Application of Subpicosecond Optical Techniques to Molecular Dynamics [and Discussion]

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Application of subpicosecond optical techniques to molecular dynamics

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New techniques that extend time resolved investigations of molecular dynamics into the subpicosecond régime are reviewed.

The last decade has seen dramatic advances in the development of short laser pulses and their application to the study of phenomena taking place on a picosecond time scale. Currently, the extension of this technology into the subpicosecond [10^{-13}s] régime offers exciting possibilities for accurate studies of previously unresolved photoprocesses in chemistry, physics and biology. In this discussion we shall describe by means of specific examples the range of techniques that have been applied to the study of molecular dynamics.

The source of the optical pulses used in the experiments that we shall describe is the passively mode-locked Rhodamine 6G dye laser (Shank *et al.* 1972; Ippen *et al.* 1972; Ippen & Shank 1977). This system is described in the paper presented by E. P. Ippen (this symposium). The subpicosecond pulses produced by this system have an energy of approximately 5 nJ. The beam quality is such that the pulses can be easily focused to energy densities of several millijoules per square centimetre or photon densities greater than $10^{16}/\mathrm{cm}^2$. Single pulses can be dumped at rates up to 10^6/s to maximize signal averaging. Alternatively, the repetition rate can be reduced if the system studied needs more time between pulses for complete recovery.

The recovery dynamics of the triphenylmethane dye malachite green provides an excellent example of the application of short pulse techniques (Ippen *et al.* 1976). Previous studies of triphenylmethane dyes of which malachite green is a particular example have revealed a number of interesting optical properties (Magde & Windsor 1974). These dyes have strong visible absorption bands but in low viscosity solvents have very low quantum efficiencies (often less than 10^{-4}).

The ground state absorption recovery is directly measurable by using short pulse techniques. The experimental set-up is shown in figure 1. Short pulses are extracted from the passively mode-locked dye laser at 10^5/s and divided into two beams. One beam (the probe) is made about ten times weaker than the other (the pump). The pump beam alone passes through a mechanical chopper. Relative delay between the pump and probe pulses is provided by varying the pump beam optical path length with a stepper motor. The pump and probe beams, parallel but not collinear, are focused by a simple lens to the same point in a cell 0.1 mm thick, containing the sample dye solution. After transmission through the cell, the pump beam is blocked and the probe beam is detected by a photomultiplier. Modulation of the probe by the chopped pump is detected in a phase lock amplifier whose output is recorded as a function of time delay. Averaging is achieved by repetitive scanning of the desired delay interval to guard

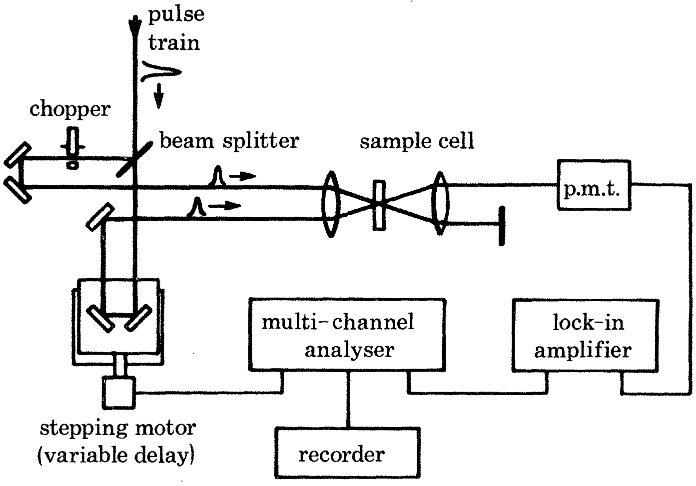


FIGURE 1. Experimental layout for measuring time resolved relaxation processes with ultra-short optical pulses.

