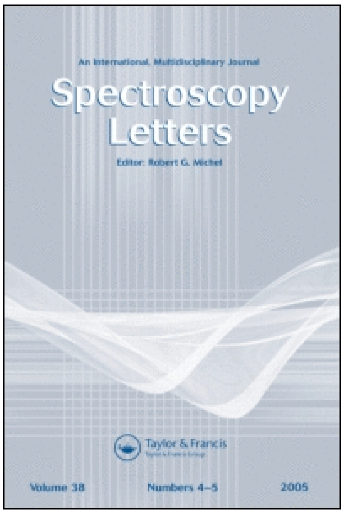

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An Application of Time-Resolved Linear Dichroism Spectroscopy: The Excited Singlet State of 1,2:5,6-Dibenzanthracene

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AN APPLICATION OF TIME-RESOLVED LINEAR DICHROISM SPECTROSCOPY: THE EXCITED SINGLET STATE OF 1,2:5,6-DIBENZANTHRACENE

Keywords: dibenz[a,h]anthracene, singlet excited state, transition moment vectors, singlet–singlet absorption, anisotropy decay, rotational relaxation.

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ABSTRACT

Time-resolved linear dichroism spectroscopy allows the relative transition moment vectors of the $S_1 \rightarrow S_n$ transitions to be obtained. This information can be used to aide in the assignment of the observed excited state and ground state transitions. The transition moment directions are constrained by the symmetry of the absorbing chromophore such that structural changes on the excited state surfaces can also be observed. The time dependence of the dichroism is related to the solution dynamics through the measurement of rotational correlation times. The spectroscopy of 1,2:5,6-dibenzanthracene is presented as an example of these measurements.

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INTRODUCTION

When an isotropic solution is irradiated with light that is linearly polarized along the laboratory Z-axis a uniaxially oriented sample of excited states is produced by photoselection. The sample is oriented with respect to the laboratory Z-axis because it is made up of those molecules that had, on average, their transition moment aligned with the laboratory Z-axis prior to absorption of the photon. If this sample is then probed with a second beam of linearly polarized light of frequency ν the measured absorbance with the electric vector of the probe beam parallel ($A_{||(\nu)}$) compared to perpendicular ($A_{\perp(\nu)}$) to the laboratory Z axis may be different. This difference, $A_{||(\nu)}$-$A_{\perp(\nu)}$, is defined as the linear dichroism of the sample (Ld_ν). There are similarities between linear dichroism measurements and fluorescence anisotropy in that they share the same theoretical basis, they are both processes described by tensors of rank two. The time dependence of the dichroism allows the rates of rotation to be measured, a valuable tool in the study of solution dynamics. Numerous examples of this type of measurement using linear dichroism [1 - 4] and fluorescence anisotropy [5 - 7] spectroscopy have appeared.

In addition, complete absorption spectra can be obtained by varying ν and the transition moment vectors (TMV) determined from the dichroism for each observed transition. The TMV are useful in determining details about the excited state molecular structure. This application of time-resolved linear dichroism has received attention only relatively recently and the information it provides is frequently not available from fluorescence anisotropy measurements.[8 - 13]

We wish to report the results of a time-resolved linear dichroism spectroscopy study of the first excited state of 1,2:5,6-dibenzanthracene (a,h-DBA, **1**). The ground state spectroscopy of a,h-DBA has been extensively studied. Six transitions in the UV-visible spectrum have been assigned and the transition moment directions obtained in stretched polymer samples.[14,15] Such large aromatic systems show small Stokes shifts and the 0:0 transitions are frequently observed. It is unlikely that a significant geometry change occurs upon excitation of this class of molecule. These features make a,h-DBA a logical starting point for these studies because the spectroscopy of the excited state is predicted to be relatively simple.

