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**MAGNETIC RESONANCE STUDIES OF PHOTO-INDUCED  
ELECTRON TRANSFER REACTIONS**

**FINAL REPORT  
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## INTRODUCTION

Photo-induced electron transfer reactions are of interest from a fundamental point of view and in connection with applications in homogeneous and heterogeneous photosensitization, photopolymerization, and solar energy conversion and storage. The objective of the research carried out in the laboratory of the PI is to contribute to the understanding of the factors that affect excited state electron transfer.

Because the reactions of interest generally involve a number of paramagnetic species, Electron Paramagnetic Resonance (EPR) can be a valuable source of kinetic and mechanistic information. EPR techniques can be used to identify paramagnetic molecules and to monitor their formation and decay. The spin polarization of products of photochemical reactions can provide information on the spin state of excited state precursors and on radical pair intermediates that cannot be studied directly with spectroscopic techniques. Finally, EPR spectra can give detailed insights into molecular motion of paramagnetic species. For the most part data given by magnetic resonance measurements complement those given by other instrumental techniques.

In the period covered by this report, research has been concerned with applications of Fourier Transform Electron Paramagnetic Resonance (FT EPR) in the study of photochemical reactions. In FT EPR a microwave pulse rotates the electron spin magnetization vector from the  $z$  (magnetic field) axis into the  $xy$  plane ( $\pi/2$  pulse). Then the time evolution of the magnetization in the  $xy$  plane, the free induction decay (FID), is sampled. The Fourier transform of the FID gives the frequency domain EPR spectrum of the free radicals present in the sample. The method is ideally suited for time-resolved studies of free radicals generated by pulsed-laser excitation. This is because the FID only reports on species present at the time of the  $\pi/2$  pulse. Hence, formation and decay of free radicals can be traced by measuring spectra for delay times between laser and microwave pulses extending from the nanosecond to the millisecond time domain.

It has been established that FT EPR can give reliable information on chemical rate constants. In addition, it can give data that may not be accessible with other spectroscopic methods:

1. The high spectral resolution makes it possible to identify paramagnetic species unambiguously.
2. Spectral data are a very sensitive function of solvent medium. This can be exploited to get information on the location of paramagnetic molecules in a heterogeneous environment.

3. The time development of the spectra, generally, is determined in part by Chemically Induced Dynamic Electron Spin Polarization (CIDEP) mechanisms. Analysis of CIDEP effects contributes to the understanding of reaction mechanisms.
4. Signal contributions can be observed of radical pairs. Measurement of the kinetics of formation and decay of these species can give an insight, at the molecular level, into substituent and medium effects on their characteristics.
5. Information on spin-lattice relaxation ( $T_1$ ) and linewidth ( $T_2$ ) can be derived. These parameters reflect the molecular motion of the free radicals.

Only recently have electronic components required for the routine application of FT EPR in the study of free radicals in solution become available. At the beginning of the period covered by this report, the construction of an FT EPR spectrometer—funded by a DOE URI grant—had just been completed. At that time only a few studies dealing with the application of the technique in the study of photochemical reactions had been published. Its full potential in this field of research remained to be explored, measurement and data analysis methodologies had to be developed. An important aspect of the work carried out over the past three years has been that it delineated the range of possible applications of the technique and that systematic methods of data analysis were developed.<sup>1</sup>

The work concerned with development of measurement techniques and data analysis methodology for the most part involved studies of radicals produced in photo-induced hydrogen abstraction reactions.<sup>2,3</sup> Investigations of electron transfer reactions focused on porphyrin (donor) - quinone (acceptor) systems. These molecules were chosen because of their favorable photochemical and photophysical characteristics, and the possibility that they may be suitable for application in man-made solar energy conversion devices. Investigations dealt with the following topics:

- I. The FT EPR study of benzoquinone anion ( $BQ^-$ ) or duroquinone anion ( $DQ^-$ ) radicals generated by pulsed-laser induced electron transfer from zinc tetraphenylporphyrin (ZnTPP) or tetra-sulfonated ZnTPP (ZnTPPS) in ethanol-water solvent mixtures.<sup>4-7</sup>
- II. The FT EPR study of photo-induced electron transfer from ZnTPP (or ZnTPPS) to benzoquinone (or duroquinone (DQ)) in micellar solutions.<sup>8,9</sup>
- III. The FT EPR study of photochemistry of reactants adsorbed on silica gel.<sup>10</sup>

In work carried out in collaboration with Dr. H. Linschitz, FT EPR has been used in the study of electron transfer quenching of triplet  $C_{60}$  by electron donors.<sup>11</sup>

## RESULTS

### I. Photo-induced hydrogen abstraction reactions

Two hydrogen abstraction reactions were studied with FT EPR:

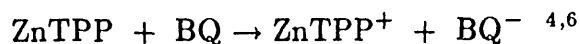
1. The photoreduction of acetone with 2-propanol yielding the acetone ketyl radical  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ .<sup>2</sup>
2. The reaction of 2-propanol with t-butoxy radicals (formed by photocleavage of t-butylperoxide) giving  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ .<sup>3</sup>

The data analysis method that was developed involves two steps. In the first, values of the spectral parameters characterizing the EPR spectrum—i.e. amplitudes, frequencies, linewidths, and phases of all hyperfine components in the spectrum—were extracted from the FIDs with the Linear Prediction/Singular Value Decomposition procedure. In the second, kinetic models were applied to account for the changes in magnitude of these parameters accompanying variations in the delay time ( $\tau_d$ ) between laser excitation and  $\pi/2$  microwave pulse. A complete analysis gives: (1) values of rate constants of formation and decay of free radicals, (2) values of spin polarization generated in the formation and decay steps, (3) information on the spin state of excited state precursor molecules, (4) lifetime of radical pair intermediates, (5) information on time evolution of spin relaxation times reflecting variations in the interaction of the free radicals with the environment.

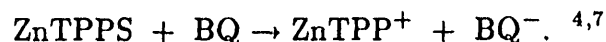
In the case of the acetone/2-propanol system, changes in  $\tau_d$  were found to cause a pronounced variation in signal phase.<sup>2</sup> Similar phase changes were found in the spectrum of duroquinone anions formed by electron transfer from photoexcited ZnTPP and were attributed to the presence of long-lived radical pairs.<sup>5</sup> Also for  $\tau_d < 1\mu\text{s}$  the linewidth decreases significantly with increasing delay time. This is due to radical-radical interactions as well and shows that translational motion of the radicals formed in the photochemical reaction is significantly slower than expected given the bulk viscosity of the solution. The data confirm that for acetone/2-propanol the photochemical reaction proceeds via triplet acetone precursors. CIDEP effects provide an insight into the spin polarization of these triplets at the time of reaction. In the case of t-butylperoxide/2-propanol, the data establish that t-butylperoxide cleavage involves the excited singlet state.<sup>3</sup> An analysis of CIDEP effects in the spectrum of  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  makes it possible to determine the spin-lattice relaxation time of the t-butoxy radical which cannot be observed directly. *It is of note that the understanding of the interplay of spin and chemical dynamics has developed to the point where time dependence of spectra can be modeled accurately for time domains spanning 5 orders of magnitude (from nanoseconds to milliseconds).*<sup>3</sup>

## II. Electron transfer in homogeneous solutions

A complete analysis was made of the time evolution of the FT EPR spectra from BQ<sup>-</sup> formed in the reactions:



and



The time domain covered by the spectra extended from nanoseconds to milliseconds. The solvent used for the study of the ZnTPP/BQ system was ethanol. ZnTPPS/BQ was studied in a series of water/ethanol solvent mixtures.

