

Single and three pulse photoselection of dye probes in nematic liquid crystals

D. A. Armoogum, J. Bryant[†], E. M. Monge and A. J. Bain*

Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

ABSTRACT

We present results of single and three pulse photoselection studies of the dynamics of a fluorescent probe (Oxazine 4) in the nematic phase of the liquid crystal 4-n-pentyl-4'-cyanobiphenyl (5CB). The combination of these techniques with time resolved fluorescence anisotropy measurements allows the unambiguous determination of the full angular motion of the probe together with the ground and excited state degrees of equilibrium (steady state) alignment. The restricted geometry imposed by the nematic host is seen to impart a marked anisotropy in θ and ϕ diffusion ($\gamma_\phi/\gamma_\theta \sim 4$).

Keywords: molecular probe, alignment, rotational diffusion, picosecond, fluorescence anisotropy, polarisation.

1. INTRODUCTION

In an ordered medium it is crucial to achieve a full resolution of the orientational (both θ and ϕ) dynamics as the imposition of order gives rise to a marked departure from conventional (isotropic) molecular relaxation¹⁻⁵. Molecular order has to date been probed using a range of optical processes including Raman scattering⁶, laser induced fluorescence⁷⁻⁹ and surface second harmonic generation¹⁰. Picosecond fluorescence anisotropy studies of molecular probes have been shown to yield useful information on molecular order, orientational dynamics and photophysical processes in both molecular and biomolecular systems^{1,11}. Recent work in our group has shown that it is possible to obtain information on the order and full angular motion of a fluorescent probe in an ordered environment using single pulse variable photoselection and picosecond polarised fluorescence^{2,4}. Here the variation of the excitation (linear) polarisation gives rise to the creation of varying degrees of (non-equilibrium) cylindrically symmetric and asymmetric probe alignment. Analysis of the subsequent fluorescence anisotropy signals yields the ground and excited state degrees of molecular alignment together with the intrinsic rates for θ and ϕ diffusion in the laboratory axis system. This approach has been highly successful in the study of systems exhibiting moderate probe alignment where the departure from (otherwise) isotropic diffusion dynamics is well described by first order perturbation theory³. In single pulse photoselection the creation of the maximum probe alignment orthogonal to the laboratory Z axis (in the case of liquid crystals the nematic director) is achieved with an excitation polarisation angle of 90° ⁴. This invariably leads to the creation of both cylindrically symmetric and asymmetric degrees of excited state alignment and whose joint evolution is reflected in the measured fluorescence anisotropy. The use of three beam photoselection which involves the net photoselection resulting from three orthogonally polarised (Z plus X and Y), temporally coincident laser pulses allows for the creation of cylindrically symmetric but orthogonal probe alignment¹². A combination of these techniques affords the unequivocal experimental determination of probe alignment dynamics within a nematic host.

Defining the measurement direction perpendicular to the Z axis as X, the probe fluorescence anisotropy $R(t)$ at time t following the application of an ultrashort pulse sequence (or single pulse) is given by¹

$$R(t) = \frac{\frac{1}{\sqrt{5}} \langle \alpha_{20}^{ex}(t) \rangle - \frac{1}{\sqrt{30}} \left\{ \langle \alpha_{22}^{ex}(t) \rangle + \langle \alpha_{2-2}^{ex}(t) \rangle \right\}}{1 + \frac{2}{\sqrt{30}} \left\{ \langle \alpha_{22}^{ex}(t) \rangle + \langle \alpha_{2-2}^{ex}(t) \rangle \right\}} \quad (1)$$

* Corresponding author, email a.bain@ucl.ac.uk

[†] Current address: Solexa Ltd, Chesterfield Research Park, Little Chesterfield, nr Saffron Walden, Essex CB10 1XL, UK.

where $\langle \alpha_{20}^{ex}(t) \rangle$ and $\langle \alpha_{22}^{ex}(t) \rangle + \langle \alpha_{2-2}^{ex}(t) \rangle$ are the time dependent cylindrically symmetric and asymmetric degrees of excited state alignment. Their initial values are dependent on the photoselection process and the degree of order in the ground state. From symmetry considerations to first order the diffusion dynamics in an aligned medium should be linear³. For a medium exhibiting global cylindrical symmetry, these are expected to follow

$$\langle \alpha_{20}^{ex}(t) \rangle = \left\{ \langle \alpha_{20}^{ex}(0) \rangle - \langle \alpha_{20}^{ex}(ss) \rangle \right\} \exp\left(-\frac{t}{\tau_{20}}\right) + \langle \alpha_{20}^{ex}(ss) \rangle \quad (2)$$

