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by

(10) Maurice W. Windsor

Department of Chemistry
Washington State University

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Maurice W. Windsor
Department of Chemistry, Washington State Univ.
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In this final report a summary of past work and a description of some recent results on triphenylmethane dyes are given.

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FOREWORD

The work described in this report was a natural outgrowth of an earlier contract (N00014-67-C-0327) that began in March 1967 and which supported my research at TRW systems, until December 1971 when I moved to Washington State University to assume the chairmanship of the Chemistry Department.

The support ONR has given my research program at WSU has enabled us to develop the technique of picosecond laser flash photolysis and kinetic spectroscopy and apply it to obtaining data on the transient photodynamic behavior of a variety of chemical systems, including laser dyes, modelocking dyes, inorganic complexes and more recently biological systems.

I owe a debt of gratitude to Dr. Rudy Marcus for his confidence in us and in our work. To both him and Dr. George Neece I want to extend a hearty vote of thanks for many things: their continuing interest and encouragement; their thoughtful advice -- both technical and otherwise; and last, but by no means least, for the very valuable semi-annual, one-day contractors review meetings, which have contributed so much to our work through the stimulus of friendship and exchange of ideas with other workers in the field.

1. INTRODUCTION

The present research program began 6 1/2 years ago in April, 1972. From its inception, it emphasized the study of molecular properties in the picsecond (10^{-12}s) to nanosecond (10^{-9}s) time range and the development of novel instrumentation suitable for such investigations. The program was founded on the twin premises that:

(1) the photodynamic behavior of molecules in the picsecond to nanosecond time range is of fundamental scientific interest, and

(ii) for technological devices operating in this time range molecules themselves constitute the natural control elements in the optical "circuitry" of various laser devices.

Support for these premises is found first by noting that the fundamental primary steps in molecular photophysics and photochemistry--vibrational and orientational relaxation, internal conversion and intersystem crossing, charge-transfer processes, cis-trans isomerizations and other geometric rearrangements of atomic nuclei, and the rupture and formation of chemical bonds--all take place in the picosecond to nanosecond time domain. Second, complex molecules such as dyes have found application not only as media for laser oscillators, e.g., dye lasers, but also as ultrafast optical shutters for tailoring laser pulses to required shapes and durations, e.g., dyes used as passive Q-switches and modelockers. Thus a happy symbiosis exists between the laser and picosecond (and nanosecond) molecular photodynamics. The laser is *a fortiori* a molecular oscillator. And the most elegant and usually most effective way of controlling the laser is also to harness appropriate molecules and their optical properties. But, in order to choose molecules for various applications in an intelligent fashion, and, further, to design molecules with improved properties, we first need to gather data on their spectroscopic and photodynamic behavior in the nanosecond to picosecond time range. Finally, it is clear that, in order to obtain short-time photodynamic data on molecules, we need instrumentation capable of exciting and observing molecular processes in the picosecond to nanosecond time range. What better way can be imagined than to exploit the short duration pulses of Q-switched and mode-locked lasers as optical probes for this purpose. Thus molecules help make picosecond pulses and these same pulses can be harnessed to observe and study how excited molecules behave in the short-time domain.

It is eighteen years since the ruby laser was first invented, and lasers of various types have now found a variety of military applications in such areas as communications and data processing, optical radar, target identification and designation, and weaponry. There is also developing an increasing need to provide protection to both men and machines against various laser devices. Other areas in which lasers show promise of playing a crucial role are isotope separation and the quest for controlled thermonuclear fusion. Most, if not all of these applications, are likely to be furthered by a better fundamental understanding of how molecular laser media and molecular laser control devices function on the picosecond to nanosecond time scale.

2. MAJOR ACHIEVEMENTS

During the course of this contract the technique of picosecond flash photolysis and kinetic spectroscopy was conceived, reduced to practice, applied to a variety of chemical problems and finally developed and refined to the point that it can be used almost as a routine chemical tool. Major achievements can be summarized as follows:

1. Construction of an apparatus that provides a series of broad-band, time-resolved, photographic spectra of transient species with time resolution of about 10 ps following excitation of the sample at 530 nm, 1060 nm or nearby wavelengths (by Raman shifting) by 10 ps monochromatic laser pulse.