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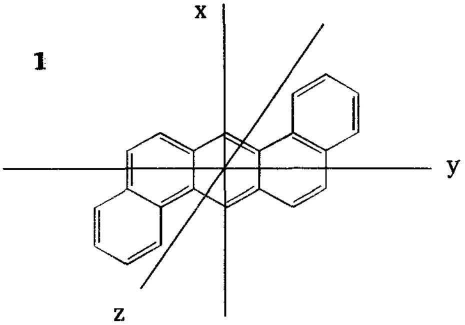

EXPERIMENTAL

Linear dichroism and transient absorption spectrum measurements were performed using the picosecond pump-probe apparatus shown in block form in Figure 1. A Continuum model PY61C Nd:YAG laser was used to produce pulses of 1064-nm light. The model PY61 is a cavity dumped active/passive mode-locked system. It delivers pulses of *ca.* 20-30 mJ in energy with 25-30 ps FWHM duration at 1064 nm. The second, third and fourth harmonics are generated using dry mounted KDP crystals. Raman shifting of the 355-nm pulse is also possible, when the excitation pulse is passed through the 33-cm cell filled with the appropriate solvent (i.e. cyclohexane, acetonitrile).

In a typical experiment, the fundamental and third harmonic are isolated using laser beamsplitters while discarding the 532-nm pulse. The

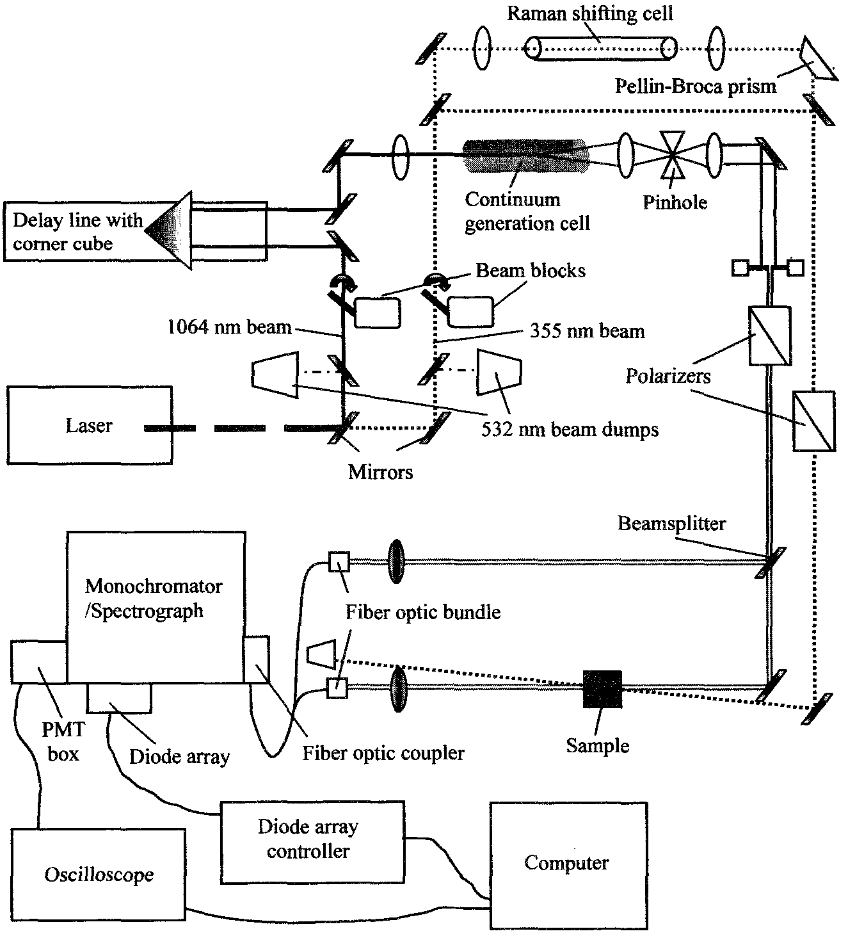

FIG. 1. Diagram of the picosecond time-resolved linear dichroism experimental setup.

UV pulse is directed toward the sample using a set of dichroic laser mirrors and is passed through an iris and a "clean-up" calcite polarizer immediately before the sample. This pulse is used as an excitation pulse with the beam diameter of approximately ≈4 mm and typical pulse energy of 300-600 μJ.