With the data analysis methodology discussed earlier it proved possible to distinguish the effect of radical formation and decay on the signal development from CIDEP and spin relaxation contributions. As a consequence, the spectral data could be used to get information on the effect of solvent composition on the electron transfer rate. It was found that the time evolution of the radical pair CIDEP signal contribution is affected by the homogeneous electron transfer reaction



Homogeneous electron transfer also makes a contribution to the linewidth of the resonance peaks. Both effects have been used to determine the rate constant of homogeneous electron transfer.

The rate constant of photo-induced electron transfer from ZnTPP(S) to BQ was found to be inversely proportional to solvent viscosity. From this it is concluded that the reaction is diffusion controlled. The rate constant of BQ<sup>-</sup> formation shows a BQ concentration dependence characteristic for a diffusion controlled reaction.

The introduction of the SO<sub>3</sub><sup>-</sup> groups in the porphyrin does not affect the forward electron transfer process. By contrast, the rate of back electron transfer is reduced markedly by the introduction of the anionic groups. This reflects the fact that close encounters between BQ<sup>-</sup> and ZnTPPS<sup>+</sup> (which carries three negative charges) is inhibited by electrostatic repulsion. It is noteworthy, however, that the repulsion does not appear to affect the radical pair CIDEP contribution. Measurements of BQ<sup>-</sup> formed by electron transfer from ZnTPPS in 100% water gave poor results. Fluorescence spectra established that this is due to ground state complexation between donor and acceptor molecules.

The presence of radical pairs at the time the microwave pulse is delivered can express itself in the form of a phase shift of the signal given by the radicals after cage escape. This makes it possible to monitor the formation and decay of radical pairs whose lifetime is too short to make a direct contribution to the free induction decay signal. The effect was used to study the temperature dependence of the lifetime of radical pairs formed in the reaction of triplet ZnTPP with DQ in ethanol.<sup>5</sup> The lifetime data show that the pairs are trapped in a shallow potential energy well generated by Coulomb interaction between the radical ions. As a consequence of the, dielectrically shielded, Coulomb interaction radical pair lifetimes are longer than expected which could affect the probability of cage escape of redox products.

### III. Electron transfer in micellar solutions

Photo-induced electron transfer reactions in micellar solutions have been subject of numerous studies in recent years. The interest in these systems stems in part from the potential relevance to applications in conversion and storage of solar energy. Also, the investigations contribute to the understanding of the factors that play a role in electron transfer across boundaries between hydrophobic and hydrophilic domains in biological systems.

The keypoint in studies of photochemical reactions in heterogeneous media with FT EPR is that the parameters that determine CIDEP signal contributions, lineshapes, and relaxation times are sensitive to the spatial distribution of reactants and products, and molecular motion (rotation, translation). As a consequence, FT EPR spectra can provide a detailed insight into the spatial distribution and stability of reactants and products in the micro-heterogeneous environment.

The following systems were studied:

- a. ZnTPP/BQ in a micellar solution of cetyltrimethylammonium chloride (CTAC),<sup>8</sup> and
- b. ZnTPPS/DQ in solutions of sodium dodecylsulfate (SDS), triton X100 (TX100), and CTAC.<sup>9</sup>

FT EPR spectra of the quinone anion radicals ( $BQ^-$  or  $DQ^-$ ), formed by electron transfer from the porphyrins, were measured as function of delay time between laser pulse and  $\pi/2$  microwave pulse. The studies established that FT EPR can provide information on these systems that cannot be derived from data provided by optical spectroscopy. For instance, in TX100 electron transfer takes place between donor and acceptor molecules that are associated with the micelles. After electron transfer, the anion radical escapes