2. Interfacing of this equipment to a vidicon optical multichannel analyzer (OMA) detection system, thus permitting absolute difference spectra (change in optical density versus wavelength) to be obtained at any chosen time delay after excitation in the range 0 - 5 ns with a resolution of about 10 ps. This apparatus required point-by-point measurements at each individual wavelength to build up the complete spectrum.
3. Further interfacing of this equipment to a dedicated microprocessor which, together with 2-dimensional control-circuitry for the vidicon detector, enables time-resolve absolute difference spectra over a range of about 300 nm to be obtained in a single shot (or a small number, 4 or 5, shots to enhance the signal/noise ratio).
4. Application of the above instrumentation to studying the short time photophysics and photochemistry of several dyes, including modelocking and laser dyes, inorganic complexes and to the study of electron transfer in several systems of biophysical interest. These studies are described in detail in the publications listed in the next section.
5. Provision of advanced training and experience to more than a dozen individuals, including four postdoctoral research associates, six graduate students and several undergraduates as summarized in section 6.

3. TECHNICAL REPORTS (TR) AND PUBLICATIONS

Twelve publications based on ONR supported research and distributed earlier as ONR Technical Reports have appeared or are in press. Several additional technical reports are in preparation and will be distributed later. Five students have written M.S. or Ph.D. theses based on the ONR supported work.

In addition, seven other publications, while resulting from other sources of research support, have made use of the unique instrumentation developed under the present program. Details follow:

3.1 Publications Based Directly on ONR Supported Research

The Technical Report Number (TR-) is given at the beginning of each entry.

TR- 1. Picosecond Internal Conversion in Crystal Violet, M. D. Magde and M. W. Windsor, Chem. Phys. Lett., 24, 144 (1974).

TR- 2. Q-Switching and Mode-Locking the Nd^{3+} -Glass Laser with the Nickel Dithienes, D. Magde, B. A. Bushaw and M. W. Windsor, IEEE J. Quant. Electronics, QE10, 394 (1974).

TR- 3. Picosecond Flash Photolysis and Spectroscopy: 3,3'-Diethyloxadicarbocyanide Iodide (DODCI), D. Magde and M. W. Windsor, Chem. Phys. Lett., 27, 31 (1974).

TR- 4. Picosecond Flash Photolysis and Spectroscopy: Bis-(4-dimethylaminodithiobenzil)-Ni(II), (BDN), D. Magde, B. A. Bushaw, and M. W. Windsor, Chem. Phys. Lett., 28, 263 (1974).

TR- 5. Picosecond Flash Photolysis: Transient Absorptions in Sn(IV), Pd(II), and Cu(II) Porphyrins, D. Magde, M. W. Windsor, D. Holten, and M. Gouterman, Chem. Phys. Lett., 29, 183 (1974).

TR- 6. Picosecond Detection of an Intermediate in the Photochemical Reaction of Bacterial Photosynthesis, M. G. Rockley, M. W. Windsor, R. J. Cogdell and W. W. Parson, Proc. Nat. Acad. Sci. USA, 72, 2251 (1975).

TR- 7. Picosecond Flash Photolysis and Spectroscopy: Transition Metal Coordination Compounds, A. D. Kirk, P. E. Hoggard, G. B. Porter, M. G. Rockley and M. W. Windsor, Chem. Phys. Lett., 37, 199 (1976).

TR- 8. Electron Transfer from Photoexcited Singlet and Triplet Bacteriopheophytin, D. Holten, M. Gouterman, W. W. Parson, M. W. Windsor and M. G. Rockley, Photochem. Photobiol., 23, 415 (1976).

TR- 9. Picosecond Flash Photolysis and Spectroscopy and Kinetics of Intermediates in Bacterial Photosynthesis, M. W. Windsor, M. G. Rockley, R. J. Cogdell and W. W. Parson, Lasers in Physical Chemistry and Biophysics, ed., J. Jourssot-Dubien, Elsevier Sc. Publ. Co., New York, 1975, p. 369-378.

TR-10. Picosecond Flash Photolysis and Spectroscopy in Photochemistry and Photobiology, Maurice W. Windsor, J. Luminescence, 12, 893 (1976).

TR-11. Picosecond Flash Photolysis Studies of Dyes, Inorganic Complexes, Biological Pigments and Photosynthetic Systems, Maurice W. Windsor, J. Phys. Chem., 20, 2278 (1976). (Special issue dedicated to Proceedings of Michael Kasha Symposium).

TR-12. Measurements in the Picosecond and Shorter Time Range, invited chapter for Chemical Experimentation Under Extreme Conditions, ed. B. W. Rossiter, Eastman Kodak Company, for publication in the Interscience Series on Physical Methods in Chemistry, S. C. Pyke and M. W. Windsor, in press, to be published June, 1979.

