rightarrow P + h\nu$) of light tends to occur at nuclear geometries corresponding to *minima* in both the ground and in the excited surface; (b) radiationless jumps from one surface to another are most facile for nuclear geometries at which two surfaces, a minimum and a maximum, come close together in energy ($*R \rightarrow R$ and $*R \rightarrow I$); (c) the location and heights of energy barriers on *both* the excited and ground state surface may determine the specific pathway of a photoreaction; (d) some minima on excited surfaces may not be readily detected by conventional absorption and emission techniques; (e) the course of a photoreaction depends on competing photophysical as well as photochemical processes. In Chapter 3 we shall learn how to use potential energy curves to describe photochemical and

photophysical transitions and then apply this knowledge to many situations in the subsequent chapters.

1.14 Structure, Energy, Time and Numbers at the Molecular Level.

Perhaps the most powerful paradigms in all of chemistry are derived from the representation of molecules as particles possessing various levels of internal structure (atoms, electrons, nuclei, spins). At a very coarse level, molecules as particles may be viewed as fuzzy blobs or even simple spheres; at a finer level the molecule is a collection of atoms. At this level, the molecule takes on a structure whose key features are the connectivity of atoms via bonds and stereochemistry of atoms in space. The atoms of molecules are of course in the state of perpetual motion. The chemist imagines that the atoms of molecules possess zero point motions of electrons in orbitals, of vibrating nuclear geometries, and of the precessing electron spins in certain configurations relative to the molecular framework or relative to some orienting magnetic field. From this exquisitely detailed visualization of the structure and dynamics of a molecule, the chemist is able to calibrate the sizes of the space occupied by the molecule and its substructural entities, the energies corresponding to transitions and the rates or transitions.

Both a qualitative and a quantitative appreciation of molecular dimensions, molecular dynamics and molecular energy is important for visualization of events and estimating their rates at the microscopic level. An understanding of the sizes of molecules and the time and energy required for electrons and nuclei to move in space are at the heart of mechanistic descriptions of molecular and spectroscopic phenomena.

In the photophysical and photochemical processes displayed in the paradigms discussed above, we seek to visualize a molecular transformation as one that transforms a given state (i.e., a molecule possessing a certain electronic-nuclear-spin structure) into a second state (i.e., a molecule differing in at least one of the key structural characteristics). The ability to achieve a transformation at the molecular level will depend on the energy of the initial state, the energy of

the final state, the amount of energy available to do work to cause the transition and the time available to execute the transformation relative to the interactions (forces) that drive the structural changes of interest. Intuitively, the rate of the transformation will depend on the efficiency of getting energy into the modes which cause a motion that can change the structure in the appropriate fashion.

In order to calibrate the energy, distance and time scales we shall now consider some benchmark values of great importance to photochemistry. Although the classical description of electrons, photons and nuclei as particles fails to explain molecular phenomena quantitatively, we shall see in Chapters 2-5 that a classical mechanical discussion of molecules and light invariably pinpoints the essential physical and chemical features of a molecular process or a process involving light. Furthermore, the classical model may then be translated into quantum mechanical language and methods.

1.15 Calibration Points and Benchmarks for Molecular Energetics

A paradigm is useful when it provides not only both qualitative but also quantitative measures that define the range and limits the energies, dimensions and dynamics of structures and the time scales of dynamics of transitions between structures. In addition, a useful paradigm provides a means of “counting” the important entities of a field. Organic chemists are accustomed to counting molecules. Photochemists are interested in counting the number of photons in a light source (the intensity of the light source), the number of photon absorbed by a molecule (the optical density of a sample) and the number of molecules of I or P produced per photon absorbed (the quantum yield of a primary process or product formation). We now try to obtain a “feel” for some of the quantities that are important in all chemical transformations, but are particularly important in photochemical transformations. In this section we shall consider some *calibration points and benchmarks for molecular and photonic energetics* and in the following section we shall consider some calibration points for molecular and photonics sizes and dynamics.

In general we shall be concerned with the *difference in energy between states of a molecule*, rather than the absolute energy of a state. The energy difference between a ground state (R) and an excited state (*R) determined the wavelength and frequency of light that is absorbed by a molecule. We need information about two kinds of energetics in order to understand photochemical behavior:

1. "static" energetics, or the inherent equilibrium energy difference between two states of a molecule;
2. "dynamic" energetics, or the change in energy of a state of a molecule as a function of time.

Typical "static" energetic quantities are the energy differences between the electronic states of a molecule (E_n), bond energies (BE), free energies (ΔG), reaction enthalpies (ΔH) and entropies (ΔS), ionization potentials (IP) and electron affinities (EA). The energy difference between an initial state and a final state are important in determining reaction *feasibility*, since this energy gap must be made up somehow during the course of a reaction in order to obey the law of conservation of energy. In addition, any transition between states must be accomplished within the limited time scale determined by the lifetime of the state.