into the aqueous phase within a few tens of nanoseconds judging from the linewidth of the hyperfine components in the EPR spectrum. By contrast, in CTAC, electrostatic attraction between the cationic headgroups of the surfactant molecules and the negatively charged electron transfer products generates long lived ( $\sim 5 \mu s$ ) radical pairs. It should be noted that in this case the radical pairs contribute directly to the FT EPR spectrum. Their presence is evident from the characteristic signal produced by these species. Linewidth data establish that, even after dissociation of the pairs,  $DQ^-$  remains associated with the micelles. The linewidth is strongly dependent on the nuclear spin quantum number. A theoretical interpretation of this hyperfine dependence makes it possible to determine the rotational correlation time of  $DQ^-$  in CTAC. Finally, in SDS electron transfer involves donor (ZnTPPS) and acceptor (DQ) molecules dissolved in the bulk aqueous phase. Since most of the DQ is found inside the micelles and ZnTPPS prefers the aqueous phase, the electron transfer reaction is slow.

It is noteworthy that in TX100 and CTAC solutions, where donor and acceptor molecules must be in close proximity, FT EPR spectra show no evidence of singlet excited state electron transfer. Even so, fluorescence spectra of these systems reveal significant singlet state quenching by acceptor molecules. Apparently, singlet state electron transfer does not produce a significant concentration of *separated redox* products. Since back electron transfer is not inhibited by spin state selection rules in this case, it can compete effectively with cage escape of free radicals. From the point of view of light energy utilization, singlet state electron transfer can be more efficient than electron transfer involving photoexcited triplets. Evidently, it is not sufficient to design a system in which donor and acceptor have a high probability to react within the lifetime of singlet excited state lifetime. Of importance as well is an assembly that promotes fast separation of redox products.

#### **IV. Photochemistry of reactants adsorbed on silica gel**

Photochemistry involving molecules adsorbed in the pores of silicas, clays, and zeolites is of interest because the confinement of reactants and products in a restricted space will affect the reaction kinetics and mechanism in a unique way. On-going research in a number of laboratories is concerned with the design of systems in which the solid support serves to promote fast photo-induced electron transfer and inhibits the energy wasting back electron transfer reaction.

The work initiated in the laboratory of the PI explores the utility of EPR measurements in monitoring the formation and decay of paramagnetic products of photochemical reactions taking place in the pores of silica gels, zeolites, and clays. It is difficult to get



detailed information on these opaque systems with the aid of optical spectroscopy. By contrast, the factors that hamper the application of UV/vis spectroscopy do not play a role in the application of magnetic resonance techniques. Of interest, of course, is the identification of free radicals formed in photochemical reactions and the determination of rates of formation and decay. It should be noted, however, that the effect solid supports have on chemical reactions depends on spatial distribution of intercalated molecules and their molecular motion. In principle, FT EPR is uniquely suited to provide an insight into these factors. High spectral resolution can make it possible to study interactions between free radicals and the environment. Spin-lattice relaxation and linewidth data can convey information on molecular motion.

It has been demonstrated that FT EPR can be used to monitor pulsed-laser induced chemistry taking place between reactants adsorbed in the pores of silica gel.<sup>10</sup> One study involved the photo-induced electron transfer from ZnTPP to BQ. The samples were prepared by adsorption of the reactants from a solution in a non-polar solvent onto the silica gel, drying of the silica, and subsequent introduction of polar solvent molecules in the silica pores by exposing the solid to solvent saturated argon gas.

