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 study is 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 which result in net physical, not chemical, changes) and the ***photochemistry of organic compounds*** (the interactions of light and organic molecules which result in net chemical changes).

What is ***molecular photochemistry***? A definition that suits this text is: "*Molecular photochemistry is the science concerned with a complete description, **cradle to grave**, of the physical and chemical processes induced by the absorption of photons, in terms of concrete mechanistic models based on molecular structures and their implied static and dynamic properties.*" We shall employ the term molecular photochemistry to include both photophysics and photochemistry, since concepts and laws of photophysics and photochemistry are intimately interwoven, as we shall see many times in the text. Indeed, it is not possible to have a proper understanding of photochemical processes without a proper understanding of photophysical processes.   We shall see that the molecular photochemistry of organic molecules is a rather broad interdisciplinary discipline embracing the fields of chemical physics, molecular spectroscopy, physical organic chemistry, synthetic organic chemistry and supramolecular chemistry. The "molecular" part of molecular photochemistry emphasizes the use of the molecule and molecular structure and their implied dynamics and substructure (electron configuration, nuclear configuration, spin configuration) as the crucial and unifying intellectual concepts for describing the possible, plausible and probable pathways of photochemical reactions from the cradle (absorption of a photon by a reactant, R) to the grave (isolation of a product, P).

1.2 Why Study Molecular Photochemistry? Content, Context, Cognitive Learning.

When a student is introduced to a new subject there are three intellectual pillars which underlie robust learning: the content of the subject, the context of the subject and the cognitive learning aspects of the subject. The content are the "facts" which compose the subject matter. Any textbook can present the information or content that has been compiled by a mature field of scientific inquiry. Textbooks are unusually valued by students in terms of their ***context***, the manner in which the "facts" are intellectually embedded with relation to the motivation of the student's interests and ***cognitive learning aspects***, the manner in which "facts" are converted into knowledge, how that knowledge is represented and how that knowledge is intellectually manipulated. This text attempts to take content, context and cognitive learning aspects into account in teaching the student the science of modern 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 and matter, interact with one another. 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 photochemistry. The intellectual structure of molecular photochemistry is inherently interdisciplinary and therefore requires a practitioner in the field to seek commonality in the ideas and methods of many scientific disciplines. In effect, molecular photochemistry must integrate many theories which initially appear to be based on disparate concepts and laws. The process of achieving such an intellectual integration cannot only be stimulating and gratifying, but can also serve as a model for knowledge creation in any area of science or ordinary decision making.

Other, more practical motivations can be found in the desire to understand 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, and vision, which is triggered by a remarkably simple photochemical reaction, a photochemically induced cis-trans isomerization which occurs in the eye. During the late 1900s the advent of the use of lasers in the field of telecommunications produced a new way of transmitting information by the use of light (through glass fibers), rather than electrons (through metal wires), and has produced a new technology termed photonics, which has many advantages over the classical technology of electronics. Photochemistry is attaining an increasingly important role in the health sciences to cure cancers through phototherapy, to repair tissues and to perform surgery with lasers. Other important applications of photochemistry in technology include the use of photoinduced polymerization to manufacture computer chips and provide protective coatings for a variety of high value materials such as optical fibers.

The cognitive learning approach of the text teaches the student (1) to convert "facts" into robust knowledge, (2) to represent that knowledge through highly pictorial representations, and (3) to organize, manage and manipulate the representations intellectually and within chosen contexts. This approach is described in the following section.

1.3   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 matter. Organic chemists are accustomed to the theory of matter in terms of molecular structure and molecular dynamics.   We shall use the molecular theory of matter as a familiar and effective approach to understanding organic photochemistry. We shall be in less familiar ground as we develop a theory of light and of the interaction of light with molecules. It is useful in exploring new theories to review the construction of scientific representations and models in general, in an effort to enhance the comfort level of developing new concepts.

A successful scientific theory of some observable phenomena, such as photophysical or photophysical processes that occur in the natural world is intended to produce an understanding of the phenomena. This understanding is developed though the creation of an organized and systematic structural or mathematical description of the phenomena. Observations which are to be understood by representation or model are often too cumbersome to describe and systematize and therefore are difficult to share with other scientists who are committed to studying the same or similar phenomena. According to most textbooks, a theory is created by a scientist who "invents" a set of key intellectual units or ***representations*** that are related in some definite way to the observations of interest and that are well suited for logical, systematic and detailed analysis. After the representations have been developed, the scientist then attempts to perceive a set of relationships (***rules*** and ***laws***) between the representations. For example, the fundamental concepts of heat, energy, work, force, velocity and acceleration are key intellectual units in many important fields of physics, such as thermodynamics and classical mechanics and are commonly represented in terms of mathematical formulae or mechanical models. In the same way, the concepts of atoms, molecules, electrons, nuclear configurations, periodicity and chemical bonding are represented in terms of mathematical or mechanical models which provide an understanding of phenomena such as chemical properties and chemical transformations. The rules and laws that interrelate representations are often easier to master than the mastery of the representations themselves. In molecular photochemistry, in addition to familiar chemical representations involving molecular structure and molecular dynamics, we must develop the perhaps less familiar concepts of spins, electromagnetic radiation, photons and quantum mechanics.

A scientific theory may be considered "mature" and a working paradigm for a community of practitioners if it repeatedly is able to make predictions about events that will occur under certain circumstances in the future and which turn out to be verified experimentally. The predictive attributes of a theory are highly admired, valued and important. Such theories may make quantitative or qualitative predictions which serve as a tool for experimental research. In this

sense the intellectual structure of the 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, and is represented by, an obscure mathematical framework. Thus, an important feature of a good everyday, working scientific theory is the ability to create a system of *qualitative* representations that are abstracted from direct experimental observations and which can be expressed *geometrically* and therefore 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 described, arranged, and interpreted. Using geometry, the scientist can develop qualitative *pictorial theories* that provide the tremendous value of being able to provide a 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. Thus, best and most readily accepted and applied theories usually provide both the language for prediction for the future observations and organization of past observations.

In the text we shall employ pictorial representations of the concepts and rules and laws of quantum mechanics to describe photochemical and photophysical processes. Many of the important concepts in quantum mechanics, such as matrix elements for observable quantities such as energy and dipole moments, selection rules for transitions, orbital correlation diagrams, oscillator strengths, spin-orbit couplings, etc. may be unfamiliar to the student, especially one who is not well versed in or is mystified by complex and abstract mathematics. This text attempts to demystify all of the important quantum mechanical concepts in terms of qualitative, pictorial analogies and models. Although these visualizations and pictures are admittedly only a partial and incomplete representation of the more "correct" and quantitative mathematics that underlie the concepts, experience has shown that geometric pictures can often capture the essence of the mathematics and can allow the student to understand each concept at a qualitative and intuitive rather than at a

mathematical level. It will be noted at the outset that it is admitted that quantum mechanics can only be properly understood in detail through the language of complex mathematics. However, it will also be noted that the judicious selection of pictorial representations of quantum mechanical concepts is all that is required for most students who are seeking to use the concepts as tools for a qualitative understanding. 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.

The text shall develop a theory of molecular organic photochemistry involving a number of qualitative pictorial and visualizable concepts that will provide an intellectual structure for a investigation and description of both photophysics and photochemistry. In organic chemistry the concept of molecular structure and its implied substructure (electrons, nuclear configuration, spins) provide the key intellectual concepts for describing, organizing and predicting the properties and transformations of organic compounds. The text will use the concepts of organic chemistry (which are assumed to be familiar to the student) and will develop new, less familiar concepts to describe a structure for light, and show how this structure provides a means of understanding the interaction of light and organic molecules.

The structures of the key molecular species (reactants, R, electronically excited states, *R, reactive intermediates, I, and products, R) will be described in terms of readily visualizable orbitals which represent electrons, wave functions which represent vibrations, and vectors which represent electron and nuclear spins. Visualizing the transitions between structures will involve the development of concepts of potential energy surfaces and the forces, energetics and interactions that determine the rates and probabilities of transitions from one structure to another. These and other concepts will be employed to determine the "selection rules" for "allowed" and "forbidden" transitions of structures involved in photochemical and photophysical processes. The concepts will allow the student to rank a transition between structures (states) as qualitatively "possible", "plausible" or "probable". The visualized transition can

then be subjected to experimental tests which, if successful, will establish a transition or occurrence of an excited state or reactive intermediate as "proven".

1.4   The Paradigms of Molecular Organic Photochemistry

In performing everyday, normal science, the relationship of the scientist to the understanding of phenomena being studied depends critically on answers to questions such as the following: What legitimate concepts should be employed to analyze, organize and predict observations? What legitimate methods of measurement 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? To what authority does a scientist appeal in making decisions on what theory to employ to answer such questions?