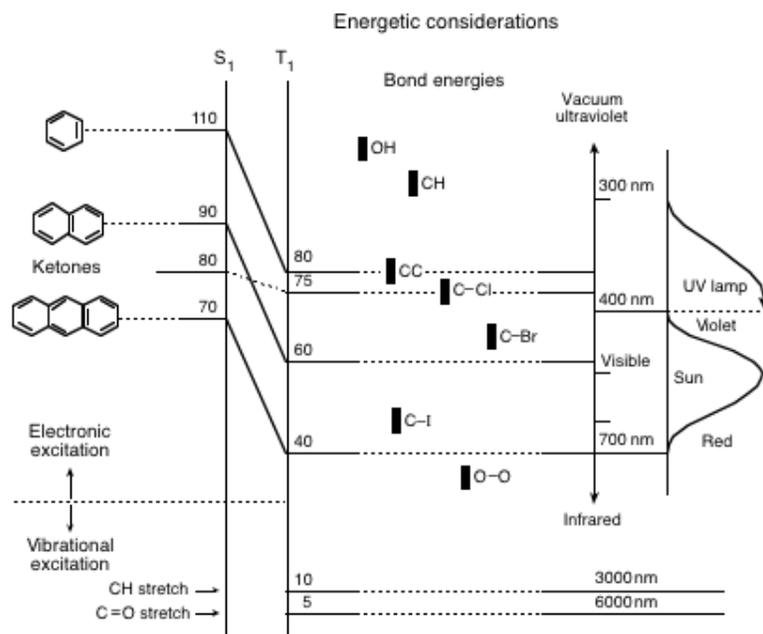
If the final state is higher in energy than the initial state (the free energy, $\Delta G^\circ > 0$, the process is endothermic and "uphill"), reaction cannot be spontaneous and a certain *minimum* activation energy must be supplied to effect reaction is the energy gap between the states. If, on the other hand, the free energy, $\Delta G^\circ < 0$, the process is exothermic and "downhill", the initial state may proceed to the final state spontaneously. However, even in this case there may be an energy barrier even for reactions that are overall exothermic, so that in such cases a certain "activation energy" (ΔG^\ddagger) must be acquired before reaction can occur. Such barriers are the result of "selection rules" requiring some degree or reorganization of the electron configuration, the nuclear configuration or the spin configuration before the two states involved in the transition "look alike" and are ready for a transition between the state. We can think of the free energy required for such reorganization as a guide to the height

of the barriers separating reactants from products. It is useful to breakdown the free energy of activation into the enthalpy of activation (ΔH^\ddagger) and the entropy of activation (ΔS^\ddagger). The value of ΔH^\ddagger can be correlated to the potential energy involved in the making and breaking of bonds, and the value of ΔS^\ddagger can be correlated with the “organizational energy” required to get an initial state to “look like” a final state.

Absorption of a photon by a molecule ($R + h\nu \rightarrow {}^*R$) transforms light energy into electronic excitation energy of a molecule. The photon uses its energy to “do work” on the orbiting electrons or vibrating nuclei or precessing spins of a molecule. Not only does the absorption of light provide the molecule with energy that it can employ to make or break chemical bonds, but it also changes the electronic configuration and therefore the electronic distribution about the nuclei. The change in the electronic configuration will generally promote a change in the nuclear configuration, which will respond as positive charges to the change in the electronic distribution. The change in electronic and nuclear configuration may also assist in changing the electron spin configuration.

$\lambda = \text{nm}$	$E = \text{kcal/mole}$	$\nu = \text{Hz (s}^{-1}\text{)}$	Einsteins in 100 kcal/mol	Type of radiation
0.0001	3×10^8	3×10^{21}		Gamma rays
0.1	3×10^5	3×10^{18}		X Ray
100	300	3×10^{15}		Deep UV
200	143	1.5×10^{15}		UV
400	95	7.50×10^{14}		Violet
500	57	6.00×10^{14}		Green
700	41	5.00×10^{14}		Red
1,000	30	3.00×10^{14}		Near IR
10,000	3	3×10^{13}		IR
10^8	3×10^{-4}	3×10^9		Microwave
10^{10}	3×10^{-6}	3×10^7		Radiowave

Table 1. Relationship between energy, wavelength and frequency.



Sch. 1.6. Comparison of energies involved in photochemical reactions and bond energies and the emission spectrum of the sun. Vibrational energies are shown for comparison.

The energy required to produce an excited state ($R + h\nu \rightarrow {}^*R$) is obtained by inspection of the absorption or emission spectrum of the molecule in question, together with the application of Einstein's famous resonance condition for the absorption of light, Eq. 1.1:

$$\Delta E = E_2({}^*R) - E_1(R) = h\nu \quad (1.1)$$

where h is Planck's constant (common units, kcal-s), ν is the frequency (common units, $s^{-1} = \text{Hz}$) and λ is the wavelength (common units, nm) at which absorption occurs, and E_2 and E_1 are the energies of a molecule in an excited state (*R) and in an initial state (R). Eq. 1.1 is of fundamental importance to spectroscopy and photochemistry, since it relates the energy gap ΔE between two states to measurable properties: the frequency (ν) and the wavelength (λ) of an absorbed photon. It is important to remember that knowledge of the absolute energies, E_2 and E_1 is not required in such energy analyses. In Sch. 1.4 the two most important values of ΔE are the energy gap between S_1 and S_0 (termed the singlet energy, E_S) the energy gap between T_1 and S_0 (termed the triplet energy, E_T). These energies reflect the power of these two states to "do work" on the making and breaking of bonds in photochemical processes in the sense that E_S and E_T correspond to excess electronic energy that can be converted into free energy to drive bond making and bond breaking in a primary photochemical process. For example shall see in Chapter 7 how the values of E_S and E_T play a critical role in photoinduced electron transfer processes and in Chapter 8 how the values of E_S and E_T play a critical role in overcoming thermodynamic endothermicity in bond breaking processes.

Photochemists use a number of different energy units which historically relate to the units of convenience to various forms of spectroscopy. An examples of the energies involved in photochemical processes we shall give exemplars of energy E in units of kcal/mol corresponding to certain frequencies (ν in s^{-1}) and wavelengths (λ in nanometers, nm). Planck's constant, h is the conversion factor between energy (E) and frequency (ν) or wavelength (λ).

