

ELEMENTS OF ORGANIC PHOTOCHEMISTRY

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Preface

In the past fifteen years organic photochemistry has undergone a greater change and has stimulated more interest than probably any other area of organic chemistry. What has resulted is a population explosion, that is, an ever-increasing number of organic chemists are publishing important and exciting research papers in this area. Professor Bryce-Smith in the introduction to a recent volume of the Specialist Periodical Report (*Photochemistry*, Volume 6), which reviews the photochemical literature in yearly intervals, states that "the flood of photochemical literature is showing some signs of abatement from the high levels of two or three years ago" However, Volume 6 of that periodical contains 764 pages of excellent but very concise reviews.

We expect the development of the mechanistic aspects of organic photochemistry to continue at the present pace as new methods are developed to probe in increasing detail and shorter time scales the photochemical dynamics of both old and new photoreactions. Since photochemistry is no longer the sole domain of the specialist, it is relatively safe to predict a dramatic increase in the near future of the synthetic and industrial uses of organic photochemistry.

In part, this book has grown out of photochemistry courses given at Hopkins during the past 13 years. In order to maintain a reasonable length, we have found it necessary to select our topics carefully, and consequently many interesting photoreactions have had to be omitted. Our goal was not to produce an encyclopedic volume but rather a textbook designed so that a student, having a background in organic and physical chemistry, can start this text and proceed to the point where he or she can read and comprehend the significance of current photochemical literature and initiate research in

this area. To accomplish our goal we have interwoven, in a gradual manner, photochemical and photophysical concepts along with the chemical and physical techniques necessary to understand a variety of photoreactions. Many of the specific examples presented in detail reflect the interests of the authors. However, the extensive documentation provided in the text will allow the student to seek out other examples of interest.

We wish to thank Ms. Tami Isaacs for her help in proofreading the text and to acknowledge our great debt to former teachers, our colleagues, and the photochemical pioneers of each generation.

Baltimore, Maryland

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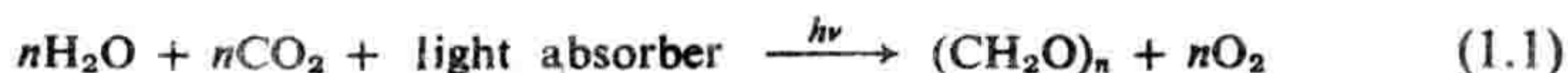
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Basic Photophysical and Photochemical Concepts

1.1. INTRODUCTION

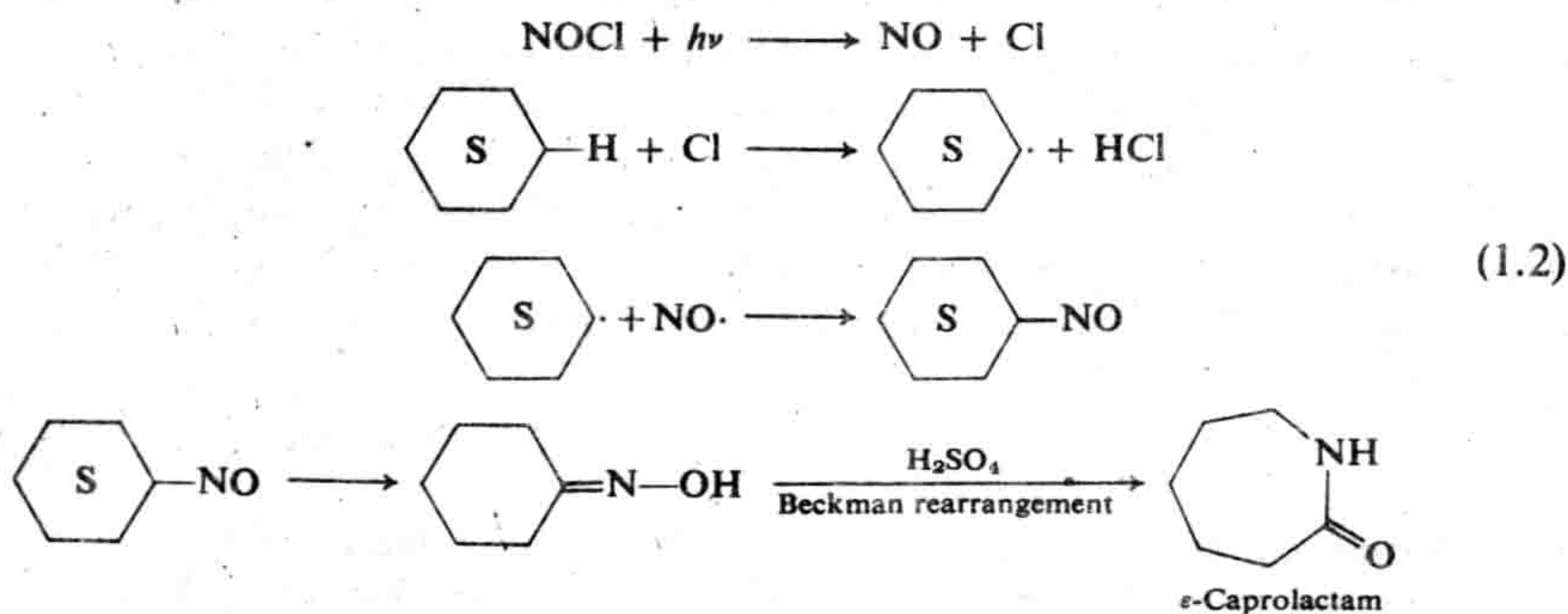
Although man was not present to observe the event, the first photochemical reaction probably occurred billions of years ago. High-energy solar radiation ($\lambda < 2000 \text{ \AA}$) undoubtedly was an important factor in the development of large molecules, polymers, and eventually polypeptides from the primitive earth's reducing atmosphere (methane, ammonia, and hydrogen). However, from man's point of view, the greatest photochemical "breakthrough" occurred when the first few quanta of light were absorbed by a rudimentary photosynthetic unit, resulting in the release of molecular oxygen to the atmosphere, thus paving the way for all higher life:



