

NOVEL ROTATIONAL DYNAMICS IN ANISOTROPIC FLUID MEDIA STUDIED BY POLARISATION RESOLVED PICOSECOND TCSPC

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INTRODUCTION

Conventional time resolved fluorescence anisotropy experiments involve the photoselection of an anisotropic array of molecular orientations in an isotropic fluid medium by an ultrashort light pulse. Collisions with the isotropic background lead to the randomisation of this distribution and the consequent decay of the fluorescence anisotropy R with time. $R(t)$ decay curves yield the second order orientational correlation functions for isotropic rotational diffusion, whose correlation times, τ_{or} , can be used to extract information on the orientationally averaged nature of microscopic frictional forces⁽¹⁾⁽²⁾⁽³⁾.

In contrast, the study of orientational dynamics in anisotropic media affords the possibility of observing collisional dynamics in a wholly new light. In particular, the interaction of polarised laser radiation with an already anisotropic molecular array leads to the preparation and subsequent evolution of additional (higher order) correlation functions for molecular motion⁽⁴⁾. Furthermore, since the dynamics are no longer averaged over an isotropic background, the conventional selection rules governing isotropic relaxation no longer hold and a radically different collisional modification of the initial distribution may result⁽⁴⁾⁽⁵⁾. It should be noted that chemical reactivity and energy exchange processes, such as Förster transfer, can be expected to be substantially modified under such conditions⁽⁶⁾ and that orientationally sensitive spectroscopic techniques should be particularly revealing in this context.

Recent developments in sapphire jet technology now afford the routine production of thin high optical quality fluid jets. In such environments the highly directional nature of molecular collisions is predicted to lead to significant molecular alignment⁽⁴⁾. The sign and magnitude of this alignment is a sensitive probe of the anisotropy of the collisional processes and the directional nature of frictional forces operating at the molecular level⁽⁸⁾.

Steady state fluorescence measurements of R6G in ethylene glycol jets show evidence of significant molecular alignment and/or anisotropic orientational relaxation with the flow⁽⁷⁾. Steady state measurements invariably convolve the initial anisotropy of the system, its interaction with polarised laser radiation and its subsequent evolution⁽⁵⁾. Picosecond time resolved fluorescence anisotropy measurements are crucial to unravel the complex dynamics of such systems. This report describes novel picosecond time correlated single photon counting (TCSPC) studies of R6G in ethylene glycol and polyethylene glycol flows together with a comparison of R6G dynamics in identical but isotropic fluid environments.

The differences between isotropic and anisotropic R6G dynamics are marked, illustrating the presence of an initial alignment along the jet axis, together with highly anisotropic orientational motion of the array following excitation.

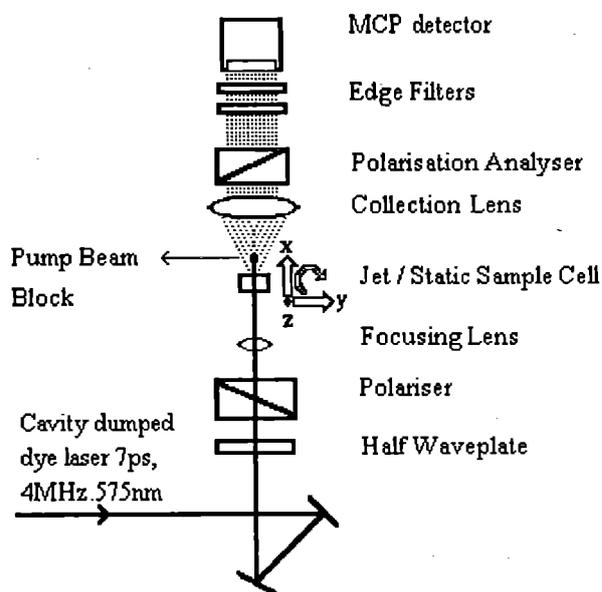


Figure 1 optical layout.

EXPERIMENTAL

The optical arrangement is shown in Figure 1. We have successfully employed a colinear fluorescence collection geometry, which is essential for polarisation dependent studies of thin samples in that the additional complication of angle dependent Fresnel factors is removed from the analysis. Direct and scattered pump radiation is prevented from reaching the MCP detector by a combination of edge filters and a small beam block. The system has non-preferential detection of any particular polarisation (a g factor of unity). This is demonstrated in Figure 2, which shows $I_V(t)$ and $I_H(t)$ curves for an isotropic sample of R6G excited with 45° polarisation at 575 nm. Both curves are identical at all times, as should be the result for an isotropic system under these excitation conditions⁽⁹⁾. The sapphire nozzle was mounted on a precision stage allowing xyz positioning and rotation about the jet axis.