The fundamental is directed along a variable delay line (Velmex model NF90, -350 ps to 9800 ps typical available delay range, computer controllable via a serial interface). It is then focused using an 18 cm focal length lens into 10 cm cell containing 50/50% mixture of H_2O and D_2O to generate continuum (the focal point is maintained at 8.5 cm from the front window). The white light continuum pulse is collected in a lens and collimated. The collimated beam is focused through a 200 μm pinhole as a spatial filter, recollimated and passed through an iris. Polarization of this beam is achieved using a second calcite polarizer. The continuum beam is then split into reference and sample beams using an evaporated metal film beamsplitter (≈40/60 ratio). The sample beam is reduced in diameter using a 30 cm focal length lens such that it is 1 mm in diameter through the sample where it overlaps in space with UV laser pump pulse. The angle between the pump and probe propagation directions through the sample is less than 4° in the laboratory horizontal (XY) plane and care is taken to insure there is not a Z component to the beams. The sample and reference beams are coupled into the separate legs of a 1 m bifurcated fiber optic bundle for optimal coupling to the spectrograph/monochromator and to insure complete polarization scrambling of the pulses, negating any polarization bias in the detector system.

The detection system is capable of acquiring either single wavelength optical density decay profiles or time-resolved absorption spectra. An Acton Research SpectraPro-300i monochromator/spectrograph (300 mm focal length, 150 gr/mm blazed at 500 nm and 150 gr/mm blazed at 300 nm gratings) equipped with two exit ports and a model FC-446-030 fiber coupler on the entrance port is used to obtain wavelength discrimination. Effective bandwidths ranged from 0.2 to 1.1 nm for the typical slit widths of 10-50 μm.

One of the spectrograph exit ports houses a Princeton Instruments, Inc. PDDA 1024 dual photodiode array detector. The detector is controlled using a ST-120 Controller, and data is collected and manipulated using Princeton Instruments Winspec software.

The second exit port on the spectrograph houses a custom-made detection system based on Hamamatsu HC 120-05 photosensor modules for single wavelength measurements. HC 120-05 integrated photosensor module combines a ½ inch (1.27 cm), side-on photomultiplier tube with a high voltage power supply, voltage divider, and operational amplifier. Output voltages from the sensor modules were measured across 1 M Ω input of a Tektronix TDS 620B (500 MHz, 2.5 GS/s) digital oscilloscope. The typical PMT voltage output trace includes a fast growth to ca. 100 mV followed by a slower (20 μs) decay. The intensity of the light pulse was taken to be proportional to the area under the voltage response profile. The high voltages applied to the PMTs were adjusted to keep the PMT response linear (generally 350-500 V), which was checked using neutral density filters. For each time delay, 150-200 probe pulses with and without excitation pulse were averaged using the reference pulses. Shutters driven by the Velmex NF90 stepping motor controller, control the acquisition sequence.

The whole experiment was automated through the use of an IBM compatible personal computer by interfacing through GPIB (scope and spectrograph) and serial (delay line and shutters) and Princeton Instruments control board (diode array).

Quantitative descriptions using spectral features as a function of wavelength requires the knowledge of the group velocity dispersion (GVD) imposed on the continuum pulse and polarization bias of the detection system. Using the system described above, GVD was evaluated by measurements of the autocorrelation zero-time position on the absorption profile at different wavelengths (benzophenone at 525 nm, DBA at 609, 700, and 866 nm). Using these measurements GVD was shown to be under 2 ps per 100 nm wavelength shift. As a consequence the transient spectra were not corrected for GVD.

Polarization bias was checked by comparison of the time-resolved decay profile measured with polarizers set at magic angle (54.7 °) with the linear combination of decay profiles obtained with the probe polarizer parallel and perpendicular to the excitation polarizer according to $1/3A_{||}+2/3A_{\perp}$. The spectra obtained were identical within experimental error.

A second test for the presence of the polarization bias was performed. The decay traces obtained with the probe polarizer set parallel and then perpendicular to the excitation polarization should converge on the time scale of a few hundred picoseconds. The traces collected, as shown below, do converge, indicating that polarization bias is not a significant problem for our system.

