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FINAL TECHNICAL REPORT

UNIVERSITY RESEARCH INSTRUMENTATION PROGRAM:

PICOSECOND LASER CHEMISTRY OF MATERIALS ADSORBED ON SURFACES

SUBMITTED BY

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Final Report of Research Accomplishments AFOSR-86-0223

Abstract

The research supported by this contract has provided new insights into photophysical and photochemical processes in condensed media, and in the liquid-air interface. Using the new picosecond laser-detection system we monitored the various channels by which photoexcitation energy is used to effect physical as well as chemical changes in molecular systems. Specifically, we have accomplished the first time resolved studies dealing with photochemical and photophysical processes in the air-liquid interface using surface specific second harmonic generation techniques. We also discovered novel relaxation effects on ultrafast photoisomerization reactions due to restricted microenvironments. The results dealing with *t*-stilbene inclusion complexes with various cyclodextrins provided a model for chemical reactions and molecular motion in restricted environments.

Completed Project Summary

The objective of our research during the course of this contract was to obtain a microscopic description of molecular processes that take place in liquids and surfaces. To this end we addressed the issue of how microenvironments can influence very fast reaction dynamics. By following the *trans-cis* photoisomerization of stilbene encapsulated inside cyclodextrins we were successful in determining the effect on the energetics and on the dynamics of the reaction caused by microheterogeneous environments. The results provided a model for reactions in restricted environments.

Most recently, we have extended our ultrafast laser studies of liquids to include a most interesting region of a liquid, namely the interface region with another bulk medium, e.g. its vapor. The asymmetry in forces experienced by molecules in this inhomogeneous region results in physical and chemical properties that can be markedly different from those of the bulk. The chemical composition and

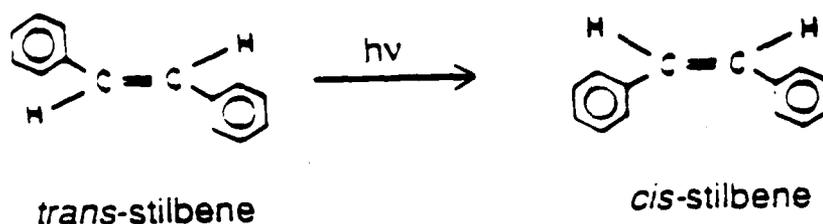
geometrical arrangement of molecules at the interface of a binary solution does not correspond to its bulk composition or to its bulk isotropic structure. The different dielectric, e.g. polarity, and transport properties, e.g. viscosity, can result in very different static and dynamic properties in the bulk and interfacial regions. To probe the liquid/vapor interface, we used the surface selective technique of second harmonic generation. We have used picosecond lasers to gain information about the composition and orientational structure of solute molecules at the air/water interface, we determined how chemical reactions differed in the air/water interface compared with the bulk, and carried picosecond time resolved measurements of excited state lifetimes in the air/water interface. In these pump/probe studies we used second harmonic generation to probe the dynamics in the interface. We also measured the bulk dynamics of the same process in the same solution using picosecond time resolved fluorescence. In this way we are able to obtain information not only about the interface, by determining how it differs from bulk dynamics, but also about the molecular process itself.

A. Effect of Restricted Environments on Photochemical Reactions

Cyclodextrins, zeolites, micelles, and other microheterogeneous structures have received increasing attention in recent years, since these systems have been found to provide so called restricted microenvironments or cavities of molecular dimensions (of the order of 10 Å) capable of sequestering and the chemistry of reactive molecules. Indeed, these systems provide molecular environments that have been shown to modify both a variety of different chemical pathways as well as the dynamics of energy relaxation for the encapsulated guest molecules. The effect on the energetics and on the dynamics caused by these microheterogeneous environments can often be rationalized by a simple "lock and key" hypothesis, which is widely used to explain the nature of the guest-host interactions in enzymatic systems. Dynamic effects may result from geometric restrictions imposed on the guest molecule, resulting from the limited space in the host cavity. For example, cyclodextrins are cone shaped oligosaccharides which have a hydrophobic cavity that varies from 5.6 Å for α -cyclodextrin up to 8 Å for γ -cyclodextrin. This space limitation could affect the chemistry of a reactive guest molecule

because it may restrict or encourage motions that are necessary for a reaction. Another factor that can affect energy relaxation of a guest molecule results from specific guest-host interactions. These interactions could provide a dramatic change in the energetics of a reaction. For example, the effective polarity around the guest molecule as it is bound inside the cavity may be substantially different than in the bulk.