Fluorescence decay curves for emission polarised parallel and perpendicular to the jet axis were recorded as a function of excitation polarisation angle θ (relative to the jet axis). Similar measurements were performed with the isotropic cell to provide a reference. The instrument response function (105 ps) was determined by light scattering from a suspension of "Coffee-mate" (a non-fluorescent scatterer).

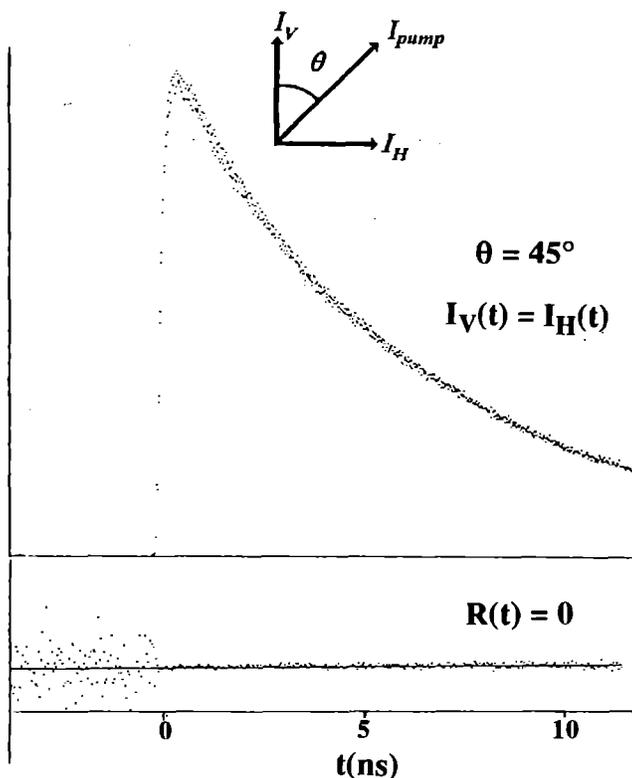


Figure 2 g factor assessment.

RESULTS AND DISCUSSION

Figure 3 shows $I_{||}(t)$, $I_{\perp}(t)$ and $R(t)$ curves for a 0.9 g^{-1} solution of R6G in an ethylene glycol / polyethylene glycol (viscosity 38 cP), excited on axis (spot size $50 \mu\text{m}$), 5.5 mm downstream from a $500 \mu\text{m}$ sapphire nozzle with a backing pressure of 8 psi. The corresponding data for the reference (isotropic) sample of the same solution, in a $500 \mu\text{m}$ strain-free quartz cuvette is displayed in Figure 3a. Figures 3b and 3c correspond to excitation polarisations parallel ($\theta = 0^\circ$) and perpendicular ($\theta = 90^\circ$) to the flow axis respectively. The $R(t)$ curves are defined (conventionally) relative to the excitation polarisation vector in each case.

The differences between the jet and isotropic fluorescence profiles are striking. It is immediately apparent that the initial anisotropy $R(0)$ is a strong function of excitation polarisation relative to the jet axis. For parallel excitation $R(0)$ is 0.40 ± 0.015 , significantly higher than the isotropic cell ($R(0) = 0.36 \pm 0.015$), whilst perpendicular excitation results in considerably reduced $R(0)$ of 0.30 ± 0.015 . These observations are consistent with the interaction of polarised laser radiation with an initially aligned array of R6G molecules about the flow axis. The variation of $R(0)$ with θ can be used to extract information on the moments of the ground distribution function⁽⁴⁾⁽⁵⁾⁽⁹⁾ and will be discussed elsewhere⁽⁹⁾.

The subsequent orientational dynamics of molecules photoselected with orientations parallel and perpendicular to the flow axis are equally distinct. In isotropic systems $R(t)$ will always decay exponentially to zero due to the isotropic nature of solvent-solute collisions, as can be seen by reference to the isotropic cell. For a photoselected array of R6G molecules, aligned parallel to the jet axis, the anisotropy decays non-exponentially to a constant value. The orientational dynamics for excitation at 90° are most marked: the $I_{||}(t)$ and $I_{\perp}(t)$ curves meet at $\tau = 4.2 \text{ ns}$, the system behaving as if it were isotropic, before reaching a final negative value corresponding to alignment along the jet axis. Neither $R(t)$ curve is consistent with isotropic rotational diffusion. The passage of $R(t)$ from positive to negative for 90° excitation is unequivocal evidence of cross relaxation between moments of the excited state orientational distribution functions, a process forbidden in isotropic systems⁽⁴⁾.