Abstracts of the above reports follow:

Abstract of TR-1

On the basis of measurements made using the second harmonic of a mode-locked Nd^{3+} laser, we demonstrate that the efficient quenching of the lowest excited singlet state in the dye, crystal violet, ($\tau_R < 10^{-8}$ sec, yet $Q < 10^{-4}$ in ethanol) involves rapid repopulation of the ground state in less than 10^{-11} sec. The repopulation time exhibits a cube root dependence on solvent viscosity. We argue that our data are best explained by a deactivation involving direct $S_1 \rightsquigarrow S_0$ internal conversion. We suggest that the class of triphenyl and diphenylmethane dyes should prove to be more efficient and versatile bleachable shutters and

passive mode-locking elements for laser construction than any dyes currently in use in the visible region of the spectrum.

Abstract of TR-2

Measurement of the relaxation time for transient bleaching of solutions of bis-(dimethylaminodithiobenzil)-nickel explains observed Q-switch and mode-locking behavior. A pronounced solvent effect permits varying relaxation time by a factor of five down to times short enough to be considered for mode-locking in special circumstances.

Abstract of TR-3

We demonstrate transient absorption spectroscopy with picosecond time resolution and nanometer spectral resolution over the entire visible region. To resolve multiple discrepancies in the literature, we studied 3,3'-diethyloxadicarbocyanine iodide. We measured both excited singlet lifetime and ground state depletion and recovery. The kinetics of the two processes are the same. The characteristic time is 1.15 ± 0.15 ns in ethanol and 560 ± 70 ps in water. We report fluorescence yield determinations and comment on the controversy over photoisomer generation.

Abstract of TR-4

The transient absorption spectrum of an electronically excited dithiene, bis-(4-dimethylaminodithiobenzil)-Ni(II), which we term BDN, was measured with 10 ps temporal resolution and 1 nm wavelength resolution. For a series of "heavy atom" solvents, both the ground state and the excited state spectra remained constant while the decay kinetics of the excited state absorption, as well as the recovery from ground state bleaching, varied; the extreme values were 9 ns in benzene and 0.22 ns in iodoethane. The excited state spectrum can plausibly be fit by a particular one electron transition between previously calculated molecular orbitals, although this clearly does not prove that these orbitals provide the best description for the excited states. Similarly, present data do not determine a unique decay scheme. We comment on three possibilities within the framework of the ground state virtual orbital picture.

We are aware of no previous direct detection of excited states of such nickel complexes either in absorption or in emission. We conclude that our recently developed techniques will be generally applicable in probing the photodynamics of presently intractable molecular species. The significance of our data for laser mode-locking is discussed.

Abstract from TR-5

From picosecond flash photolysis and spectroscopy, the absorption spectra of the first excited singlet S_1 and of the first excited triplet T_1 of $(OEP)SnCl_2$ are determined; we also determine triplet quantum yield, $\phi_T \sim 0.80$. Similar S_1 and T_1 phototransient absorption spectra occur in (OEP)Pd. However, two Cu porphyrins show only one phototransient absorption spectrum. Our T_1 absorption results are generally consistent with the available earlier spectroscopic studies made with other techniques. Our value for ϕ_T lies intermediate between values given by two earlier studies, which were based on two different methods.

Abstract from TR-6

Preparations of photosynthetic reaction centers from Rhodopseudomonas sphaeroides were excited with flashes lasting approximately 8 psec. Immediately after the excitation, there appeared a transient state which was characterized by new absorption bands near 500 and 680 nm, by a bleaching of bands near 540, 600, 760, and 870 nm, and by a blue shift of a band near 800 nm. The transient state decayed with an exponential decay time, τ, of 246 ± 16 psec after the flash. As the transient state decayed, the radical cation of the reaction center bacteriochlorophyll complex appeared. This indicates that the transient state is an intermediate in the photo-oxidation of the bacteriochlorophyll. The absorption spectrum of the transient state shows the state to be identical with a state (P^F) which has been detected previously in reaction centers that are prevented from completing the photooxidation, because of chemical reduction of the electron acceptor. Analysis of the spectrum suggests that the formation of P^F involves electron transfer from one bacteriochlorophyll molecule to another within the reaction center, or possibly from bacteriochlorophyll to the bacteriopheophytin of the complex. The initial absorbance changes after flash excitation also include a bleaching of an absorption band at 800 nm. The bleaching decays with ≈ 30 psec. The bleaching appears not to be a secondary effect, but rather to reveal another early step in the primary photochemical reaction.

