Meetings

Photosensitization in Solids

Photosensitization refers to the enhancement of the response of a system to light of longer, usually visible, wavelengths. The significant response may be chemical, optical, electrical, or biological, and frequently a combination of effects. Most inorganic and organic crystals, glasses, polymers, and biological structural materials absorb little visible light so that sensitization makes possible the utilization of more readily available long wavelengths. Furthermore, the energy per photon is smaller and photosensitized systems can operate at high efficiency. The sensitizer may be incorporated in the substrate as a "dopant," located immediately adjacent to it as an adsorbed molecule, monolayer, or multilayer, or else situated at some distance from the reactive region. In order to discuss fundamental aspects of photosensitization relevant to different systems and to consider reports of recent work in specific areas, an international conference on photosensitization in solids was held at the Illinois Institute of Technology, Chicago, 22–24 June 1964.

The basic problems of photosensitization are concerned with the elementary processes involved in light absorption, conversion, and utilization. G. Wilse Robinson (California Institute of Technology), discussing energy transfer mechanisms, suggested that a useful model for complex chemical and biological systems consists of two active molecules connected by a molecular coupling system. The response to optical excitation was discussed in terms of possible elementary events: vibrational relaxation, electronic relaxation, emission of radiation, resonance and nonresonance excitation transfer, absorption of a second quantum, and energy escalation by exciton-exciton processes. The initial processes of light absorption and emission are reasonably well explained for isolated molecules by the theories of atomic and molecular spectroscopy. This is not the case, however, for molecules which interact with their surroundings. This point was emphasized by the report of E. Lendvay (Research Institute for Technical Physics of the Hungarian Academy of Sciences, Budapest) on the luminescence of dyes adsorbed on inorganic substrates. For example, the wavelength maximum and bandwidth of the aqueous fluorescein fluorescence is altered markedly when the dye is adsorbed on $Sr(OH)_2$, $Ca(OH)_2$, and $Mg(OH)_2$. In cases where the substrate was luminescent, for example ZnO and ZnS, the fluorescence of both the dye and the substrate was excited by ultraviolet light. The results were explained by the influence of the substrate on the probability of radiationless transitions from the vibrational states of the excited dye.

An even more striking example of the effect of a matrix on molecular excitation was described by A. C. Albrecht (Cornell University) in a report on the photoconduction of 3-methylpentane rigid glasses containing *N,N,-N′,N′*-tetramethylparaphenylenediamine (TMPD). It is known that light absorption by TMPD at 77°K oxidizes it to Wurster's Blue. However, it is not apparent how this can be done with 3.5-electron volt photons, since the gaseous ionization potential of TMPD is 6.5 electron volts. Albrecht and his co-worker, G. E. Johnson, have found that the glass is photoconducting and that the rise of primary photocurrent depends quadratically on the incident light intensity, which they interpret by means of a two-photon process. Furthermore, after excitation of primary photocurrent it was possible to generate a "spike" photocurrent with green light and a quasi-steady state photocurrent with near-ultraviolet light. The dependence of these effects on viscosity, electric field strength, and oxygen led to a model in which the complete ionization of TMPD is a two-photon process, with a Franck-Condon vibronic state of the first excited electronic state as the short-lived intermediate. The "spike" induced by green light was attributed to excitation of electrons trapped in the matrix, and the quasi-steady state photocurrent to a metastable intermediate state attained after absorption of the first photon.

Situations are known where excitation energy migrates for considerable distances from the site of initial light absorption prior to utilization. The exciton transfer of energy between like molecules in a lattice differs from transfer by inductive resonance, such as described by Th. Foerster. New work on the former was reported by A. Schmillen (Physikalisches Institut der Universität Giessen) where energy transfer from a host aromatic hydrocarbon crystal to low-concentration guest molecules was investigated. A phase fluorimeter was used to measure the decay times of the host lattice fluorescence, of the direct guest molecule fluorescence, and of the guest molecule fluorescence excited by transfer from the host lattice.

