ULTRAVIOLET PICOSECOND PUMP–PROBE SPECTROSCOPY WITH A SYNCHRONOUSLY PUMPED DYE LASER.
ROTATIONAL DIFFUSION OF DIPHENYL BUTADIENE

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The second harmonic of a picosecond synchronously mode-locked dye laser has been used to study orientational relaxation of 1,4-diphenyl-1,3-butadiene in dilute solution. The dye laser was amplified by a novel high repetition rate (~1–5 MHz) amplifier. The motion of diphenylbutadiene in tetradecane is well described by hydrodynamics with a slip boundary condition.

1. Introduction

Over the last few years synchronously pumped dye lasers have been used to study a range of relaxation processes [1]. The wide wavelength tunability available gives an important advantage over passively mode-locked systems [2,3] when sub-picosecond time resolution is not required. In order to study smaller molecules more amenable to theoretical description it is important to extend the high repetition rate techniques into the ultraviolet. For example, rotational diffusion times of 1,4-diphenyl-1,3-butadiene (DPB) measured with UV excitation and probing would complement our recent studies of DPB photoisomerization dynamics [4]. The friction felt by the molecule rotating as a whole can be used as a measure of the friction felt along the isomerization coordinate, thus allowing theories of activated barrier crossing to be tested without making an assumption of hydrodynamic friction [5]. Direct time-resolved studies of rotation correlation functions are also of interest for testing boundary conditions and the influence of molecular size, shape, and charge. To date the majority of studies has been made on charged dye molecules in polar solvents [6–8] where a stick boundary condition (BC) is frequently observed. By contrast light scattering studies on a range of small molecules are consistent with a slip boundary condition [9]. Extension of the time-resolved studies to uncharged molecules with well-defined shape is important to clarify how the solvent–solute interaction influences the boundary condition for the motion and to establish the influence of molecular shape and size on the form of the motion.

The low pulse energy of synchronously pumped dye lasers (~1 nJ) means that second-harmonic generation is inefficient, and to our knowledge no experiments have been reported in which the second harmonic of the unamplified dye laser has been used in pump–probe type experiments. (Time-correlated single-photon counting fluorescence lifetime experiments with UV excitation have been carried out for several years [10,11] but only a few pJ of pulse energy is required for these experiments.) Present amplification schemes involve low repetition rate high power lasers [11,12]. In this note we describe data obtained with a high repetition rate amplifier (~<5 MHz). The amplifier preserves the tunability, pulse duration, and high repetition rate of the basic synchronously pumped dye laser. Data are presented on the rotational reorientation of DPB. The rotational correlation function for DPB is consistent with a slip boundary condition and decays as a single exponential.
2. Experimental

The experimental arrangement is shown in fig. 1. The synchronously pumped dye laser and detection system have been described in detail elsewhere [13, 14]. The amplifier consists of a pair of simple lenses (5 cm focal length), a standard dye laser nozzle and a pair of mirrors which enable the picosecond pulse to pass twice through the gain medium during the passage of the pumping pulse. The amplifier is pumped by a cavity-dumped 3 W argon ion laser operating all lines. The average power at 756.7 kHz dumping rate was 1.2 W. The cavity dumper of the 3 W laser was synchronized to the mode locker of the oscillator argon laser. We have performed experiments using both the full repetition rate of the synchronously pumped dye laser (i.e. amplifying one pulse in a hundred) and with the dye laser also cavity dumped at 756.7 kHz. The maximum double-pass gain obtained for a non-cavity-dumped dye laser is ≈30 times, while significantly lower gains (2.75 times) are obtained when the dye laser is cavity dumped. We believe this large decrease is mainly attributable to poor beam quality and changes in confocal parameter rather than saturation, since lower gains were also observed when the cavity dumper was operated as a cw output coupler. Significantly improved gains should be possible with an improved optical design, however, even the initial system used here provides sufficient UV for pump-probe spectroscopy.

Frequency doubling was carried out in a temperature tuned ADA crystal (5 cm long) with 55 mW average visible power at 760 kHz the maximum doubling efficiency was 7.6%. Higher efficiencies were obtained from a 2 mm LiIO₃ crystal (Cleveland Crystals). However, the beam quality and stability of the UV power were significantly better with the ADA crystal.

No pulse broadening was observed in the amplifier, in fact a small shortening was observed when the cavity-dumped dye laser pulses were amplified. A detailed description of the amplifier characteristics will be presented elsewhere [15].

