Rotational Diffusion of Stilbene in Alkane and Alcohol Solutions

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An amplified colliding pulse modelocked laser system is described which is capable of subpicosecond resolution flash-photolysis studies. As an application of this system we used the anisotropic absorption technique (polarization spectroscopy) to measure the rotational reorientation of trans-stilbene. These measurements give a more accurate estimate of the microscopic friction involved in the isomerization dynamics of this molecule. When the friction is assumed proportional to the reorientation times, the isomerization rates in alkane solvents are adequately described by activated barrier-crossing theory.

Introduction

It is now possible to generate visible and near-ultraviolet light pulses with a duration of only a few optical cycles. Thus the 50 fs–5 ps time regime is now accessible for flash photolysis studies. Many of the techniques developed for picosecond spectroscopy rely only on the pulse duration for their time resolution and can therefore be carried over directly into the femtosecond regime. Colliding-pulse ring lasers produce pulses of duration 35–150 fs and when combined with high-power amplifiers are readily capable of generating a broadband continuum stretching from 300 to 1400 nm with a duration similar to that of the original laser pulse. This continuum can be used to record a spectrum at a particular time or a decay at a particular wavelength in direct analogy with the original spectroscopic and kinetic flash photolysis methods.

There is much current interest in the dynamics of chemical reactions in liquids and solutions. Subpicosecond spectroscopy provides a valuable probe of the exchange of momentum and vibrational energy between solvents and solutes and of the response of solvents to a newly created charge or dipole. Activated crossing over a barrier represents a simple model for chemical reactions in solution. The overall, solvent-dependent barrier crossing rate depends on the barrier height and the balance between two antagonistic solvent effects: (i) a retardation (or friction) arising from repeated crossing and recrossing of the barrier which results from momentum exchange between reactant and solvent and (ii) an acceleration resulting from vibrational energy exchange between reactant and solvent that maintains the population of reactant molecules and deactivates the product molecules. We have carried out studies of photochemical isomerization in stilbene from isolated molecules, through dense gas to the solution phase to characterize the timescales of these processes. In this paper, following a description of our subpicosecond spectrometer, we concentrate our attention on the validity of the Stokes–Einstein relationship for describing the friction felt along the isomerization coordinate.

Laser System

Fig. 1 shows a sketch of the laser and amplifier system used to produce subpicosecond pulses of ca. 0.4 mJ per pulse at 10 Hz. The colliding pulse modelocked (CPM) laser
is based on two flowing dye jet solutions. The gain medium (rhodamine 6G) is pumped 'all lines' by an argon-ion laser at ca. 5 W. The saturable absorber is DODCI flowing through a thin jet. The stability is improved by maintaining the dye slightly below room temperature. The DODCI pump module is constructed entirely of plastic and stainless steel to prevent excessive dye degradation. Four Brewster-angle prisms arranged to adjust the cavity dispersion are incorporated into the laser. Symmetrical placement of the prisms at Brewster's angle is required and is most easily accomplished by maximizing the deflection of the dye fluorescence spot. Two of the prisms are mounted to translate perpendicular to the prism base and two are arranged to translate parallel to the original beam direction. High-quality prism tables are also a useful feature. The two counterpropagating pulses produce two output beams with a repetition rate dependent on the cavity length (ca. 80 MHz) and pulse energies <100 pJ. One of the CPM beams is amplified and the other is continuously monitored by a real-time autocorrelator and a monochromator/vidicon spectrum-analyser. A typical autocorrelation trace is shown in fig. 2.

Four stages of longitudinally pumped flowing-dye amplifiers are used to produce the high energies which are necessary for efficient frequency doubling and/or 'white-light continuum' generation.11,12

A grating pair is used to compensate for group velocity dispersion in the amplifier cells and optics. One of the gratings and a mirror are mounted on a translation stage which is arranged so that the spacing can be varied without changing the beam direction. We use 2400 g mm⁻¹ holographic gratings spaced ca. 5 mm apart at close to the Littrow

† 3,3'-Diethyloxadicarbocyanine iodide.
angle. Coarsely ruled gratings allow larger beam waists. The amplifier cells are separated by flowing jets of the saturable absorber dye malachite green. All the jets (including the laser) flow vertically so that the entire system is arranged with p-polarization. Although the same amplifier dye solution can be used in all the cells we find separate pumps and well filtered dye reservoirs are more practical. Contaminants on the inner surfaces of the dye cell easily result in damage to optics, so the cells are constructed with replaceable windows. We prefer water as the solvent if solubility is not a problem (for stability and ease of cleaning). Since the oscillator is passively modelocked, the synchronization of the YAG pump laser is accomplished by using a photodiode. Home-made digital logic (MECL) provides the Q-switch signal with jitter comparable to the internal YAG laser jitter (ca. 0.25 ns). A fine Q-switch delay (± 8 ns) is used to adjust the relative timing of the pump pulse and a CPM pulse for optimum amplification. The timing system easily isolates a single pulse from the ring laser. It is particularly undesirable to use countdown logic with a passively modelocked system since the ‘system clock’ will be corrupted if the laser temporarily flashes off. Instead a next pulse flip/flop arrangement is used.