The case of fluorene containing pyrene is particularly interesting in that the fluorescence of a minute anthracene impurity was observed, but not at higher pyrene concentrations. It was suggested that anthracene-pyrene complex centers are present in the fluorene lattice; the presence of such centers indicates a direct energetical coupling between the two molecules. At higher pyrene concentrations the long wavelength "excimer" fluorescence —that is, light emission by an excited dimer—was observed. Exciton generation in inorganic crystals is interesting also, particularly in that characteristic lines can be identified on the absorption spectra. A. Coret (University of Strasbourg) reported work performed in the laboratory of S. Nikitine on the relationship between exciton absorption and photoelectric effect of single crystals of Cu_2O, HgI_2, PbI_2, and GaSe. Coret pointed out that exciton decay can lead to photoconduction when one carrier is trapped and the other is elevated to a conduction level. For the case of Cu_2O, which was studied in most detail, the absorption spectrum at 4°K shows maxima corresponding to indirect band-to-band transitions, to the first-class and second-class exciton spectra, and to the intrinsic absorption. The photoconductivity spectrum at 4°K shows sharp maxima at the peaks of the second-class exciton spectrum and sharp minima at the peaks of the first-class exciton absorption spectrum. The minima were explained by the high surface absorption and were reversed for some exciton lines on related measurements of the photoelectromagnetic effect and the photo-Hall effect.

Direct evidence for long-range radiationless energy transfer between unlike molecules was presented by H. Kuhn (Physikalisch-Chemisches Institut of the University of Marburg) in a remarkable paper. Monolayers of sensitizer dye were separated from monolayers of acceptor dye by multilayers of barium stearate or arachidate, produced by the method of Langmuir and Blodgett. The irradiation of sensitizer dye with light, absorbed only by the sensitizer, excited the sensitizer fluorescence when the separation distance was approximately 1000 Å. Only the fluorescence of the acceptor dye was excited when the distance was 50 Å. Since reabsorption by the monolayer of the acceptor dye was negligible, this result is direct proof of radiationless energy transfer. Good numerical agreement with the Foerster theory was obtained for various sensitizer-acceptor pairs, with characteristic transfer distances of 70 to 100 Å. When the acceptor dye was nonfluorescent, it still could quench the fluorescence of sensitizer dye and was bleached. Furthermore, a nonfluorescent sensitizer dye could excite fluorescence in the acceptor; the rate of bleaching of the acceptor showed that the excited singlet state of the sensitizer was the transfer state. Direct evidence for transfer was obtained also from a cyanine dye monolayer to a gold film, from a dibenzoylmethane complex of europium (III) to a gold film, and from a dye monolayer to a cadmium sulfide film. Other results reported by Kuhn were capacitors containing a single monolayer of barium stearate which could maintain 10^7 v/cm, monolayers of merocyanine dye between stearate layers which were photoconductive, and monolayer donor-acceptor systems (for example, perylene and *o*-chloranil) sandwiched between layers of stearate which were photovoltaic.

In view of the evidence for long-range energy transfer it might be supposed that this process adequately explains how light absorbed in a dye sensitizer can excite conduction in an adjacent inorganic substrate. A. Terenin and his associates (University of Leningrad) have given continued support to this view, and submitted a written paper for the case of *n*-type dye films on *p*-type semiconductor substrates. However, for *n*-type substrates their latest results do not distinguish between charge and energy transfer but do impose an upper time limit on the former of 10^{-9} second. Nevertheless, sensitizing dye films are photoconductors and photovoltaic couples are produced between such dye films and semiconducting substrates. Therefore, there is considerable evidence to favor charge transfer sensitization. Speaking from this viewpoint, R. C. Nelson (Ohio State University) proposed three regimes of sensitization: isolated sensitizer molecules, close-packed monolayers, and multilayers. The principal requirements for charge-transfer sensitization by the last two cases are: (i) charge carriers must be separable in the sensitizer or sensitizer-substrate system in reasonable yield; (ii) transfer of a carrier to the substrate must be energetically possible; and (iii) the pair of charge carriers must possess a large fraction of the energy of the photon absorbed. H. Meier (Staatliches Forschungsinstitut für Geochemie, Bamberg) continued the discussion of charge-transfer sensitization and proposed a "*pn*-photoeffect" theory in which equilibration of the sensitizer and substrate Fermi levels is necessary for sensitization, with the establishment of a photovoltaic potential. This theory explains how *n*-type dyes can sensitize *n*-type and *p*-type substrates and vice versa. The results of photovoltaic measurements on organic dye–semiconductor systems were reported; the observed polarities are in agreement with the predictions of the theory.