Abstract from TR-7

Lifetimes of excited states of a number of transition metal compounds have been investigated with picosecond time resolution by following excited state absorption ground state bleaching and repopulation. The lowest excited quartet state of octahedral chromium(III) compounds is found to have a lifetime with respect to intersystem crossing to a doublet state too short to be followed by this technique. The lifetimes of excited states of some non-luminescent compounds of iron and ruthenium have been established in the sub-nanosecond range.

Abstract from TR-8

Nanosecond and picosecond kinetic techniques have been used to study electron transfer from the first excited singlet state (Bph*) and the first excited triplet state (Bph^T) of bacteriopheophytin to p-benzoquinone. Quenching of the first excited singlet state by 40 mM p-benzoquinone results in a decrease in the lifetime of Bph* but does not lead directly to the formation of the π-cation radical ($\mathrm{Bph}\overset{+}{\cdot}$). In the presence of 8 M methyl iodide and 40 mM p-benzoquinone together, the singlet lifetime is reduced further; however, the quantum yield of Bph^{T} is enhanced due to the increased rate of intersystem crossing between Bph* and Bph^{T}. Electron transfer from Bph^{T} to p-benzoquinone leads to the formation and detection of $\mathrm{Bph}\overset{+}{\cdot}$. The results are discussed in terms of the spin-selectivity of the reverse electron transfer process within the intermediate charge transfer complexes.

Abstract from TR-9

We have used the techniques of picosecond flash photolysis and kinetic spectroscopy to examine the primary photochemical reaction of bacterial photosynthesis. Immediately following excitation of reaction centers (RC's) of *Rhodospeudomonas Sphaeroides* with 530 nm wavelength laser pulses of 8 ps duration, a transient state is observed that decays with an exponential lifetime of 246 ± 16 ps. As the transient state decays, the radical cation of the RC bacteriochlorophyll complex appears. The absorption spectrum of the transient state shows that it is identical with a state (P^{F}) that has been detected previously in RC's that are prevented from completing the photo-oxidation, because of chemical reduction of the electron acceptor. Thus the results demonstrate conclusively that P^{F} is a direct intermediate in the photo-oxidation of the bacteriochlorophyll.

Abstract from TR-10

The application of the technique of picosecond flash photolysis and kinetic spectroscopy in the author's laboratory to a variety of chemical and biological systems is reviewed and briefly discussed. Reference is made to studies of internal conversion in crystal violet and bis-(4-dimethyl amino dithio benzil)-Ni(II), BDN, as a function of solvent; to the excited singlet and triplet state spectra and lifetimes of several porphyrins; and to studies of the primary electron-transfer reaction, both in bacterial photosynthesis and in model systems, such as bacteriopheophytin quenched by p-benzoquinone.

Abstract from TR-11

The application of the technique of picosecond flash photolysis and kinetic spectroscopy in the author's laboratory to a variety of chemical and biological systems is reviewed and briefly discussed. Reference is made to studies of internal conversion in crystal violet and bis-(4-dimethyl amino dithio benzil)-Ni(II), BDN, as a function of solvent; to the excited singlet and triplet state spectra and lifetimes of several porphyrins. Studies of non-radiative processes that quench luminescence in inorganic complexes of chromium, manganese, ruthenium and iron are also reported. A novel technique for measuring quantum yields of intersystem crossing, made possible by picosecond spectroscopy, is described and its application to the dye, rose bengal, is reported. Studies of the primary electron-transfer reaction, both in bacterial photosynthesis and in model systems, such as bacteriopheophytin quenched by p-benzoquinone, were also made.

Abstract from TR-12

Instrumentation and techniques for chemical measurements in the picosecond and shorter time range are reviewed and described in detail. Representative applications in photochemistry and photobiology are given.

3.2 Reports and Manuscripts in Preparation

TR-13. A Study of the Photodegradation of the Blue-Green Laser Dye, AC3F, A. C. Craig, S. C. Pyke and M. W. Windsor.

TR-14. Predicted and Measured Picosecond Lifetimes of Several Cyanine Dyes, A. C. Craig, D. W. Warner and M. W. Windsor.

TR-15. Picosecond Absorption Measurements of Electronic Relaxation in Triphenylmethane Dyes, D. Cremers and M. W. Windsor.

TR-16. An Analysis of the Conformations of the Triphenylmethane Dye, Crystal Violet Using Molecular Orbital Theory, B. A. Bushaw, D. Cremers and M. W. Windsor.

TR-17. A Possible Mechanism for the Viscosity Dependence of the Electronic Relaxation of Crystal Violet, D. Cremers and M. W. Windsor.

