MASTER

Technical Progress Report

Radiationless Energy Conversion of Photoexcited
Triplet States of Organic Molecules

Progress Report for
May 1, 1975 - April 30, 1977

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I. Progress Report (5/1/75 - present)

A. Abstract

During the initial two years of our ERDA-supported research program we have attempted to define and understand the mechanisms active in the intersystem crossing processes of large polycyclic hydrocarbons and chlorophyll. To study these excited states energy conversion processes we have utilized optical detection of magnetic resonance spectroscopy, as developed in our laboratory, which is uniquely applicable to these molecular systems. Our results on polycyclic hydrocarbons have shown that an understanding of triplet state radiationless transitions in planar aromatic molecules can be obtained from a consideration of the symmetry-selected spin-orbit interactions and positions of available mixing states; this work provides a predictive model of triplet state nonradiative energy conversion with general applicability to aromatic systems. This treatment has been applied successfully to chlorophyll triplet state dynamics and provides a basis for the utilization of the triplet state of chlorophyll as a (nondestructive) spin probe into the makeup of more complex chlorophyll-containing systems in vitro and in vivo.

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A. Abstract

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B. Progress Report

Over the past two years our laboratory has been investigating the dynamical processes involved in the activation and deactivation of paramagnetic excited states of organic molecules. The overall goal of our research program is aimed at defining and understanding the mechanisms involved in the highly efficient intersystem crossing processes characteristic of a variety of large aromatic ring systems. To study these excited state energy conversion processes we have employed optical detection of magnetic resonance (ODMR) techniques which were developed in our laboratory. These techniques combine the sensitivity of optical

spectroscopy with the resolution of magnetic resonance and are uniquely applicable to molecular systems with fast nonradiative processes of excited state energy conversion. Our experiments take advantage of the fact that at low temperatures in an optically pumped triplet state intersystem crossing produces unique population distributions among the magnetic sublevels which can be altered by a microwave field. The microwave-induced population changes characteristic of a particular molecular system and molecular environment may be monitored by the optical spectrum of any level of the system, since all energy levels are dynamically coupled. Thus, in our laboratory we have demonstrated the generality of ODMR spectroscopy for studying triplet excited state dynamical processes. We have applied these techniques to the investigation of the following systems:

1. Triplet State Radiationless Transitions in Polycyclic Hydrocarbons.

The group of polycyclic hydrocarbons includes a number of molecules which exhibit weak phosphorescence and short (< 1 sec) triplet state lifetimes. These molecules have low energy triplet states and are expected to undergo efficient intersystem crossing (isc) from the triplet to the ground state by nonradiative transitions. The central importance of the aromatic hydrocarbons as model systems for the understanding of nonradiative transitions in organic molecules makes the measurement and characterization of such transitions of considerable interest. Recent theoretical work on triplet state radiationless transitions have attempted to calculate the rates of isc for the individual spin sublevels of the triplet state by evaluating specific vibronic and spin-orbit interactions expected to be important for polycyclic hydrocarbons, and generalizations of these results have been reported. We have completed a study of the zero-field EPR transitions and spin sublevel intersystem crossing rates for the lowest triplet states of a series of polyacenes by ODMR techniques. The rates of spin sublevel isc are primarily nonradiative in these systems, and our analysis of these, as well as

our analysis of the triplet state dynamics of several groups of polycyclic hydrocarbons investigated by other laboratories, suggests that nonradiative transitions for all aromatic ring systems may be qualitatively understood and predicted by a determination of the symmetry-selected one-center spin-orbit coupling mechanisms available to each triplet sublevel.

In all the data collected on T_1 spin sublevel lifetimes one feature of non-radiative triplet state isc processes in polycyclic hydrocarbons is evident. Superimposed on the general lifetime trend which follows from the positions of T_1 above the ground state (the energy gap law) is an isc selectivity among the T_1 spin sublevels. In all of the systems studied there is one, and in some cases two, spin sublevels which dominate the population and decay of the lowest triplet state. These data suggest that differences in T_1 isc rates reflect differences in spin sublevel properties among the various molecular systems and that mechanisms for T_1 nonradiative transitions can be deduced from an analysis of the spin sublevel properties in each molecule. Since isc involves transitions between states of different spin multiplicity, the important property to be considered is the relative value of spin-orbit coupling (soc) interactions for each spin sublevel. The most efficient spin-orbit coupling terms for $^3\pi\pi^*$ states of polycyclic hydrocarbons is well known to be to the $\sigma\pi$ states for each spin sublevel. Thus, the qualitative understanding of triplet state radiationless rates in polycyclic hydrocarbons reduces to a determination of the symmetry-selected $\sigma\pi$ soc mechanisms available to each spin sublevel.