In order to address the issue of how microenvironments can influence very fast reaction dynamics, we have investigated the photoisomerization of *t*-stilbene complexed to cyclodextrins. The *trans-cis* photoisomerization of stilbene was chosen because it has been extensively studied in homogeneous solution. It is known, for example, that the reaction occurs by a thermally



activated twisting around the central double bond, which thus provides the principal mode of deactivation of the excited singlet state of stilbene. From picosecond time resolved methods we have been able to show for the first time that the nature of the complex is different for different cyclodextrins, being dependent mainly on the cavity size. Furthermore, we found that two distinctly different complexes are formed for the larger β - and γ -cyclodextrins, which yield vastly different kinetics for the photoisomerization process.

In the presence of α -cyclodextrin a *single-exponential fluorescence decay* behavior was observed for *t*-stilbene. In contrast, in the presence of β - and γ -cyclodextrin the excited singlet state decay of *t*-stilbene was non-exponential but could be fitted to the sum of two exponentials, (Fig. 1). The short-lived component (of about 50 ps) is similar to the fluorescence lifetime of *t*-stilbene in low-viscous alcohols (methanol and ethanol). The second, long-lived component (of several hundred picoseconds), had values typical for the decay times

of stilbene fluorescence in highly viscous or rigid environments. The contribution of the long component to the decay curve is also strongly dependent on temperature, as shown in Fig. 2.

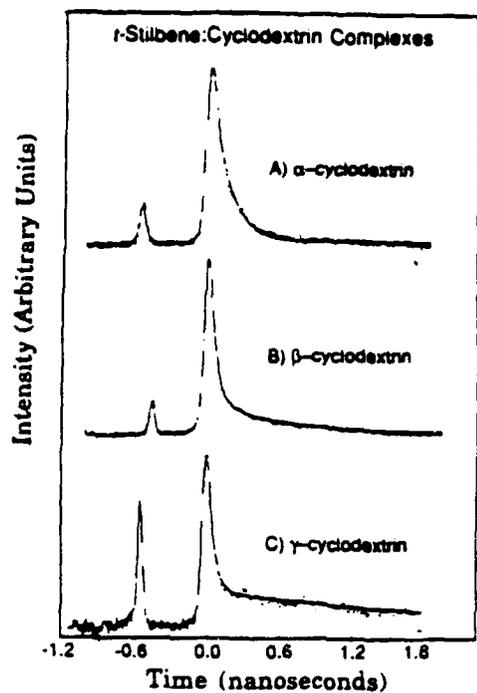


Fig. 1 Fluorescence decay of *t*-stilbene in presence of: a) α -cyclodextrin; b) β -cyclodextrin and c) γ -cyclodextrin, at room temperature

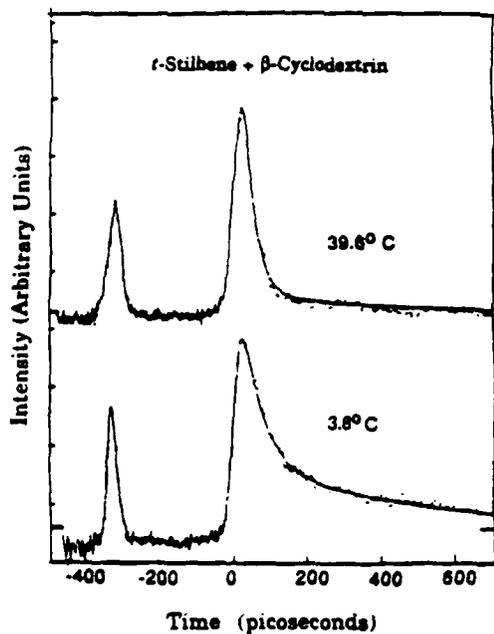
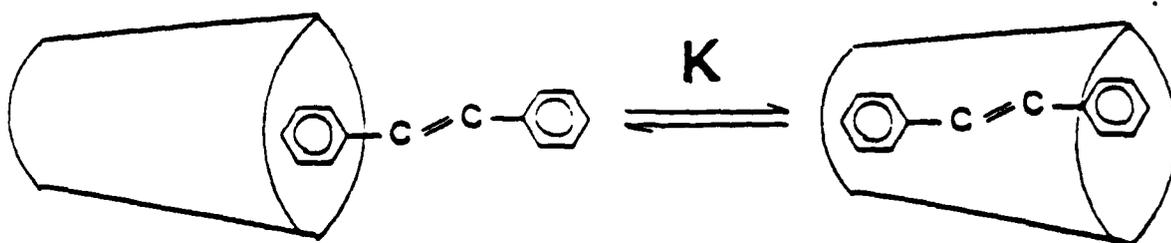