Since photochemistry is concerned with the making and breaking of chemical bonds, it is useful to have calibration points or "energetic benchmarks" for the energy of absorbed photons and to compare these energies to the

energies required to break bonds that commonly occur in organic molecules and to also relate these bond energies to the frequency (ν) and wavelength (λ) of light. In Chapter 4 we shall develop a model of light as a photon treats light as consisting of “particle” or quanta of energy. Macroscopic particles, such as atoms or molecules can be counted and chemists are used to employing the mole as a standard unit for the number of particles in a macroscopic system. It follows that photochemists are concerned with counting photons that are emitted from a light source or adsorbed by a molecule during a photoreaction. Eq. 1.2, the second famous Einstein light-energy relationship, relates the energy of a *single* photon to the wavelength (frequency) of light. Thus, through Eq. 1.2 we can “count” photons if we know the energy emitted by a light source. The idea is that a mole of photons of light of a given wavelength (frequency) corresponds to a definite energy, E , so if we know the energy of the light source we can compute the number of photons through Eq. 1.2. Since we will be dealing with E in kcal/mol, with λ in nm and with ν in Hz (s^{-1}) we need appropriate units for the values of the constants h and c . These constants are $h = 1.59 \times 10^{-37}$ kcal-s as the energy of a single photon, and $c = 10^{17}$ nm/s as the speed of light.

$$E = h\nu = h(c/\lambda) \quad (1.2)$$

A mole, N_0 , of photons is termed an *einstein* in honor of the intellectual father of the photon. (*It is important to distinguish Eq. 1.2, which relates the energy of a single photon to a light wave's frequency and wavelength, to the resonance condition (Eq. 1.1) which relates the energy gap, ΔE , between two states and the frequency of the light wave that corresponds to a photon whose energy is exactly equal to ΔE .)* From Eq. 1.2, the energy contained by an einstein of photons depends on the wavelength (frequency) of the corresponding light wave, which leads directly to Eq. 3, where N is a mole of photons.

$$E = N_0 h\nu = N_0 h(c/\lambda) \quad (1.3)$$

In Eq. 1.3 $N_0 = 6.02 \times 10^{23} / \text{mol}$ so that $N_0 h = 9.57 \times 10^{-14} \text{ kcal-s}$ for a mole of photons. The energy of a mole (N_0) of photons given by Eq. 1.3 provides a direct relationship between the amount of light energy absorbed by a system and the number of photons absorbed. Thus, *by measuring the energy of light absorbed, E, and knowing the wavelength (or frequency) of the absorbed light, we have a way to count photons!*

As an exemplar, consider a “green” photon whose wavelength is 500 nm and whose frequency, ν , is therefore $c/\lambda = 3.00 \times 10^{17} \text{ nm-s}^{-1} / 500 \text{ nm} = 6.00 \times 10^{14} \text{ s}^{-1}$. From Eq. 1.3 and the conversion factors we compute that the energy of a mole of green photons of wavelength $\lambda = 500 \text{ nm}$ is $E(500 \text{ nm}) = N_0 h(c/\lambda) = [9.57 \times 10^{-14} \text{ kcal-s/mol}] \times [3.00 \times 10^{17} \text{ nm-s}/500 \text{ nm}] = 57.4 \text{ kcal/mol}$. Or we can compute from the frequency of the light that $E(6.00 \times 10^{14} \text{ s}^{-1}) = N_0 h\nu = [9.57 \times 10^{-14} \text{ kcal-s/mol}] \times 6.00 \times 10^{14} \text{ s}^{-1} = 57.4 \text{ kcal/mol}$.

Table 1 uses Eq. 1.3 to show how the energy of a mole of photons (an einstein) is related to the corresponding wavelength of light (λ in nm) and frequency of light (ν in $\text{s}^{-1} = \text{Hz}$). Historically, because different energy units were used for investigating light in different regions of the electromagnetic spectrum (see right hand column of Table 1), a number of different energy units are commonly used in both spectroscopy and photochemistry. Values of the energies corresponding to a mole of photons of varying ν or λ are commonly given in terms the following energy units: kcal/mole, kJ/mole, cm^{-1} and eV. The units employed in this text will typically be kcal/mole since this unit is commonly employed in chemistry and are associated with bond energies and reaction activation energies. The practical range of electromagnetic radiation extends from gamma rays (high frequency, short wavelength limit) to radiofrequency waves (low frequency, long wavelength limit). For practical purposes, the highest energy photon corresponds to a gamma ray (for $\lambda = 0.0001 \text{ nm}$ or $3.0 \times 10^{21} \text{ s}^{-1}$, a mole of gamma ray photons = ca $3 \times 10^7 \text{ kcal/mole}$!) and the lowest energy photons correspond to a radiofrequency wave (for $\lambda = 1 \times 10^{10} \text{ nm}$ or $3.0 \times 10^6 \text{ s}^{-1}$, a mole of radiowave photons = ca $3 \times 10^{-6} \text{ kcal/mole}$). Thus, the practical range of energies corresponding to a mole of photons spans about 13 orders of magnitude!

However, the range of energies of interest to the organic photochemist is just a tiny region of the electromagnetic spectrum and corresponds to light with wavelengths in the range of approximately 200-1000 nm. This range corresponds to the ultraviolet (UV, 200-400 nm), the visible (VIS, 400-700 nm) and near infrared (NIR, 700-1000 nm) regions of the electromagnetic spectrum. The cutoff at short wavelengths (200 nm = ca 140 kcal/mole) is determined by practical considerations such as the need for a transparent "material" from which to construct photolysis vessels. The most transparent material commonly available is quartz, which becomes strongly absorbing at wavelengths shorter than 200 nm, thereby setting the practical short wavelength cutoff for organic photochemical reactions. The cutoff at long wavelengths (1000 nm = ca 29 kcal/mole) is somewhat arbitrary and corresponds to the longest practical wavelength for electronic excitation of organic molecules.