$$\left\{ \langle \alpha_{22}^{ex}(t) \rangle + \langle \alpha_{2-2}^{ex}(t) \rangle \right\} = \left\{ \langle \alpha_{22}^{ex}(0) \rangle + \langle \alpha_{2-2}^{ex}(0) \rangle \right\} \exp\left(-\frac{t}{\tau_{22}}\right)$$

where (ss) denotes the equilibrium or steady state value of the probe alignment. The cylindrically symmetric and asymmetric alignment rates τ_{20} and τ_{22} are related to the θ and ϕ diffusion rates in the laboratory frame D_{\perp}^{LAB} and D_{\parallel}^{LAB} respectively through

$$1/\tau_{20} = 6D_{\perp}^{LAB} \quad (3)$$

$$1/\tau_{22} = 2D_{\perp}^{LAB} + 4D_{\parallel}^{LAB} \quad (4)$$

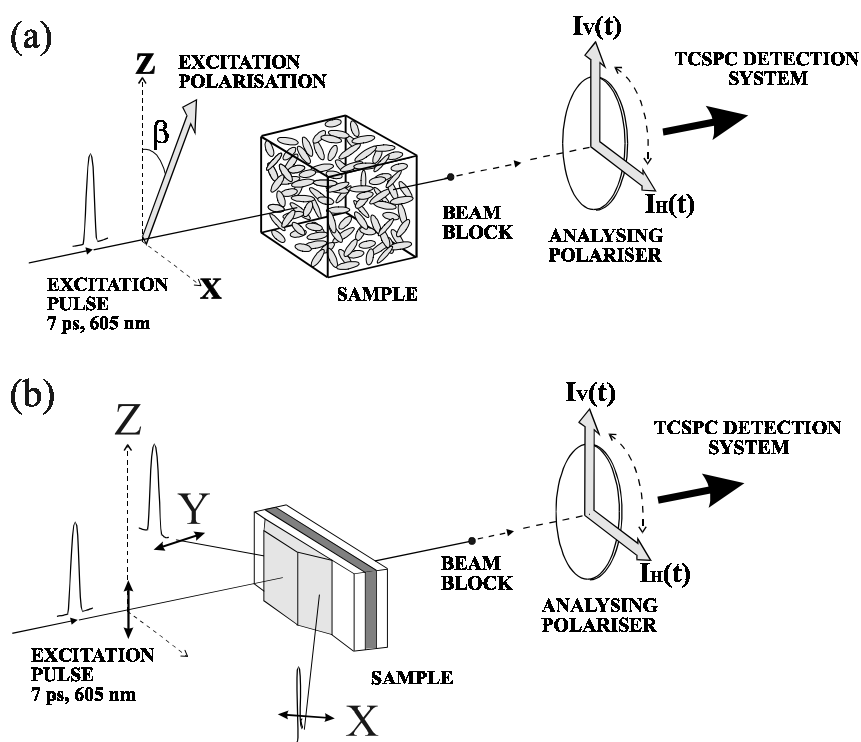


Figure 1. (a) A schematic representation of the experimental arrangement and 180° excitation-detection geometry for single pulse polarised photoselection. The excitation polarisation angle β is varied to create varying degrees of cylindrically symmetric and asymmetric excited state alignment. (b) Experimental arrangement used for three beam photoselection. The excitation from three orthogonally polarised coincident pulses results in a cylindrically symmetric excited state; variation of the Z polarised beam intensity relative to the (equal) X and Y beam intensities allows the cylindrically symmetric alignment to be controlled. Prism coupling is required to ensure the necessary $\pm 45^\circ$ propagation angles for the horizontally polarised pulses.

2. SINGLE PULSE PHOTOSELECTION

The experimental arrangement for single pulse photoselection using a variable linear polarisation is shown in Fig 1a. The excitation polarisation angle β is tuneable between 0° to 90° resulting in a transition probability of the form,

$$W_{abs}^{lab}(\theta, \phi, t) = |\mu_a|^2 \frac{(4\pi)^{\frac{1}{2}}}{3} \left[Y_{00}(\theta, \phi) + \frac{2}{\sqrt{5}} \sum_Q d_{0Q}^2(-\beta) Y_{2Q}(\theta, \phi) \right] \quad (5)$$

In a medium with an axis of cylindrical symmetry parallel to the laboratory Z-axis the degrees of initial excited state alignment are given by³

$$\langle \alpha_{2Q}^{ex}(0) \rangle = \frac{\sum_{K'Q'} \langle \alpha_{K'Q'}^{gs}(ss) \rangle \langle 2Q \left[Y_{00}(\theta, \phi) + \frac{2}{\sqrt{5}} \sum_Q d_{0Q}^2(-\beta) Y_{2Q}(\theta, \phi) \right] | K'0 \rangle}{\sum_{K'Q'} \langle \alpha_{K'Q'}^{gs}(ss) \rangle \langle 00 \left[Y_{00}(\theta, \phi) + \frac{2}{\sqrt{5}} \sum_Q d_{0Q}^2(-\beta) Y_{2Q}(\theta, \phi) \right] | K'0 \rangle} \quad (6)$$

where $\langle \alpha_{K'Q'}^{gs}(ss) \rangle$ are the normalised steady state moments of the ground state distribution function ($\langle \alpha_{00}^{gs}(ss) \rangle = 1$).