3.3 Students Theses Based on ONR Supported Work

1. B. A. Bushaw, M.S., Washington State University, 1978, "Picosecond Flash Photolysis Kinetic Spectroscopy: The Effect of Viscosity Upon Rotationally Coupled Internal Conversion in Crystal Violet."
2. J. Dewey Holten, III, Ph.D., University of Washington, 1976, "Excited States and Electron Transfer Dynamics for Some Porphyrins and Chlorophylls."
3. A. B. Nielsen, M.S., Washington State University, 1978, "The Comparative Photophysics of Two Xanthene Dyes."
4. D. W. Warner, M.S., Washington State University, 1978, "Picosecond Spectrokinetic Measurements of Singlet and Triplet States in Some Aromatic Compounds."
5. D. A. Cremers, Ph.D., Washington State University, 1979,"Picosecond Studies of Electronic Relaxation in Some Triphenylmethane Dyes."

3.4 Other Publications Benefiting from the ONR Program

1. Picosecond Flash Photolysis in Biology and Biophysics, invited chapter for Vol. 7 of the Annual Review of Biophysics and Bioengineering, D. Holten and M. W. Windsor, 7, 189-227 (1978).
2. Primary Photochemical Processes in Isolated Reaction Centers of Rhodospeudomonas Viridis, D. Holten, M. W. Windsor, W. W. Parson and J. P. Thornber, Biochim. Biophys. Acta, 501, 112-126 (1978).
3. Models for Bacterial Photosynthesis: Electron Transfer from Photoexcited Singlet Bacteriopheophytin to Methyl Viologen and m-Dinitrobenzene, D. Holten, M. Gouterman, W. W. Parson, and M. W. Windsor, Photochem. Photobiol., in press, 1978.
4. Isolated Photochemical Reaction Centers from Bacteriochlorophyll b-Containing Organisms, J. P. Thornber, P. L. Dutton, J. Fajer, A. Forman, D. Holten, J. M. Olson, W. W. Parson, R. C. Prince, D. M. Tiede and M. W. Windsor, Proc. Fourth Intl. Cong. Photosynthesis, Reading, England, September, 1977.
5. Picosecond Studies of Electron Transfer in Bacterial Photosynthesis and In Model Systems, Dewey Holten, Maurice W. Windsor and W. W. Parson, Proc. Topical Meeting on Picosecond Phenomena, 1978. To be published by Springer-Verlag, eds. S. L. Shapiro, C. V. Shank and E. P. Ippen.
6. Kinetics of Photochemical Electron Transfer Reactions In Vivo and In Vitro, W. W. Parson, C. C. Schenck, R. E. Blankenship, D. Holten, M. W. Windsor and C. V. Shank. Proc. Johnson Foundation Symposium, 1978, in press.
7. Picosecond Studies of Excited State Decay Kinetics in Chromium(III): Trans-Diiosothiocyanatobis(ethylenediamine)chromium(III), S. C. Pyke and M. W. Windsor, accepted for publication as a Communication to the Editor, J. Am. Chem. Soc., Oct/Nov, 1978.

4. Invited Lectures and Presentations

1973	January, :	IBM Research Laboratory, San Jose.
1974	May :	University of Oregon.
	June, :	Eleventh Informal Conference on Photochemistry, Vanderbilt University.
	September, :	University of Southampton, University of Paris, "General Discussion on Radiationless Processes," Munich.
1975	February 4 & 5:	University of British Columbia, Vancouver and University of Victoria.
	April, 28 :	Eastman Kodak Research Laboratories, Rochester, New York.
	May, 2 :	Optical Sciences Division, Naval Research Laboratory, Washington, D.C.
	June 17-20 :	Invited lecturer at 27th International Reunion of Societe de Chimie Physique on "Lasers in Physical Chemistry and Biophysics," Paris.
	July 21-25 :	Invited participant in Gordon Conference on "Physico-chemical Aspects of Photosynthesis," Tilton, N.H.
	August 7-13 :	Invited lecturer at Eighth International Conference on Photochemistry, Edmonton, Canada.
	September 1-5 :	Invited lecturer at the 1975 International Conference on luminescence, Tokyo, and Chairman of Group Discussion on Picosecond Spectroscopy.
1976	January 8-10 :	Plenary address at The Michael Kasha Symposium on Energy Transfer in Organic, Inorganic and Biological Systems, Florida State University, Tallahassee, Florida.
	February 18-20:	Invited address at the American Society for Photobiology Annual Meeting, Denver, on "Picosecond Flash Photolysis Studies of Dyes, Biological Pigments and Photosynthetic Systems."
	April 26 :	Biophysics Chemistry seminar at University of California, Berkeley.
	October 5-7 :	Invited lecturer on "Laser Investigations of Primary Events in Photosynthesis," at a Symposium on The Molecular Mechanisms of Light Transformation in Photosynthesis, held in Moscow, USSR.
	October 20 :	The Davy Faraday Laboratory, The Royal Institute of Great Britain, London.