The instrument response function was measured using the solution of benzophenone in hexane (absorbance 0.3 at 355 nm and polarizers oriented at "magic" angle) by monitoring the growth of the triplet state at 525 nm and iteratively deconvolving the resulting trace using a Simplex least squares minimization program with an assumption of overlapping Gaussian profiles and infinite lifetime of the triplet state.

1,2:5,6-dibenzanthracene (a,h-DBA) was purchased from Aldrich Chemical Company and was purified by recrystallization from benzene twice. The solvents *n*-hexane (distilled) and n-decane and obtained from EM Science and used as received. Solutions of DBA were purged with nitrogen and sealedin a1-cm quartz cuvet prior to the experiment. The samples were stirred using a magnetic stirrer during all experiments.

RESULTS and DISCUSSION

Transition Moment Vector Directions

The ground state absorption and emission spectra of a,h-DBA are shown in Figure 2. The 0:0 transition is clearly identifiable at 25,400 cm^{-1} and six additional transitions are also observed. The transition energies are collected in Table 1.

These assignments are taken from Birks,[16] with the exception of the transition at 36,495 cm^{-1} which was mistaken for vibrational progression of a very strong band centered at 33,560 cm^{-1}, but was later shown to have different orientation factor in stretched polymer samples.[6]

The singlet excited state spectrum is also included in Figure 2 with an axis offset by an energy equal to the 0:0 transition energy to allow direct comparison with the ground state spectrum. a,h-DBA is centrally-symmetric and the parity selection rule applies. The states are divided into gerade and ungerade parity depending on the sign of transformation through the inversion center. Transitions between states with the same parity are forbidden while transitions between states of different parity may be allowed. For a,h-DBA the ground state is gerade and the first excited state is ungerade. Thus the ground state spectrum and the first excited state spectrum should be mutually exclusive and should not have transitions in common. Examination of the spectra in Figure 2 highlights this difference. Five well-defined peaks are observed in first excited state transient absorption spectrum, and the energies are also collected in Table 1. In addition, the peak at 14,260 cm^{-1} has two shoulders at 12,610 and 13,130 cm^{-1}, the peak at 16,420 cm^{-1} has a shoulder at 15,690 cm^{-1}, and the peak at 20,280 cm^{-1} has a shoulder at 21,460 cm^{-1}. The onset of a sixth transition at around 23,000-24,000 cm^{-1} is also evident, but stimulated emission and ground state bleaching in conjunction with the low intensity of continuum in this region prevent accurate analysis of this band. This transition is tentatively assigned at *ca.* 23,600 cm^{-1}.

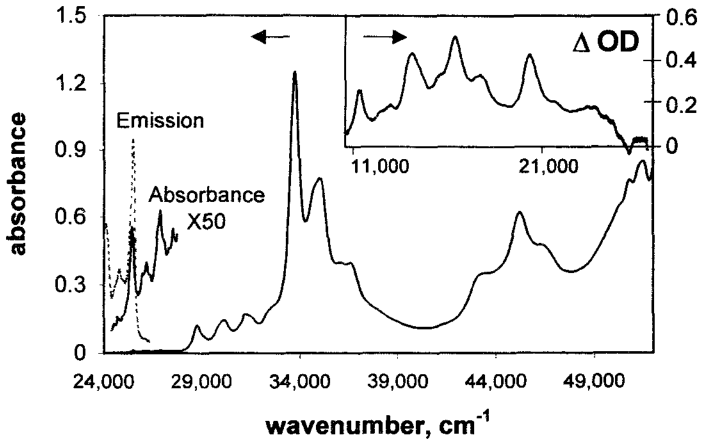

FIG. 2. Ground state absorption spectrum of 1,2:5,6-dibenzanthracene ($1.5*10^{-4}$ M in n-hexane, absorbance 0.332 at 355 nm). Inset – transient absorption spectrum of 1,2:5,6-dibenzanthracene obtained by exciting the identical solution with 355-nm pulse with a probe delay of 100 ps and polarizers oriented at the magic angle. The inset x-axis is offset from the main x-axis by an energy increment equal to 0:0 transition energy.