It may seem that there would be many subjective opinions concerning how to answer the above questions, and, as a result, that the performance of everyday science would be a matter of constant controversy so that it would be difficult to obtain a consensus on how to describe and interpret laboratory observations. However, this is not the case in mature sciences such as Physics and Chemistry because of the existence of *scientific paradigms* that make it easy for scientists to agree on important questions. Indeed, scientific paradigms allow for the practicing scientist to perform everyday research and for a student to be readily initiated into a mature field of science. The development of a *scientific paradigm for molecular photochemistry of organic molecules* is a critical objective of this text and serves as the basis 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 and interpreting the observable phenomena of the universe in a systematic and reproducible manner. According to Kuhn,

paradigms are the authority to which scientists appeal in deciding on the course of everyday, normal scientific activities. Scientists readily accept and employ the authority of 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, theory 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 **paradigms of modern molecular organic photochemistry***.

One of the most important features of a successful paradigm is its authority over what are the legitimate issues which should be of concern to the community and what are the appropriate methods to address these issues. The authority of the paradigm prevents practitioners in a field from wasting time quibbling over fundamentals; because they share the same paradigm, practitioners can proceed rapidly to advanced levels of inquiry without arguing over basic issues. The nature of a successful paradigm is to possess a structure which is necessary and sufficient to describe all observable phenomena in a field. For example, the paradigm of atomic and molecular structure is so authoritative that no modern chemist 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. 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. Yet today we are convinced that all observable chemical phenomena, no matter how complex, can be understood and investigated based on the paradigm of atomic and molecular structure!

Typically, a textbook will implicitly employ paradigms which constitute the assumptions, concepts, strategies, methods and techniques of the field of

interest. Indeed, the explicit consideration of a field's paradigms and specific exemplary examples, or **exemplars**, provides an excellent pedagogical vehicle to introduce students to new fields of science, and that approach is the one which is taken in this text.   For example, 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 interpretation and prediction of those reactions. In this text we shall explicitly use Kuhn's concepts of paradigms to assist the student in understanding organic photochemical reactions from the initial act of light absorption by an organic molecule to the isolation of a product of some photochemical process. This represents a "cradle to grave" ***mechanistic approach*** to molecular organic photochemistry.

In closing this section on paradigms, the student must be warned that the ruling paradigms are not permanent, but are subject to change. The history of science over the past two centuries has shown that paradigms which were considered unshakable, were not only shakable, but completely replaced by new governing paradigms. For example the classical paradigm of light as a continuous electromagnetic wave has been replaced by the quantum mechanical paradigm in which light is viewed as a quantized entity which possesses 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.

1.5   Global Paradigms and Exemplar Paradigms

It is useful to classify paradigms as being of two types: (1) **global paradigms** which encompass the entire collection of beliefs, values, techniques, methods and successful achievements of a scientific discipline such as molecular organic photochemistry and (2) **exemplar paradigms** referring to universally recognized outstanding specific accomplishments in the field that serve as guiding examples to practitioners on how to solve research puzzles in the field.

The global paradigms provide an authoritative and general framework for performing scientific research and organizing, predicting and interpreting the observable phenomena of a field. The exemplar paradigms guide scientists in the every day activities of the design, execution and interpretation of specific experiments and permit the replication of many examples, any one of which could, in principle, be substituted for the exemplar. For example, exemplar paradigms or "case studies" in photochemistry supply the photochemist with examples of past achievements that are accepted by the community as the foundation for current practice. The judicious selection and use of exemplar paradigms allows the scientist to "visualize" or to "infer" the future by analogous examples that has been successful in the past. There is an intellectual mapping of one established exemplar onto an example which is in progress. The mapping processes consists of identifying the features of the new system which are analogous to those of the exemplar system. In this text exemplars are selected to provide the student with outstanding examples or representations which test and verify important concepts and rules that are the heart of the paradigm of molecular organic photochemistry.

Molecular photochemistry blends together the global paradigms of chemistry and the interaction of electromagnetic radiation (or less rigorously but more familiarly, light) with matter. The paradigm of chemistry employs the molecule (with its implied electronic, nuclear and spins configurations) as key organizing structural concepts; the paradigm of electromagnetic radiation employs the photons or oscillating waves as its key organizing structural concepts. In the paradigm of chemistry, all observable phenomena involving matter are interpreted in terms of the behavior of atoms and molecules; in the paradigm of electromagnetic radiation all observable phenomena are interpreted in terms of the behavior of photons (or oscillating electromagnetic waves). Thus, ***the field of molecular photochemistry is concerned with interaction of light (represented by photons or oscillating electromagnetic waves) and matter (represented by molecules).*** Molecular organic photochemistry is simply the subdiscipline of molecular photochemistry dealing with organic molecules.

1.6   The Role of Structure in the Global Paradigms of Molecular Organic Photochemistry

Successful paradigms usually possess a structure which attracts communities of practitioners. A structure may be defined in an abstract mathematical manner in terms of the following properties: (1) composition; (2) constitution; (3) configuration; (4) conformation. Note that these are the same terms that 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, which describes the number and kinds of atoms in a molecule. Constitution refers to the way that the entities of a geometric structure are connected. 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. 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 not 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 bonded atoms in 3 D space about a central atom such as carbon. Finally, conformation refers to the specific global 3 D geometry of a geometric object. For an organic molecule the term refers to the shapes produced by rotations about single bonds, such as carbon-carbon bonds.

In this text we shall use molecular structures as the intellectual representation to think about molecular organic photochemistry. By visualizing structures and the transitions between structures we shall produce a paradigm for understanding organic photochemical reactions from "cradle to grave".

It is important for the student to recognize that the global paradigm, which has authority in a scientific field, determines the fundamental structures which the practitioners assume can and cannot exist and, therefore, defines the structures which are accessible for observation, characterization, investigation

and use in interpretation. The paradigm also has the authority to determine which transitions are "allowed" between structures and which are "forbidden". The text will teach how the photochemist uses the paradigms of molecular photochemistry of organic compounds to define a complete list of possible structures which are assumed to exist, and how to predict which transitions between structures are "allowed" and which are "forbidden". 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!

   For example, 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.

1.7   A Global Paradigm for Molecular Organic Photochemistry.

   It is now time to get more specific about the structures and transitions involved in molecular organic photochemistry. Scheme 1.1 is a global paradigm that schematically represents the "mechanistic pathway" of the overwhelming majority of known organic photochemical reactions from cradle to grave. This paradigm implies that, in general, organic photochemical reactions which convert a reactant(s) R to a product, P(s), can be understood in terms of the structures of reactant molecules (R), photons (hν), electronically excited molecules (*R) and reactive intermediates (I) produced from electronically excited molecules. By global we mean that the concepts expressed in Scheme 1.1 are independent of the specific structures of interest and have been observed to successfully explain the pathways of organic photochemical reactions repeatedly in the past and therefore is a plausible initial paradigm to explain pathways of any organic photochemical reaction without specifying the detailed structures of R, *R, I or P.

$$\text{R} + \text{h}\nu \longrightarrow {}^{*}\text{R} \longrightarrow \text{I} \longrightarrow \text{P}$$
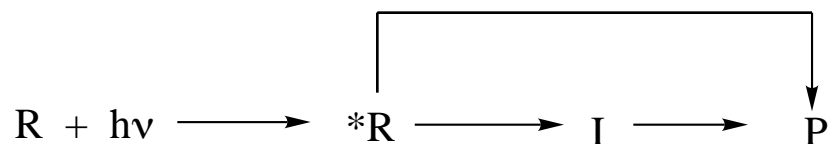
Scheme 1.1. A global paradigm for organic photochemical reactions.

Based on Scheme 1.1, molecular organic photochemistry has developed a mature global paradigm for describing the possible, the plausible, the probable and the proven pathways (transitions) involved in an overall photochemical process R + hν → P. This paradigm guides photochemists with respect to the effective methods to investigate and to prove these pathways experimentally.

Let us now consider what we mean by the concepts possible, plausible, probable and proven in the context of the paradigm of molecular photochemistry. For a pathway to be ***possible***, molecules (and their components) 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*** pathways that a photochemical reaction can follow. Only the set of pathways which obey the conservation laws are considered ***possible***. 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 coupling interactions and mechanisms of momentum exchange. These considerations lead to a set of "selection rules" that indicate the ***plausible*** reactions from the set of possible reactions. Next, one considers specific details of structure and the available energy and time scales available to the structure. After taking these considerations into account, the remaining, much smaller set of plausible pathways, are considered to be the most ***probable***, i.e., those which proceed at the fastest rates. The text will teach how to employ structures and interactions between structures to decide on whether a pathway is possible, plausible or

probable. It will also teach how to experimentally **_prove_** which of the probable pathway is actually the one which occurs under a given set of conditions.

The task, therefore, in understanding an overall photochemical transformation, R + hv → P, is to first be able to list **_all of the plausible pathways_** that are available to *R after the absorption of a photon by R and the rates of the pathway(s) to P compared to the rate of all other plausible pathways. 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 judgements based on knowledge of measured rates or the theoretical ability to estimate rates based on structure, 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 + hv → P.

Scheme 1.1 teaches that for many organic photochemical reactions the following steps are generally involved:

(1) **_absorption of a photon of light_**, hv, by a reactant molecule, R to produce an electronically excited state, *R;

(2) **_primary photochemical reaction_** of an electronically excited state, *R, to produce reactive intermediate, I;

(3) **_thermally induced reaction_** of I to produce the observed product(s), P.

(4) the direct conversion of *R to P, which we shall see occurs is a special manner in photochemical reactions.