Evaluating matrix elements yields

$$\frac{\langle \alpha_{20}^{ex}(0) \rangle}{\sqrt{5}} = \frac{\left[\frac{3\cos^2 \beta - 1}{5} + \frac{\langle \alpha_{20}^{gs}(ss) \rangle}{\sqrt{5}} \left[1 + \frac{2}{7}(3\cos^2 \beta - 1) \right] + \frac{6\langle \alpha_{40}^{gs}(ss) \rangle}{35} (3\cos^2 \beta - 1) \right]}{\left[1 + \frac{(3\cos^2 \beta - 1)}{\sqrt{5}} \langle \alpha_{20}^{gs}(ss) \rangle \right]} \quad (7)$$

$$\frac{\langle \alpha_{22}^{ex}(0) \rangle + \langle \alpha_{2-2}^{ex}(0) \rangle}{\sqrt{30}} = \frac{\sin^2 \beta}{5} \left[1 - \frac{10\langle \alpha_{20}^{gs}(ss) \rangle}{7\sqrt{5}} + \frac{\langle \alpha_{40}^{gs}(ss) \rangle}{7} \right] / \left[1 + \frac{(3\cos^2 \beta - 1)}{\sqrt{5}} \langle \alpha_{20}^{gs}(ss) \rangle \right]$$

Variation of the excitation polarisation angle β from 0 to 90° allows the preparation of a range of initial degrees of excited state alignment with increasing cylindrical asymmetry as β approaches 90° . This is accompanied by a decrease in $\langle \alpha_{20}^{ex}(0) \rangle$ which will tend, depending on the ground state order, towards a negative value as β nears 90° . The variation of the cylindrically symmetric and asymmetric contributions to the excited state alignment of oxazine 4 in nematic 5CB with excitation polarisation angle β is shown in figure 2, with those for an isotropic system shown for comparison.

Observation of the alignment dynamics for an excitation polarisation angle of $\beta=0^\circ$ will clearly reveal the θ diffusion dynamics of probe molecules aligned predominantly along the laboratory Z-axis. For single beam photoselection (in a positively aligned medium) the observation of θ diffusion for probe molecules aligned orthogonally to Z is invariably convoluted with the asymmetric alignment dynamics. In a highly ordered environment such as an aligned mesophase of a liquid crystal it is possible that the diffusion dynamics may well not be linear and the simple picture of alignment relaxation above described in equation (2) will not hold. In these circumstances as clear an experimental picture of the full alignment dynamics is highly desirable. To this end the ability to control the initial photoselected excited state alignment whilst retaining an axis of cylindrical symmetry is highly desirable. This novel approach to alignment control in polarised fluorescence experiments has recently been demonstrated and uses the net photoselection produced by Z, X and Y polarised excitation pulses¹¹.

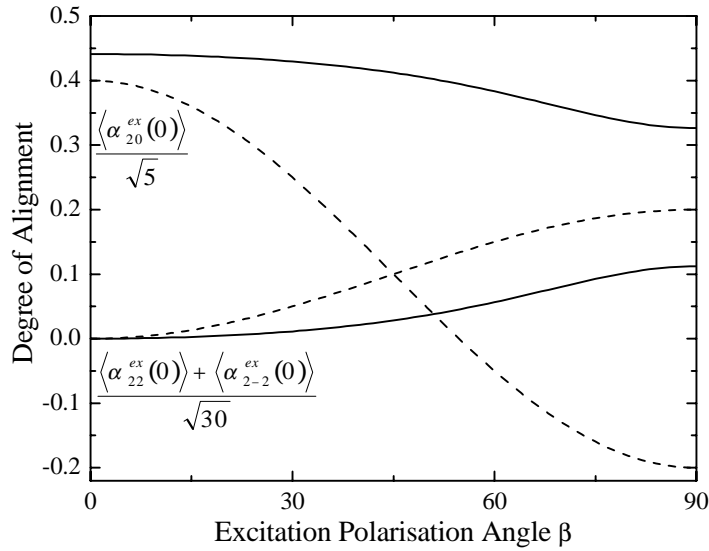


Figure 2. Excitation polarisation dependence of the cylindrically symmetric and asymmetric contributions to the initial fluorescence anisotropy for oxazine 4 in 5CB (solid lines) and for an isotropic system (dashed lines). As the excitation polarisation angle β is increased from 0° , increasing cylindrical asymmetry is introduced into the excited state alignment.

