MASTER

Technical Progress Report

Investigation of the Triplet States of Chlorophylls

Progress Report for

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I. Progress Report (5/1/77 - present)

A. Abstract

Triplet state properties of solutions containing chlorophyll monomers and dimers have been determined by optically detected magnetic resonance spectroscopy. Using a simple exciton formalism, the triplet state zero-field splittings and intersystem crossing rate constants found for the chlorophyll dimers and for the isolated chlorophyll molecule are utilized to determine the orientation of the pigment molecules in the dimer. The triplet state results indicate that water-linked chlorophyll dimers in vitro form single plane-parallel structures. Similar calculations using monomeric measurements by ODMR on bacteriochlorophyll and zero-field splittings for in vivo preparations of photosynthetic bacteria indicate that the dimer structures in vivo may be more complex than those observed in solution.

B. Progress Report

The past year saw the development in our laboratory of an approach to utilize triplet state properties as a structural tool in evaluating chlorophyll aggregated complexes.

Work on the photoexcited triplet state of the isolated chlorophyll by optically detected magnetic resonance (ODMR) has provided a detailed description of the triplet electronic distribution and mechanisms of intersystem crossing. The triplet state zero-field splittings and individual spin sublevel decay rates have been obtained for a series of chlorophyll b molecules -- pheophytin b, calcium chlorophyll b, chlorophyll b and cadmium chlorophyll b. A comparison of the triplet intersystem crossing rates in these systems suggests that the nonradiative deactivation of chlorophylls may be understood by consideration of the effect of the metal center interaction on the spin-orbit coupling centered on the pyrrole nitrogens of the chlorophyll ring. Thus, the dynamical processes of energy conversion from the triplet state of what appears to be a rather complex π -electron system may be understood essentially by consideration of the electron orbitals associated with the ring nitrogen atomic centers. And the metal-free and metal-substituted chlorophyll b series provides a striking example of the controlling effect of the metal center on the one-center spin-orbit mechanisms determining the intersystem crossing rates in chlorophylls.

With this basic understanding of the triplet state properties in the isolated pigment molecule, we set out to utilize the triplet state

as a probe into the makeup of aggregated chlorophyll systems. Using a simple exciton formalism we have shown that the triplet state properties of a chlorophyll dimer in which the triplet excitation is shared between the two molecules may be calculated from the properties of the monomer and the geometry of the pair. Therefore, since our previous work had characterized the isolated chlorophyll triplet state, solutions containing dimers of chlorophyll could be probed in their triplet state to investigate the orientation of the pigment molecules in the pair. Our first ODMR experiments measured the zero-field splittings for a hydrocarbon solution containing chlorophyll and an excess of water. This solution has been previously shown to exhibit a fluorescence band at low temperatures which can be assigned to a water-linked chlorophyll dimer. Detecting our ODMR transitions on the dimer fluorescence peak we find zero-field splittings very close to what our exciton model would predict for a dimer in which all axes of the paired molecules were either parallel or antiparallel. We calculate that the planes of the two molecules in the dimer are within 10 degrees of being parallel. This ODMR data is the first triplet state experimental conformation of the structure water-linked chlorophyll dimers proposed by Fong, Katz and Closs.

In addition we also calculated the dimer structure for the bacteriochlorophyll reaction center "special pair" using our exciton model, the ODMR values obtained in our laboratory for the bacteriochlorophyll monomer triplet state, and literature values for the triplet state zero-field splittings in a variety of photosynthetic bacteria. In the case of the bacteria, all calculations gave a consistent value - the angle made by the

normal to the planes of the two molecules in the pair was always 50 ± 10 degrees. The marked difference between chlorophyll dimer structures in vitro and in vivo obviously requires further study for its understanding, but this may be an indication that the dimer structure in vivo is influenced by the protein environment which surrounds it in the bacteria.

As part of our research program to evaluate chlorophyll dimer structures we have also examined covalently-bound pyrochlorophyllide a molecules in their unfolded (monomeric) and folded (dimeric) form in the presence of alcohols. The preliminary ODMR spectra of these systems are also consistent with a plane-parallel structure, as was found in the chlorophyll-water in hydrocarbon solutions. More information is required, however, before generalizations about water-linked chlorophyll dimers may be conclusively stated.

C. Personnel Involved in Research Program (5/1/77 - present)

1. Richard H. Clarke - principal investigator
2. Harry A. Frank - graduate student, full time, 5/1/77 - 8/31/77,
received Ph.D. degree in August 1977, presently postdoctoral
fellow at University of California, Berkeley.
3. David R. Hobart - graduate student, full time, 5/1/77 - present,
Ph.D. candidate.
4. Pradip Mitra - graduate student, full time, 5/1/77 - present,
Ph.D. candidate.
5. Surya Jaganathan - graduate student, full time, 9/1/77 - present,
Ph.D. candidate.
6. David Michaels - graduate student, full time, 5/1/77 - present,
M.S. candidate.

D. Publications Acknowledging DOE Support (cumulative listing)

1. 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 Rhodo-
spirillum Rubrum.
J. Am. Chem. Soc., 97, 7178 (1975).
2. R.H. Clarke and H.A. Frank
Triplet State Radiationless Transitions in Polycyclic Hydrocarbons.
J. Chem. Phys., 65, 39 (1976).
3. 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).
4. 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).
5. R.H. Clarke and R.E. Connors
Optically Detected Zero-Field Triplet State Magnetic Resonance in
Photosynthetic Bacteria.
Chem. Phys. Letters, 42, 69 (1976).

6. 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.

Che. Phys. Letters, 45, 523 (1977).

7. 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.

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

8. R.H. Clarke and D.R. Hobart

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

F.E.B.S. Letters, 82, 155 (1977).

E. Publications in Press and Talks Given Related to DOE-Supported Research Program, 5/1/77 - present.

1. Publications 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 (publication delayed until 1978).

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. Semiconductors and Metals, January 1978 (in press).

2. Talks given on Results of Research Program

Departmental Seminar, Department of Molecular Physics, Agricultural University Wageningen, The Netherlands, June 2, 1977.

Title of Talk: "Triplet State of Chlorophylls."

Third Specialized Colloque Ampere

Trinity College, Dublin, Ireland, August 29 - September 1, 1977.

Title of Talk: "Investigation of the Triplet State of Chlorophylls and Chlorophyll Complexes by ODMR."

Fourth International Congress on Photosynthesis

University of Reading, Reading, England, September 4-9, 1977.

Title of Talk: "The Triplet States of Chlorophylls and Chlorophyll
Complexes."

Departmental Colloquium, Chemistry Department, Iowa State University, Ames, Iowa, December 15, 1977.

Title of Talk: "The Triplet State As a Structural Probe in
Photosynthesis."

~~Thirteenth~~ Thirteenth Informal Conference on Photochemistry

Clearwater Beach, Florida, January 4-7, 1978.

11 Title of Talk: "Structural Aspects of Chlorophyll Aggregates
in vitro and in vivo from Triplet State Properties."