Eq. 1.4 is a convenient formula, derived from consideration of the units involved in Planck's constant discussed above (rounded off slightly), for the conversion of the wavelength of an electromagnetic wave into the energy (kcal) of a mole of photons (for a handy web unit converter, see <http://www.ilpi.com/msds/ref/energyunits.html>).

$$E \text{ (kcal/mole)} = N_0 h(c/\lambda) = \frac{2.86 \times 10^4}{\lambda \text{ (nm)}} \quad (1.4)$$

Thus, from Eq. 1.4 an einstein (mole of photons) possessing a wavelength of 700 nm (red light) is equal to

$$E \text{ (kcal/mol)} = \frac{2.86 \times 10^4}{700 \text{ nm}} = 40.8 \text{ kcal/mole} \quad (1.5)$$

while an einstein of light possessing a wavelength of 200 nm (UV) is equal to

$$E \text{ (kcal/mol)} = \frac{2.86 \times 10^4}{200 \text{ nm}} = 143 \text{ kcal/mole} \quad (1.6)$$

For comparison with photochemical excitation energies in the UV-visible region, some typical bond energies are shown in Sch. 1.5. The weakest single bonds commonly encountered in organic molecules have strengths of ~ 35

kcal/mole (e.g., an O-O bond) and the strongest single bonds have strengths of the order of ~ 100 kcal/mole (e.g., a O-H bond). A photon of wavelength of ca 820 nm carries sufficient energy to break an O-O bond, whereas a photon of wavelength of ca 290 nm would be required to break an O-H bond. We might ask whether absorption of 250 nm light (114 kcal/mole) leads to random rupture of any of the single bonds of an organic molecule. The answer is negative. In fact, many photoreactions proceed with remarkable selectivity, even if UV light corresponding to photons of energy much greater than that of the strongest bonds of organic molecules is absorbed. Indeed, only certain bonds are made or broken even when the energy per photon absorbed is higher than the energy of most of the individual bonds of a molecule. The reason for this selectivity is due to a combination of the rapid deactivation of excess vibrational energy by electronically excited states, the localization of electronic excitation on certain atoms and the specificity with which this electronic excitation is employed to make or break bonds. In other words, specific mechanisms exist for the conversion of electronic excitation energy into the nuclear motion which in a net chemical reaction ($*R \rightarrow I$). In this text we shall seek an understanding of these mechanisms in order to understand photoreactions.

Light of wavelength in the range of ca 1000 nm-10,000 nm (3×10^{14} - 3×10^{13} s⁻¹) corresponds to photons in the "infrared" region of the electromagnetic spectrum. Photons in this energy region excite fundamental and overtone vibrations (stretches and bends) of organic molecules. For example, a photon corresponding to $\lambda = 3000$ nm corresponds to an energy of ca 10 kcal/mole (energy required to stretch a C-H) and $\lambda = 10000$ nm corresponds to an energy of ca 3 kcal/mole (energy required to stretch a C-C bond).

Light of wavelength in the region of ca. 1×10^6 nm (1 cm, 3×10^9 s⁻¹) corresponds to photons in the "microwave" region of the electromagnetic spectrum, and light of wavelength in the region of 1×10^{10} nm (10 m, 3×10^6 s⁻¹) corresponds to photons in the "radiofrequency" region of the electromagnetic spectrum. The value of ΔE for electron spin and nuclear spin states depends on the size of the magnetic field in which they are placed. In a field of $\sim 10,000$ gauss typical electron spin energies correspond to microwave frequencies ($\sim 10^9$ - 10^{10} s⁻¹)

which correspond to energies of $\sim 10^4$ - 10^5 kcal/mole). In a magnetic field of $\sim 10,000$ gauss, typical nuclear spin energies correspond to radiofrequency frequencies ($\sim 10^6$ - 10^7 s⁻¹) which correspond to energies of $\sim 10^6$ - 10^7 kcal/mole.

Finally, it is of interest to relate the *number* of photons, n , and the moles of photons, $N = n/N_0$, that corresponds to a given amount of energy. As an exemplar, let us compute the number of photons corresponding to 100 kcal/mol for light of different wavelengths (frequencies). From reorganization of Eq. 1.3 the value of n is given by Eq. 1.7 and the value of $N =$ is given by Eq. 1.8.

$$n(\text{number of photons}) = E\lambda/hc \quad (1.7)$$

$$N(\text{number of moles of photons}) = n/N_0 = E\lambda/N_0hc \quad (1.8)$$

Setting $E = 100$ kcal/mol and $n = 6.02 \times 10^{23}$, we find that solving for λ leads to a value of ca 284 nm. This means that one mole of photons whose $\lambda = 284$ nm contains 100 kcal of energy. This serves as a benchmark for computation at other wavelengths as is shown in Table 1. We note that for X-Ray photons $\lambda = 0.1$ nm), 100 kcal corresponds to 3.5×10^{-4} moles of photons, that for IR photons (1000 nm), 100 kcal corresponds to 3.5 moles of photon, that for microwave photons (10^8 nm) corresponds to 3.3×10^5 photons and for radiowave photons (10^{10} nm) corresponds to ca 3.3×10^7 photons. These benchmarks show that the number of photons corresponding to 100 kcal of energy varies over many orders of magnitude depending on the value of λ .

1.16 Calibration Points and Benchmarks for Molecular Dimensions and Time Scales

Chemists often think of molecules in terms of “ball and stick” models that are useful for evaluation of many static (time independent) properties of molecules such as molecular geometries (bond lengths and bond angles), but it is important to remember that microscopic particles (electrons, nuclei and spins) are never at rest. We are accustomed to the notion of “zero point” motion of nuclei, i.e., the postulate because of the uncertainty principle nuclei undergo

vibrational motions even at temperature close to 0° K. In addition, electrons and their associated magnetic spin moments execute characteristic zero point motions. Indeed, even the electromagnetic field has a zero point motion (which corresponds to the absence of photons in the field!). As we shall see in Chapter 3, physical and chemical radiationless transitions may be viewed as changes in zero point motions, i.e., reorganization of the nuclear, electronic, or spin structure of a molecule. Understanding how this reorganization of structure over distances of the order of the dimensions of molecules occurs as a function of time is critical for an understanding of photophysical and photochemical processes. Thus, we need to some benchmarks for dimensions and time scales.