3. THREE PULSE POLARISED PHOTSELECTION

The background theory for three beam photoselection has been described in detail elsewhere¹¹. The experimental arrangement for three pulse polarised photoselection is shown in fig1b. We have shown in previous work that the implementation of coincident equal intensity X and Y polarised beams with propagation angles of $\pm 45^\circ$ to the collinear Z polarised beam photoselects an excited state with no cylindrically asymmetric alignment¹¹. For single photon transitions within the mutual excitation volume the net excitation operator is given by an intensity weighted sum of the individual transition probabilities

$$W_{abs}^{lab}(\theta, \phi, t) \propto |\vec{\mu}_a|^2 \frac{\sqrt{4\pi}}{3} \left[Y_{00}(\theta, \phi) + \frac{2}{\sqrt{5}} B(I) Y_{20}(\theta, \phi) \right] \quad (8)$$

where $B(I)$ is given by the ratio of the input intensities,

$$B(I) = \frac{I_z(t) - \frac{1}{2}[I_x(t) + I_y(t)]}{I_z(t) + I_x(t) + I_y(t)} \quad (9)$$

where I_x and I_y represent the equal intensity horizontally polarised excitation beams that propagate at $\pm 45^\circ$ to the Z-polarised beam. By varying the ratio of I_x and I_y to I_z , $B(I)$ can be varied from 1 ($I_x=I_y=0$) to -0.5 ($I_z=0$). For an isotropic medium this leads to an initial excited state anisotropy range tuneable between 0.4 to -0.5 . Typical initial excited state orientational distribution probabilities $P^{ex}(\theta, \phi, 0)$ arising from three beam photoselection for an isotropic system as beam ratio $B(I)$ is varied from 1 to -0.5 are shown in figure 3.

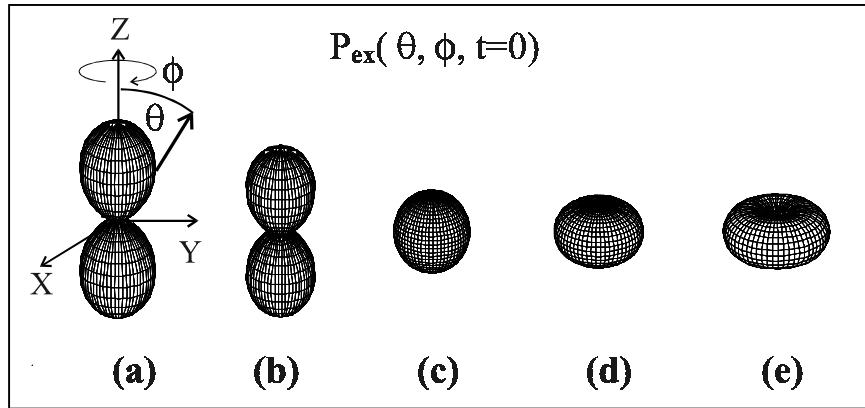


Figure 3. In an isotropic medium, three beam photoselection allows for the control of excited state alignment whilst retaining cylindrical symmetry as beam ratio $B(I)$ is varied. For $B(I)=1$, an excited state orientational distribution (a) is formed which yields an initial fluorescence anisotropy of 0.4. For $B(I)=-0.5$, an excited state orientational distribution (e) is formed which yields an initial fluorescence anisotropy of -0.5 . Although cylindrical symmetry is retained in the experiments with oxazine 4 in nematic 5CB, isotropic and negatively aligned distributions such as in (c)-(e) are not observed, due to the intrinsic positive steady state alignment.

3.1 Application to an aligned medium

For an anisotropic medium the degree of excited state alignment is not only dependent upon the photoselection process but also upon the intrinsic alignment of the ordered ground state. In the presence of an axially symmetric ground state the initial fluorescence anisotropy is given by

$$R(0) = \frac{\langle \alpha_{20}^{ex}(0) \rangle}{\sqrt{5}} = \frac{\frac{k-1}{A} + (2k+1) \left[\frac{\langle \alpha_{20}^{gs}(ss) \rangle}{\sqrt{5}} + B(I) \left(\frac{2}{5} + \frac{4}{7} \frac{\langle \alpha_{20}^{gs}(ss) \rangle}{\sqrt{5}} + \frac{12}{35} \langle \alpha_{40}^{gs}(ss) \rangle \right) \right]}{\frac{k+2}{A} + 2(k-1)B(I) \frac{\langle \alpha_{20}^{gs}(ss) \rangle}{\sqrt{5}}} \quad (10)$$

where k and A are experimental correction factors (see section 4.1.1)

