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A sophisticated picosecond laser and detection system has been constructed and used to obtain new information on key energy relaxing phenomena in molecular systems.

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FINAL TECHNICAL REPORT

The aim of the research undertaken with ARO support was to investigate ultrafast molecular relaxation phenomena and to develop the necessary picosecond laser methods to carry out these studies. During the period of the ARO contract a significant part of our efforts have involved putting together a picosecond laser, detection and data analysis system to enable us to carry out picosecond transient absorption and emission measurements. The present experimental set-up consists of a mode-locked Nd:glass laser as the excitation source, a picosecond streak camera serving as the detection system for emission or for the transient absorption of a probe flash lamp source, an optical multichannel analyzer for recording the time dependent optical signals, and finally a small computer for data collection and manipulation. The major stumbling block we have encountered has been with the picosecond streak camera system. The camera portion has performed adequately but the intensifier performance has been erratic and may require replacement with a more reliable unit.

To carry out transient absorption measurements covering nanoseconds or longer, but with picosecond resolution, an intense white light source was required. The time duration of the white pulse should not exceed 10-100 microseconds, at high intensities, to avoid secondary exposure effects in the streak camera. There was no suitable commercial system available. We originally purchased a Xenon Corporation system but it did not meet specifications. We have built a flash lamp system with a rise time of less than 15 nsec and an adjustable time duration. The flash lamp is laser triggered and has therefore solved a key problem, namely synchronization of the flash lamp pulse with the picosecond laser pulse used to excite the sample. We have successfully coupled together the laser triggered flash lamp - streak camera to an optical multichannel analyzer and small computer. A schematic of the overall set-up is shown in Figure 1.

A key mechanism by which molecules in excited electronic states degrade their electronic energy is by charge transfer interactions between the excited molecule and surrounding ground state molecules. We have expanded our studies of these processes from free donor and acceptor molecules to the case of a donor and and acceptor molecule connected by three methylene groups. The molecule we are studying is $A-(CH_2)_3-D$ where A represents an anthracene acceptor and D a dimethylaniline donor. Using transient absorption techniques we have measured the charge transfer dynamics in polar and nonpolar solvents. The picosecond laser experiments included the following steps:

Excitation: $A-(CH_2)_3-D + \hbar\omega \longrightarrow A^*-(CH_2)_3-D$

Charge Transfer: $A^*-(CH_2)_3-D \longrightarrow \left[\cdot A^- -(CH_2)_3-D^+\cdot\right]^*$

Detection: $\left[\cdot A^- -(CH_2)_3-D^+\cdot\right]^* + \hbar\omega' \longrightarrow \left[\cdot A^- -(CH_2)_3-D^+\cdot\right]^{**}$

Radiative and Radiationless Decay: $\left[\cdot A^- -(CH_2)_3-D^+\cdot\right]^* \longrightarrow A-(CH_2)_3-D$

Hooked together molecules, such as the one we are studying, serve as a powerful tool for gaining information not only on the charge transfer process but on the dynamics of intramolecular motions. From the transient absorption measurements we conclude that there are strong geometrical requirements for electron transfer in the nonpolar (low dielectric solvents) hexane and hexadecane. In the high dielectric solvent acetonitrile the electron transfer is very rapid, occurring in less than 5 psec. In acetonitrile we also find that back electron transfer occurs in 760 ± 80 psec whereas in the nonpolar solvents the exciplex state lasts many nanoseconds. We are currently supplementing this transient absorption work with the measurement of emissions from the excited charge transfer state in a variety of solvents. It should be noted that this work represents the first picosecond laser research on intramolecular charge transfer interactions and has provided the first picosecond information of these ultrafast processes. Another class of problems that we are addressing is the nonlinear interactions of an intense picosecond laser pulse with molecules in the condensed phase. In particular we have been investigating the photoionization of organic molecules in polar media and the dynamics of the subsequent electron solvation process. The system we have been investigating has been anthracene and more recently pyrene in alcohols. The dynamics of the solvation process in the simple alcohols, e.g. methanol and ethanol, has been studied only by pulse radiolysis methods. We have generated the electron in our experiments by a two photon ionization process. The time evolution of the quasi-free electron via interactions with the alcohol to the trapped and finally solvated form was monitored by transient absorption methods. The excitation pulse was a frequency tripled Nd:glass picosecond pulse at 351 nm and the formation kinetics of the solvated electron was monitored with the flash lamp - picosecond streak camera system. In Figure 2 are shown the experimental and theoretical curves we have obtained using pyrene as the solute in methanol. These results can directly compare the pulse radiolysis and laser methods. Our results yielded solvation times which were 30% to 70% higher than the pulse radiolysis results. For the solvation in ethanol there are a considerable number of different values appearing in the literature. The value of 26 ± 5 psec which we obtain by probing at 600 nm is found to be exponential in its rise and is probably the most reliable value for solvation in ethanol. To further understand the dynamics of photoionization, electron return and capture, solvent trapping and solvation we are extending our measurements to other temperatures, solvents and other probe wavelengths.

