MASTER

Technical Progress Report

Investigation of the Triplet State of Chlorophylls

Progress Report for the period
May 1, 1978 through April 30, 1979

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I. Abstract

The photoexcited triplet state properties of chlorophyll dimer systems in vitro were investigated by zero-field optically detected magnetic resonance (ODMR) spectroscopy at 2°K. Measurements of the triplet state zero-field splittings, overall triplet lifetimes, and individual spin sublevel inter-system crossing rate constants were obtained for solutions of chlorophyll a and zinc-substituted chlorophyll a and for the covalently linked dimeric derivative of pyrochlorophyllide a. The triplet state properties found for these systems are interpreted within the framework of the triplet exciton model to assess the applicability of the exciton approach in determining the geometry of chlorophyll aggregate systems and to evaluate structural features of chlorophyll systems proposed as models for in vivo chlorophyll.

II. Progress Report (5/1/78 - present)

In the past year our research program has concentrated on triplet state studies of the water-linked chlorophyll dimer in solution. Since the chlorophyll dimer, the so-called chlorophyll special pair, has been postulated to be of central importance in the primary photophysical events of photosynthesis, our research program attempted to characterize its properties in solution by excited state optically-detected magnetic resonance (ODMR) spectroscopy. The research program proceeded by first determining the conditions under which the simple triplet exciton description was applicable to chlorophyll dimers, then utilizing triplet exciton theory to interpret the ODMR transition frequencies and intersystem crossing rates found for the chlorophyll hydrate dimer.

Measurements of the photoexcited triplet state zero-field splittings, overall triplet lifetimes and individual spin sublevel intersystem crossing rate constants were obtained at 2°K for the covalently linked dimeric derivative of pyrochlorophyllide a and for aggregated solutions of chlorophyll a and zinc-substituted chlorophyll a containing water, methanol and ethanol in hydrocarbon solvents. The value of ODMR spectroscopy in the investigation of structural features of the components in these solutions is evident from our experiments. By selecting the appropriate detection wavelength it was possible to measure triplet state properties of the monomeric and dimer triplet state properties to evaluate geometrical features of the dimer.

The ODMR results of the covalent pyrochlorophyllide a dimer, a system known to assume a plane-parallel configuration in the presence of a hydrogen bonding, metal-coordinating ligand, established the applicability of the simple triplet exciton model to the study of the chlorophyll dimer. Both the triplet state zero-field splittings and individual spin sublevel intersystem crossing

rate constants observed for the folded form of the covalent dimer are in agreement with the results derived from the exciton relationships derived in our earlier work, in terms of the monomer properties and the geometry of the dimer of particular importance was the demonstration from these results that no new intermolecular terms (charge transfer, intermolecular spin orbit coupling) are introduced into the intersystem crossing mechanism upon dimerization of ordinary chlorophylls. It was not, however, possible to distinguish between a coherent or an incoherent description for the intersystem crossing on the basis of the chlorophyll dimer systems studied to date. Zinc substitution into the pyrochlorophyllide dimer demonstrated the limiting case of interterms in the triplet exciton description, but such effects may be reasonably expected to be negligible for in vivo chlorophylls.

Results of the ODMR investigation of water-linked chlorophyll dimer systems in toluene and in octane provided an opportunity to investigate the structural features of this highly modeled chlorophyll aggregate. As interpreted through the equations from the triplet exciton description, verified as applicable from the pyrochlorophyll covalent dimer results above, both the zero-field splittings and intersystem crossing rates provided an internally consistent structure for the dimer in which all molecular axes are parallel (or antiparallel, our experiments do not distinguish). These results support the hypotheses, with experimental data, in which magnesium-coordinated ligands hydrogen bond to the carbonyl ring substituents to form plane parallel dimer structures in vitro.

An important next step, then, is to determine whether these same structures are, indeed, the preferred conformations for the in vivo chlorophylls within the reaction center of green plants.

III. Personnel Involved in Research Program (5/1/78 - present)

1. David R. Hobart - graduate research assistant.
Graduate student, working 100% of time on this research.
Ph.D. candidate, degree expected in 1979.
2. Pradip Mitra - graduate research assistant.
Graduate student, working 100% of time on this research.
Ph.D. candidate, degree expected in 1980.
3. Surya Jaganathan - graduate research assistant.
Graduate student, working 50% of time on research, 50% of
time as teaching assistant.
Ph.D. candidate, degree expected in 1980-81.
4. K. Vinodgopal - graduate research assistant.
Graduate student, working 50% of time on research, 50% of
time as teaching assistant.
Ph.D. candidate, degree expected in 1981.
5. David Michaels - graduate research assistant
Graduate student, working 50% of time on research, 50% of
time as teaching assistant.
6. Richard Ciccarelli - undergraduate research assistant
B.A. degree expected 1979.
7. Mark DeBenedetto - undergraduate research assistant
B.A. degree expected 1979.

IV. Publications Acknowledging DOE 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 Photo-excited 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).

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 Optically Detected Zero-Field Magnetic Resonance."
Chem. Phys. Letters, 50, 61 (1977)

R.H. Clarke and H.A. Frank

"Investigation of the Effect of Metal Substitution on the Triplet State of Chlorophyll by Optically Detected Zero-Field Magnetic Resonance."

Chem. Phys. Letters, 51, 13 (1977).

R.H. Clarke and D.R. Hobart

"Structural Aspects of the Reaction Center of Photosynthetic Bacteria Calculated from Triplet State Zero-field Splittings."

FEBS Letters, 82, 155 (1977).

R.H. Clarke, D.R. Hobart and W.R. Leenstra

"Investigation of the Structure of the Reaction Center Chlorophyll Complex by Optical Detection of Triplet State Magnetic Resonance."

Semicond. Insul., 4, 313 (1978).

V. Publications in Press and Talks Given Under DOE Support (5/1/78-present)

A. Publications in press (accepted for publication)

R.H. Clarke, Dr. Hobart and W.R. Leenstra
"The Triplet State of the Chlorophyll Dimer"
J. Am. Chem. Soc., 101, XXXX (1979).

R.H. Clarke
"The chlorophyll Triplet State and the Structure of Chlorophyll Aggregates"
A chapter in Light Reactions in Photosynthesis, F. Fong, ed.
To be published by Springer-Verlag (Berlin), 1979.

B. Talks on Results of Research Program

Departmental Colloquium, Department of Chemistry, Michigan Technological University

Houghton, Michigan, June 12, 1978

Title of talk: "Structural Features of Photosynthetic Systems by Excited State Magnetic Resonance Spectroscopy."

Twentieth Congress Ampere

Tallinn, USSR, August 21-26, 1978

Title of talk: "Structural Features of Chlorophyll Complexes in vitro and in vivo as Determined by Triplet State ODMR"

Sixth International Biophysics Congress

Kyoto, Japan, September 3-9, 1978

Title of talk: "Structural Features of Chlorophyll Complexes in vitro and in vivo."

Departmental Colloquium, Department of Chemistry, New York University
New York, N.Y., March 28, 1979

Title of talk: "Structural Features of Photosynthetic Systems by Excited State Magnetic Resonance Spectroscopy."

VI. Budget (5/1/78 - 4/30/79)

It is projected that all funds provided for this contract period will be fully expended in the course of this research program, and no funds will remain after April 30, 1979.