TABLE 1 Transition Energies for a,h-DBA

Ground state absorption transition energies (cm^{-1})		Excited state absorption transition energies (cm^{-1})	
1	25,380	1*	11,540
2	28,610	2*	14,260
3	33,560	3*	16,420
4	36,495	4*	17,740
5	42,920	5*	20,280
6	44,840	6*	~23,600
7	51,280		

Dichroic spectra of a,h-DBA obtained during excitation with 355 nm laser pulse are shown in Figure 3. The methods used to analyze these spectra are identical with those used for ground state spectra obtained by steady state or matrix isolation techniques. The low symmetry of a,h-DBA (C_{2h}) does not completely constrain the allowed TMV directions, and it is possible for each transition to assume a unique direction within the molecular plane. The angular deviation, $\Delta\phi_i$, of the transition moment associated with the absorption of the probe beam, $\mathbf{M}_{1i}$, relative to the transition moment direction associated with the absorption of the initial excitation, $\mathbf{M}_{02}$, can be calculated from the expression: [17]

$$tg^2(\Delta\phi_i) = \frac{K_Z - K_i}{K_i - K_Y} \qquad (1)$$

Photoselection theory predicts the orientation factors for the excited state molecule based on alignment with the laboratory Z axis, K_Z=0.6 and K_X=K_Y=0.2.[18] These values assume that absorption at 355 nm occurs in a purely polarized transition and that depletion of the ground state is negligible. The first assumption appears to be justified based on the published ground state dichroism spectra in stretched polyethylene. The second assumption is also justified because less than 10% of the ground state molecules are excited in these experiments. Using these values for K_Z and K_Y, the angles corresponding to each observed $S_1 \rightarrow S_n$ transition can be calculated directly from the values of dichroic absorbances at corresponding maxima using the following expression for K_i,[18]

$$K_i = \frac{A_\parallel}{A_\parallel + 2A_\perp} \qquad (2)$$

The resultant angles are collected in the Table 2.

Graphical reduction is a pictorial way of determining these angles. This method is based on the fact that a spectral feature due to a transition in the molecular YZ plane that has its transition moment at an angle $\Delta\phi_i$

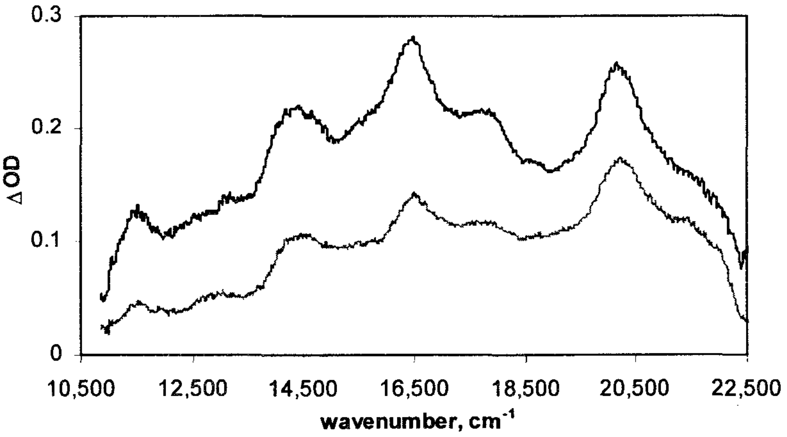

FIG. 3. Dichroic spectra of 1,2:5,6-dibenzanthracene in n-decane at 0 ps delay time, excitation at 355 nm, excitation pulse energy ~600 μJ, 10 spectra (50 laser shots each) averaged for each trace. (——) probe perpendicular to excitation, (——) probe parallel to excitation.