In a typical experiment 50% of the amplified pulse is focussed into a 1 cm cell of water to generate a continuum probe. The remaining 50% is frequency-doubled in KDP for the pump pulse. The probe beam transmitted through the sample and polarizers is measured as a function of optical delay. A monochromator is used to discriminate against scattered pump light and interference filters select the probe wavelength. A photomultiplier or diode and a current integrating analogue-to-digital converter (LeCroy 2249A) interfaced to an IBM system 9000 microcomputer collect the data and control the delay stage. Typically a decay curve is obtained by averaging 25 shots at each delay position and scanning the entire decay 3-4 times. Other diodes monitor the performance of the YAG laser and amplifier shot-to-shot so that abnormal shots can be rejected. For anisotropic absorption measurements the requirement of low-birefringence optics is less severe for the high-energy pulses obtained with this system.

**Stilbene Isomerization**

The trans-cis photoisomerization of stilbene has been extensively investigated by picosecond spectroscopy as a model system for activated barrier crossing in solution.\(^9,14,15\) A typical timescale for trans-cis isomerization is 75 ps (in hexane at 23 °C).
Rotational Diffusion of Stilbene

Fig. 3. $S_1 \rightarrow S_n$ absorption decay of cis-stilbene in hexane at room temperature. The solid line corresponds to a single exponential decay with $\tau = 1.0$ ps.

The cis-trans isomerization is much faster, and had to await the development of subpicosecond laser pulses before direct time-resolved studies were possible. Greene and Scott$^{16}$ and Doany et al.$^{17}$ measured the decay of excited cis-stilbene in hexane solution to be 1.35 ps. Fig. 3 shows the decay of $S_1 - S_n$ absorption in cis-stilbene measured with the apparatus described. The solid line is an exponential decay with a time constant of 1 ps. Apparently there is essentially no barrier for isomerization of the excited cis-stilbene molecule, and the resistance to isomerization comes entirely from the friction of the solvent. Systematic studies of such 'barrierless' isomerizations should provide useful checks of current theories of solution-phase reaction dynamics involving little or no barrier.$^{18}$

In contrast the trans-cis isomerization has a barrier of ca. 14.6 kJ mol$^{-1}$ in alkane solvents and the Kramers model of activated escape over a barrier$^{19}$ might be expected to apply. Previous studies$^{9,15,20}$ have shown that Kramers theory does not work well when the normal zero-frequency shear viscosity of the alkane solvents was used as the measure of solvent friction. In a study of isomerization in the dye molecule DODCI, Velsko et al.$^{21}$ suggested using the rotational reorientation time as a microscopic measure of the solvent friction. By using the Hubbard relation$^{22}$ rotational and isomerization data obtained over a range of temperatures can be combined into a single plot. In the case of DODCI the rotational reorientation times follow the Stokes-Einstein relation rather closely and the fit to Kramers equation was not improved by using rotation times instead of viscosity. This failure led to the suggestion that the large curvature in the region of the barrier might necessitate the use of frequency-dependent friction. Rothenberger et al.$^{15}$ applied the Grote-Hynes$^{23}$ theory of frequency-dependent friction to stilbene and found reasonable agreement, but rather unphysical potential parameters.

To explore further the applicability of the Stokes–Einstein relation to motion of stilbene we have measured rotational reorientation time using the polarization spectroscopy or anisotropic absorption$^{24}$ method. Fig. 4 shows a typical trace for stilbene in hexadecane. The decay is exponential with a time constant, $\tau_M$, of 25 ps. The data shown were recorded for 305 nm excitation and 610 nm probe. Identical decay times were obtained when the probe pulses were selected from a white-light continuum. For
Fig. 4. Example excited-state absorption anisotropy of trans-stilbene in hexadecane. The fundamental wavelength was used as the probe and the single exponential decay time is 25 ps.

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^a Interpolated from Arrhenius plots.

