Physical Processes in Radiation Biology

Proceedings of an International Symposium Sponsored by the U.S. Atomic Energy Commission and held at the Kellogg Center for Continuing Education, Michigan State University

EDITED BY

LEROY AUGENSTEIN, RONALD MASON, and BARNETT ROSENBERG

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PREFACE

The core problems of radiation biology are concerned with how high energy packets (photons or particles) are absorbed, distributed, and utilized in biological systems. There are many naturally occurring biological pathways—in structures such as chloroplasts, visual cells, and skin melanins—which normally handle energy packets on the order of a few electron volts. In such organelles the absorption act is relatively simple, and the absorbing pigments are, at present, well characterized. If, however, one asks what are the next steps in the distribution and utilization of the absorbed energy, no clear answers exist, although many mechanisms have been postulated. In the case of higher energy packets, a simple understanding of even the primary act of absorption does not exist, and greater complexities arise since distribution and "utilization" presumably involve non-normal biological pathways.

The International Symposium on Physical Processes in Radiation Biology, the heart of which is represented by the papers and discussions contained in this volume, was called to discuss these core problems. It brought together scientists of many disciplines, biologists, biophysicists, physical chemists, and physicists, all of whom share a common interest in these problems, but all of whom also bring different backgrounds and techniques to their research. Such cross-fertilization is essential, for the statistical improbability of finding a biologist who can handle exciton theory, is almost matched by the population density of physicists who dare work with the complexities of a living organism. Thus, this volume will have something of value for most scientists, and much of value for radiation biologists.

This symposium is, in many ways, a continuation and development of the Symposium on Bioenergetics, sponsored by the U.S. Atomic Energy Commission and held at Brookhaven National Laboratories in the Fall of 1959. A major objective of that conference was to act as a meeting ground for biologists and physical scientists. That the symposium was at least partially successful in its aim is attested to by a large number of recent publications.

It also became apparent that this first symposium inadequately covered a number of vital topics. The present volume reflects an attempt to correct some of these omissions by emphasizing the nature of exciton processes,

and the mechanisms of charge transport in biological materials, the interactions of fast and slow electrons with model systems, the importance of liquid structures in determining the development of radiation damage and, finally, the nature of the metastable species formed.

For the radiation biologist, the papers presented and the final discussions will help to provide some definite answers to questions such as:

(1) How extensive is exciton migration in biological systems? How much orderliness, or more importantly, how little orderliness is consistent with extensive exciton migration? Do liquids have appropriate configurations for extensive excitation transfer? In particular, how well are the conditions fulfilled in water?

(2) What is the nature of the initial interactions between electrons and absorbing molecules? How much correspondence is there between the events observed in gases and those in condensed systems? What is the distribution of absorbed energy among various excitation processes? In particular, how many ionizations actually occur in condensed systems?

(3) What is the importance of charge migration in energy transfer processes in different biological systems? What is the significance of higher excited levels in charge migration and energy transfer? What is the nature of the hydration of electrons and protons in aqueous systems?

The above list illustrates the kind of questions which were considered during the planning of the conference. Clearly, this list is not all-inclusive since additional and perhaps more crucial problems are to be found in these proceedings. We should also emphasize that the questions raised and the principles and techniques discussed have pertinence in most of the major areas of biology (e.g., in vision, photosynthesis, carcinogenesis, macromolecular organization, perhaps nerve functioning, and a host of others).

We are very appreciative of the financial support provided by the U.S. Atomic Energy Commission, and also the fact that their staff have shown a continuing interest in this area of research. We also wish to express our sincere thanks to the College of Natural Science and the Kellogg Center for Continuing Education for serving as sponsors for the symposium.

THE SYMPOSIUM COMMITTEE:
Leroy Augenstein
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June, 1964

CONTENTS

ABSORPTION, EXCITATION, AND TRANSFER PROCESSES IN MOLECULAR SOLIDS

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I. Introduction

In molecular solids light absorption may produce an excited state of the whole solid, or a large zone of it, and not a stationary state in which the excitation is localized on one molecule. Moreover, in terms of a non-stationary state approximation, the transfer of excitation from one molecule to another does not take place by emission and reabsorption of radiation, but through the static coupling of the two molecules without the "mediation" of a free photon. These two statements are associated with a particular approximate method of dealing with the absorption of ultraviolet excitation in condensed phases, broadly described as the exciton method. In the following paper those results of the application of this method to molecular crystals will be described that may have relevance to biological systems.

The approximate character of the exciton description of phenomena in solids lies in ignoring much of the complexity of the situation in which the radiation field, the exciton field, and the phonon field are interacting together. Separate treatment of the exciton part of the problem implies assumptions about the magnitudes of the couplings between the fields that may not be well based. However, in the phenomena to be described there is a degree of agreement with experiment that justifies it to a considerable extent.