First let us consider the dimension of a typical “chromophores”, the group of atoms that is responsible for the absorption of light. If we consider the atoms or groups involved in the absorption of light ($R + h\nu \rightarrow {}^*R$), the “size” of these groups generally of the order of 2 Å to 6 Å and involve a relatively small number of connected atoms. A photon traveling at the speed of light moves at $c = 3 \times 10^{10}$ cm/sec = 3×10^{17} nm/sec. Put in a different perspective, a photon travels 1 cm (10^7 nm) in 33×10^{-12} s (33 picoseconds, ps)! If we associate the wavelength of light, λ , with the “length” or “dimension”, d , of a photon, then photons corresponding to blue light have a “dimension”, d , of the order of 400 nm (Table 1). We may interpret the “dimension” or length of photons in terms of the ability to collide (interact) with a molecule. Thus, the time it takes a “blue” photon with the length of 400 nm to pass a point is $\tau = d/c = 400 \text{ nm} / 3 \times 10^{17} \text{ nm/sec} \sim 10^{-15}$ sec (a femtosec, fs). Crudely, this corresponds to an order of magnitude for the “interaction time” available for absorption of a photon by a molecule. If absorption does not occur in this time period the photon zips past the chromophore and absorption does not occur.

Can an electron make an orbital jump from one orbital to another or from one atom to another in this period of time, or does the photon zip by a molecule too rapidly? Let’s use a concrete physical model, the Bohr atom, to make an estimation of the time required for an electron to make an orbital jump from one atom to an adjacent atom. The time it takes an electron to make one complete circuit in a Bohr orbit is $\sim 10^{15}$ Å/sec. Thus, an electron may move on

the order of 0.1 nm in 10^{-16} and 1 nm in 10^{-15} s. Since 0.1-0.3 nm is the order of common bond lengths of organic molecules, we can conclude that the time scales of photon interaction and electron motion overlap.

For absorption of light to cause an electron to jump from one orbital to another (the $R + h\nu \rightarrow {}^*R$ process), the frequency of the light must match a possible frequency of motion of an electron, i.e., the resonance condition of Eq. 1.1 ($\Delta E = h\nu$) must be satisfied. Thus, if the resonance condition is met, the energy of the photon may be absorbed and an electron may be excited. In the wave picture, when light is absorbed energy is transferred from the oscillating electromagnetic field to the electrons, which are simultaneously sent into oscillation of excitation. In Chapter 4 we shall discuss the quantum mechanical selection rules that make plausible the absorption of light by a molecule. The time period of $\sim 10^{-15}$ sec sets an upper limit to the scale of chemical events, since no chemistry can occur before electron motion has occurred. Thus, a 10^{-15} s (femtosecond) serves as a benchmark time for the fastest events of chemical or photochemical interest. Remarkably, modern laser techniques have allowed the measurement of processes occurring on the time scale of 10^{-15} s. For his work in developing these techniques Ahmed Zewail was awarded the Nobel Prize in 1999 (4).

Let us now obtain a feeling for the magnitudes of processes that can occur during the lifetime of an excited state, *R , i.e., the processes shown in the state energy diagram of Sch. 1.3. What are calibration points or benchmark rates of the slowest and fastest available to *R ? What limits the lifetime of *R ?

Radiative processes limit the maximum lifetimes of electronically excited states, *R . In other words, *R cannot live longer than its natural radiative lifetime; if no other process deactivates *R , it will eventually emit a photon and the ${}^*R \rightarrow R + h\nu$ process will take the excited molecule back to its ground state. Thus, any radiationless transition (photophysical or photochemical) from S_1 or T_1 must occur at a rate faster (in a time scale shorter) than the rate of emission, or the latter will be the “default” deactivation process; i.e., the molecule will deactivate by emitting a photon faster than undergoing a photophysical or photochemical event. It is therefore natural to ask: “what are the limits for the fastest and the

slowest pure radiative processes?" We shall see in Chapter 4 that the largest *fluorescence* ($S_1 \rightarrow S_0 + h\nu_f$) rates of organic molecules are of the order of 10^9 s^{-1} and the smallest fluorescence rate constants are of the order of 10^6 s^{-1} . This puts the time scale for competitive processes from S_1 in a time period shorter than the range of 10^{-6} to 10^{-9} s. In other words, a radiationless process that takes 10^{-5} s or longer from S_1 will be inefficient, even for the longest lived S_1 states.

On the other hand, the largest *phosphorescence* ($T_1 \rightarrow S_0 + h\nu_p$) rate constants for organic molecules, k_p , are of the order of 10^3 s^{-1} and the smallest phosphorescence rate constants are of the order of 10^{-2} s^{-1} . This means that the time scale for competitive processes from T_1 to occur in a time period that is shorter than the range of 10^{-3} to 100 s. Thus, a radiationless process taking place in the time period of 10^{-5} s (which is far too long to compete with fluorescence from S_1) or longer may be quite efficient for a T_1 state. The values of k_f and k_p will be shown in Chapter 4 to be related to the structure of *R , but for now we have some calibration points for the limits of the rates of processes that can occur competitively from S_1 or T_1 .

Let us compare the time scales for emission of light to the time scales for internal nuclear motions such as vibrations. The fastest vibrations of organic molecules occur with a frequency of 10^{14} sec^{-1} (C-H stretching vibrations) and the slowest occurs with a frequency of $\sim 10^{12} \text{ sec}^{-1}$ (C-Cl stretching vibrations). This means that it takes somewhere between $\sim 10^{-12}$ to $\sim 10^{-14}$ sec to complete a zero point vibration for the bonded groups in organic molecules. Since the lifetime of fluorescence is in the range of 10^{-6} to 10^{-9} s, S_1 states will undergo thousands to millions of vibrations before emitting! The T_1 state, which takes 10^{-3} s or longer to emit, will have executed $\sim 10^{11}$ to 10^{14} vibrations before emitting photons! The point of this comparison is to show that there is plenty of time for nuclear motion to become equilibrated during the lifetime of an electronically excited molecule that deactivated through a radiative process.