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

(1)   What are the possible and plausible **pathways** for the photochemical transformation of R → P?

(2)   What are the possible and plausible **structures, energetics and dynamics** of the *R and I which occur along the reaction pathway from R → P?

(3)   What are the legitimate **experimental and theoretical strategies** for experimentally "observing" the *R and I that occur along the reaction pathway from R → P?

(4)   What are legitimate **techniques** for executing strategies for "observing" *R and I that occur along the reaction pathway from R → P?

(5)   When does the photochemical transformation occur directly from *R , and when does the photoreaction proceed through an intermediate I?

(6)   What are the competing pathways for photophysics and photochemistry of *R?

Questions such as these are handled through the establishment of a working paradigm or by reference to exemplar investigations.

1.8   From the Global to the Working Paradigm.

As with all mature and successful paradigms, the paradigm of molecular photochemistry is a powerful intellectual tool because it informs photochemists how to avoid wasting their time pursuing implausible structures and transitions. As a result, the photochemist can emphasize what experience has proven to be most important through the application of the global paradigms.

In solving normal every day scientific puzzles, a great deal of time is saved by employing a "working paradigm" which applies to many common situations and which is found to be generally *probable* based on considerable experience. This shortcut of using a working paradigm prevents 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. Let us use Scheme 1.1 as an example of a global paradigm of molecular organic photochemistry and see how we can refine it into a more specific everyday, working paradigm for molecular organic photochemistry.

The global paradigm of Scheme 1.1 may be expanded and elaborated into a useful ***working*** paradigm for the photoreactions of common families of organic molecules. For any family of organic molecules (ketones, alkenes, enones, aromatic compounds, etc.) the working paradigm will consider molecular orbital and spin descriptions (configurations) of the entities (R, *R, I and P) shown in Scheme 1.1. For example, a typical working paradigm will start by classifying R, *R and P according to the orbital nature and spin orientation of the electrons as shown in Scheme 1.2. It is assumed that all of the remaining electrons are spin paired in orbitals of lower energy and are of secondary importance in determining the course of the photochemical processes. For R, *R and P, the starting point for analysis of a photophysical or photochemical process will be the assignment of the electronic nature of highest occupied orbital (HO) and the lowest unoccupied orbital (LU), where the orbitals are ranked in energy from highest to lowest. The reactive intermediate(s) I is classified according to the occupancy of two electrons in two orbitals of (usually) similar energy, as in a radical pair or biradical. In all cases the orbitals assigned to the HO and LU will be simply one electron orbitals that are familiar to the student from courses in organic chemistry and physical chemistry.

$$R \xrightarrow{h\nu} P$$

$$R \xrightarrow{h\nu} {}^*R \longrightarrow I \longrightarrow P$$

$$R \xrightarrow{h\nu} {}^1{}^*R \xrightarrow{ISC} {}^3{}^*R \longrightarrow {}^3I \xrightarrow{ISC} {}^1I \longrightarrow P$$

LU

HO

S_0 S_1 T_1 ^3I ^3I S_0
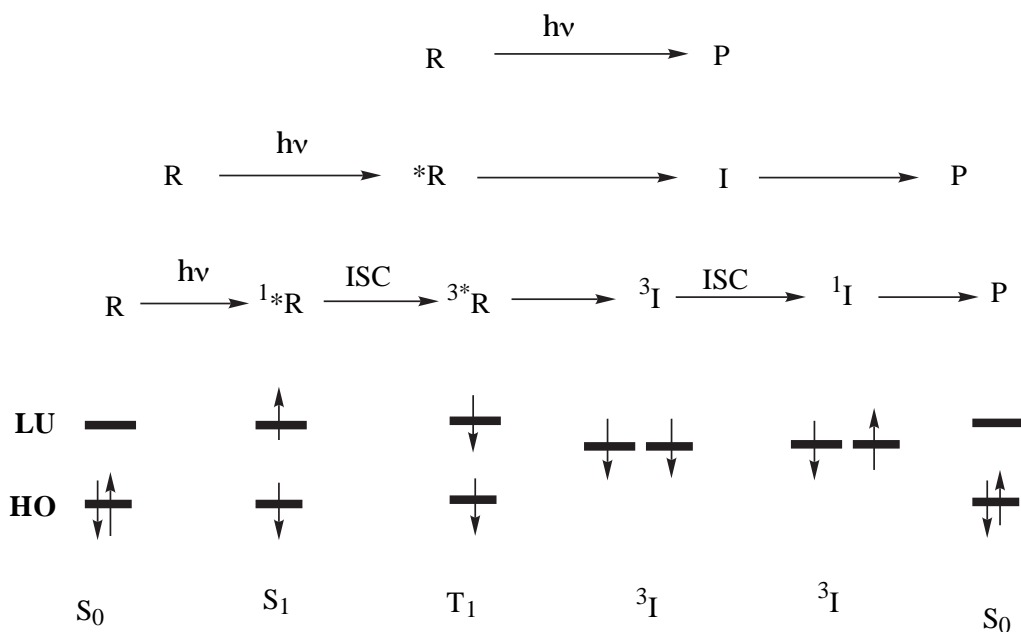
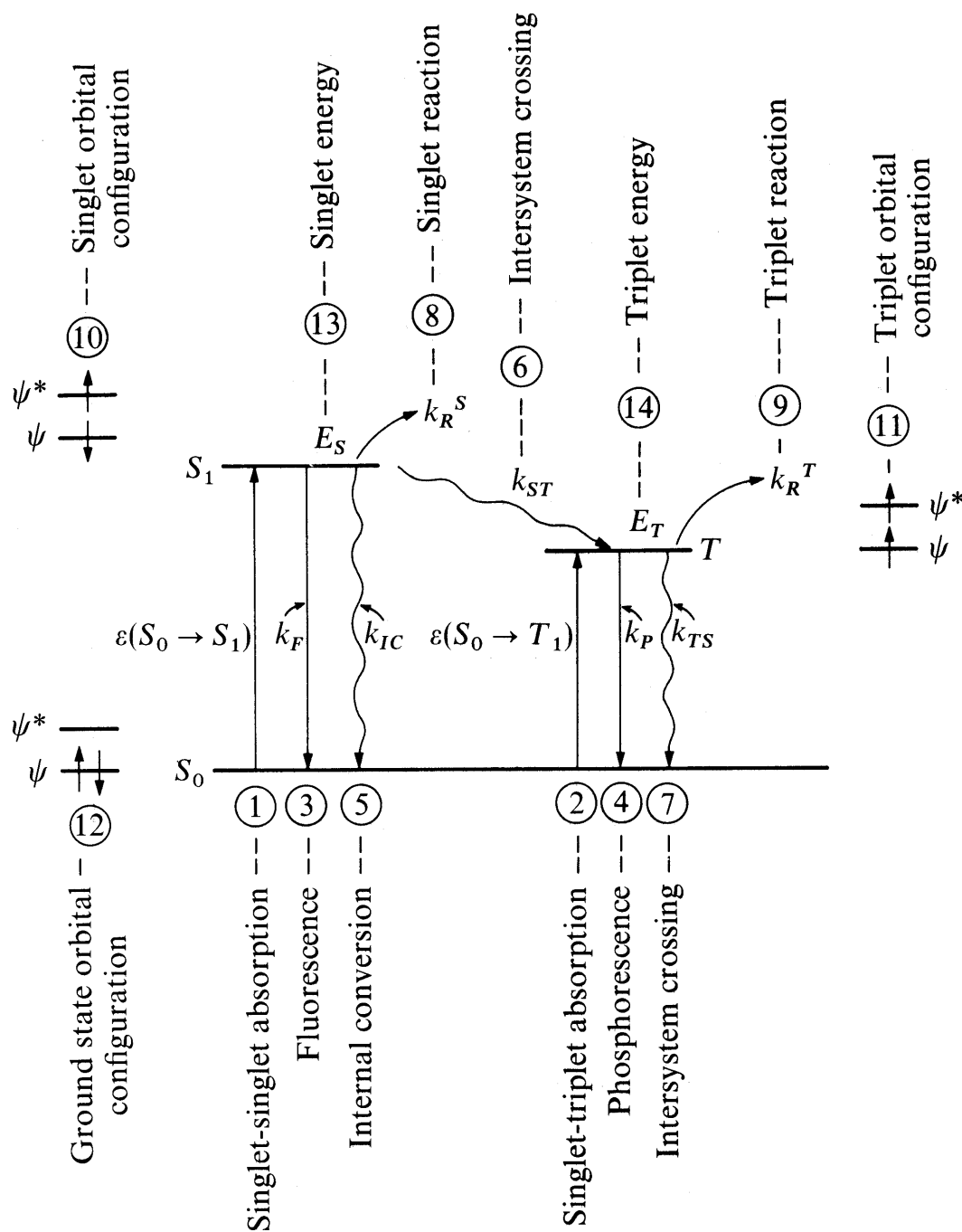**Scheme 1.2.** Working paradigm for organic photochemical reactions.