In the absence of the polar solvent molecules no EPR signal from electron transfer products is observed. Time-resolved cw EPR measurements give the spectrum from ZnTPP in the photoexcited triplet state. CW EPR demonstrates that, in the absence of solvent molecules, there is no rotational motion of ZnTPP triplets. Exposure of the silica gel samples to solvent vapor leads to quenching of the triplet EPR spectrum. This demonstrates that the introduction of solvent molecules in the pores has a strong effect on the rotational motion of the porphyrin molecules. In the presence of acceptor molecules, well resolved spectra of  $BQ^-$  were obtained after introduction of the solvent. The measurements are facilitated by the fact that the electron transfer process is almost 100% reversible. This makes it possible to record spectra for different delay time settings between laser pulse and microwave pulse over an extended period of time. The spectra exhibit a fast rise time and a major portion of the signal decays within a few microseconds. However, a significant fraction of the signal is still observed tens of milliseconds after the laser flash. The following model is proposed to explain the experimental results. (1) The laser pulse excites ZnTPP molecules positioned near the surface of the particles. (2) Electron transfer involves ZnTPP triplets that happen to have an acceptor within reaction distance. (3) A small fraction of  $BQ^-$  diffuses away from the surface and the probability of an encounter of these anions with a counter ion is very small. As in the case of the micellar systems, the FT EPR spectra show no sign of generation of  $BQ^-$  via singlet excited state electron

transfer. This is attributed to fast back electron transfer.

A second set of measurements focused on the reaction between photo-excited benzophenone and 2-propanol in which a hydrogen atom is transferred from alcohol to benzophenone giving two ketyl radicals. This system gives rise to strong FT EPR spectra as well. However, since the reaction is not reversible, some method of sample replenishment must be devised to make it possible to study the details of the time evolution of the spectra.

## V. Electron transfer quenching of $C_{60}$ triplets

Flash photolysis measurements have shown that  $C_{60}$  in the photoexcited triplet state can be reduced by amines and hydroquinone. In polar solvents, triplet quenching gives rise to formation of relatively long-lived anion and cation radicals. FT EPR was applied to get further information on the characteristics of the triplet state of  $C_{60}$  and on the electron transfer reactions.

The application of FT EPR appeared of special interest because of a report that photoexcitation of  $C_{60}$  in fluid solution gives rise to a narrow, transient EPR signal. The signal was assigned to  $C_{60}$  triplets. However, the assignment has been questioned because it would be very unusual for the rotational motion of the triplets to be fast enough to average out the anisotropic dipole-dipole interaction between the unpaired electrons. The effect of the presence of donor molecules on the decay of this unusual signal could confirm the assignment. Furthermore, if the interpretation is correct, the signal could provide an alternative way to measure rates of photo-induced electron transfer.

The FT EPR results provide compelling evidence that the single-line spectrum is indeed due to triplet  $C_{60}$ . The spectra show that the triplets are formed with a spin polarization which is a fraction of the Boltzmann value. The spin-lattice relaxation time of the triplets corresponds to a rotational correlation time  $\tau_r \sim 10^{-13}$  s. This is considerably shorter than would be expected given the solvent viscosity. It is consistent with an earlier proposal that the dipole-dipole interaction between the unpaired electrons is averaged out by pseudo rotation of the zero-field axes in the molecule caused by a dynamic Jahn-Teller effect. The analysis of the time dependence of the FT EPR signals due to triplet  $C_{60}$  and doublet radical products give values for the rate constant of electron transfer which are in close agreement with results obtained with flash photolysis methods.

## REFERENCES

- (1). For an overview of this work see: van Willigen, H.; Levstein, P.R.; Ebersole, M.H. *Chem. Rev.* **1993**, in press.
- (2). Levstein, P.R.; van Willigen, H. *J. Chem. Phys.* **1991**, *95*, 900-908.
- (3). Levstein, P.R.; Doering, P.; van Willigen, H. *Chem. Phys. Letters* **1992**, *197*, 265-272.
- (4). Ebersole, M.H. *Ph.D. Thesis, University of Massachusetts at Amherst* **1992**.
- (5). Kroll, G.; Plüschau, M.; Dinse, K.P.; van Willigen, H. *J. Chem. Phys.* **1990**, *93*, 8709- 8716.
- (6). Ebersole, M.H.; Levstein, P.R.; van Willigen, H. *J. Phys. Chem.* **1992**, *96*, 9311.
- (7). Ebersole, M.H.; van Willigen, H. *Z. Phys. Chem.* **1992**, submitted.
- (8). Levstein, P.R.; van Willigen, H.; Ebersole, M.H.; Pijpers, F.W. *Mol. Cryst. Liquid Cryst.* **1991**, *194*, 123-131.
- (9). Levstein, P.R.; van Willigen, H. *Chem. Phys. Letters* **1991**, *187*, 415-422.
- (10). Levstein, P. R.; van Willigen, H. *J. Colloid and Interface Chem.*, **1992**, in press.
- (11). Steren, C.A.; Levstein, P.R.; van Willigen, H.; Linschitz, H. *J. Phys. Chem.* **1993**, submitted.