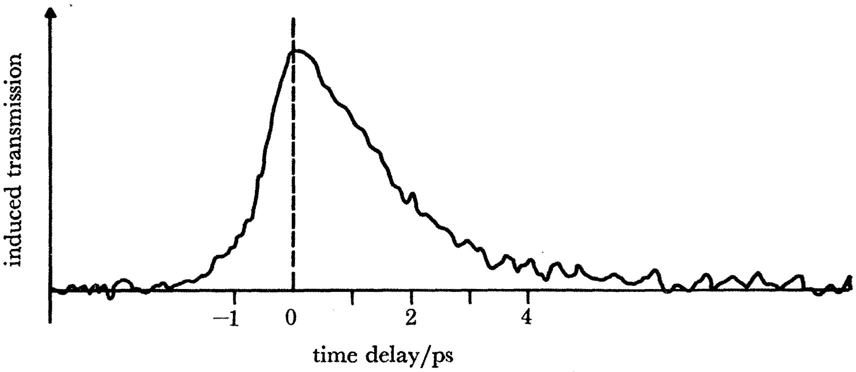


FIGURE 2. Relaxation of malachite green in methanol.

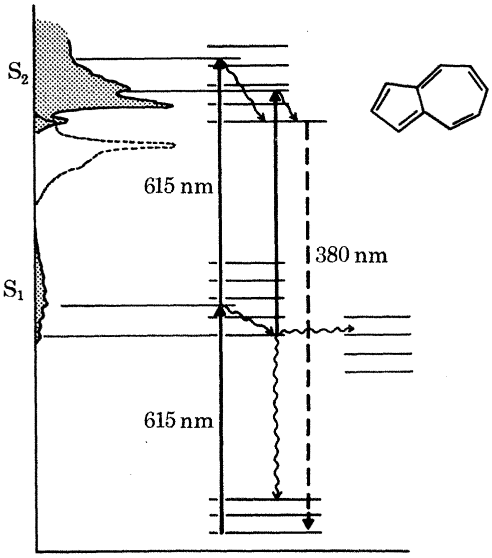


FIGURE 3. Energy level diagram for azulene.

against the possibility of signal drift during a particular trace. A single measurement made over a period of several minutes utilizes more than 10^7 pulses.

An experimental trace of the picosecond response of malachite green in methanol is shown in figure 2. The absorption recovery is characterized by single exponential behaviour with the time constant of 2.1 ps. To our knowledge this is the fastest absorption recovery of a dye ever measured. Further measurements of the recovery in high viscosity solvents reveal a complex behaviour which has been reported previously.

Another example is the molecule azulene, with interesting photophysical properties that have been the subject of extensive investigations in recent years (Rentzepis 1968; Birks 1972). The measurement of the S_1 lifetime in azulene is facilitated by the anomalous fluorescence behaviour of the molecule. The excitation scheme is illustrated in figure 3. A short optical pulse of wavelength 615 nm excites the azulene molecule into an excited vibrational level of the S_1 state. A second delayed pulse then excites these molecules to the second singlet S_2. The pulse wavelength is such that this second step can occur even after relaxation within S_1. Excitation to S_2 results in easily detectable fluorescence ($S_2 \rightarrow S_0$; quantum efficiency *ca.* 0.031). Thus, the number of molecules in S_1 as a function of time is determined by measuring the amount of induced ($S_2 \rightarrow S_0$) fluorescence as a function of delay between the two pulses. The experiments were performed again by dividing the extracted laser pulses into two beams that arrived at the sample with variable delay. Both pulses were focused to the same 10 μm diameter spot in the 0.1 mm azulene cell. The optical density incident on the sample was about 1 mJ/cm^2.

Since the two excitation pulses are identical in wavelength and temporal behaviour, the measured fluorescence delay curve is expected to be symmetrical. That is, the total number of excitations to S_2 is independent of which pulse comes first. If both pulses have the same intensity, the peak of the signal at pulse coincidence has a contrast of 3:1 over the signal level at large delay, where excitation is due to each pulse individually. An advantage of the high repetition rate of our system is that we are able to enhance this contrast ratio considerably. One beam of pulses is made somewhat weaker than the other and the weak beam is chopped mechanically at a low rate. The fluorescence signal is processed with a phase lock amplifier which detects only the strong-weak cross product signal and the weak beam background. For a pulse intensity ratio of 10:1 the fluorescence trace can have a peak:background contrast of 41:1.