4. EXPERIMENTAL REALISATION

4.1 Procedure

A schematic representation of the experimental apparatus is shown in fig 1b. The oxazine 4 doped (c.a. $10^{-4}M$) nematic 5CB was held in $100\mu m$ thick quartz cells. To provide a homogeneous alignment for the liquid crystal environment, the cells were coated with a surfactant (polyvinyl alcohol solution) and rubbed mechanically. A cell path length of $100\mu m$ was chosen because it falls within the $300\mu m$ range over which homogeneous alignment persists¹³. The sample was contacted by index matching fluid to a coupling prism, fluorescence collection and analysis utilised a collinear geometry with respect to the normally incident Z-polarised excitation pulse (605nm, 7ps). Fluorescence was detected and recorded using time correlated single photon counting (TCSPC) electronics. Particulars of sample preparation, the TCSPC system and associated components have been described in detail elsewhere^{4,14}.

Two preliminary measurements were made using a single pulse at 0° incidence with excitation angle $\beta=0^\circ$ and $\beta=90^\circ$. The initial values of the two fluorescence anisotropies can be used to determine the K=2 and K=4 moments of the ground state distribution. In order to determine accurately these and other fluorescence observables it is necessary to take account of the alteration of the fluorescence anisotropy by the ordered sample and optical system, this results in the determination of two parameters and is described below.

4.1.1 Corrections to the fluorescence anisotropy

In a birefringent medium the vertical and horizontally polarised components of the fluorescence anisotropy are unequally affected by local field effects and differential reflection losses at the boundary between the sample the cell wall¹⁵. Application of these considerations to emission from a molecular probe in a nematic host we obtain¹⁶ the anisotropy correction factor k given by,

$$k(\lambda, T) = \left(\frac{n_e}{n_o} \left(\frac{n_o + n_g}{n_e + n_g} \right) \right)^2 \left(\frac{n_e^2 + 2}{n_o^2 + 2} \right) \quad (11)$$

In this analysis k is uniquely determined by the extraordinary and ordinary indices of refraction of the medium (n_e and n_o) and the refractive index of the sample cell wall n_g . The temperature and wavelength dependence of these for 5CB are well known¹⁷, however correction for the change in the nematic isotropic phase transition and averaging over the fluorescence emission spectrum is necessary¹⁴. We have recently shown that it is possible to determine k independently by a series of fluorescence lifetime and anisotropy measurements^{16,18}, the values yielded by both methods are in general agreement. For oxazine 4 in 5CB at T=25°C k=1.12463.

The second correction factor labelled the A parameter takes into account the reduction in the fluorescence anisotropy from theoretical values due the possible contribution of a number of molecular and experimental factors. Principally these are the non-parallelism of absorption and emission transition dipole moments³, depolarisation due arising from sample concentration and path length effects¹⁹ and depolarisation by the collection optics. The A parameter is determined by the departure of the initial fluorescence anisotropy from its theoretical value in an isotropic sample⁴. For liquid crystalline media the sample is raised to the a few degrees above the nematic isotropic phase transition temperature where departure of R(0,β) from theory is then determined¹⁴. For oxazine 4 in 5CB this approach yielded a value for A of 0.881.

4.1.2 Prism Coupling

In order to achieve the conditions whereby net cylindrical symmetry is maintained by three pulse photoselection, it is necessary for the horizontally polarised beams to propagate through the sample at $\pm 45^\circ$ to the Z polarised excitation pulse. From Snell's Law for propagation at 45° to the normal the incident light angle ξ_{air} at the air glass interface for a sample must satisfy

$$\sin \xi_{air} = n_{sample} / \sqrt{2} \quad (12)$$

It is clear therefore that $n_{sample} \leq \sqrt{2}$, however in highly ordered media such as 5CB n_{sample} is greater than $\sqrt{2}$, so prism coupling is necessary to achieve 45° sample propagation. Details of this are described elsewhere¹².