Excitation processes in molecular crystals and in solids with a lower degree of organization such as mixed crystals and solutions in glassy solvents have usually been treated theoretically under rather restrictive assumptions. The results will have validity for the migration of excitation and other phenomena in biological systems only if these same assumptions continue to hold. The most important is that the centers, or sites, in which the excitation can be localized are far enough apart to interact with one another only weakly. In molecular solids like crystalline benzene or naphthalene the excitation sites are individual molecules, which interact (in their

ground states) only through van der Waals coupling. Formally, in an array of interacting systems the requirement is that the Hamiltonian for the system should differ from the sum of Hamiltonians for the separate parts by correcting terms that are small. If we write $\mathbf{H}_k$ for the kth molecule Hamiltonian and $\mathbf{V}_{lk}$ for the interaction between molecules k and l the total Hamiltonian is given in expression (1)

$$\sum_{k=1}^{N} (\mathbf{H}_k + \sum_{l>k} \mathbf{V}_{kl}) \tag{1}$$

In this expression the interaction terms are taken to be small compared with the free-molecule terms. If this were not true, individual excitation units between which transfer could take place could not be distinguished, and some other description appropriate to a tight-binding limit would have to be used.

The possibility of using the same model for excitation transfer in biological systems rests on identifying weakly interacting localized excitation sites belonging to the same or to different large molecules. These are the active sites for the long wavelength ultraviolet absorption; one can suppose them to be aromatic residues in the various amino acids. These sites will usually fall into several sets, the members of one set being the same in structure and nearly the same in excitation energy, but different from those in other sets.

While it seems reasonable to postulate that weakly coupled uv absorption sites exist in biological systems, one cannot expect to find crystalline regularity in the full sense. Even in a biological system with all the excitation sites of one type the differences from a crystalline molecular array would be (1) lack of translational symmetry, and (2) spread of excitation energies of absorbing units over a range, i.e., a range narrow compared with the mean excitation energy. Thus the analogy between exciton processes in a perfect molecular crystal and those in an irregular network of absorbing centers in a biological system cannot be expected to hold closely; but it provides a useful starting point, and some of the refinements necessary are suggested by the properties of imperfect crystals, such as those containing impurity centers or traps.

II. Absorption by Pure Molecular Crystals (*1–3*)

Let us suppose that the terms $\mathbf{V}_{kl}$ in expression (1) are small, allowing the excitation processes in a crystal to be described in terms of the free molecules and their electronic states. In order to form an idea of the scale of events we note that the interaction energy between two neighbor molecules in a crystal, one excited and the other not, usually lies in the range 100–4000

cm^{-1}, in the equivalent wave number units. The lifetime of the excitation on one site is then in the range 3×10^{-13} to 10^{-14} sec. It is several orders of magnitude shorter than the radiative lifetime. Thus radiation from an excited pure crystal will almost certainly take place from a delocalized crystal excited state. It is easily shown that small lattice deformations caused by excitation, or defects, will not alter this situation; bigger disturbances, such as the presence of impurity traps, or perhaps gross surface imperfections in the crystal structure will be necessary to change it.

If we assign 100 cm^{-1} as the lower limit of interaction energies it follows that the transfer times will be shorter, even if only slightly shorter, than the time required for a displacement of the lattice. Lattice fundamentals in simple molecular crystals are of 100 cm^{-1} or less, the higher values in this range applying to torsional oscillations. Thus at least in most cases the absorption process in a pure molecular crystal is to an excited state of the undisplaced lattice. It cannot usually be said, however, that it takes place in a lattice of *rigid molecules*. The frequencies of molecular vibrations, in molecules of about the complexity of anthracene, fall in the same range, namely 100–3500 cm^{-1}. Thus an excited molecule may have time to relax into a new equilibrium configuration before transferring its excitation. In a very strongly coupled case, with coupling energy near 4000 cm^{-1}, excitation transfer is quicker than molecular deformation. But couplings of this strength are rare in molecular crystals, and are out of the question in biological systems. The more interesting cases are those of coupling energies less than the energies of skeletal deformation motion of about 1000 cm^{-1}; then a molecule changes shape and size to some extent before transferring its excitation, and the whole process involves nuclear, as well as electronic, motion.

In a pure crystal we let the ground state wave function for the molecule on the ith site of the pth unit cell be ϕ_{ip}, and that for its rth excited state be ϕ_{ip}^r. The zeroth order excited state wave function for the crystal, with excitation localized on the ipth site is given in expression (2)

$$\phi_{ip}^r = \phi_{11}\phi_{12}\cdots\phi_{ip}^r\cdots\phi_{h,\,N/h} \tag{2}$$

The product includes all the sites in the crystal, N in all, distributed over h equivalent sites in each unit cell. Wave functions giving an equal probability of excitation to every molecule in a given position in the unit cell are given in expression (3)

$$\Phi_j(\mathbf{k}) = \sqrt{\frac{h}{N}} \sum_q e^{i\mathbf{k}\cdot\mathbf{r}_{iq}} \phi_{jq}^r \tag{3}$$

In light absorption the wavelength is so much greater than the lattice spacing that the active upper states in absorption are those for very small