Electron spin plays an important role in many photochemical reaction pathways and is the key structural feature of all singlet-triplet interconversions. In general the rate of spin interconversions are slow relative to vibrational motions and very slow relative to electronic motions. The fastest spin

interconversions occur at a rate of ca 10^{12} s^{-1} . The slowest spin interconversions occur at a rate of ca 10^{-1} s^{-1} . The dynamics of spin interconversions will be discussed in Chapter 3.

The rates of efficient photoreactions (k_R , Sch. 1.3) vary from $\sim 10^{13} \text{ s}^{-1}$ to $\sim 0.01 \text{ sec}^{-1}$. The faster reactions are limited by vibrational motion and electron transfer (ionization) and the slowest are limited by the slowest phosphorescence rates. Whether or not photoreaction occurs from S_1 or T_1 depends on both k_R and Σk where the latter represents the sum of the rates of all deactivating pathways of the excited state.

Up to this point we have considered only the molecule and not intermolecular time scales. The latter become important for bimolecular events involving *R . Let us close this section on calibration of dynamic processes by considering the time scales of molecular diffusion and collisions and the movement of entire molecules, both of which are critical in bimolecular photochemical processes. As a starting calibration point, let us consider a molecule in the vapor phase where the number of collisions (Z) that a small organic molecule undergoes with another molecule per sec at one atm is of the order:

$$Z (\text{s}^{-1}) \sim 8 \times 10^9 \text{ sec}^{-1}. \quad (1.9)$$

In liquids, collisions between adjacent molecules, or between a solute molecule with the walls of its solvent cage, occur with a rate similar to the rate of vibrations of heavy atoms, i.e., $Z \sim 10^{12} \text{ sec}^{-1}$, i.e., we can think of two molecules colliding in solution as possessing a weak bond between them. This high collision rate means that an electronically excited molecule is subjected to a large number of collisions with neighboring molecules before even the fastest fluorescence emission ($\max k_f \sim 10^9 \text{ s}^{-1}$) is likely to occur. Collisions with solvent molecules may serve as an energy source (to boost the excited molecule up to transition states for photoreactions) or as an energy sink (to remove energy from excited vibrational levels of an excited molecule) as we shall see in Chapters 3 and 6.

In addition to the internal nuclear motion of vibrations and collisions, typical small organic molecules undergo diffusional motion in which the

molecule as a whole is transported through a solvent. A molecule in a fluid solvent diffuses with a rate constant given by Eq. 1.10.

$$k_{\text{diff}} = 2 \times 10^5 T/\eta \quad (1.10)$$

where T is the temperature in degrees Kelvin and η is the viscosity in units of poise. A non-viscous organic solvent (e.g., acetonitrile, benzene) possesses a viscosity of ca. $\eta \sim 0.1$ poise so that at room temperature ($\sim 300^\circ \text{K}$);

$$k_{\text{diff}} = 2 \times 10^5 (300)/0.1 = 6.9 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1} \quad (1.11)$$

If a second molecule M in solution is present in concentration of 1M, the rate of encounter of this molecule with an excited state is approximately given by:

$$k_q[\text{M}] = (6.9 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1})(1\text{M}) = 6 \times 10^9 \text{ sec}^{-1}. \quad (1.12)$$

In other words, M will undergo a diffusive encounter with the excited state on the order of 6×10^9 times each sec. This rate is clearly competitive with the fastest fluorescence rates.

Finally, let's consider the distances that a molecule travels in solution as a result of random motions which are the result of thermal energy collisions with neighboring molecules. The distance traveled in a given time, t, by a molecule, making a "random walk", in solution is given by Eq. 1.13

$$R = (2Dt)^{1/2} \quad (1.13)$$

where D is the diffusion coefficient of the molecule in a given solvent. For organic molecules in fluid solvents $D \sim 10^{-5} \text{ cm}^2/\text{sec}$. Thus, in 10^{-6} sec a molecule will diffuse $\sim (2 \times 10^{-5} \times 10^{-6})^{1/2} = 4.5 \times 10^{-6} \text{ cm} = 450 \text{ \AA}$. In 30 sec, a molecule will diffuse $\sim 2.5 \times 10^{-2} \text{ cm} = 2.5 \times 10^6 \text{ \AA}$.