The most obvious isc selectivity is reflected in the isc values for the out-of-plane spin sublevel τ_z for the hydrocarbons. The fact that the isc rate for τ_z is always less than for τ_x , τ_y (the in-plane levels) is indicative of the symmetry-selective spin-orbit coupling of the in-plane spin sublevels compared to the out-of-plane spin sublevel. τ_z requires higher order vibrational spin-orbit

coupling than τ_x , τ_y to mix with $\sigma\pi$ levels and is expected to be always less efficient than τ_x , τ_y in isc for all planar aromatic molecules (excluding those containing heavy atoms) with lowest $^3\pi\pi^*$ states, as long as the molecule retains a plane of symmetry. The only exception observed in polycyclic hydrocarbons is in a molecule (3,4-benzpyrene) for which there is evidence of distortion away from planarity. In fact, an increase in the value of k_z approaching that for k_x , k_y may be a useful indicator of molecular distortion in polycyclic hydrocarbons.

Further, in several of the molecules one of the in-plane T_1 sublevels dominates the isc dynamics, despite the fact that both τ_x and τ_y are expected to utilize the same order vibrational soc mechanism. All of the molecules displaying a dominance of isc through either τ_x or τ_y have C_{2v} symmetry or higher (excluding benzpyrene, as discussed above) and utilize $\sigma\pi$ levels of different symmetry in their soc schemes. It is known that the introduction of a nitrogen atom into an aromatic three-ring system increases the depopulating rates of T_1 spin sublevels, not by changing the mechanism of isc (still vibrational soc through one-center terms), but by introducing a more energy accessible level available for soc to symmetry-selected T_1 sublevels. A similar effect appears responsible for the differences in isc rates for τ_x and τ_y in high symmetry polycyclic hydrocarbons, whose symmetry-selected $\sigma\pi$ levels for spin-orbit interactions are at energies sufficiently different to affect the nonradiative rate constants.

The approach to determining radiative and radiationless transition rates for the T_1 sublevels of polycyclic hydrocarbons is similar in that in both cases one is interested in the one-center soc available for each sublevel. The main difference, however, is that the soc of T_1 to the $\sigma\pi$ levels for radiative transitions has the additional requirement of coupling to levels with appreciable oscillator strength to provide radiative intensity. For the linear polyacenes, for example, this requirement implies that one must include a large number of high

energy $\sigma\pi^*$ and $\pi\sigma^*$ states in considering the soc, since the low energy $\sigma\pi^*$ levels have vanishingly small oscillator strength (the allowed low energy $\sigma\pi^*$ levels are calculated to be very weak and have never been observed). However, for radiationless transitions one is looking primarily for available singlet character to efficiently mix into T_1 , and energy accessibility of the $\sigma\pi$ levels becomes an important factor. Thus, calculations of radiationless transitions may be more sensitive to the exact positioning of the $\sigma\pi$ levels than radiative transitions.

Further refinements of the theoretical attempts to calculate isc rates for the polycyclic hydrocarbons are needed to properly evaluate all contributing terms to the isc transition probabilities. However, our work has shown that a qualitative explanation for nonradiative transitions in planar aromatic molecules can be obtained by a consideration of symmetry-selected spin-orbit coupling interactions and the position of the mixing states, and provides a predictive model whose applicability to aromatic systems appears general.

The investigation described above represents a completed phase of our research project. Since we believe that we can understand the dynamical features of polycyclic hydrocarbons, we now wish to extend our studies to more complex systems as described below.

2. Triplet State Dynamics of Chlorophylls.

Deactivation of the lowest triplet states of chlorophylls is primarily by nonradiative isc into the ground state. Triplet state populations in chlorophylls can be quite large and our ODMR techniques are especially well suited to investigation of the dynamics of these systems. In our work over the past year we have attempted to detail the general features of chlorophyll triplet state isc as revealed through magnetic resonance measurements over a range of temperatures, in varied solvent systems, and with metal center and substituent changes in the chlorophyll molecule. An understanding of the properties of the triplet state of

chlorophylls is of importance from several points of view. First, since chlorophyll molecules contain large conjugated units, the mechanisms of intersystem crossing active in these molecules and their derivatives provide new tests for existing models of radiationless transitions in multi-ring organic systems. For studies of triplet state intersystem crossing in organic molecules, magnetic resonance spectroscopy has proven to be a most useful tool. Second, in recent low temperature EPR experiments on both the intact cells of photosynthetic bacteria and the reaction centers extracted from the cells, photoexcited triplet state EPR signals have been observed under conditions where electron-transfer processes have been blocked by chemical reduction of the electron acceptors. These experiments have renewed interest in the possible role of the excited triplet state of chlorophylls in the initial photophysical processes of photosynthesis, although further work is necessary to clearly identify the function of the triplet state in photosynthetic mechanisms. Finally, since triplet states are paramagnetic, an understanding of their magnetic properties and the changes which can occur in these properties would allow the use of the triplet state as a magnetic probe into chlorophyll-containing systems, providing information concerning the structure and molecular interactions within such systems.