## PAPERS ACKNOWLEDGING DOE SUPPORT

Steren, C.A.; Levstein, P.R.; van Willigen, H.; Linschitz, H. "FT EPR STUDY OF TRIPLET STATE C<sub>60</sub>", *J. Phys. Chem.* **1993**, submitted.

Ebersole, M.H.; van Willigen, H., "SOLVENT EFFECTS ON PHOTOINDUCED ELECTRON TRANSFER; A FT EPR STUDY", *Z. Phys. Chem.*, **1992**, submitted.

Levstein, P. R.; van Willigen, H. "CHEMICALLY INDUCED DYNAMIC ELECTRON POLARIZATION IN PHOTOGENERATED ACETONE KETYL RADICALS; A FT-EPR STUDY", *Z. Phys. Chem.*, **1992**, submitted.

Levstein, P. R.; van Willigen, H. "PHOTOCHEMISTRY IN HETEROGENEOUS MEDIA: A FT-EPR STUDY", *J. Colloid and Interface Chem.*, **1992**, in press.

van Willigen, H.; Levstein, P. R.; Ebersole, M. H. "APPLICATION OF FOURIER TRANSFORM ELECTRON PARAMAGNETIC RESONANCE IN THE STUDY OF PHOTOCHEMICAL REACTIONS", *Chem. Rev.*, **1992**, invited contribution, in press.

Levstein, P. R.; Ebersole, M. H.; van Willigen, H. "FOURIER TRANSFORM EPR STUDIES OF PHOTOINDUCED ELECTRON TRANSFER IN HOMOGENEOUS AND MICELLAR SOLUTIONS", *Proc. Indian Acad. Sc.*, **1992**, in press.

Ebersole, M. H.; Levstein, P. R.; van Willigen, H. "THE PHOTOOXIDATION OF ZINC TETRAPHENYLPORPHYRIN BY BENZOQUINONE: A FOURIER TRANSFORM ELECTRON PARAMAGNETIC RESONANCE INVESTIGATION", *J. Phys. Chem.*, **1992**, *96*, 9311-9315.

Levstein, P. R.; Doering, P.; van Willigen, H. "FT-EPR STUDY OF SPIN POLARIZATION IN THE ACETONE KETYL RADICAL FORMED BY PHOTOLYSIS OF t-BUTYLPEROXIDE IN 2-PROPANOL", *Chem. Phys. Lett.*, **1992**, *197*, 265-272.

van Willigen, H.; Levstein, P. R.; Ebersole, M. H. "FOURIER TRANSFORM EPR STUDIES OF PHOTOCHEMICAL REACTIONS" in *Magnetic Resonance: Current Trends*; eds. Khetrpal, C. L.; Govil, G., **1991**, Vedams Books International, Delhi.

Levstein, P. R.; van Willigen, H. "PHOTOINDUCED ELECTRON TRANSFER FROM PORPHYRINS TO QUINONES IN MICELLAR SYSTEMS: AN FT-EPR STUDY", *Chem. Phys. Lett.*, **1991**, *187*, 415-422.

Levstein, P. R.; van Willigen, H. "FOURIER TRANSFORM- EPR STUDY OF THE PHOTOCHEMICAL REACTION OF ACETONE WITH 2-PROPANOL", *J. Chem. Phys.*, **1991**, *95*, 900-908.