Fig. 2 Fluorescence decay of *t*-stilbene in the presence of β -cyclodextrin in aqueous solution at two different temperatures: a) at 39.9°C; b) at 3.8°C

Using picosecond dynamic measurements of the photoisomerization reaction of *t*-stilbene, we have been able to show the effect of restricted environments caused by

complexation to cyclodextrins on reaction rates. We also determined that the nature of the complex depends on the cavity size. A single complex is formed between *t*-stilbene and α -cyclodextrin molecules, resulting in a relatively slow single exponential decay, compared to nonviscous homogenous media. In the presence of the larger cavity size β - (and γ -) cyclodextrin, on the other hand, two distinct complexes are formed that result in a double exponential fluorescence decay of *t*-stilbene. The nature of the two complexes for the large cavity cyclo-



Scheme 1. Dynamic equilibrium between "loose" and "tight" stilbene/cyclodextrin complexes

dextrins can be viewed as a tightly bound form (inside the cavity), leading to a relatively long decay time (comparable to the fluorescence lifetime in rigid environments), and a loose association, displaying a comparably fast decay of the stilbene fluorescence like in nonviscous media. In the case of complexation with β -cyclodextrin, values of $\Delta H = -33 \pm 3$ kJ/mol and $\Delta S = -127 \pm 9$ J mol⁻¹ K⁻¹ were determined for the differences of enthalpy and entropy between the two forms of complexes between *trans*-stilbene and β -cyclodextrin. It is emphasized that which type of complex is formed, is determined by the size of the cyclodextrin cavity. With α -cyclodextrin, providing a fit for only one half of the stilbene molecule, only a tightly bound complex is formed, whereas with β - (and γ -) cyclodextrin both types of complexes are formed. In summary, picosecond time resolved methods permitted for the first time the identification of two distinctly different complexes that yield vastly different reaction dynamics for the photoisomerization reaction of *t*-stilbene. The results provide a model for reactions in restricted environments.

B. Dynamics at the Liquid/Vapor Interface

To initiate our studies of dynamic processes at the liquid/vapor interface, and thereby learn about its pitfalls and problems, we chose a molecule that has a strong absorption at the laser wavelength. In addition, we required that the molecule have a large nonlinear polarizability, $\alpha^{(2)}$, which would be further enhanced by one and two photon resonances at the probe wavelength. The process we chose to study was the excited singlet state relaxation of Rhodamine 6G at the air/H₂O interface. A great deal is known about the spectroscopy and excited state relaxation, energy transfer and rotational motion of Rhodamine 6G, a molecule that we have had a good deal of experience with in our laboratory. The bulk concentration of the Rhodamine 6G was 2×10^{-4} M which results in a surface concentration that is well below a monolayer coverage as we determined from surface tension measurements. The experiment consisted of exciting Rhodamine 6G to S₁ with a 532 nm pump pulse and monitoring the dynamics by detection of a second harmonic signal at 266 nm generated by a time delayed 532 nm probe pulse. The pump and probe pulses arrived at the solution surface at sharply different angles to insure, as we determined, that the pump pulse was not producing any second harmonic that could be detected at the photomultiplier. With this arrangement we obtained the first excited state dynamics at a liquid interface, as shown in Fig. 3. The SH