4.1.3 Propagation angle determination.

The correct propagation angle of 45° for the X and Y polarised beams can be established from measurements of the initial anisotropy relation for horizontally polarised excitation ($\beta=90^\circ$) with varying external propagation angle ξ . The variation of R_H with ξ is given by¹²,

$$R_H(0, \xi) = \frac{\frac{k-1}{A} \left[1 - \frac{\langle \alpha_{20}^{gs} \rangle}{\sqrt{5}} \right] + (2k+1) \left[-\frac{1}{5} + \frac{5}{7} \frac{\langle \alpha_{20}^{gs} \rangle}{\sqrt{5}} - \frac{6}{35} \langle \alpha_{40}^{gs} \rangle \right] - \frac{3}{5} \cos(2\xi) \left[1 - \frac{10}{7\sqrt{5}} \langle \alpha_{20}^{gs} \rangle - \frac{\langle \alpha_{40}^{gs} \rangle}{7} \right]}{\frac{k+2}{A} \left[1 - \frac{\langle \alpha_{20}^{gs} \rangle}{\sqrt{5}} \right] + 2(k-1) \left[-\frac{1}{5} + \frac{5}{7} \frac{\langle \alpha_{20}^{gs} \rangle}{\sqrt{5}} - \frac{6}{35} \langle \alpha_{40}^{gs} \rangle \right] + \frac{6}{5} \cos(2\xi) \left[1 - \frac{10}{7\sqrt{5}} \langle \alpha_{20}^{gs} \rangle - \frac{\langle \alpha_{40}^{gs} \rangle}{7} \right]} \quad (13)$$

The predicted variation in R_H with propagation angle ξ for oxazine 4 in 5CB is shown in figure 4, 45° propagation in the sample corresponding to an initial anisotropy of 0.325. The angle of incidence of the horizontally polarised beam was varied until the target anisotropy of 0.325 was reached. The second horizontally polarised beam was similarly aligned and care was taken to ensure the three beams were spatially and temporally overlapped in the sample. Fluorescence anisotropy measurements were then made with varying values of beam intensity ratio $B(I)$ from 1 [Z-polarised excitation] to -0.5 [X and Y polarised excitation].

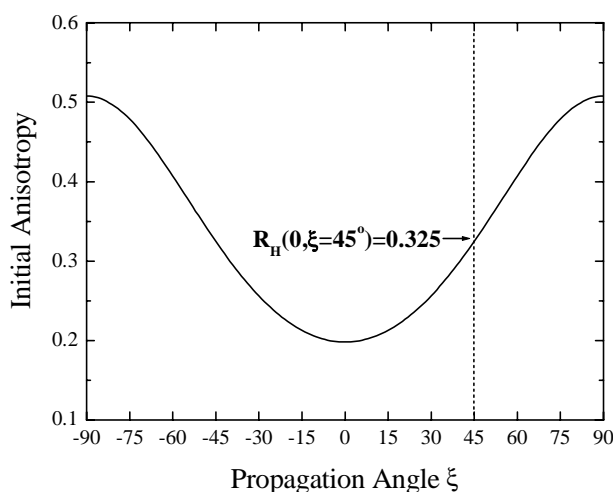


Figure 4. A plot of the variation in the initial anisotropy with angle of incidence $R_H(0, \xi)$ for oxazine 4 in 5CB predicted by the ground state moments. The predicted (target) initial anisotropy value for 45° propagation is 0.325.

5. RESULTS

Fluorescence anisotropy decays following three beam photoselection for oxazine 4 in 5CB are shown in figure 5. All the decays can be fitted to a single exponential lifetime, which is in excellent agreement (within experimental uncertainties) with the lifetime obtained for a single beam photoselection experiment using vertically polarised light. The single beam anisotropy decay with an excitation polarisation angle $\beta=90^\circ$ for oxazine 4 is included for comparison.

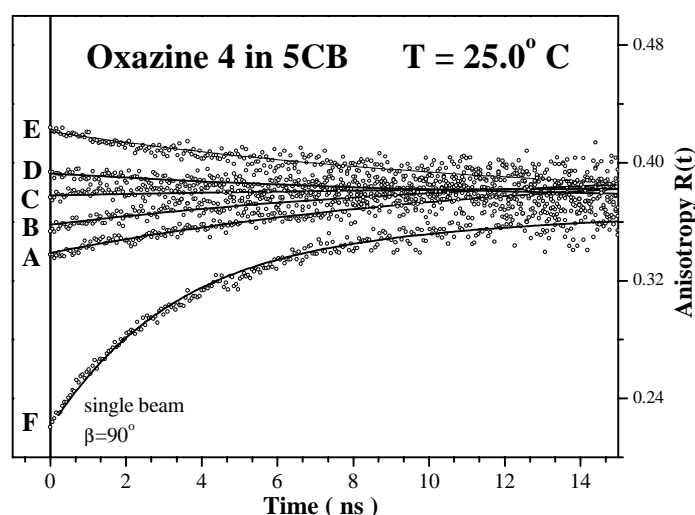


Figure 5. Three beam anisotropy decays (curves A to E) obtained for Oxazine 4 in 5CB ($5 \times 10^{-4} \text{M}$), with a single beam $\beta=90^\circ$ anisotropy decay (curve F) shown for comparison. The intensity ratio $B(I)$ is varied from -0.5 (X and Y polarised photoselection) through to 1 (Z polarised photoselection).