Reddy, D.; Reddy, N. S.; Chandrashekar, T. K.; van Willigen, H. "OXIDATION OF COBALT(II) TETRAPYRROLES IN THE PRESENCE OF AN ELECTRON ACCEPTOR", *J. Chem. Soc. Dalton Trans.*, **1991**, 2097-2101 .

Levstein, P. R.; van Willigen, H.; Ebersole, M. H. "FT-EPR STUDY OF PHOTOINDUCED ELECTRON TRANSFER IN A MICELLAR SYSTEM", *Mol. Cryst. Liq. Cryst.* **1991**, 194, 123-131.

Kroll, G.; Plüschau, M.; Dinse, K. P.; van Willigen, H. "FOURIER TRANSFORM EPR SPECTROSCOPY OF CORRELATED RADICAL PAIRS", *J. Chem. Phys.* **1990**, 93, 8709-8716.

### THESIS

Marie H. Ebersole, *A FT EPR STUDY OF A PHOTO-INDUCED ELECTRON TRANSFER REACTION*, Ph.D. Thesis, University of Massachusetts at Amherst, **1992**.

### ABSTRACTS OF CONFERENCE PAPERS

Levstein, P.R.; van Willigen, H. "FT-EPR STUDY OF PHOTOCHEMISTRY IN HETEROGENEOUS MEDIA", *Abstracts 6th Int. Symposium on Magnetic Resonance in Colloid and Interface Science*, Florence (Italy), **1992**.

Levstein, P.R.; Ebersole, M.H.; van Willigen, H. "FT-EPR INVESTIGATIONS OF PHOTOCHEMICAL REACTIONS", *Int. Symposium on Magnetic Field and Spin Effects in Chemistry*, Konstanz (Germany), **1992**.

Levstein, P.R.; van Willigen, H. "FT-EPR STUDY OF PHOTOCHEMISTRY IN HETEROGENEOUS MEDIA", *Abstracts 14th IUPAC Symposium on Photochemistry*, Leuven (Belgium), **1992**.

Dinse, K. P.; Plüschau, M.; Kroll, G.; van Willigen, H. "FT EPR INVESTIGATION OF PHOTO-INDUCED CHARGE TRANSFER IN THE Zn TETRAPHENYL-PORPHYRIN/DUROQUINONE SYSTEM", *Abstracts 25th Colloque Ampere*, Stuttgart (Germany), **1990**.

van Willigen, H.; Levstein, P. R.; Ebersole, M. H.; Dinse, K. P. "FT-EPR STUDY OF PHOTOINDUCED ELECTRON TRANSFER REACTIONS", *Abstracts VIII<sup>th</sup> IUPAC Symposium on Photochemistry*", Warwick (England), **1990**.

van Willigen, H.; Levstein, P. R.; Ebersole, M. H.; Dinse, K. P. "FT-EPR STUDY OF PHOTOINDUCED ELECTRON TRANSFER", *Abstracts Symposium on Photoinduced Charge Transfer*, Rochester (NY), **1993**.

## **PERSONNEL INVOLVED IN RESEARCH**

Dr. Patricia R. Levstein, postdoctoral fellow, 100% of time, July 1989 through July 1992.

Dr. Carlos Steren, postdoctoral fellow, 100% of time, since June 1992.

Marie Ebersole, graduate student, 80% of time, June 1990 through November 1991.

Patrick Doering, graduate student, 50% of time, September 1990 through December 1991.

Mei Hing Chu, graduate student, since September 1992.

Martin Dunne, undergraduate assistant, July 1991 through August 1991.

Thomas Lepkowski, undergraduate assistant, October 1991 through December 1991.

Bryant Salvesen, undergraduate assistant, September 1991 through December 1991.

## **ESTIMATE OF UNOBLIGATED BALANCES**

It is estimated that no funds will remain unencumbered at the end of the current grant period.

**END**

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