       Thus, in the working paradigm the structures of the excited states and reactive intermediates of the global paradigm of Scheme 1.1 are expanded to produce a working paradigm which includes both the orbital and spin configurations of *R and I. As mentioned above, in many organic photoreactions the intermediate, I, is a radical pair or a biradical. The electronically configuration of *R and I, both of which generally possess one electron in each of two orbitals, can have the electrons either paired or unpaired. When *R or I possess two orbitally unpaired electrons and the electron spins are antiparallel (spin paired) the structure is termed a **_singlet_** state. In general, R and P will be singlet states ground states (to be discussed in detail in Chapter 2) and are labeled S_0, where the subscript indicates that the state is a stable ground state of lowest energy for a particular nuclear configuration. If the electrons are spin paired in *R (i.e., ${}^1{}^*R$ in Scheme 1.2), we term this an singlet _excited_ state and label it S_1 where the subscript indicates that the state is the _first excited_ singlet state (in contrast to the ground state, S_0). If the electrons are unpaired in *R (i.e., ${}^3{}^*R$ in Scheme 1.2), 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. Likewise, the reactive intermediate I (often a radical pair or biradical) may either be a singlet or a triplet, and for the

case where I is a radical pair, we label the intermediates ^{1}RP (^{1}I) and ^{3}RP (^{3}I), respectively. In this case we use a superscript where 1 indicates a singlet state and 3 indicates a triplet state.

In summary, Scheme 1.2 represents a "zero order" working paradigm for many photochemical reactions of organic molecules which 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 to deduce the nature of *R and the probable reactions to produce I. Predicting and understanding photochemical reactions will require a knowledge of the structures of the entities, R (S_0), ^{1*}R (S_1), ^{3*}R (T_1), ^{3}I, ^{1}I, and P (S_0) and of the probabilities of the transitions between the structures connected by the pathways shown in the paradigm.

1.9   State Energy Diagrams: Electronic and Spin Isomers

A *state energy diagram* is an important working paradigm which displays 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 for a given, fixed nuclear geometry (Scheme 1.3). Higher energy singlet states (S_2, S_3, etc) and higher energy triplet states (T_2, T_3, etc) are usually not 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 x coordinate has no physical meaning and it is generally assumed that the nuclear geometries of all states displayed in a single state diagram are not very different from the equilibrium nuclear geometry of the ground state. Since all of the structures in the state energy diagram have the same composition and the same constitution as S_0, but are chemically different from S_0, ,**S_1 and T_0 are both isomeric with S_0**. Indeed, all

Singlet orbital configuration — ⑩

Singlet energy — ⑬

Singlet reaction — ⑧

Intersystem crossing — ⑥

Triplet energy — ⑭

Triplet reaction — ⑨

Triplet orbital configuration — ⑪

ψ^* — $\uparrow$
ψ — $\uparrow\downarrow$

S_1 $\qquad$ E_S $\nearrow k_R^S$

k_{ST}

E_T $\quad T$

ψ^* — $\uparrow$
ψ — $\uparrow$

$\varepsilon(S_0 \to S_1)$ $\quad k_F$ $\quad k_{IC}$ $\quad \varepsilon(S_0 \to T_1)$ $\quad k_P$ $\quad k_{TS}$ $\quad k_R^T$

ψ^* ____
ψ $\uparrow\downarrow$

S_0

① ③ ⑤ $\qquad$ ② ④ ⑦

⑫ — Ground state orbital configuration

Singlet-singlet absorption —

Fluorescence —

Internal conversion —

Singlet-triplet absorption —

Phosphorescence —

Intersystem crossing —

Scheme 1.3. The State Energy Diagram. A basic paradigm of modern molecular photochemistry.

of the states in the state diagram 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 S_n and T_n states are related to each other as ***spin-electronic isomers***. In addition to the spin-electronic isomerization the states in the energy diagram in the state energy diagram may be stereoisomers of one another (same constitutions, same spin-electronic configurations, different configurations).

As a working paradigm, the state energy diagram indicates the 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* photochemical and photophysical processes as those which represent transitions between any two 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.

With reference to the state energy diagram, *photophysical processes* are defined as transitions which interconvert excited states with each other or excited states with the ground state. The important photophysical processes, in turn, are classified as *radiative* and *radiationless* photophysical processes. The state diagram defines the *plausible* photophysical radiative processes, as shown in Scheme 1.3:

1. "Allowed" or singlet-singlet absorption ($S_0 + h\nu \rightarrow S_1$), characterized experimentally by an extinction coefficient $\varepsilon(S_0 \rightarrow S_1)$;
2. "Forbidden" or singlet-triplet absorption ($S_0 + h\nu \rightarrow T_1$), characterized experimentally by an extinction coefficient $\varepsilon(S_0 \rightarrow T_1)$;
3. "Allowed" or singlet-singlet emission, called *fluorescence* ($S_1 \rightarrow S_0 + h\nu$), characterized by a radiative rate constant, k_F:
4. "Forbidden" or triplet-singlet emission, called *phosphorescence* ($T_1 \rightarrow S_0 + h\nu$), characterized by radiative rate constant, k_P.

The *plausible* photophysical *radiationless* processes are:
5. "Allowed" transitions between states of the same spin, called *internal conversion* (e.g., $S_1 \rightarrow S_0 + heat$), characterized by a rate constant, k_{IC};

6. "Forbidden" transitions between excited states of different spin, called *intersystem crossing* (e.g., $S_1 \rightarrow T_1$ + heat), characterized by a rate constant, k_{ST};

7. "Forbidden" transitions between triplet states and the ground state - also called intersystem crossing (e.g., $T_1 \rightarrow S_0$ + heat) - and characterized by a rate constant, k_{TS}.

       In terms of the state energy diagram, *primary photochemical processes* may be defined as transitions from an electronically excited state to yield molecular structures of different constitution or configuration than that of S_0. These chemically different molecular structures are the reactive intermediates, I, of Schemes 1.1 and 1.2 and are produced by

8.   Photochemical reaction from S_1 to produce a reactive intermediate, ^1I, called primary *photochemical reaction from S_1*, (e.g., $S_1 \rightarrow {}^1I$) and characterized by a rate constant k_R^S.

9.   Photochemical reaction from T_1 to produce a reactive intermediate, ^3I, called primary *photochemical reaction from T_1*, (e.g., $T_1 \rightarrow {}^3I$) and characterized by a rate constant k_R^T.

       The theory of organic photoreactions (Chapter 6) will provide us with the rules for deciding on the *plausible* primary photochemical processes for common electronic configurations of S_1 and T_1.

       The ***thermal*** reactions which transform I in the product(s) P (Scheme 1.2) are not explicitly included in the state energy diagram. These processes are called secondary thermal reactions and are considered to be exactly the same reactions of I that occur when I is produced thermally. Such processes are, however, necessary for a complete description of the overall process R + hν → P, and this description is provided by the working paradigm of a potential energy surface, which will be described in the next sections.

       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 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.

1.10 An Energy Surface Description of Molecular Photochemistry

In proceeding from the state energy diagram (fixed nuclear geometry) 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 bookkeeping is nicely handled by the paradigms associated with potential energy surfaces (which will be discussed in detail in Chapters 3 and 6). We now present a preview of how this paradigm handles the problem of simultaneously considering the structure, energetics and transition dynamics involved in photochemical processes. Strictly speaking, potential energy surfaces are multidimensional and difficult to visualize. As a reasonable "zero order" energy surface we shall employ an approximation which uses two-dimensional "potential energy curves" (however, for simplicity we shall employ the term surface to describe these curves).
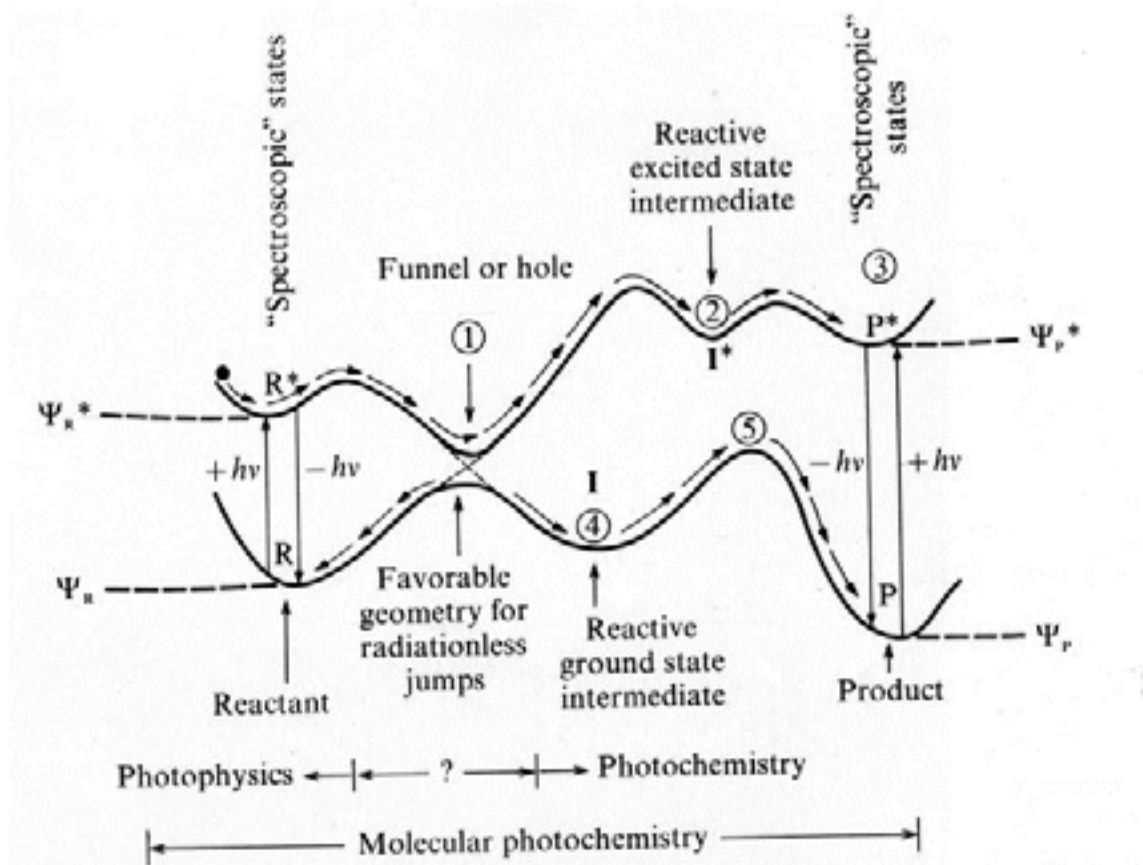
A potential energy surface is a natural extension of the concept of a state energy diagram and describes the possible structures involved in the photochemical transformation of R → P (hypothetical example shown in Scheme 1.4). Whereas in the state energy diagram a nuclear geometry similar to that of 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.