Considering the importance of photochemistry in man's history, it is surprising that it is only within the past ten to fifteen years that photochemical reactions have been extensively investigated. However, during this period the field has developed at such an explosive rate that the amount of literature reporting new photochemical discoveries increases daily. This is not to say that photochemistry was totally neglected prior to the 1950's. In fact, as far back as 1912, one of the earliest photochemists, Giacomo Ciamician, realizing the enormous potential of photochemistry, predicted: "Solar energy is not evenly distributed over the surface of the earth; there are privileged regions, and others that are less favored by the climate . . . On the arid lands

there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere.”* Although the realization of Ciamician’s prediction would be attractive in view of today’s pollution-troubled industry, much of the recent rapid progress in photochemistry has arisen from the technological development of convenient and efficient high-intensity light sources, making dependence on the whims of the sun unnecessary. Consequently a reaction that fifty years ago might have taken weeks of irradiation with sunlight to obtain a yield of product large enough to characterize can now be done in the laboratory in a few hours on a rainy day. Of equal importance in the burgeoning of this field have been the development and utilization of spectroscopic techniques and the development of molecular orbital theory. Using information obtained from these sources, the organic photochemist may in the future be able to both predict and control the products of his photochemical reaction.

Future developments are expected not only to yield a greater understanding of the mechanisms of many photochemical reactions, but also to provide a means for the adaptation of these reactions to large-scale industrial syntheses. A glimpse of the latter is seen in the production of ϵ -caprolactam (Nylon 6 monomer) by the Toyo Rayon Company using the photonitrosation of cyclohexane. In this process nitrosyl chloride is cleaved by light and the following sequence of reactions takes place:



One plant in the Nagoya (Japan) region alone is capable of producing 120 tons of caprolactam *per day*. In addition, the Nylon 12 monomer, lauryl lactam, is being prepared by a similar route from cyclododecane.

In this chapter we introduce many of the basic concepts and the vocabulary necessary for the study of photochemistry.

* Quoted in: R. C. Cookson, *Quart. Rev.* **22**, 423 (1968).

1.2. ENERGY DISTRIBUTION IN THE EXCITED MOLECULE

The various intramolecular processes initiated by light absorption are illustrated schematically in Figure 1.1. Such a schematic representation of the energy levels and photophysical processes which can occur in the excited