J. Bourdon (Kodak-Pathé, Paris) reviewed work on sensitization of zinc oxide and silver halide photographic blackening and noted that they are closely related processes, an electronic step being followed by a primary chemical step. Emphasizing this point, S. Namba (Institute of Physical and Chemical Research, Tokyo) reported that certain cyanine dyes on zinc oxide powder show long wavelength "J band" absorptions, which may be caused by oriented aggregates of dye molecules. Sensitization of electrical conduction in the substrate is particularly high for irradiation in the "J band"; such sensitization closely resembles the supersensitizing action of "J band" aggregation on photographic emulsions. G. Oster (Polytechnic Institute of Brooklyn) reported the effect of oxygen in the photoconductivity, luminescence, and photochemical reactions of zinc oxide. He proposed that excited dye in the triplet state interacts with adsorbed oxygen to give an unstable photoperoxide which can oxidize a substrate, such as allyl thiourea, and thus restore the dye.

A number of papers were presented on the sensitizing properties of charge-transfer complexes, that is, highly colored compounds produced by the reaction of an electron donor with an electron acceptor. H. Hoegl (Institut Battelle, Geneva) reported work on the sensitization of polymeric *N*-vinylcarbazole and other host substances with a large number of donor and acceptor compounds. Photosensitivity was investigated by an ingenious method in which the photo-induced discharge rate was measured after charging from a corona. Donor behavior is shown by π-electron systems with electron-repelling groups, such as amino, alkylamino, alkoxy, acetoxy, and alkyl, and acceptor behavior is shown by π-electron systems with electron-attracting groups, such as nitro, cyano, carbalkoxy, acetyl, carboxylic acid anhydride, and halogen. The unique properties of such compounds were further emphasized by G. Tollin (University of Arizona) who prepared single crystals of a riboflavin-hydroquinone-acid complex and reported that both electrons and holes carry photocurrent, and that the irradiated crystal gives an EPR signal which he associated with a riboflavin semiquinone.

Application of solid state arguments to biological sensitization received considerable attention. The essential problem is that the solid state physics which must be applied is not very well understood. In this connection, R. Mason (University of Sheffield) discussed the molecular exciton model for weakly bonded molecular aggregates. Noting that biological systems do not have long-range translational symmetry, Mason calculated the wave functions for one-dimensional exciton motions where the interaction energy varies gradually with position. It was found that tunneling of the quasi-particles into energetically forbidden regions is possible. Mason suggested that small irregularities may have considerable effects on the lowest states of the exciton band and that energy transfer for more than 50 Å in biopolymers is not likely.

Nevertheless, it may not be the case that only long-range translational symmetry will satisfy the basic requirements for describing biological sensitization by solid state concepts. As noted by W. Arnold (Oak Ridge National Laboratory), nature has been developing suitable mechanisms for 2 billion years. Further information on the structure of photoreceptors was presented by J. J. Wolken (University of Pittsburgh); his data were based on high-resolution electron microscopy. Simplified structural models for the chloroplast and retinal rods were proposed; these models permit maximum efficiency for energy capture and transfer by the pigments. The photoreceptors resemble a quasi-crystalline network, in which the pigment-lipid-protein complexes have the proper molecular shape for stabilization. Arnold proposed an electron-hole model to explain the primary step in photosynthesis, whereby a first exciton produced by light absorption in a photosynthetic unit dissociates to give a trapped electron and a free hole, and a second exciton dissociates to give a trapped hole and a free electron. The trapped carriers are available for the initial chemical oxidation and reduction processes, and the free carriers recombine eventually to give the delayed light which accompanies photosynthesis. The saturation of traps explains why the quantum yield decreases at high light intensities. Arnold emphasized that his model poses two questions, the first being whether two 1.8 ev excitons can dissociate as required, and the second concerning how electrons and holes move in a unit of 500 to 600 molecules. R. Livingston (University of Minnesota) presented a "prejudiced review of solid state mechanisms in photobiology" in which he noted that the recent great improvements in methods of detection of extremely small transient changes in the physical properties of biological systems require cautious interpretation. Referring to the model of Arnold, Livingston suggested that delayed light can be explained by induced chemiluminescence. The question was not resolved.