In Scheme 1.4 two hypothetical surfaces are shown for the overall reaction R + hν → P for two different starting electronic configurations. The lower energy surface is termed the **ground state electronic surface** and the higher energy surface is termed the **excited state surface** (in this hypothetical example we shall assume it is a single surface). Both surfaces correspond to the same overall R + hν → P transformation in terms of changes in nuclear configuration, since it is assumed that the representative point of the system must be on one surface or the other on the way from *R to P. To the extent that these

hypothetical surfaces are valid, they allow a visualization or "map" of all plausible pathways for the R → P transformation. Let us consider some of the *a priori* plausible pathways for the electronically excited state *R based on the nuclear geometry changes which are "mapped out" by the two curves of Scheme 1.4.

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. 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 is for is R* to proceed along the excited surface to region (1) which happens to be close in energy to the ground state 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*

"Spectroscopic" states

"Spectroscopic" states

Reactive
excited state
intermediate

Funnel or hole

③

② P*

① I* — $\Psi_p{}^*$

R*

$\Psi_R{}^*$

+hv −hv ⑤

R −hv +hv

Ψ_R I

Favorable
geometry for
radiationless
jumps ④

P

Reactant Reactive
ground state
intermediate Product Ψ_p

Photophysics ←|← ? →|→ Photochemistry

|← ——— Molecular photochemistry ———→|

Scheme 1.4. 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 which represents a molecule whose nuclear geometry is moving aong the reaction coordinate from left to right.

(we shall see why in Chapter 3). Some electronically excited molecules may thus "jump" to the ground surface and "spill" into the R minimum (resulting in a net "photophysical" cycle R + hv → R* → R). Other molecules of *R 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 the 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* → (1) → (4) → (5) → P the nuclear motion was controlled by the excited-state surface for part of the reaction, *R → (1), and by the ground-state surface, (4) → (5) → (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).

Both the absorption and emission of light occur near minima corresponding to the nuclear geometry of the reactants and products (we will see why in Chapter 4). Thus, there is both a radiative and a radiationless 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. It is also possible that *R may proceed to an electronically excited *I and *P, although this pathway is rarely found.

Although Scheme 1.4 represents an arbitrary and hypothetical photochemical reaction R + hv → P, the pathways and processes shown represent examples of most of the important photochemical and photophysical processes and allows for some generalizations based on considerable theoretical and experimental experience: (a) absorption (R + hv → *R) and emission (*R → R+ hv and *P → P+ hv) of light tends to occur at nuclear geometries which correspond 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 → R and *R → 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.

1.11   Dimensions, Structure, Energy, and Time at the Molecular Level. Visualizing Structures and Dynamics at the Molecular Level.

The most effective paradigms in all of chemistry are derived from the concept 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 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. At a still finer level of structure the chemist sees the zero point motions electrons in orbitals, certain vibrating nuclear geometries, and the precessing electron spins in certain configurations relative to the molecular framework or some orienting magnetic field. From this finely detailed structure of a molecule, the chemist is able to calibrate the rates of zero point motions and is able to estimate the rates at which plausible processes may occur and thereby estimate which of these is most probable.

At the macroscopic level we are accustomed to understanding events that occur by identifying geometrical structural changes as a function of time. By geometric structure we mean the shape or topography (in the broadest sense) of an object or collection of objects. The amount of change is usually identified with the energy available to do work on a system and the rate of change is identified with the rate at which the available energy is placed into structural modes that accomplish the desired change of structure. A qualitative appreciation of molecular dimensions, molecule size and molecule 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 it takes for electrons and

nuclei to move in space are at the heart of mechanistic descriptions of molecular phenomena.

We seek to visualize any 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. Intuitively, rate of the transformation will depend on the efficiency of getting energy into the modes that cause a motion which can change the structure in the appropriate fashion.

In order to visualize molecular processes, we should have a means of visualizing events at the microscopic level in terms of structural changes of atoms, electrons and spins. We should also have a means of estimating the rates of change of structure. We shall do this in the following manner:

1.   We assume that molecules are composed of an assembly of electrons, nuclei and spins;

2.   We assume that the electrons generally move much more rapidly than the heavier and sluggish nuclei;

3.   We assume that nuclei, because of their relatively slow movement, may be visualized as classical point masses, i.e., as points located in a precise manner in space.

4.   We assume that electrons, because of their relatively fast motion compared to nuclei and spins, are quantum particles and their location in space must be associated with a probability function we call orbitals.

5.   We assume that electron spins are associated, not with mass or motion, but with angular momentum and may be visualized as vectors that precess about an axis determined by the molecular structure and the presence or absence of an external field.

Let us now consider sizes and time scales associated with molecules and molecular motions, after which we will consider energetic features of molecules. Although the classical description of electrons, photons and nuclei as particles

fails to explain molecular phenomena quantitatively, we shall see in Chapter 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.

1.12   Calibration Points for Molecular Energetics

A paradigm is useful when it provides both qualitative and quantitative measures which defines the limits of properties of structures and the time scales of dynamics of transitions between structures. For example, in molecular photochemistry we are interested in the energetics, the sizes of structures, the number of photons, the rates of transitions between structures, etc. 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 for molecular and photonic energetics*** and in the following section we shall consider some calibration points for molecular and photonics sizes and dynamics.

By energetics we shall mean the ***difference in energy between states of a molecule***, rather than the absolute energy of a state. 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;
2. "dynamic" energetics, or the change in energy of a state as a function of time.

Typical "static" energetic quantities are the energy differences between the electronic states of a molecule, bond energies, reaction enthalpies and entropies, ionization potentials and electron affinities. 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 or any transition between states and this must be done 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 the ***minimum*** energy that 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, there may be an energy barrier even for reactions which are exothermic, so that in such cases a certain "activation energy" must be acquired before reaction can occur.

Absorption of a photon by a molecule transforms light energy into electronic excitation energy. The photon uses its energy to "do work" on the electrons or nuclei or spins or 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

Table 1.1 Energy Conversion Table

Region	λ Å	λ nm	$\tilde{\nu}$ cm^{-1}	ΔE kcal/mole	ν sec^{-1}	Structure and motion involved in absorption or emission
Ultraviolet	2,000	200	50,000	143.0	15×10^{15}	
	2,500	250	40,000	114.4	12×10^{15}	
	3,000	300	33,333	95.3	1.0×10^{15}	Electrons-orbital motion
	3,500	350	28,571	81.7	8.7×10^{14}	
	4,000	400	25,000	71.5	7.5×10^{14}	
	4,500	450	22,222	63.5	6.6×10^{14}	
	5,000	500	20,000	57.2	6.0×10^{14}	
Visible	5,500	550	18,182	52.0	5.4×10^{14}	
	6,000	600	16,666	47.7	5.0×10^{14}	
	6,500	650	15,385	44.0	4.6×10^{14}	
	7,000	700	14,286	40.8	4.2×10^{14}	
Infrared	10,000	1,000	10,000	28.6	3×10^{14}	Nuclei-vibrational motion
	50,000	5,000	2,000	5.8	6×10^{13}	
	100,000	10,000	1,000	2.86	3×10^{13}	
Microwave	10^8	10^7	10	3×10^{-2}	3×10^{11}	Electron spin-precessional motion
	10^{10}	10^9	0.1	3×10^{-4}	3×10^9	
Radiowave	10^{12}	10^{11}	0.001	3×10^{-6}	3×10^7	Nuclear spin-precessional motion

distribution. The change in electronic and nuclear configuration may also promote a change the electron spin configuration.