Oxazine 4 curve label	Beam ratio $B(I)$	τ_{20} (ns)
A	-0.500	11.9 ± 0.3
B	0.096	12.0 ± 0.5
C	0.477	12.5 ± 0.2
D	0.738	12.2 ± 0.9
E	Single pulse photoselection, $\beta=0^\circ$: $B(I)=1$, $\tau_{20}=12.06 \pm 1.15 \text{ns}$	
F	Single pulse photoselection, $\beta=90^\circ$: $\tau_{22}=4.04 \pm 0.01 \text{ns}$	

Table 1. The anisotropy decays for oxazine 4 in 5CB yield (within experimental uncertainty) the same corrected single exponential lifetime as that obtained for single beam Z-polarised excitation.

The three beam photoselection experiment provides a variable degree of alignment selectivity whilst retaining cylindrical symmetry. The tuning range of initial anisotropy depends upon the value of beam ratio B(I) for a given set of ground state parameters and correction factors. The predicted maximum and minimum degrees of initial alignment can be determined from equation (10) where B(I) is 1 and -0.5 respectively: this gives,

$$R(0, \max) = \left[\frac{k-1}{A} + (2k+1) \left[\langle P_2 \rangle + \left(\frac{2}{5} + \frac{4}{7} \langle P_2 \rangle + \frac{36}{35} \langle P_4 \rangle \right) \right] \right] / \left[\frac{k+2}{A} + 2(k-1) \langle P_2 \rangle \right]$$

$$R(0, \min) = \left[\frac{k-1}{A} + (2k+1) \left[\langle P_2 \rangle - \left(\frac{1}{5} + \frac{2}{7} \langle P_2 \rangle + \frac{18}{35} \langle P_4 \rangle \right) \right] \right] / \left[\frac{k+2}{A} - (k-1) \langle P_2 \rangle \right] \quad (14)$$

where $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are the more commonly used 2nd and 4th rank order parameters used to describe cylindrically symmetric samples²⁰ these are related to the alignment moments through

$$\langle P_K \rangle = \langle \alpha_{K0} \rangle / \sqrt{2K+1} \quad (15)$$

The tuning range of initial anisotropy measured for oxazine 4 in excellent accordance (i.e. within experimental error) with the predicted maximum and minimum initial anisotropy values, as shown in table 2.

OXAZINE 4, T=25° C	B(I)	R _{predicted}	R _{observed}
$\langle P_2 \rangle = 0.3949$	1	0.42	0.42 ± 0.01
$\langle P_4 \rangle = -0.2245$			
k = 1.12463	-0.5	0.33	0.32 ± 0.01
A = 0.861			

Table 2. The ground state parameters obtained from the single beam $\beta=0^\circ$ and 90° curves predict the initial anisotropy tuning range that should be possible using three beam photoselection. The observed tuning range is in excellent agreement with predictions for oxazine 4 in 5CB.

The symmetric and asymmetric alignment relaxation times (τ_{20} and τ_{22}) can be determined by fitting the single photon photoselection anisotropy decays for $\beta=0^\circ$ and $\beta=90^\circ$. Including correction factors, the fitting function for the anisotropy decays took the following form:

$$R(\beta, t) = \left[\frac{k-1}{A} + \frac{\alpha_{20}(2k+1)}{\sqrt{5}} - 3\alpha_{AS} \right] / \left[\frac{k+2}{A} + \frac{\alpha_{20}(2k-2)}{\sqrt{5}} + 6\alpha_{AS} \right] \quad (16)$$

where

$$\frac{\alpha_{20}}{\sqrt{5}} = \left[\frac{3 \cos^2 \beta - 1 + \langle P_2 \rangle \left(1 + \frac{2(3 \cos^2 \beta - 1)}{7} \right) + \langle P_4 \rangle \left(\frac{18(3 \cos^2 \beta - 1)}{35} \right)}{1 + \langle P_2 \rangle (3 \cos^2 \beta - 1)} - \alpha_{SS} \right] \exp\left(-t/\tau_{20}\right) + \alpha_{SS} \quad (17)$$

and

$$\alpha_{AS} = \frac{\frac{\sin^2 \beta}{5} \left(1 - \frac{10}{7} \langle P_2 \rangle + \frac{3}{7} \langle P_4 \rangle \right)}{1 + \langle P_2 \rangle (3 \cos^2 \beta - 1)} \exp\left(-t/\tau_{22}\right) \quad (18)$$

Knowledge of the ground state order parameters and correction factors[‡] allows τ_{20} to be determined from the $\beta=0^\circ$ curve. Analysis of the $\beta=90^\circ$ curve a known value for τ_{20} is thus straightforward allowing τ_{22} to be determined. It is assumed in this step that θ diffusion (symmetric alignment relaxation) is independent of the initial molecular alignment. This is confirmed by the three beam excitation measurements where cylindrically symmetric alignment relaxation is seen to be independent of initial molecular orientation. From equations (3) and (4) the cylindrically symmetric and asymmetric alignment relaxation times can thus be used to determine the intrinsic θ and ϕ diffusion rates in the laboratory frame (D_{\perp}^{LAB} and D_{\parallel}^{LAB}), these are displayed in table 4.