The proceedings were reviewed by a panel including R. C. Nelson, B. H. Carroll (Rochester Institute of Technology), R. K. Clayton (Charles F. Kettering Research Laboratory), J. F. Hornig (Dartmouth College), and J. R. Platt (University of Chicago). Discussion was given to a request from Platt that theoretical scientists emphasize concepts which can be tested with crucial experiments.

Papers given at the conference will be published in the *Journal of Physical Chemistry*. Support was provided by the Office of Naval Research, Air Force Cambridge Research Laboratories, and the National Institutes of Health. The conference will reconvene in 1967 at the University of Arizona, Tucson.

L. I. GROSSWEINER
Illinois Institute of Technology, Chicago

Mass Spectrometry

Mass spectral studies and allied topics were reviewed at the 12th Annual Conference on Mass Spectrometry held at McGill University, Montreal, Canada, 7–12 June 1964. This conference, sponsored by ASTM Committee E-14, marked the first time this meeting was held on a university campus and the first time it was held outside the United States.

The use of mass spectrometers to study gaseous reaction systems was discussed. Various problems have been encountered in relating the quantities of species detected by the mass spectrometer to the composition of the reactive mixture in the low pressure flames, flash photolysis, and pyrolytic flow reactors being sampled. P. Le Goff (University of Nancy) discussed calculations of the role played by surfaces in low pressure reactors attached to the ion source. Based on Monte Carlo type calculations, he concluded that, for the typical pressures and reactor dimensions in his apparatus, the region preceding the actual reactor was the primary region of reaction. J. Cuthbert (UKAEA, Harwell) pointed out that, for pinhole sampling from sources at atmospheric pressure, supersonic flow results downstream from the pinhole. The resultant cooling from isentropic expansion can cause considerable condensation which explains the polymeric ions that have been observed in these systems. A. W. Tickner (National Research Council, Ottawa) discussed observation of two different ion generation mechanisms in the negative glow of a glow discharge. From the shift of the peak ion concentration and the nature of the species, it was established that ions are formed by electron impact and by Penning-type ionization from collision with metastable atoms generated by electron impact.

Considerable disagreement about the rate constants for the reaction of oxygen atoms with oxygen and ozone has arisen in the study of the role of these species in atmospheric aeronomy. This controversy now appears to be clarified by the results of several conclusive experiments reported by Schiff. Two reactive species (O and O_2^*) were detected in the laboratory system. It was found that the relative amounts of these species were dependent on the operating pressure; this explains the variety of results yielded by different experiments. From analysis of their results, Schiff determined the contributions due to the oxygen atoms alone.

J. Berkowitz (Argonne) reported on extension of the Stern-Gerlach experiments to several polyatomic molecules by use of mass spectrometric detection. In this way a particular species in the molecular beam may be studied. Initial emphasis is on choosing one of two possible ground states of a molecule after qualitative observation; the choice is based on whether it possesses a magnetic moment.

Considerable effort has been devoted in recent years to experimentally obtaining monoenergetic electron beams for the study of fine structure in the ionization efficiency curves. The retarding potential difference source, originated by R. E. Fox and co-workers (Westinghouse), and electrostatic electron selectors (E. M. Clark, St. Francis Xavier University, and P. Marmet and L. Kerwin, University of Laval) have been the principal experimental approaches to this problem. Both techniques have been plagued by lack of sufficient signal-to-noise for application to anything but the simplest compounds. There was therefore considerable interest in the paper by J. D. Morrison (CSIRO, Melbourne). He discussed his recently published procedure for mathematically removing the effects of the electron energy spread from data obtained with a source having the normal energy distribution. The effective reduction in signal-to-noise ratio by this procedure is considerably less than that observed experimentally for the same gain in energy resolution. P. Marmet also discussed the effects of radial energy distribution in space charge, limited electron guns on the ionization efficiency curves based on