The energy required to produce an excited state is obtained by inspection of the absorption of emission spectrum of the molecule in question, together with the application of equation 1:

$$\Delta E = E_2 - E_1 = h\nu = hc/\lambda \qquad\qquad (1)$$

where h is Planck's constant (kcal-s), ν is the frequency (sec^{-1}) and λ is the wavelength (nm) at which absorption occurs, and E_2 and E_1 are the energies of a single molecule in the final and initial states.

It is useful to have calibration points for the energy of absorbed photons and the energy of bonds that commonly occur in organic molecules. Table 1 shows how the energy of a mole of photons is related to the corresponding wavelength of light (λ, typical units Ångstroms, Å, or nanometers, nm) and frequency of light (ν, typical units nanometers, nm). Since different energy units are commonly employed, the Table presents values in terms of kcal/mole, kJ/mole, cm^{-1} and eV.

The minimum energy required for electronic excitation of organic molecules is ~ 30-40 kcal/mole and corresponds to "red" light (λ = 700 – 800 nm). The maximum energy commonly employed by organic photochemists corresponds to ~ 140 kcal/mole and corresponds to far ultraviolet light (λ ~ 200 nm). This cutoff at short wavelengths is determined by practical considerations: the absorption of quartz, which is required to serve as a reaction vessel for photochemical reaction becomes strongly absorbing at shorter wavelengths that 200 nm.

The position of an absorption band is often expressed by its wavelength (λ in nanometers, nm), by its wave number ($\mathbf{\nu}$ = $1/\lambda$ in reciprocal centimeters, cm^{-1}) or by its frequency (ν in s^{-1}). For example, 300 nm is equivalent in wave numbers to

$$\mathbf{\nu}\ (cm^{-1}) \quad = \quad \frac{1}{300\ nm} = \frac{1}{3 \times 10^{-5}\ cm} \quad = 3.33 \times 10^{4}\ cm^{-1} \qquad (2)$$

300 nm is equivalent in frequency to

$$\nu \ (s^{-1}) \ = \ \underline{c} \ = \ \underline{3 \times 10^{10} \ cm/sec} \ = \ 10^{15} \ sec^{-1} \qquad (3)$$
$$\lambda \qquad 3 \times 10^{-5} \ cm$$

Eq. 1 may be rewritten in terms of kcal/mole the unit usually used for chemical bonds:

$$\Delta E \ (in \ kcal/mole) \ = \ E_2 - E_1 = \ h\nu = \ \underline{2.86 \times 10^4} \qquad (4)$$
$$\lambda \ (in \ nm)$$

The amount of energy produced through the absorption of one mole of photons by a compound at a given wavelength is equivalent to the energy of 6.02×10^{23} photons. The energy of a mole of photons is termed an einstein. Thus, an einstein of light possessing a wavelength of 700 nm (14,300 cm^{-1}) is equal to

$$E_2 - E_1 = \ \underline{2.86 \times 10^4} \ = \ 40.8 \ kcal/mole \qquad (5)$$
$$700 \ nm$$

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

$$E_2 - E_1 = \ \underline{2.86 \times 10^4} \ = \ 143 \ kcal/mole \qquad (6)$$
$$200 \ nm$$

ENERGETIC CONSIDERATIONS

S_1 T_1 BOND ENERGIES

VACUUM ULTRAVIOLET

110

OH
CH

300nm

90

80 80 CC
75 C-Cl

KETONES

UV LAMP
400nm
VIOLET

70

C-Br

60 VISIBLE SUN

C-I

ELECTRONIC EXCITATION

40 700nm RED

O-O

INFRARED

VIBRATIONAL EXCITATION

CH stretch → 10 3000nm
C=O stretch → 5 6000nm
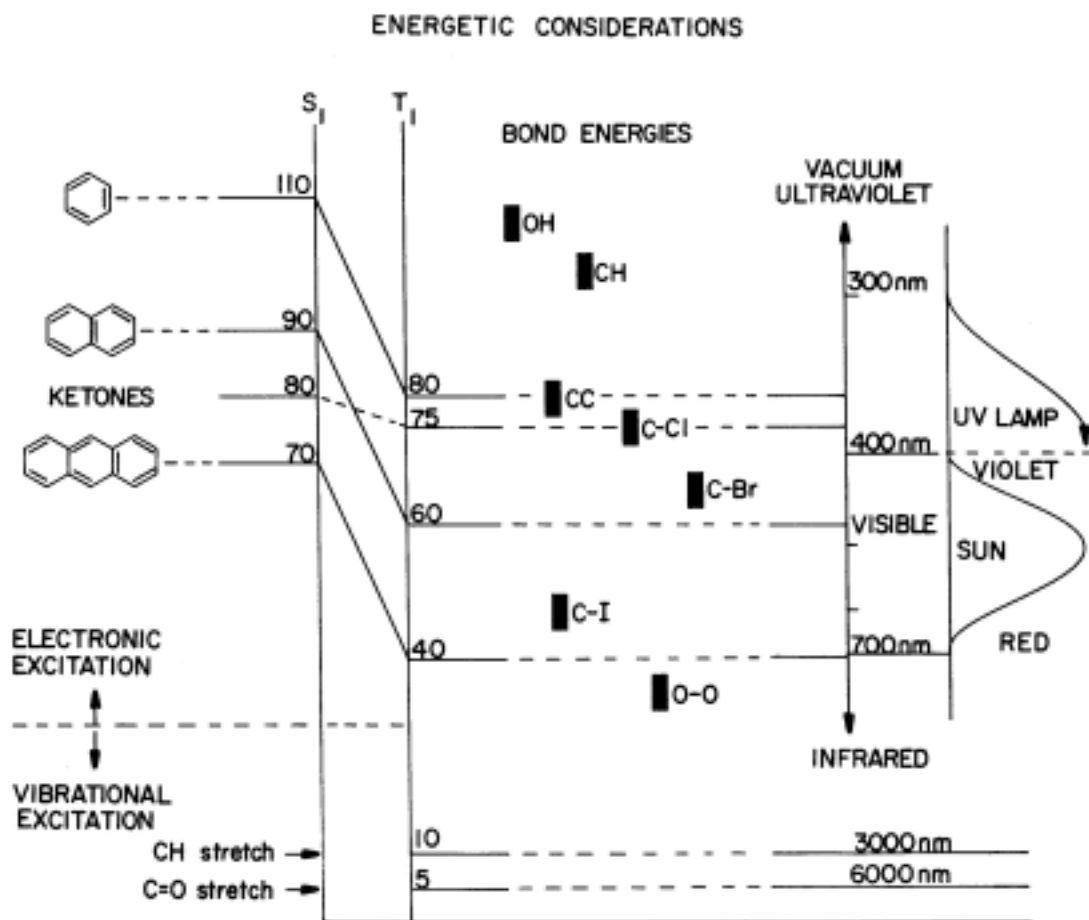
Scheme 1.5. Comparison of energies involved in photochemical reactions and bond energies and the emission spectrum of the sun. Vibrational energies are show for comparison. Electron spin and nuclear spin energies depend on the size of the magnetic field in which they are placed. In a field of ~ 10,000 gauss typical electron spin energies correspond to microwave frequencies ($\sim 10^9$-10^{10} s^{-1}, which correspond to $\sim 10^{-4}$-10^{-5} kcal/mole) while typical nuclear spin energies in a magnetic field of 10,000 gauss correspond to radiofrequency frequencies ($\sim 10^6$-10^7 s^{-1}) which correspond to $\sim 10^{-6}$-10^{-7} kcal/mole. We shall see in following chapters why nuclear and electron spin energies

For comparison with photochemical excitation energies, some typical bond energies are shown in Scheme 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 C-H bond). We might ask whether absorption of 250 nm light (114 kcal/mole) leads to random rupture of all the single bonds of an organic molecule? The answer is negative. In fact, many photoreactions proceed with remarkable selectivity, i.e., only certain bonds are made or broken. The reason for this selectivity is due to the localization of electronic excitation 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 nuclear motion that results in a net chemical reaction. In this text we shall seek an understanding of these mechanisms in order to understand photoreactions.

1.13 Calibration Points for Molecular Dimensions and Time Scales for Molecular Dynamics

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 that nuclei undergo vibrations even at 0^oK. In addition, electrons and their associated magnetic spin moments execute characteristic zero point motions. 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.

If we consider the atoms or groups involved in the absorption of light (R + h$\nu \rightarrow$ *R), the "size" of these groups (termed "chromophores") generally of the order of 2 Å to 10 Å involve a relatively small number of connected atoms. A particle (photon) travelling at the speed of light moves 3 x 10^{10} cm/sec = 3 x 10^{18}Å/sec. If we associate the wavelength of light with the "length" or "dimension", d, of a photon, then photons corresponding to blue light have a "dimension", d, of the order of 4000Å. We may interpret the "dimension" of photons in terms of the ability to collide (interact) with a molecule. Thus, the time it takes a "blue" photon to pass a point is τ = d/ν = 4000Å/3 X 10^{18}Å/sec

~10^{-15} sec. Crudely, this corresponds to the maximum "interaction time" available for absorption of a photon by a molecule.