In summary, we have succeeded with ARO support in constructing a sophisticated picosecond laser and detection system and we have obtained new information on key energy relaxing phenomena in molecular systems.

FIGURE 1

PICOSECOND TRANSIENT ABSORPTION AND EMISSION ARRANGEMENT

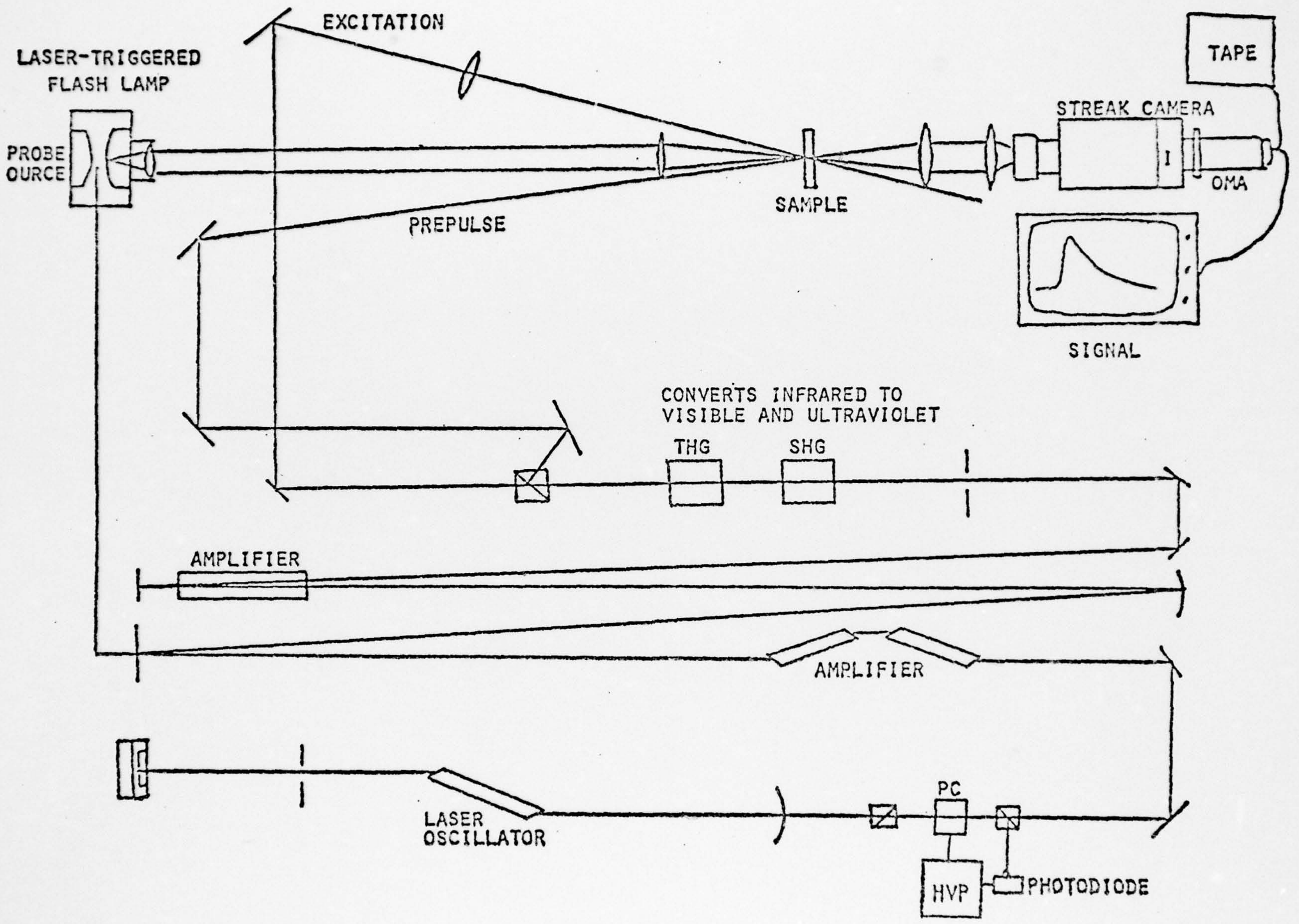
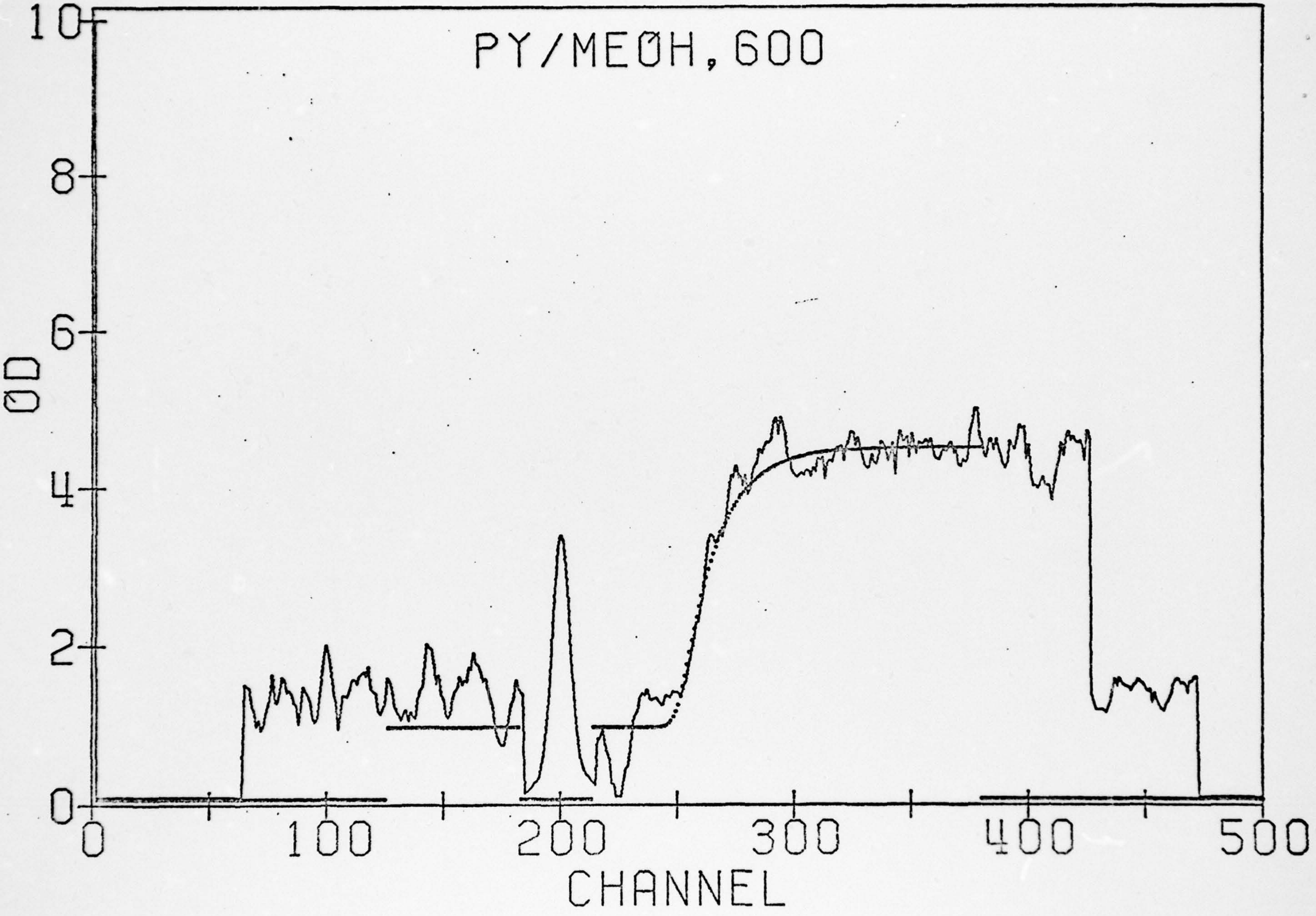


FIGURE 2

PHOTOIONIZATION OF PYRENE IN METHANOL
ELECTRON SOLVATION



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"Picosecond Spectroscopy," Annual Review of Physical Chemistry, Vol. 28, B. S. Rabinovitch, J. M. Schurr, H. L. Strauss (Eds.), Annual Reviews Inc., Palo Alto, Calif., 1977, pp. 207-232.

"Picosecond Relaxation Processes in Chemistry," Topics in Applied Physics, Vol. 18: Ultrashort Light Pulses, Picosecond Techniques and Applications, S. L. Shapiro (Ed.), Springer-Verlag, New York, 1977, pp. 275-315.

"Picosecond Kinetics of Excited Charge-Transfer Interactions," K. B. Eisenthal and K. Gnadig, Chem. Phys. Lett. 46, 339 (1977).