From our experimental data on the chlorophyll triplet state zero-field splittings and intersystem crossing rates several points emerge which provide a basis for a qualitative understanding of the nature of the triplet state in chlorophyll. The general trends in the chlorophyll intersystem crossing rate constants of the triplet spin sublevels may be explained by consideration of the one-center spin-orbit and spin-vibronic coupling activity of the chlorophyll ring system, as has been done successfully in simple planar aromatic molecules. Implicit in this description is the suggestion that the magnesium atom coordinated in the center of the chlorophyll ring system is relatively unimportant in the description of chlorophyll triplet state dynamics. Thus, the chlorophylls prove to be another

example of in-plane spin sublevel dominance of the population and decay processes in $\pi\pi^*$ triplet states. In contrast, the replacement of magnesium with zinc results in a redirection of spin sublevel activity away from planar aromatic behavior, due, most likely, to important spin-orbit coupling interactions involving mixing of Zn orbitals into the chlorophyll ring system and a dominance of the z spin sublevel in population and decay. Thus, it seems possible to explain the essential features of the triplet state ODMR investigations of the chlorophylls on the basis of our previously described model for radiationless transitions in aromatic systems and the electronic nature of the ring substituents. With these data defined and qualitatively understood for isolated chlorophyll species it is now possible to begin to apply triplet state ODMR measurements to more complex chlorophyll-containing systems in vitro and in vivo.

C. Personnel Involved in Research Program (5/1/75 - present)

1. Harry A. Frank - Graduate study 5/1/75 - present.

Ph.D. candidate, degree expected 1977-78.

2. Robert E. Connors Postdoctoral Fellow 5/1/75 - 8/31/76.

presently Assistant Professor of Chemistry,

Worcester Polytechnic Institute, Worcester, MA.

3. Jeffrey C. Hoch - Undergraduate Research Assistant 5/1/76 - 8/31/76.

presently graduate student, Harvard University.

4. Daniel Lichtin - Undergraduate Research Assistant 5/1/76 - 8/31/76.

presently undergraduate study, University of Rochester.

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D. Publications Acknowledging ERDA Support 5/1/75 - present

R.H. Clarke, R.E. Connors, J.R. Norris, and M.C. Thurnauer

"Optically Detected Zero-Field Magnetic Resonance Studies of the Photoexcited Triplet State of the Photosynthetic Bacterium Rhodospirillum Rubrum"

J. Am. Chem. Soc., 97, 7178 (1975).

R.H. Clarke and H.A. Frank

"Triplet State Radiationless Transitions in Polycyclic Hydrocarbons"

J. Chem. Phys., 65, 39 (1976)

R.H. Clarke, R.E. Connors, T.J. Schaafsma, J.F. Kleibeuker, and R.J. Platenkamp

"The Triplet State of Chlorophylls"

J. Am. Chem. Soc., 98, 3674 (1976)

R.H. Clarke, R.E. Connors, and H.A. Frank

"Investigation of the Structure of the Reaction Center in Photosynthetic Bacteria by Optical Detection of Triplet State Magnetic Resonance"

Biochem. Biophys. Res. Comm., 71, 671 (1976).

R.H. Clarke and R.E. Connors

"Optically Detected Zero-Field Triplet State Magnetic Resonance in Photosynthetic Bacteria"

Chem. Phys. Letters, 42, 69 (1976).

E. Publications in Press and Talks Given Related to ERDA-Supported Research Program 5/1/75 - present.

1. Publications in Press.

R.H. Clarke, R.E. Connors, H.A. Frank and J.C. Hoch

"Investigation of the Structure of the Reaction Center in Photosynthetic Systems by Optical Detection of Triplet State Magnetic Resonance"
Chem. Phys. Letters, March 1977 (in press).

R.H. Clarke and R.E. Connors

"The Triplet States of Photosynthetic Pigments"
Proceedings of 3rd Intl. Seminar on Energy Transfer in Condensed Matter,
K. Vacek, editor, Charles University Press, Prague, 1977 (in press).

2. Talks on Results of Research Program.

Conference on Modern Aspects of Photosynthetic Research

Wageningen, The Netherlands, June 10, 1975

Title of talk: "Triplet State Dynamics of Chlorophylls"

Eighth International Conference on Photochemistry

Edmonton, Alberta, August 8-13, 1975

Title of talk: "Radiationless Deactivation of Triplet States of Chlorophylls"

Departmental Colloquium, Chemistry Department, Boston College

Boston, MA, October 1, 1975

Title of talk: "Triplet State of Chlorophylls"

Departmental Colloquium, Chemistry Department, M.I.T.

Cambridge, MA, October 7, 1975

Title of talk: "Triplet State of Chlorophylls"

Departmental Colloquium, Chemistry Department, Harvard University

Cambridge, MA, March 5, 1976

Title of Talk: "Triplet State of Chlorophylls"

Conference on Molecular Spectroscopy

Columbus, Ohio, June 14-18, 1976

Title of talk: "Optical Detection of Magnetic Resonance in Aromatic Hydrocarbons"
(talk given by H.A. Frank)

3rd International Seminar on Energy Transfer in Condensed Matter

Prague, Czechoslovakia, June 29-July 2, 1976

Title of talk: "The Triplet States of Photosynthetic Pigments"

7th International Congress on Photobiology

Rome, Italy, August 29 - September 3, 1976

Title of talk: "Optically-Detected Zero-Field Triplet State Magnetic Resonance
in Photosynthetic Bacteria"