Can an electron make an orbital jump from one orbital to another in this period of time or does the photon zip by too rapidly? Let use a concrete physical model, the Bohr atom, to make an estimation and approximate an orbital jump as taking an electron from one atom to an adjacent atom. The time it takes an electron to make one complete circuit in a Bohr orbit is ~ 10^{16} Å/sec. Thus, an electron may move on the order of 1 Å in 10^{-16} and 10 Å in 10^{-15} s.   Since 1Å 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 + hv $\rightarrow$ *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 must be satisfied.   Thus, if the resonance condition is met, the energy may be absorbed from the oscillating light wave by electrons which are simultaneously sent into oscillation. In Chapter 4 we shall discuss the selection rules which make the absorption of light by a molecule probable or improbable. The time period of ~ 10^{-16} sec sets an upper limit to the scale of chemical events, since no chemistry can occur before electron motion has occurred. Thus, it serves as a calibration point for the fastest events of chemical or photochemical interest. Remarkably, modern laser techniques have allowed the measurement of processes which occur on the time scale of 10^{-15} s, a femtosecond. For his work in developing these techniques Ahmed Zewail was awarded the Nobel Prize in 1999 (4).

Let us now obtain a feel for the magnitudes of processes that can occur from the excited state, *R. What are calibration points for the slowest processes of direct photochemical interest from *R, such as the emission of light (the *R $\rightarrow$ R + hv process)? *Radiative processes limit the lifetimes of electronically excited states, *R.* Thus any radiationless transition (photophysical or photochemical) from S_1 or T_1 must occur at a rate faster than emission or the latter will be the "default" process, and 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 radiative processes?" We shall see in Chapter 4 that the largest fluorescence 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 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. This means that a radiationless process that takes place in the time period of 10^{-5} s (which is far too long to compete with florescence 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 to be related to the structure of *R in Chapter 4, but for now we have some calibration for the limits of the rates of processes which can occur competitively from S$_1$ or T$_1$.

Let us compare the time scales for emission of light to the time scales for nuclear motions such as vibrations, and molecular motions such as collisions and diffusion. 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 ~10^{12} sec^{-1} (C-Cl stretching vibrations). This means that it takes ~10^{-12} to 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 long to emit, will have executed ~10^{13} to 10^{14} vibrations before emitting photons! The point of this comparison is to show that there is plenty of time for nuclear motion during the lifetime of an electronically excited molecule.

The rates of photoreactions (k_R, Scheme 1.3) vary from ~ 10^{13} s^{-1} to ~ 0.1 sec^{-1}. The faster reactions are limited by vibrational motion 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.

Let us close this section on calibration of dynamic processes by considering the time scales of molecular collisions and the movement of entire molecules, both of which are critical in bimolecular processes. In the vapor phase, the number of collisions (Z) that a small organic molecule undergoes per sec is of the order:

$$Z \sim 10^7 \times P \tag{7}$$

where P is the pressure in nm of mercury. Thus, at 1 atm (~ 760 nm),

$$Z \sim 8 \times 10^9 \text{ sec}^{-1}. \tag{8}$$

Collisions between adjacent molecules occur with a rate similar to that of vibrations or heavy atoms, i.e., $Z \sim 10^{12} \text{ sec}^{-1}$. This high collision rate means that an electronically excited molecule is subjected to a large number of collisions with neighboring molecules before emission is likely to occur. These collisions may serve as an energy source or energy sink to boost the excited molecule up to transition states for photoreactions or remove energy from excited vibrational levels of an excited molecule.

In addition to the internal nuclear motion of vibrations and collisions, typical small organic molecules undergo translational 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. 9.

$$k_{diff} = 2 \times 10^5 \, T/\eta \tag{9}$$

where T is the temperature in degrees Kelvin and η is the viscosity in 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 (~ 300° K);

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

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:

$$k_q[M] = (6.9 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1})(1M) = 6 \times 10^9 \text{ sec}^{-1}. \tag{11}$$
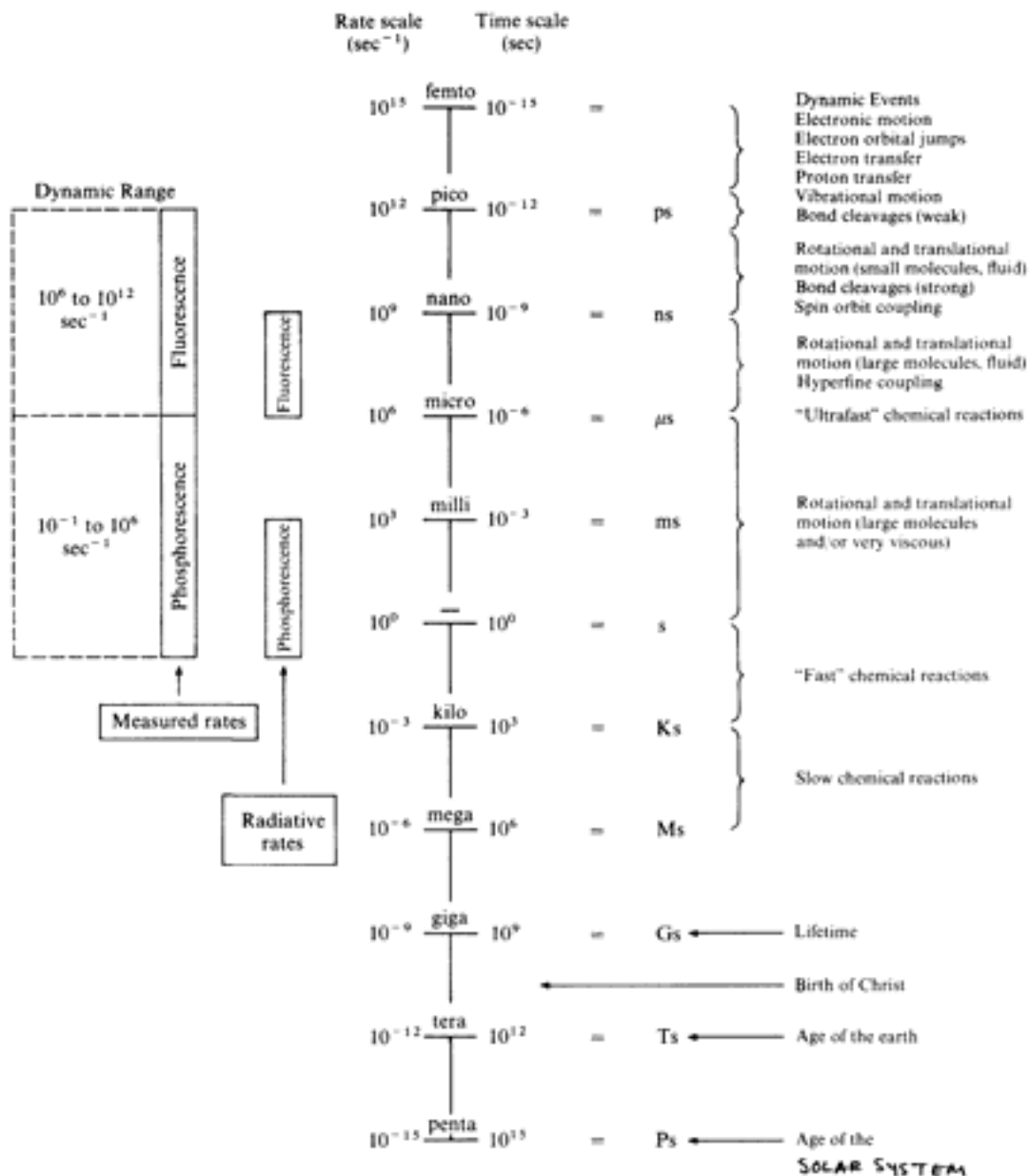
In other words, M will undergo a diffusive encounter with the excited state on the order of 6×10^9 times each sec. This rate is clearly competitive with the fastest fluorescence rates.

The distance traveled in a given time, t, by a molecule, making a random walk, in solution is given by:

$$R = (2Dt)^{1/2} \qquad\qquad\qquad (12)$$

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

These calculations indicate the limits of nuclear motion and molecular motion 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

Rate scale
(sec^{-1})

Time scale
(sec)

Dynamic Range

Fluorescence

10^6 to 10^{12}
sec^{-1}

Fluorescence

Phosphorescence

10^{-1} to 10^6
sec^{-1}

Phosphorescence

Measured rates

Radiative
rates

	femto				Dynamic Events
10^{15}		10^{-15}	=		Electronic motion
					Electron orbital jumps
					Electron transfer
	pico				Proton transfer
10^{12}		10^{-12}	=	ps	Vibrational motion
					Bond cleavages (weak)
					Rotational and translational
					motion (small molecules, fluid)
	nano				Bond cleavages (strong)
10^9		10^{-9}	=	ns	Spin orbit coupling
					Rotational and translational
					motion (large molecules, fluid)
					Hyperfine coupling
	micro				
10^6		10^{-6}	=	μs	"Ultrafast" chemical reactions
	milli				Rotational and translational
10^3		10^{-3}	=	ms	motion (large molecules
					and/or very viscous)
10^0		10^0	=	s	
					"Fast" chemical reactions
	kilo				
10^{-3}		10^3	=	Ks	
					Slow chemical reactions
	mega				
10^{-6}		10^6	=	Ms	
	giga				
10^{-9}		10^9	=	Gs ←	Lifetime
				←	Birth of Christ
	tera				
10^{-12}		10^{12}	=	Ts ←	Age of the earth
	penta				
10^{-15}		10^{15}	=	Ps ←	Age of the SOLAR SYSTEM

Scheme 1.6. 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 (~ 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.