TABLE 2 Transition Moment Angles for a,h-DBA

#	$\Delta\phi_i$	Transition Moment Angles*
1*	± 40 °	3 (or 83)°
2*	± 32 °	11 (or 75)°
3*	± 29 °	14 (or 72)°
4*	± 28 °	15 (or 71)°
5*	± 12 °	31 (or 55)°

*The transition moment angles are taken as a counter-clockwise rotation from the molecular y axis as depicted in the diagram of **1** above (see text for details).

with respect to the Z axis will disappear for a specific linear combination of the dichroic spectra according to equation 3.[14]

$$\left(\frac{1-K_Z+(K_Z-K_Y)\sin^2\Delta\phi_i}{1+K_Z-(K_Z-K_Y)\sin^2\Delta\phi_i}\right)A_{\parallel(\nu)}-\left(2\frac{K_Z-(K_Z-K_Y)\sin^2\Delta\phi_i}{1+K_Z-(K_Z-K_Y)\sin^2\Delta\phi_i}\right)A_{\perp(\nu)}=0$$

(3)

Here the coefficient in front of $A_{||(v)}$ (referred to as *a*) and in front of $A_{\perp(v)}$ (referred to as *b*) in this linear combination must add up to 1. Results of the graphical reduction of the spectra is shown in Figure 4 with varying coefficients *a* and *b*. Notice that different spectral features disappear with different values of *a* and *b* indicating different transition dipole moments for each of the observed transitions. For example, examination of the reduced spectra in Figure 4 shows that the 1* transition disappears for a = 0.274 and b = 0.726. Using this value of *a* and setting once again $K_z=0.6$, $K_y=0.2$ gives the angle $\Delta\phi_i = \pm 40°$. Our evaluation of the error in the determination of the excited state TVM directions gives an accuracy of ±6° in the determined angles.

Because of the way $\Delta\phi_i$ is related to the dichroism (as a squared term) the sign of the angles can not be determined from a single experiment. Theoretical calculations may be used to aide in the choice of sign for each angle, as has been done on many ground state determinations and in this report as well, but in this case this is not necessarily required. Excitation of different ground state transitions in the photoselection process allows the absolute angles to be experimentally determined. Experiments aimed at demonstrating this aspect of time-resolved linear dichroism are in progress. Unfortunately, nothing can be said about the placement of the TMVs within the molecular frame and calculations must be consulted if this type of information is desired. Such a comparison has been done for a,h-DBA to obtain the ground state TMVs in stretched polymer

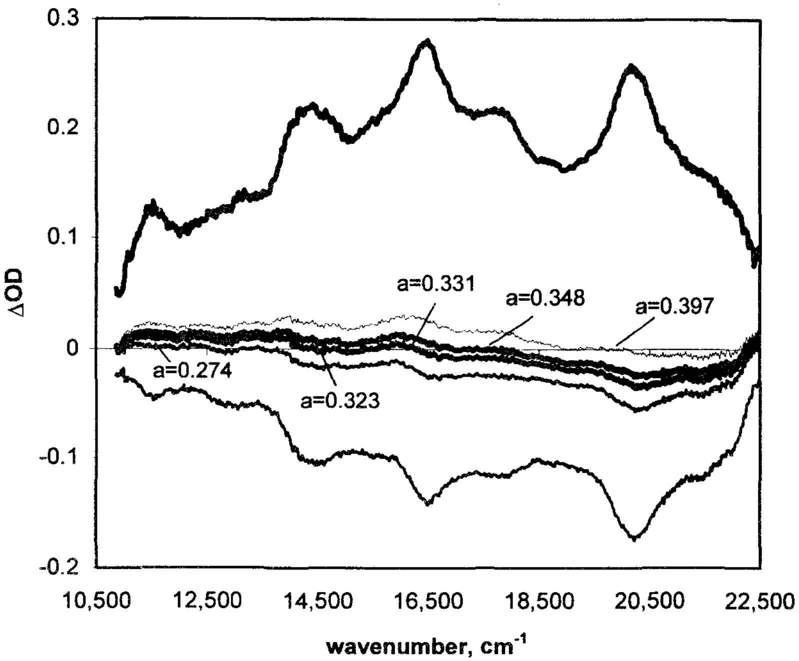

FIG. 4. Graphical reduction of the dichroic spectra of 1,2:5,6-dibenzanthracene shown in Figure 3.

samples.[14] The third column in Table 2 contains the best values of the excited state TMVs using an angle for the 355-nm transition, $\mathbf{M}_{02}$, of +43° with respect to counter clockwise rotation from the molecular y-axis as depicted in the diagram of **1** above.