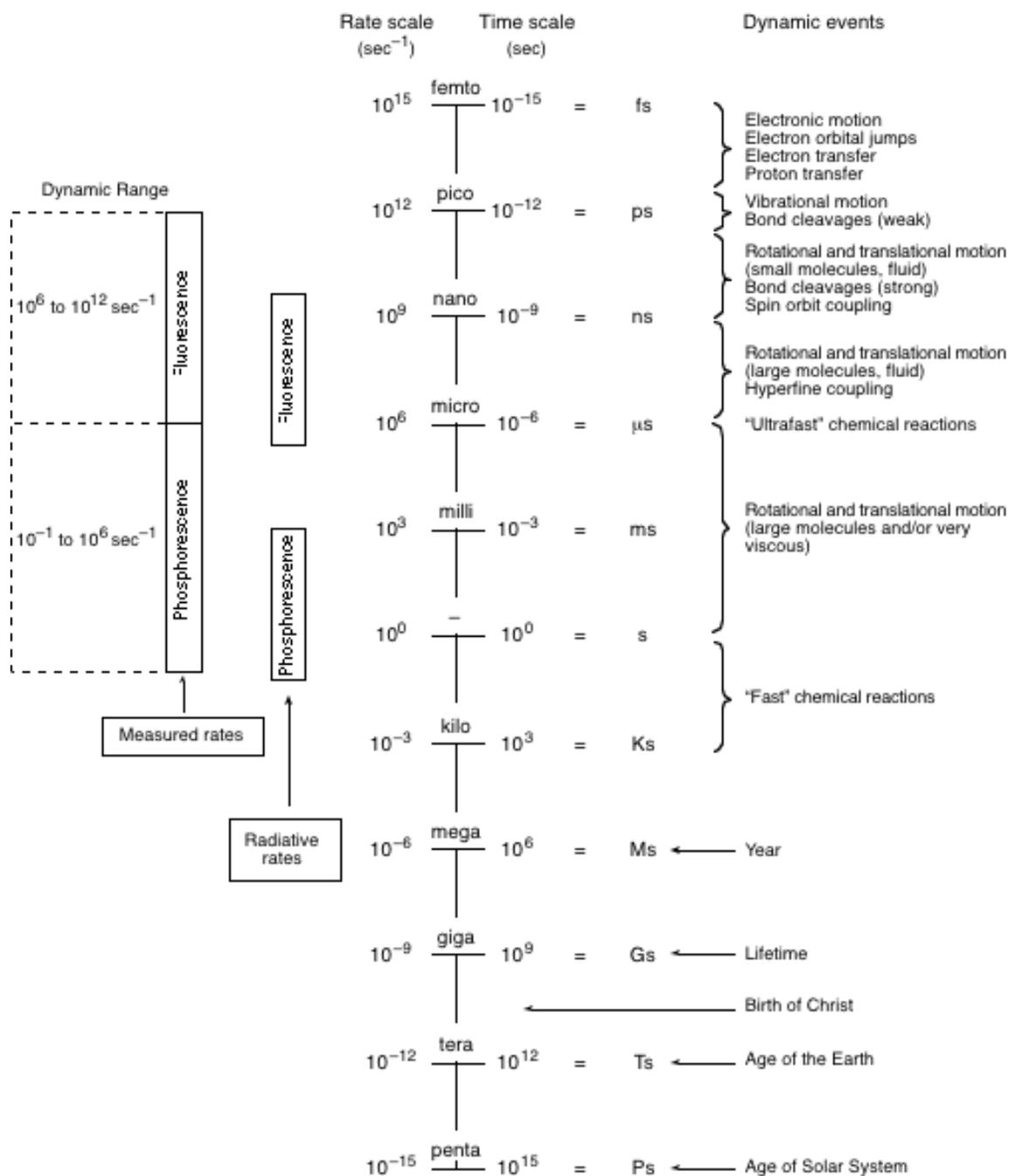
These calculations indicate the limits of nuclear motion (vibrations) and molecular motion (diffusion) that can occur while a molecule is in an excited

singlet state or an excited triplet state. Of course, if the excited state lifetime is shortened because of radiationless processes, less time is available for nuclear motion during the excited state lifetime, i.e., fewer vibrations, fewer collisions and less molecular translational diffusion will occur during the excited states' lifetime.

The rate of change of electron spin motion (orientation of the spin magnetic moment) is slow relative to electronic and nuclear motion. The fastest time period for changing electronic spin motion ("flipping" an electron's spin) for organic molecules is $\sim 10^{-10}$ to 10^{-11} sec. We shall see in Chapter 3 that electron spin flips commonly are much slower than this upper limit and that special molecular mechanisms are needed to allow spin flips to approach their maximum rate.

In general, the rate of electron motion in orbitals is very much faster than that of nuclear vibrational motion and spin motion. These time scales for motion will be shown to have a profound effect on the probabilities of transitions in photophysical and photochemical processes.

Sch. 1.6 compares the spread of time scales for events of photochemical interest (from ca. 10^{-15} s (femtosecond) to ca. 1 sec) with the same spread of history going back into the past (from ca. 1 sec to ca. 10^{15} s (pentasecond)). When compared in this manner, the history of a photoreaction passes through as many "decades" of time as the "history" of the earth!



Sch. 1.7. Comparison of time scales. Using a second as the standard, about 10^{15} seconds have passed since the creation of the solar system. With a femtosecond as a standard, 10^{15} femtoseconds must pass to add up to a second. Thus, taking the "heart beat" of an electron as a cycle around an atom ($\sim 10^{-15}$ s per cycle), the time scale of events that an electron "feels" up to one second is of the same order as all of the events that have occurred since the creation of the solar system.

1.17 Photons as Massless Reagents. Moles of Photons. Quantum Yields and Counting Photons of Photochemical Processes.

A photon may be profitably viewed as a “massless” reagent which, when absorbed by a molecule, causes the molecule to undergo a photoreaction. In the same way that chemists have developed stoichiometric methods to count molecules in order to determine the number of moles of a reagent to add to get a reaction to proceed, photochemists have developed methods to count photons. We start with the notion that we are dealing with a monochromatic beam of light, i.e., photons of a single precise energy. In order to approximate the number of photons in a beam of light, as well as the energy associated with the photons in a beam of light, it is useful to think of absorption of light by an organic molecule as a reaction where the photon behaves as a “mass-less” reagent. Thus, just as a mole of a compound equals 6×10^{23} molecules (Avogadro’s number), one “mole of light (photons)” is defined as 6×10^{23} photons of light of a particular wavelength (frequency). As mentioned earlier, a mole of photons is termed an einstein.

The total energy of a mole of photons of 350 nm light is ~ 82 kcal, and the energy of two moles of 700 nm light is also ~ 82 kcal. However, absorption of one photon of 350 nm light instantaneously provides the molecule with the equivalent of the entire 82 kcal, i.e., this energy, in principle, could be employed to break a bond whose energy is ~ 82 kcal/mole in a single molecule. Absorption of one photon of 700 nm light only provides the equivalent of ~ 41 kcal of energy to a single molecule. The simultaneous absorption of two photons by the same molecule is very unlikely (analogous to an improbable termolecular collision or reaction), it would be improbable to efficiently break bonds whose dissociation energy is ~ 82 kcal/mole with 700 nm light, no matter how intense the beam. In the latter example the total energy is clearly not as important as the energy per photon, i.e., an intense “red” lamp with a large total energy of photons would be useless to efficiently break 82 kcal/mole bonds, but a weak “blue” lamp could do the job. This relationship of the requirement of a “threshold” energy to break a bond in an organic molecule is completely

analogous to the familiar photoelectric effects for which there is a threshold of photon energy to remove an electron from a metal (discussed in Chapter 4). Indeed, Einstein's interpretation of the photoelectric effect was the first interpretation of light in terms of quantized photons and was made in analogy to Planck's interpretation of quantization of energy.