October 26-27 : One of eight invited speakers in a Lecture Series on *The Chemical Impact of Lasers*, sponsored by the Department of Chemistry, Northwestern University, Evanston, Illinois.

1977 April 16-21 : Invited seminars at the University of Western Ontario and the University of Guelph, Canada.

August 11-19 : Invited speaker on "Picosecond Laser Studies in Biophysics" at the Gordon Conference on "Non-Linear Optics and Lasers," Plymouth, N.H.

1978 February 15 : Seminar at University of Maryland.

February 16 : "Picosecond Studies of Primary Events in Bacterial Photosynthesis," M. W. Windsor and D. Holten. Presented at the "Picosecond Lasers in Chemistry" symposium of the American Association for the Advancement of Science, Washington, D.C.

September 11-14: "Picosecond Studies of Electron Transfer in Bacterial Photosynthesis and in Model Systems," M. W. Windsor and Dewey Holten. National Meeting of the American Chemical Society, Miami, Florida.

Dr. Windsor was a member of the Program Committee for the first Topical Meeting on Picosecond Phenomena, held May 24-26, 1978 at Hilton Head, South Carolina and presented an invited paper on "Picosecond Studies of Electron Transfer in Bacterial Photosynthesis and Model Systems."

In addition, he was Program Chairman for the Session on "Laser Studies in Photosynthesis" at the Gordon Research Conference on Lasers in Medicine and Biology, June 26-30, Kimball Union Academy, Meriden, New Hampshire and also presented an invited talk.

5. Work in Progress - Unpublished to Date

5.1 Crystal Violet and Triphenylmethane Dyes

Three manuscripts are in preparation as detailed in 3.2. These will be distributed as ONR Technical Reports (TR's 15, 16, 17) at the same time as they are submitted for publication.

We have concluded recently a study of the viscosity dependence of electronic relaxation of some triphenylmethane (TPM) dyes (see Fig. 1). This dependence is believed to be due to the effects of viscous drag upon the rate of charge of molecular conformation which occurs in the excited state.[1,2] The new conformation is characterized by fast rates of internal conversion which produce rapid depopulation of the excited state. The more viscous the medium the slower the conformational charge and the slower the total rate of electronic relaxation. It has been proposed that in TPM dyes the dominant structural change is rotation of the phenyl rings about the bond between the central and ring carbon atoms (bonds α, β, and γ of Fig. 1.a). The main efforts of this study have been to (1) experimentally monitor electronic relaxation of some TPM dyes using a variety of solvents and to (2) correlate the observed behavior with potential energy surfaces calculated using molecular orbital theory.

The experimental data indicate the following about ground state recovery (GSR) and excited state absorption (ESA) in the dyes studied:

(1) the rates of GSR and of the decay of ESA decrease with increases in solvent viscosity,

(2) GSR and the decay of ESA do not obey a simple exponential function,

(3) the rates of both increase with increased temperature.

The difference optical density spectra at times of +20ps, +80ps, and +2733ps following excitation indicate several facts. First, GSR and the decay of ESA proceed homogeneously across the spectrum and secondly, less than 3% of the molecules populate the triplet state with excitation by a picosecond pulse. Finally, three distinct regions are apparent in the difference spectrum: GSR (500-630 nm), ESA (380-500 nm), and stimulated emission (630-860 nm) producing amplification of the probe light. Measurements of GSR in the dyes crystal violet (CV), ethyl violet (EV), and parafucshin (PF) reveal that the rate of recovery increases in the order EV < CV < PF. This result may be attributed to increased viscous drag, due to increased end group size on the phenyl rings, which occurs in the order EV > CV > PF (see Fig. 1).

A conformational analysis, based upon the Pariser-Parr-Pople molecular orbital method, has been performed assuming that ring rotation and bond expansion (of bonds α, β, γ of Fig. 1.a) are the important conformational coordinates. The conclusion of this analysis is that molecular excitation leads to a state in which a single phenyl ring is driven towards greater angles by steric and electrostatic effects. This, in turn, leads to a narrowing of the S_1 to S_2 energy gap, and enhanced rates of internal conversion. These calculations also indicate that the ground state equilibrium conformation is the symmetric propeller structure with $\theta = 40°$, in agreement with experiment. The observed temperature dependence is not directly predicted by these calculations. However, the potential surfaces are such as to allow the possibility of a thermal diffusion mechanism initiating ring rotation which, once started, proceeds via a driven mechanism.