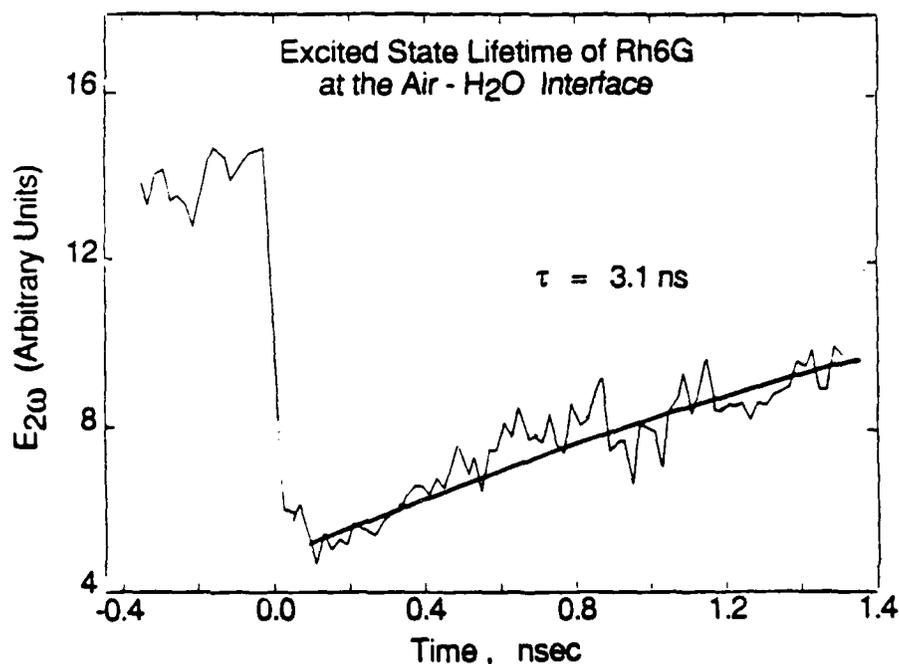


Fig. 3 Excited state dynamics of Rh6G at the air-water interface, as measured by surface second harmonic techniques

signal decreases on excitation of the ground state molecules and then recovers with a time constant of 3.1 ns. The observed decrease in SH signal can arise from the smaller nonlinear susceptibility of the excited molecules due to the absence of the strong one photon resonance of the ground state molecules. In addition the phases of the ground and excited molecules are likely of opposite sign and thus diminish the SH signal. To compare the ground state recovery with the excited state lifetime in the bulk we measured the fluorescence decay from the bulk Rh 6G excited molecules using a picosecond streak camera. Fluorescence from the interfacial Rhodamine 6G is swamped by the bulk fluorescence and can therefore be neglected. The decay time of the bulk molecules is 3.7 ± 0.2 ns, which for Rhodamine 6G would be the same as the ground state recovery time since the quantum yield of fluorescence is close to unity. The small difference between the interface and bulk lifetimes can be a consequence of the smaller average separation between Rhodamine molecules in the surface, about 15 Å, compared with roughly 130 Å in the bulk. At the interface there can be some excited state quenching due to energy transfer to a trapping site, e.g. a dimer, whereas in the bulk the efficiency of energy transfer is much smaller because of the larger intermolecular separations. Using Rhodamine 6G as a pilot study we varied the pump intensity to determine if the surface and bulk excited state decays were intensity-dependent and found that they were not.

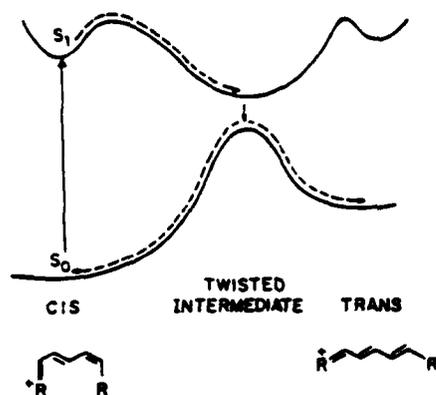
C. Dynamics of Chemical Reactions at the Vapor/Liquid Interface

We all recognize that a chemical reaction can be vastly different in a bulk liquid from its gas phase counterpart. Not only the products but also the related kinetics can differ due to the effects of interactions of the reacting molecules with the solvent molecules of the liquid. Even for a unimolecular reaction, such as a dissociation or isomerization, the kinetics and channels for chemical change can be markedly different. In a photochemical process electronic and vibrational energy relaxation can compete with chemical change in the initially excited state and thereby vitiate chemical change, or introduce new channels by relaxation to other states and thus yield different products or distribution of products.

Just as gas and liquid phase chemistry can differ we see that similar considerations suggest that a chemical reaction at an air/liquid or liquid/liquid interface can be markedly different from that in the bulk liquid. As a consequence of the interfacial chemical composition and geometrical structure, its dielectric and transport properties such as solvent polarity and viscosity, can be very different from that in the bulk liquid. The spatial and orientational restrictions on a molecule at the interface can modify its motions, and the potential surface and dynamics of its chemical reactions.