The single-exponential anisotropy decay the reorientation time is obtained from

$$\frac{1}{\tau_{OR}} = \frac{1}{2\tau_M} \frac{1}{\tau}$$

where τ is the excited-state lifetime obtained separately. The data for trans-stilbene in a series of alkane and alcohol solvents are summarized in table 1 and shown in fig. 5 as a function of η/Τ, where η is the macroscopic shear viscosity. The solid lines show the upper and lower limits calculated for a slip boundary condition assuming trans-stilbene is a prolate ellipsoid of revolution with transition moments along the symmetry
axis. In this model calculation the numerical results of Hu and Zwanzig were interpolated. The longer semi-axis was taken to be 7.4 Å and the shorter semi-axis was allowed to vary from 1.7 to 3.4 Å. The reorientation times in the alkane solvents are not too dissimilar from slip boundary-condition predictions, but the overall increase in rotation time does not depend linearly on the solvent viscosity. The failure of Stokes–Einstein predictions is much more evident in the alcohol solutions where reorientation times are much faster than slip predictions. 'Subslip' behaviour has been observed for small solute molecules using frequency-domain techniques [see ref. (26) for a review] and more recently for p-terphenyl and p-quaterphenyl in relatively high-viscosity hydrocarbon mixtures by time-resolved fluorescence anisotropy. This behaviour can be rationalized by viewing the solvent not as a continuum but as molecular. While the solute-solvent interactions for trans-stilbene are expected to be similar in the alkane and alcohol series, the solvent–solvent interactions are much stronger in alcohols. The solute reorientation time, to which both solute–solvent and solvent–solvent interactions contribute, is then expected to vary less in the alcohols than in the alkanes as a function of macroscopic viscosity. More explicitly one can consider the association of alcohol molecules in supramolecular structures, or consider a perturbation of the local solvent structure by the presence of the solute. Both of these effects could contribute to reducing the viscosity felt by the solute.

According to barrier-crossing theories the isomerization rate is

\[ k_{\text{ISO}} = F(\xi_{\text{ISO}}) \exp \left( -\frac{E_0}{RT} \right) \]  

where \( F(\xi_{\text{ISO}}) \) is a function of solvent friction and \( E_0 \) the barrier height. Following Velsko et al. we can use the reorientation times of fig. 5 as a measure of solvent friction by assuming that

\[ \xi_{\text{ISO}} \propto \xi_{\text{OR}}; \quad \xi_{\text{OR}} = \left( \frac{6kT}{I_{\text{OR}}} \right) \tau_{\text{OR}} \]  

where \( \xi_{\text{ISO}} \) and \( \xi_{\text{OR}} \) are friction coefficients for isomerization and reorientation, respectively. The latter equality is the Hubbard relation. The Kramers equation can now
be written as

$$F(\zeta_{\text{ISO}}) = \frac{A}{C} \{[1+(C/\tau_{\text{OR}})^2]^{1/2} - 1\}$$

(4)

where

$$A = \omega Q^2/2\pi Q'$$

$$C = \omega_B I^{\text{ISO}}/3kTf$$

and $f$ is a proportionality constant. In this expression $\omega$ is the angular frequency of the reactive mode and $\omega_B$ is the frequency corresponding to the barrier curvature. $Q'$ and $Q''$ are partition functions for the reactant and transition state, respectively. The prime indicates that the reactive mode has been factored out of $Q$. Fig. 6 shows a fit of isomerization data for stilbene in normal alkanes to eqn (4). The fit is much better than when shear viscosity is used as the measure of friction: evidently the deviations from Stokes-Einstein behaviour are sufficient to account for previous poor fits to the data.

Recently Hochstrasser and coworkers independently came to the same conclusion for stilbene and a diphenylbutadiene analogue. Using the average of the short-axis moments of inertia reported in ref. (29) ($I = 3.3 \times 10^{-44} \text{kg m}^2$), and $E_0 = 14.6 \text{kJ mol}^{-1}$, the parameters derived from the fit in fig. 6 are

$$\omega Q^2/Q' = 3.64 \times 10^{13} \text{s}^{-1}$$

and

$$\omega_B/f = 3.43 \times 10^{13} \text{s}^{-1}.$$
the rotational reorientation of trans-stilbene in alkane and alcohol solvents. We believe that this is the first report describing the use of continuum generated probe wavelengths for anisotropic absorption measurements. The rotational diffusion times of stilbene in both solvent series deviate from the linear viscosity dependence predicted by Stokes-Einstein-Debye theory. When the rotation times in alkane solvents are used as a measure of the friction felt for the stilbene isomerization, good fits are obtained using Kramers equation. This procedure, of course, simply shifts the problem to that of understanding friction in complex molecular solvents. It is clear that this latter area warrants much more study.

In the near future we expect improvements in femtosecond dye laser systems. Signal-to-noise ratios should improve as repetition rates for high-energy amplifier pump lasers increase. Currently probe wavelengths can be conveniently generated, but tunable pump wavelengths can only be produced by amplifying continuum. Recent reports indicate that this complication is likely to be eliminated by femtosecond tunable laser sources.

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References


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