Just as we measure the theoretical yield of a conventional thermal reaction in terms of the number of product molecules produced per reagent molecule consumed, we may measure the yield of a photochemical reaction in terms of the number of product molecules produced per reagent photon absorbed (consumed). The ratio of molecules of product to photons absorbed is called the *quantum yield* of a photochemical reaction and is given the symbol Φ .

$$\Phi \text{ (quantum yield)} = \frac{\text{molecules reacted}}{\text{photons absorbed}} \quad (1.14)$$

The notion of quantum yield may be extended to any process for which a number of molecular events may be measured. For example, if emitted photons can be measured, then we may define a quantum yield of fluorescence and a phosphorescence as follows:

$$\Phi_F \text{ (quantum yield of fluorescence)} = \frac{\text{number of photons emitted from } S_1}{\text{number of photons absorbed}} \quad (1.15)$$

$$\Phi_P \text{ (quantum of phosphorescence)} = \frac{\text{photons emitted from } T_1}{\text{photons absorbed}} \quad (1.16)$$

The quantum yield is an experimental quantity that measures the efficiency with which absorbed photons are converted into measurable molecular processes.

1.18 Plan of the text

Now that we have described a broad overview of modern molecular organic photochemistry and have indicated the paradigm and exemplar approach that will be adopted in the text, we conclude this Chapter with a review of the plan of the text. We have seen that the concepts of structure, energetics, and dynamics are crucial for understanding molecular photochemistry. To get started, we need to understand the structures of the species R, *R , I and P of the global paradigm of Sch. 1.1-1.3. **Chapter 2**, "*Electronic, Nuclear and Spin States of Electronically Excited States*" describes how we can visualize the electronic, vibrational and electronic spin structures of R, *R , I and P to a zero approximation. Each stable configuration of electrons and electron spins corresponds to a stable nuclear geometry and possesses an associated energy. The enumeration, classification, and visualization of molecular states of electronically excited molecules and their relative energies in terms of orbital configurations, nuclear configurations and spin configurations are the topics of Chapter 2.

Given the knowledge of the plausible structures we will encounter in organic photochemistry, we next consider the problem of the interconversion of an initial structure into a different final structure, i.e., processes such as $R + h\nu \rightarrow ^*R$, $^*R \rightarrow I$, $I \rightarrow P$ and $^*R \rightarrow P$. These issues are approached in **Chapter 3**, "*Transitions between Molecular States*" which ties together the concepts of structure, dynamics, and energetics in terms of potential-energy surfaces, that allow an effective and concrete visualization of the plausible pathways by which molecular states may be interconverted.

Chapter 4, "*Radiative Transitions Between States*", reviews how radiative transitions (absorption, $R + h\nu \rightarrow ^*R$ and emission, $^*R \rightarrow R + h\nu$) can be understood and visualized, and how these radiative transitions are qualitatively and quantitatively related to molecular electronic structure and the structure of the electromagnetic field. **Chapter 5**, "*Radiationless Transitions Between States*", reviews the mechanisms of radiationless transitions between excited states and each other and between excited states and ground states. The transitions considered in Chapters 4 and 5 are termed "photophysical", because they occur between initial and final molecular states of very similar *nuclear geometry* and do

not correspond to traditional chemical processes in which bonds are clearly broken or formed to create different nuclear configurations. In **Chapter 6**, “Theoretical Organic Photochemistry”, we consider radiationless transitions corresponding to chemical reactions, and we develop a theory and paradigms for the understanding and visualization of photochemical reactions in terms of energy surfaces. Chapter 6 will describe the theoretical aspects of photochemical reactions after the electronically excited state, *R , has been formed by the absorption of a photon, $h\nu$. The *primary photochemical* processes $^*R \rightarrow I$ and $^*R \rightarrow P$ will be considered in theoretical terms of orbital interactions and orbital (and state) correlation diagrams.

Chapter 7, “Energy and Electron Transfer Processes”, will review the impact of two closely related processes involving *R . The close orbital interaction relationship between electron and electronic energy transfer will be described and a number of exemplars of each process will be reviewed within the current paradigms.

Chapter 8, “Mechanistic Organic Photochemistry”, will review the ways that plausible and probable mechanisms of organic photochemistry are “proven” experimentally. This Chapter will describe how the rates of primary photochemical processes are measured experimentally and how the reactive intermediates such as *R and I are examined experimentally.

Chapters 9, 10, 11 and 12, “Photochemistry of Carbonyl Compounds”, “Photochemistry of Alkenes and Related Compounds”, “Photochemistry of Enones and Related Compounds”, and “Photochemistry of Aromatic Compounds”, respectively, will use the theoretical and experimental paradigms developed in the earlier chapters to assist the student in developing the ability to predict, analyze and understand the photochemistry of the common functional groups of organic chemistry. In these Chapters the global paradigm of Sch. 1.1 and the working paradigm of Sch. 1.2 will take on a concrete character through the examination of many examples that can be coordinated through the paradigms.

The final two chapters will describe a series of important “special topics” in molecular organic photochemistry.

Chapter 13, “Medium Effects on Photochemical Processes”, will explore, as a special topic, the role of organized and constraining media on the course of photochemical processes.

Chapter 14, “The Role of Molecular Oxygen in Photochemistry”, will explore, as a special topic, the role of ubiquitous molecular oxygen in photochemical processes.