Photoisomerization of DODCI at Vapor/Liquid Interface

Let us consider the photoisomerization of the cyanine dye DODCI, a molecule that has a large nonlinear polarizability $\alpha^{(2)}$ and thus is readily pumped and probed at the visible frequencies of a dye laser. The potential surface for isomerization about a bond in the polymethine chain can be shown as follows,



It has been established in bulk studies that the dynamics of the photoisomerization of DODCI is strongly dependent on interactions with surrounding solvent molecules. One of the chief factors influencing the kinetics is the friction the molecule experiences as it undergoes a rotation about a central bond and crosses the barrier between the cis and trans forms.

The experimental approach for probing the photoisomerization dynamics in the interface is the same as has been described for Rhodamine 6G, i.e. the pump excitation pulse and the time delayed probe pulse that generates the SH signal. The surface results are shown in Fig. 4. To obtain the bulk kinetics, which was measured in the same solution as used for the SH interfacial study, we used a lens to collect fluorescence from the excited bulk molecules, and focused it onto the slit of our picosecond streak camera. This yielded the decay from the photoexcited S_1 cis singlet state. Its value was

determined by the isomerization rate since this is the fastest decay channel from S_1 . For DODCI in water the excited state lifetime in the bulk was found to be 520 ps, Fig. 5.

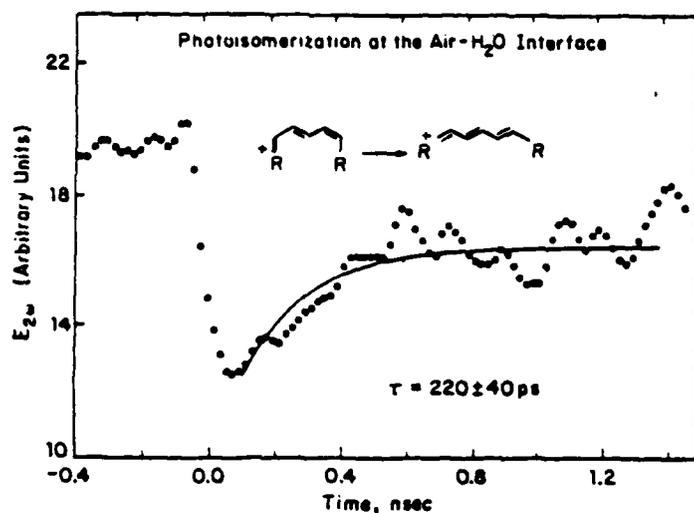


Fig. 4 Surface second harmonic field, $E_{2\omega}$, as a function of time following photoexcitation of an aqueous solution containing DODCI

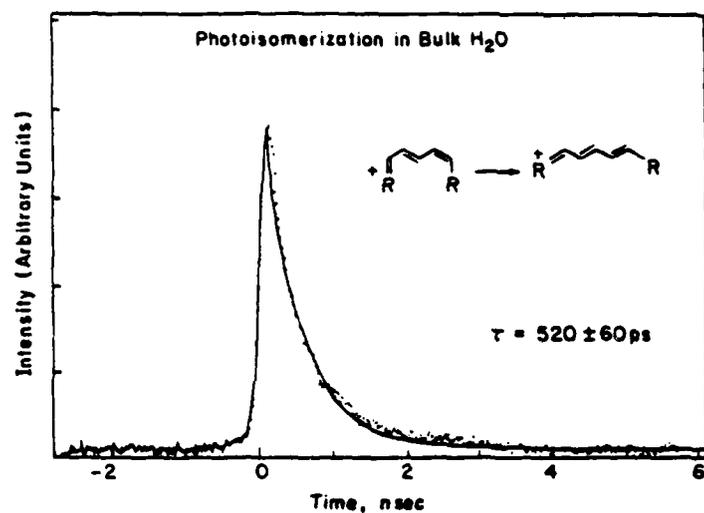


Fig. 5 Fluorescence decay of DODCI in water

To extract the kinetics of isomerization in the air/water interface we make the following observations. The SH signal $I_{2\omega}$ generated at time t after the pump pulse is proportional to the square of the surface nonlinear susceptibility $\chi^{(2)}(t)$, a quantity which is time dependent.

$$I_{2\omega} \sim |\chi_{\text{Total}}^{(2)}|^2$$

The total nonlinear susceptibility has contributions from the ground state S_0^{cis} molecules, the excited state S_1^{cis} molecules, and at some later time the ground state photoisomer S_0^{trans} . The lifetime in the