To determine accurately a molecular response from any time resolved measurement, it is necessary first to define precisely the instantaneous response of the experimental system. In our case here this can be accomplished by utilizing two-photon fluorescence from a molecule that has no intermediate state. The pulse autocorrelation is directly obtained by inserting the α-NPO sample into the apparatus. Pulse autocorrelation curves are also obtained by second harmonic generation in KDP and are equivalent to the fluorescence traces in α-NPO. Figure 4 curves *a* and *b* are the experimentally measured autocorrelation traces measured by second harmonic generation and by two-photon fluorescence respectively. This measurement represents the response time of our measurement system. Inserting the azulene into the measurement system results in the trace *c*. Clearly the relaxation time has been resolved (Ippen *et al.* 1977), and upon deconvolution we find that the lifetime, τ, is 1.9 ± 0.2 ps.

To elucidate further the non-radiative relaxation processes, the above measurements were repeated with deuterated azulene (Shank *et al.* 1978). Deuteration of the azulene molecule might be expected to modify the vibrational relaxation pathways. Previous work by Hochstrasser & Li (1972) has indicated a reduction in the $S_1 \rightarrow S_0$ line width for the O–O absorption band of azulene at 1.2 K. In figure 5 we have plotted the results for azulene-h_8 in benzene and azulene-d_8 in deuterated benzene. The lifetime measured in both cases was $\tau = 1.9 \pm 0.2$ ps.

Direct comparison of these results with the earlier low temperature spectroscopic measurements of Hochstrasser & Li is quite complicated. In solution the absorption bands are broadened and unresolved, unlike the low temperature spectra. The short pulse technique measures an average over several bands while the low temperature spectroscopic data are from a clearly defined O,O band.

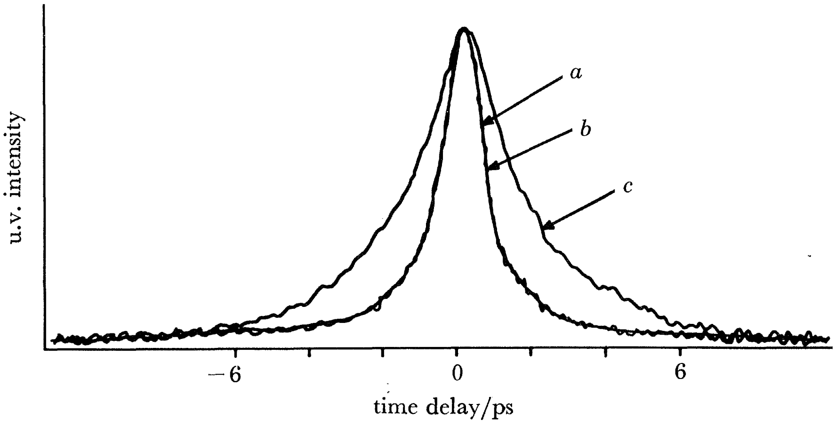


FIGURE 4. Experimental traces: (*a*) pulse correlation by second harmonic generation; (*b*) pulse correlation by two-proton fluorescence; (*c*) time-resolved excited state absorption in azulene.

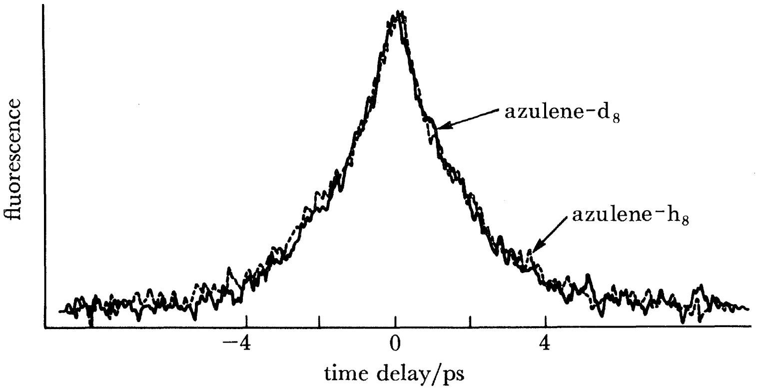
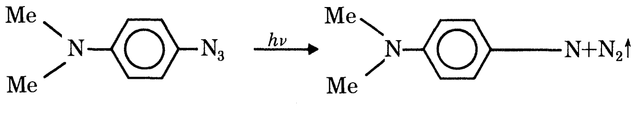


FIGURE 5. Experimental results for azulene-d_8 and azulene-h_8.