The optical arrangement for the anisotropic absorption experiment [16] is essentially identical to that described previously [14] except that NRC mirrors were used as high reflectors for the ultraviolet and quartz focusing and collecting optics were used. A Soleil–Babinet compensator (Karl-Lambrecht) was used to adjust the polarization of the probe beam. As described in detail in our earlier study, the signal observed in the experiment shown in fig. 1 may arise from either induced dichroism, induced birefringence, or both. In the limit of perfect optics the observed signal intensity \( T(t) \) is [14]

\[
T(t) = |r(t)K(t)|^2, \tag{1}
\]

where \( r(t) \) is the rotational correlation function and \( K(t) \) the excited-state decay law. If the focusing and collecting lens are inside the crossed polarizers (see fig. 1) or if a sample cell is used (in the present work a free flowing jet was used), the time dependence of the signal may be significantly distorted by the presence of strain birefringence in the optics [14]. Care was taken to avoid these effects in the present experiments.

3. Results and discussion

Fig. 2 shows the anisotropic absorption signal from diphenylbutadiene (DPB) dissolved in tetradecane. The excitation and probe wavelengths were both 303 nm. The decay is well fit by a single exponential of 62 ps. If DPB is approximated as a prolate rotor a single exponential rotational correlation function is expected [17]. (The rapid spinning motion in DPB is not observable by this technique since it does not influence the transition moment direction.)
Fig. 2. Anisotropic absorption decay of DPB in tetradecane. The single exponential fit gives a lifetime of 62 ps.

Since the excited-state decay is known to be single exponential [4] the measured decay time $\tau_M$ can be written [14,16]

$$\tau_M^{-1} = 2(\tau_{or}^{-1} + \tau^{-1}), \quad (2)$$

where $\tau_{or}$ is the rotational reorientation time and $\tau$ is the excited-state lifetime. Using the measured values of $\tau_M$ and $\tau$ (740 ps [4]) $\tau_{or}$ is obtained as 149 ps. At 25°C the viscosity of tetradecane is 2.25 cP giving a reorientation time of 66 ps/cP. Since the excited-state lifetime is long the observed motion is almost entirely that of (rigid) ground-state molecules.

The rotational relaxation rate can be calculated from Stokes–Einstein–Debye theory. The calculations were performed for a symmetric prolate ellipsoid with a volume of 205.4 Å³ and an axial ratio of 3.2 [17,18]. The result for a stick boundary condition is 127 ps/cP; for a slip boundary condition 62 ps/cP is obtained in excellent agreement with the experimental result. Systematic studies of solvent and temperature effects are required before firm conclusions can be drawn, but it seems likely that hydrodynamics with a slip boundary condition will provide a good description of the rotational relaxation of DPB in alkane solvents. It will be of particular interest to see if the anomalously slow isomerization rates observed in the cyclic alkanes [4] are reflected in the rotational diffusion data in those solvents. A slip boundary condition is entirely reasonable for an uncharged non-polar molecule in a non-polar solvent [9]; however there have been rather few direct experimental demonstrations of slip behavior by time-resolved techniques.

The coherence spike [19,20] in fig. 2 is of the height expected and previously observed in our experiments with the fundamental [5,14]. The free flowing jet sample and average powers of a few mW make steady-state heating of the sample negligible.

The excited-state lifetime of DPB is significantly shorter in alcohols than in alkane solvents. This is probably due to the stabilization of the twisted excited state (which is thought to be biradical-like in character [21]) by the polar solvent. The effect of the stabilization is to lower the barrier height for twisting in the alcohol solvent (see fig. 4 of ref. [4]). In the anisotropic absorption experiment the measured decay time, $\tau_M$, was 25 ± 3 ps for DPB in ethanol. The excited-state decay now contributes significantly to the measured relaxation time and the observed decay is notably shorter than would be expected simply from the change in viscosity between tetradecane (2.25 cP) and ethanol (1.2 cP). We do not have at present a sufficiently accurate excited-state lifetime to obtain a value of the rotational reorientation time in ethanol.

4. Concluding remarks

We have described a simple and versatile technique for extending high repetition rate pump–probe spectroscopy into the ultraviolet. Our initial results have demonstrated a slip boundary condition for the rotational motion of diphenylbutadiene in an alkane solvent. We expect a wealth of new data from this technique in the future.

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