The experimental data indicate a connection between solvent viscosity and rates of electronic relaxation. The direct measurements made in this laboratory substantiate the results of the more indirect measurements of fluorescence quantum yields made previously.[1] The results obtained with the dyes EV, CV, and PF are particularly important. In addition, the molecular orbital calculations indicate that phenyl ring rotation can, qualitatively at least, account for the observed viscosity effects. The final task of this study is to determine if the experimental data and MO calculations agree quantitatively as well as qualitatively. Numerical calculations are now being made to establish if this is the case.

1. T. Förster and G. Hoffmann, Z. Physik. Chem. N.F., 75, 63 (1971).
2. D. Magde and M. W. Windsor, Chem. Phys. Lett., 24, 144 (1974).

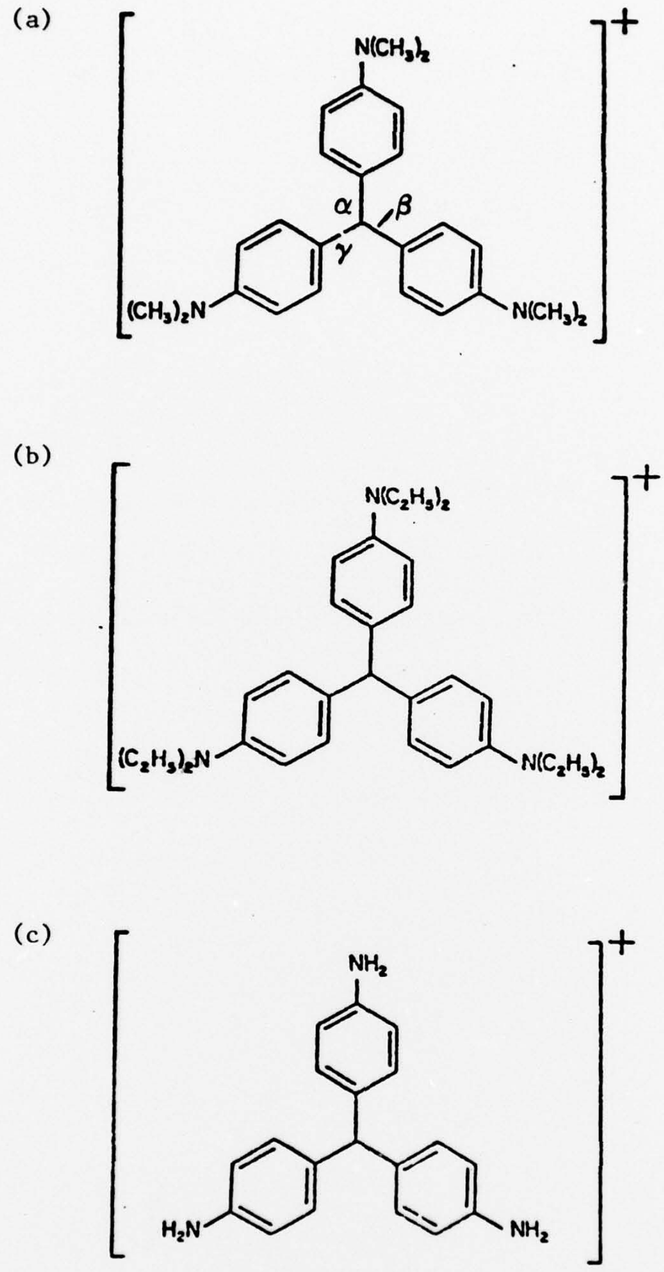

Fig. 1. Some triphenylmethane dyes used in this study: (a) crystal violet, (b) ethyl violet, and (c) parafucshin.

5.2 Cyanine Dyes

Mr. Warner has completed for his M.S. thesis a picosecond study of internal conversion in a series of cyanine dyes (see QSR, No. 21-25). The measured lifetimes correlate well ith values predicted by Professor A. C. Craig of Montana State University, based on integrated absorption and quantum yield data. A manuscript (TR-17) is in preparation.

5.3 Xanthene Dyes

Mr. Nielsen has completed for his M.S. thesis a comparative study of two substituted xanthene dyes, rose bengal and phloxine B (see QSR, No. 21-25 for details).

5.4 Degradation of Laser Dyes

During the last six months of the contract a preliminary study of the photodegradation of the laser dye, AC3F [Blue-Green Dye Laser Development, Annual Report F4-75, NELC F233 by Celto, Schimitschek and Trias] has been made in collaboration with Professor A. C. Craig of Montana State University. The results will be inssued as Teechnical Report No. 13.