τ_{20} (ns)	τ_{22} (ns)	$\gamma_{\theta} \equiv D_{\perp}^{LAB} (\times 10^{-7} \text{s}^{-1})$	$\gamma_{\phi} \equiv D_{\parallel}^{LAB} (\times 10^{-7} \text{s}^{-1})$	$\gamma_{\phi} / \gamma_{\theta}$
12.06 \pm 1.15	4.04 \pm 0.01	1.3820 \pm 0.0007	5.4971 \pm 0.0007	3.98 \pm 0.02

Table 4. Values for the cylindrically symmetric and asymmetric relaxation times for oxazine 4 in 5CB together with the corresponding θ and ϕ diffusion rates relative to the nematic director (laboratory Z axis).

The anisotropy in the intrinsic θ and ϕ diffusion rates is marked with $\gamma_{\phi} \cong 4\gamma_{\theta}$. The relative reduction in the θ diffusion rate is seen to go hand in hand with the restricted range of θ orientations the probe is allowed to adopt in the nematic host. Following the analysis¹⁵ of Durbin et al. the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ order parameters can be used to determine the oxazine 4 ground state distribution. At 25° this is seen to be sharply peaked at $\theta=40^\circ$ and 140° to the nematic director with an approximate Gaussian width of 31° . Diffusion of the probe in the ϕ co-ordinate is unrestricted, the steady state value of all moments with $Q \neq 0$ are necessarily zero in a cylindrically symmetric host.

A direct experimental verification of the difference in cylindrically symmetric and asymmetric relaxation is provided by a comparison between the evolution of the fluorescence anisotropy from cylindrically symmetric (3 beam excitation) and asymmetric molecular arrays (single beam excitation $\beta>0^\circ$) with the same initial anisotropy. Figure 5 shows that the range of initial anisotropy that can be created by single pulse photoselection covers the entire three beam tuning range. It is therefore possible to create an excited state via single photon photoselection with the same initial anisotropy as that created by three beam photoselection. The clearest case is provided by purely horizontal excitation ($B(I)=-0.5$) the corresponding single beam excited state will have the highest asymmetric alignment contribution. This offers a direct observation of the difference between cylindrically symmetric and asymmetric probe alignment relaxation, as shown in figure 7.

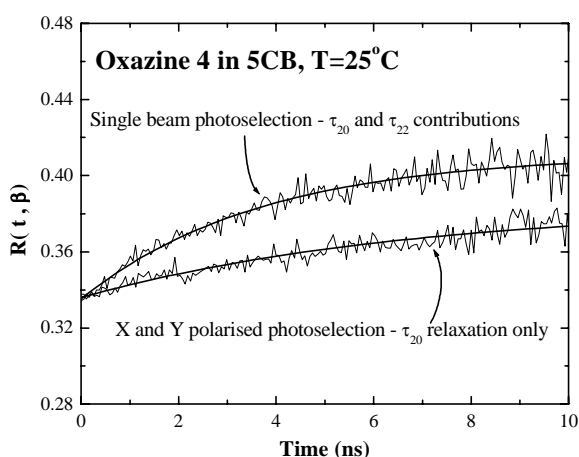


Figure 7. Fluorescence anisotropy evolution in oxazine 4 doped 5CB, relaxation back to the steady state anisotropy ($\langle P_2^{EX} \rangle$) of c.a. 0.37 is clearly more rapid in the case where the cylindrically asymmetric alignment is maximised.

[‡] The inclusion of correction factors result in a correction to the lifetimes of c.a. 10% only.

6. CONCLUSIONS

The combination of three and single pulse photoselection has proven to be a powerful tool in understanding the dynamics of a molecular probe in an ordered host. In the oxazine 4-5CB system in spite of the high degree of intrinsic probe order ($\langle P_2^{\text{EX}} \rangle$ c.a. 0.37) the alignment dynamics are seen to be wholly independent of the initial molecular orientation and conform well to first order relaxation processes as predicted by perturbation theory and simple symmetry considerations.

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