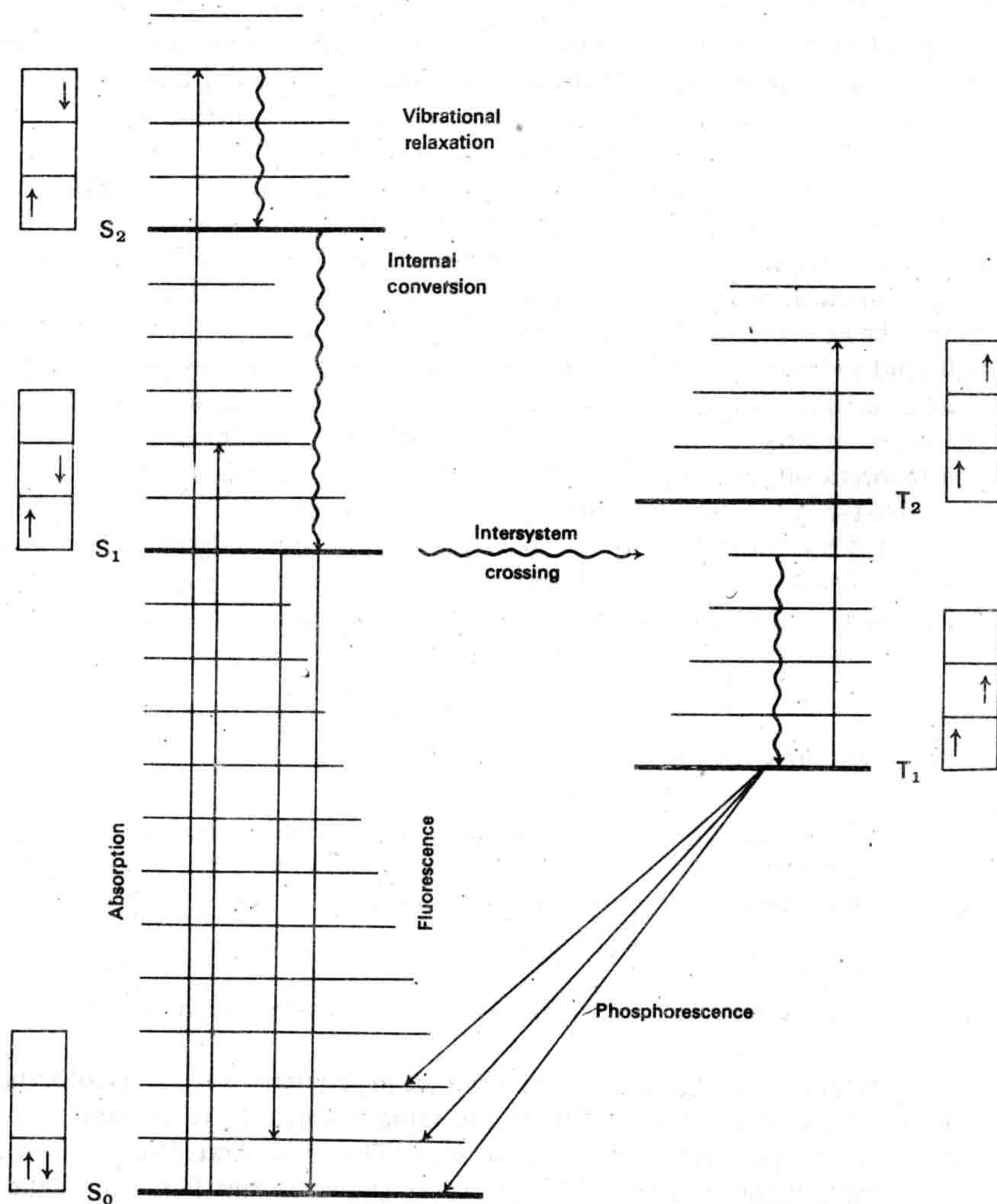


FIGURE 1.1. Jablonski diagram.

molecule is commonly called a *Jablonski diagram*. In this diagram the vertical direction corresponds to increasing energy; the horizontal direction has no physical significance. The electronic states are represented by the heavy horizontal lines; the symbols S_0 , S_1 , and S_2 represent the ground state and first and second excited singlet states (electron spins antiparallel or paired), respectively, and T_1 and T_2 represent the triplet states (electron spins parallel or unpaired). These sets of energy levels are frequently referred to as the singlet and triplet manifolds. Excitation is represented by the promotion of one electron from the ground state (S_0) to a higher electronic level. The position and spin of the excited electron relative to those of the electron in the ground state are noted in the boxes. Finally, the light horizontal lines correspond to the vibrational levels of the electronic states.

The lowest triplet level (T_1) is placed below the lowest excited singlet level (S_1), in accordance with Hund's rule, which states that the state of maximum multiplicity (highest number of unpaired electrons) lies at the lowest energy. Since two electrons having the same spin quantum number (spins unpaired) cannot be at the same place at the same time (Pauli exclusion principle), they will tend to avoid each other. This results in a lowering of the energy of the state since there is less repulsion between the negatively charged electrons in the triplet relative to the corresponding singlet state in which the electrons can theoretically be in the same region in space simultaneously. Each of the radiative-type processes (light absorption, fluorescence, and phosphorescence), designated by straight lines, and nonradiative processes (internal conversion and intersystem crossing), designated by wavy lines in Figure 1.1, will be briefly described in this section and discussed in greater detail in later chapters.

1.2a. Light Absorption

Molecular excitation by light absorption takes place during the period of one vibration of the exciting light wave. For light with a wavelength λ equal to 300 nanometers (nm), this corresponds to 10^{-15} sec:

$$\text{frequency } \nu = c/\lambda = (3 \times 10^{10} \text{ cm/sec})/(3 \times 10^{-5} \text{ cm}) = 10^{15}/\text{sec}$$

The time for excitation equals the time for one cycle, which equals $1/\nu$, or 10^{-15} sec.

This time period is too short for a change in geometry to occur (molecular vibrations are much slower). Hence the initially formed excited state must have the same geometry as the ground state. This is illustrated in Figure 1.2 for a simple diatomic molecule. The curves shown in this figure are called Morse curves and represent the relative energy of the diatomic system as a