5.5 Instrumentation

We have successfully completed the interfacing of our picosecond spectrometer via a 2-dimensional vidicon-OMA detector to a dedicated microprocessor (Southwest Technical Instruments), purchased in kit form and assembled in our laboratory. Absolute difference spectra (optical density versus wavelength) over a wide spectral range (∿300 nm can now be obtained in a single shot. O.D. changes down to 0.01 can be resolved and a series of time resolved spectra at 10 ps intervals in the range 0 - 5 ns can be obtained as required. We have been working towards this goal for several years and its achievement will greatly reduce the time and effort required to acquire picosecond spectroscopic and kinetic data on a wide range of chemical and biophysical systems. A manuscript describing the equipment is in preparation and will be submitted as a Technical Report when ready.

6. Personnel

The following is a list of the various research associates, graduate and undergraduate students who have contributed to the ONR supported research and in return received training in my laboratory:

Postdoctoral Research Associates

Dr. M. Douglas Magde, now Assistant Professor of Chemistry at University of California, San Diego.

Dr. M. G. Rockley, now Assistant Professor of Chemistry at Oklahoma State University.

Dr. J. Dewey Holten, still at WSU.

Dr. S. C. Pyke, still at WSU.

Graduate Assistants

Bruce A. Bushaw, M.S., 1975, now Research Chemist at Batelle Northwest in Richland, Washington.

Dewey W. Warner, M.S., 1978, now a Research Technician in College of Veterinary Medicine, WSU.

Andrew B. Nielsen, M.S., 1978, now at Boeing Company, Seattle.

David B. Cremers, Ph.D. expected 1979.

Sadiq Shah, Ph.D. expected 1981.

Francis Tsang, left in 1975 to pursue studies in nuclear engineering at University of Missouri.

Undergraduate Assistants

Robin M. Anderson

Mrs. Anderson, who was an undergraduate research assistant in my laboratory, received her B.S. degree in June, 1976. She has accepted a position with the Energy Research & Development Administration (ERDA) at Richland, Washington. During her sojourn in my laboratory she learned how to operate the picosecond flash photolysis apparatus and assisted significantly in gathering and reducing data for several of our research studies.

Jerry Owens

Mr. Owens, a senior in Chemistry, worked in my laboratory during 1975 and the first half of 1976. Initially he assisted Dr. Rockley in gathering and reducing picosecond spectral and kinetic data on inorganic complexes (chromium, ruthenium, iron). More recently he has assisted Mr. Cremers in constructing and characterizing various solvent mixtures of glycerol/water and glucose/glycerol that would provide constant viscosity solvents for crystal violet at several different temperatures. He also built an insulated constant temperature bath to thermostat the sample cell for the laser experiments. Mr. Owens received his B.S. degree in June, 1976.

Nils Petersen

Mr. Petersen, a junior chemistry major at Whitman College, Walla Walla, spent a month in the laboratory in the summer of 1976 purifying a supply of crystal violet for the temperature-dependence studies. He also assisted in mode-locking experiments with the dye laser. He is now a graduate student in Veterinary Medicine at WSU.

Ron Selensky

Mr. Selensky, a junior chemistry major from the College of Great Falls, Montana, spent the summer of 1976 in my laboratory supported by an NSF-URP program awarded to the WSU Chemistry Department. He learned how to operate the picosecond apparatus and studied the quenching of di-tertiary butyl)indigo in its excited state by phenol. He also assisted Mr. Cremers in mode-locking studies of the Candela dye laser. He received his B.S. degree in 1977, spent a year working in industry and has this Fall entered graduate school at WSU. He plans to work for a Ph.D. in my laboratory.

David Jaffer

Mr. Jaffer, a junior chemistry major at Reed College, worked in my laboratory for 10 weeks in the summer of 1975, funded by an NSF-URP (Undergraduate Research Participation) award to the Chemistry Department. His main project was to try passing the 1060 nm single picosecond pulse a second time through the amplifier rod with the object of obtaining a higher pulse energy for harmonic generation. Mr. Jaffer completed his B.S. degree in 1976 and was awarded both a NATO study abroad fellowship, and a Churchill Fellowship. He is now pursuing a Ph.D. program in fast photochemical kinetics at Churchill College, University of Cambridge.

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Scientific Advisor
Commandant of the Marine Corps (Code RD-1)
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University of California
Department of Chemistry
Los Angeles, California 90024 1

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