Rotational Correlation Times

The time dependence of the dichroism does allow a determination of the average rotational time constant for a,h-DBA. While for highly asymmetric molecules such as a,h-DBA can have up to five exponential terms in the dichroism decay, the time resolution of our experiments allows a single determination of a weighted average value. The traces for n-hexane solution of a,h-DBA can be adequately fit to a single exponential term corresponding to the average rotation rate. For a,h-DBA, the lifetime of the excited singlet state is long, ca. 37 ns, and its decay is not significant on the time scale of these experiments. Thus, an average value of rotational correlation time is obtained τ_{rot}=46 ps. This value is consistent with what is expected based on Stokes-Einstein diffusion theory

$$\tau_{rot} = \frac{\eta_s \overline{V}}{RT} \qquad (4)$$

where η_s is the solvent viscosity, V is the molar volume of the solute, R is the gas constant, and T is absolute temperature. Numerical evaluation of τ_{rot} gives the value of ~30 ps in n-hexane with a viscosity of 0.32 cP and an approximation of the molar volume of a,h-DBA by taking the ratio of the molecular weight to its density. The traces shown in Figure 5 for the n-decane solution of a,h-DBA can still be adequately fit to a single exponential term with the average rotation rate τ_{rot}=162 ps. This value is consistent with the threefold increase in viscosity of the solvent. A better fit can be achieved if a double exponential model is used: $\tau_{rot\,1}$=98 ps and $\tau_{rot\,2}$=208 ps. Further improvements to our experimental apparatus, including better signal to noise ratio, are required before we can definitely say that rotation of a,h-DBA in decane is indeed anisotropic.

CONCLUSIONS

Transient absorption spectrum of 1,2:5,6-dibenzanthracene has a considerable number of transitions in the region of 400-900 nm when compared with many other polyaromatic molecules. This at once facilitates and hampers achievement of the goal of our investigation. A wealth of information can be obtained from the dichroic spectra. However, considerable overlap in transitions prevents precise determination of TMVs directions. Nevertheless the ability to obtain the transition moment

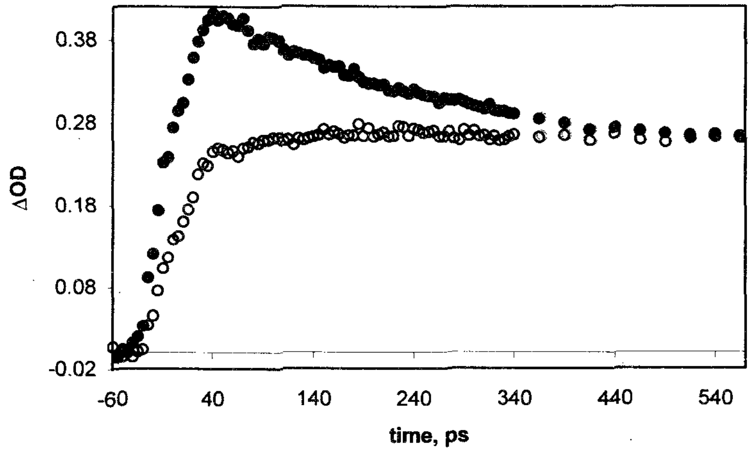

FIG. 5. Dichroic time decay of transient absorption of 1,2:5,6-dibenzanthracene, ~$1.5*10^{-4}$ M in n-decane, excitation pulse 355 nm, probe pulse 609 nm, 200 laser shots per point averaged. (○) perpendicular to excitation, (●) parallel to excitation.

directions for excited states paves the way for structural determinations of these states. The allowed TMV directions are constrained by the symmetry elements in molecules. If a plane of symmetry or rotational axis is removed by changes in geometry on the excited state surface, the allowed transition moment directions will be affected. Comparison of the measured TMVs for a series of polyaromatic systems with those obtained based on simple calculations is underway.

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