Using the pump probe technique described previously for malachite green, we have measured the ground state recovery time of azulene have found the result to be 1.9 ± 0.5 ps. Complete recovery of the ground state with the rate that agrees with our S_1 lifetime measurement suggests that $S_1 \rightarrow S_0$ internal conversion is the rate-limiting process for relaxation of optically excited azulene. Also, the deuteration results seem to indicate that vibrational energy relaxation is fast on the time scale of our measurements.

So far, the experiments that we have thus described have utilized the low-power 5 nJ pulses from the passively mode-locked Rhodamine 6G dye laser. It is useful to have pulses with a high peak optical power to extend the range of possible measurement techniques. Amplification with a three-stage dye amplifier has produced pulses in the gigawatt range while maintaining the subpicosecond optical pulse width. These short pulses, when focused into a 1 cm pathlength of H_2O, readily generate a subpicosecond continuum (Alfano & Shapiro 1970) which extends from 0.31 to 1.65 μm. The continuum is a useful probe for measuring optical absorption spectra with subpicosecond resolution. The experimental techniques are quite similar to those described previously. The optical pulse excites the sample and a delayed continuum pulse is used to probe an induced change in the optical transmission. The complete spectrum can be measured by using a two-dimensional optical multichannel analyser.



(DMAPA) (DMAPN)

Figure 6. Photodissociation of dimethylaminophenylazide.

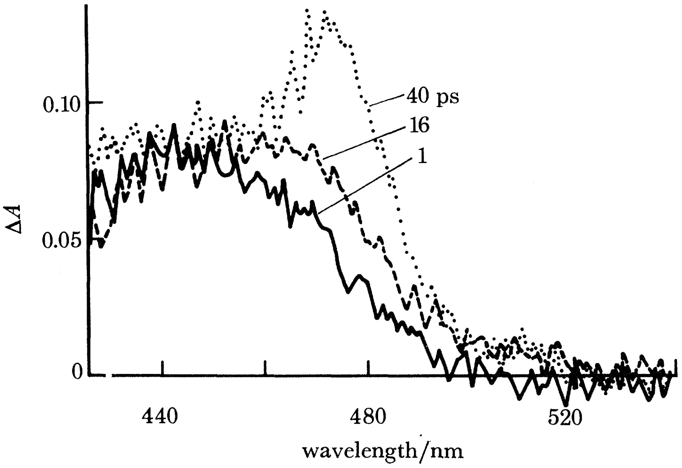


Figure 7. Time-resolved spectra following excitation at 305 nm.

An interesting application for this measurement technique is the photodissociation of dimethylaminophenylazide (DMPA). A subpicosecond pulse at 305 nm is utilized to excite the molecule. The resulting fragments produced are shown in the reaction described in figure 6. Dimethylaminophenylnitrene (DMPN) is produced with the emission of nitrogen. By measuring the absorption spectra as a function of time, we are able to measure the dynamics of this process. The results are shown in figure 7, where we have plotted the experimentally measured induced absorption change against wavelength. Within the first few picoseconds, a broad diffuse absorption is observed. As time progresses, a sharp feature in the absorption spectrum near 48 nm begins to appear which we associate with the formation of the nitrene compound. The long delay in the formation of the nitrene peak is somewhat surprising. The quantum efficiency of emission from the parent compound is extremely small, indicating a rapid conversion to the nitrene intermediate. One possible interpretation is that the parent compound photodissociates on a very short time scale, less than our measurement time, leaving a fragmented molecule in a non-equilibrium energetic and/or spin state. Subsequent equilibration then follows resulting in the clearly defined absorption peak observed at later times.

In conclusion, we have shown just a few of the many possible pieces of new information that can be obtained with the subpicosecond spectroscopic techniques. These techniques should play an important role in the future in the experimental investigations of the dynamics of molecular relaxation.

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Discussion

Sir George Porter, F.R.S. (*Royal Institution, London*). Although the ground state of a nitrene will be of triplet multiplicity, dissociation of an azide (singlet) into nitrogen (singlet) and nitrene (triplet) is spin forbidden and singlet nitrene may be expected to appear first. If the absorption that Dr Shank observes to grow with 100 ps lifetime is ground-state (triplet) nitrene, the process can therefore be interpreted as a singlet → triplet intrasystem crossing.