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 spin motion (orientation of the spin magnetic moment) is slow relative to electronic and nuclear motion. The fastest time period for changing spin motion ("flipping" an electron's spin) for organic molecules is $\sim 10^{-10}$ to 10^{-11} sec. We shall see that 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 is much faster than that of nuclear 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.

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

1.14   Photons as Reagents. Moles of Photons. Quantum Yields and Stoichiometry of Photochemical Processes.

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. In the same way that we measure reactants and products of a conventional thermal reaction in terms of moles, it is useful to measure the number of photons in a beam of light. 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). A mole of photons is called an einstein.

Photochemists are generally interested in the "size" (energy, wavelength, frequency) of an individual photon and in the "concentration" (photons per unit area or volume) of photons in a beam of light. From

eq. 1 $$E = h\nu = c/\lambda$$

we can make a connection between the properties of light as a collection of particles and light as a wave. Energy is a characteristic property of particles, whereas ν is a characteristic property of waves. Length and size are common properties of waves and particles. We may view the ratio E/ν (units = energy-time) as a term that controls the "size" of photons, i.e., from eq. 1, the ratio E/ν is always equal to h, Planck's constant. So to speak, h tells us about the "size" of particles whose frequency is ν. Since $\nu = c/\lambda$, an alternate expression of h is $E(\lambda/c)$, where the "size" in terms of energy is clearly connected to the size of a photon as measured by λ or ν.

In order to gain an appreciation of the energetic "size" of a photon in terms of a quantity related to molar concentration, let us consider how to convert light, the intensity of a given light beam, into moles of photons (remember 1 mole of photons = 1 einstein). The common unit of energy absorbed in a unit time is the joule (equal to a watt-sec., i.e., J = W (work) x sec). The number (N) of quanta or photons in a light beam of monochromatic light of wavelength λ (in nm) and of total energy J is given by eq. 13.

N (no. of photons) = 5 x 10^{15} x λ (nm) x E (joules)   (13)

In other words, the number of photons depends on their corresponding wavelength, λ, and the total energy of the beam, J (1 J = 2.4 x 10^{-4} kcal/mole). Note that 1 J of green light ($\lambda \sim 500$ nm) is equivalent to 2.5 x 10^{18} quanta, whereas 1 J of infrared light ($\lambda \sim 5000$ nm) is equivalent to 2.5 x 10^{19} quanta, 1 J of microwave photons (10^8 nm) is equivalent to 5 x 10^{23} photons and 1 J of radiofrequency photons (10^{11} nm) is equal to 5 x 10^{25} photons!

The total energy of a mole of photons of 350 nm light is $\sim$ 82 kcal and the energy of two moles of 700 nm light is also $\sim$ 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 $\sim$ 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 absorption of two photons by the same molecule is very unlikely (analogous to an improbable termolecular reaction), it would be improbable to efficiently break bonds whose dissociation energy is ~ 82 kcal/mole with 700 nm light, 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 efficiently 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. 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.

In making a comparison between photons and molecules, the total energy, E, of N photons of a specific λ or ν may be compared to the total weight m of N identical molecules. Thus, we are naturally led to the concept of a mole of photons as being equal to Avogadro's number of photons. In order to calculate the number of molecules N contained in a mass, m, of a pure compound, we must know the molecular weight, MW, of the compound. From this information we use eq. 14 to calculate N.

$N = m/MW \times 6 \times 10^{23}$ number of molecules of molecular   (14)
                                weight MW in a mass m

Similarly, to calculate the number of photons, N, in a beam of monochromatic light of energy E, we must know the frequency (comparable to the molecular. MW) or wavelength of the light. From this information we use eq. 15 to calculate N.

$N = E/h\nu \times 6 \times 10^{23}$ number of photons of frequency   (15)
                                ν in a beam of energy E

Notice that the ratio m/MW provides a feeling for the "size" of a molecule. If MW is larger for a given molecule than for a given m, the number of molecules is small relative to the same mass of a second molecule with a small

MW. Similarly, for a given total energy, a large value of ν means a smaller number of photons relative to a small value of ν. Thus, the notion of "size" of a molecule in the sense of MW is carried over to the notion of "size" of photons in the sense of frequency of light.

The advent of lasers has provided photochemists with intense sources of light (intensity = photons s^{-1} in a given volume) and with the ability to deliver a large number of photons to a system in a very short period of time. Power is a measure of the ability to deliver energy in a given period of time, and a convenient unit to express power is the watt (= joule/sec). It is now possible to deliver 1 J of energy to a system via absorption of a pulse of light from a laser in time periods of the order of 10^{-6} to 10^{-9} sec. This corresponds to powers of 10^6 to 10^9 watts (megawatts to gigawatts).

For a steady continuous source of light, the intensity, I, is given by

$$I \text{ (quanta/sec)} = \quad 5 \times 10^{15} \times \lambda(nm) = P \text{ (watts)} \qquad (16)$$

$$I \text{ (einsteins/sec)} = 8 \times 10^{-11} \times \lambda(nm) \times P \text{ (watts)} \qquad (17)$$

The idea of intensity of a continuous light beam is analogous to the idea of "steady state" concentration of a reactive intermediate, whereas the sudden injection of a pulse of photons is analogous to the idea of quickly adding a certain molar quantity of a reagent.

The steady state concentration [M*] of an excited molecule, M* (or intermediate) produced by light absorption is given by

$$\text{Steady state } [M^*] = I \text{ (einsteins/sec) } \tau_{M^*} \text{ (sec)} \qquad (18)$$

Where I is the intensity of light absorbed and τ_{M^*} is the lifetime of M* under the experimental conditions. As an example, suppose that $I = 10^{19}$ photon/sec = 1.65 $\times 10^{-5}$ einsteins/sec (a value typical of an intense commercial light source) and τ_{M^*} = 10^{-5} sec (a value typical of T_1 states) and the sample is contained in a volume of 1, then

$$[M^*]_{S1} = 1.65 \times 10^{-5} \times 10^{-9} \sim 2 \times 10^{-14} \text{ M} \qquad (19)$$

$$[M^*]_{T1} = 1.65 \times 10^{-5} \times 10^{-5} \sim 2 \times 10^{-10} \text{ M} \qquad (20)$$

There are very low concentrations, indeed. The concentration of M* may be increased by (a) focusing the exciting beam so that the same intensity is absorbed by a smaller volume; (b) increasing the lifetime of M*. Lasers are

capable of being focused so that for a given energy, a very high concentration of photons (I) may be continuously delivered to a small volume.

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.

$$\Phi \text{ (quantum yield)} = \frac{\text{molecules reacted}}{\text{photons absorbed}} \qquad (21)$$

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:

$$\Phi_F \text{ (quantum yield of fluorescence)} = \frac{\text{number of photons emitted from S}_1}{\text{number of photons absorbed}} \qquad (22)$$

$$\Phi_P \text{ (quantum of phosphorescence)} = \frac{\text{photons emitted from T}_1}{\text{photons absorbed}} \qquad (23)$$

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

1.15   Plan of the text

Now that we have some a broad overview of what modern molecular organic photochemistry is all about and the paradigm approach that will be adopted, we review the plan of the text. We have seen that the concepts of

structure, energetics, and dynamics are crucial for understanding molecular photochemistry. For starts we need to understand the structures of the species R, *R, I and P of Scheme 1.1. **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 is the topic of Chapter 2.

Given the existence of various possible structures, we next consider the problem of the interconversion of an initial structure into a different final structure, i.e., the processes R + hv → *R, *R → I, I → P and *R → P. This problem is approached in **Chapter 3**, "*Transitions between Molecular States*" which ties together the concepts of structure, dynamics, and energetics in terms of potential-energy surfaces, which allow an effective and concrete visualization of the possible and plausible pathways by which molecular states may be interconverted.

Chapter 4, "*Radiative Transitions Between States*", reviews how radiative transitions (absorption, R + hv → *R and emission, *R → R + hv) can be visualized and how they are qualitatively and quantitatively related to molecular structure. **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 that correspond to chemical reactions, and we develop a theory for the 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, hν. The *primary photochemical* processes *R → I and *R → 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 on photochemical reactions.

Chapter 8, "Mechanistic Organic Photochemistry", will review the ways that, plausible and probably, 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 Scheme 1.1 and the working paradigm of Scheme 1.2 will take on a concrete character though the examination of many examples which can be coordinated through the paradigms.

The final three chapters will describe a series of important "special topics" in molecular organic photochemistry. **Chapter 13** "The Role of Molecular Oxygen in Photochemistry", will explore, as a special topic, the role of ubiquitous molecular oxygen in photochemical processes.

Chapter 14, "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 15, "Photochemical Sensors and Switches", will explore, as a special topic, some important applications of photochemical reactions.

References

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