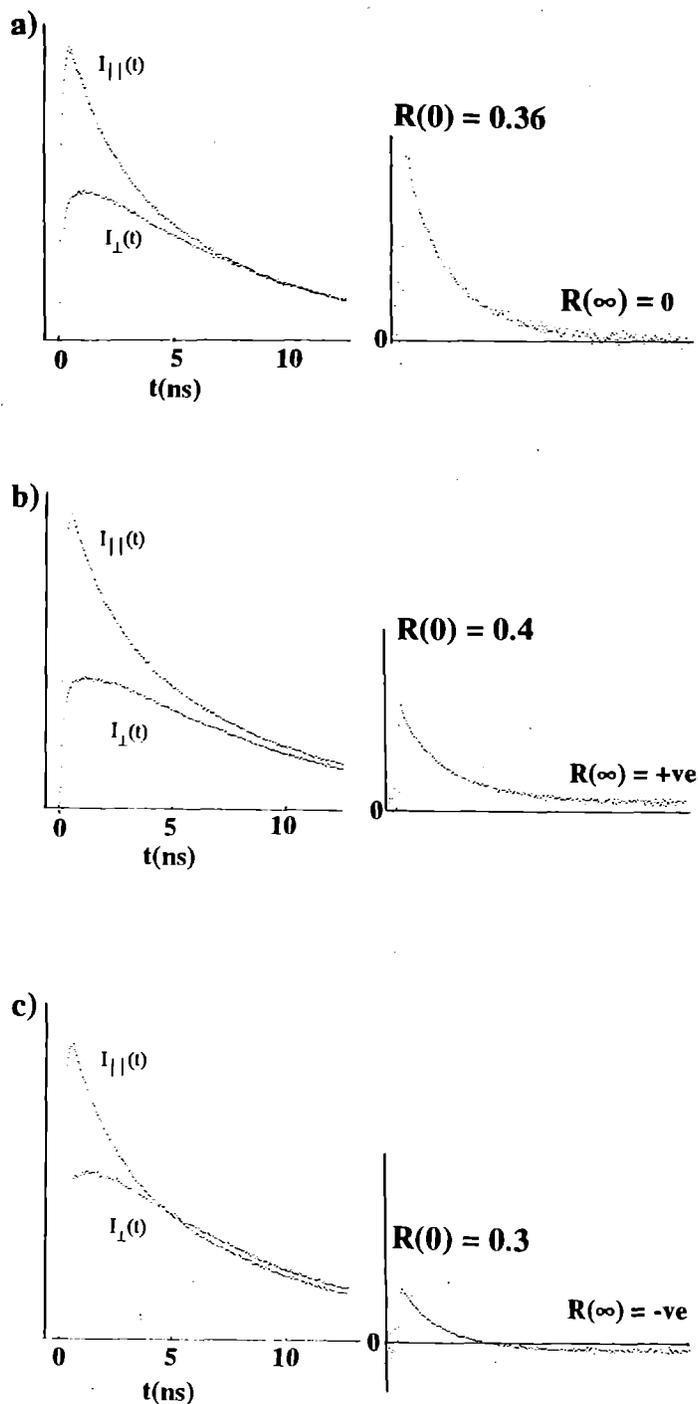


Figure 3 $I_{||}(t)$, $I_{\perp}(t)$ and $R(t)$ curves as a function of excitation polarisation angle θ a) isotropic cell, $I_{||}(t)$, $I_{\perp}(t)$ and $R(t)$ are independent of θ b) jet with excitation polarisation parallel to the jet axis $\theta = 0^\circ$ c) jet with excitation polarisation perpendicular to the jet axis $\theta = 90^\circ$

The long time anisotropy of the system in both cases corresponds to a residual alignment parallel to the jet axis and if the fluorescence observables are defined in terms of the jet axis system (I_V , I_H), this yields an identical residual anisotropy (to within experimental error) of approximately 3% for both $\theta = 0^\circ$ and $\theta = 90^\circ$.

Subsequent investigations of R6G jet dynamics have focused on the variation of $I_V(t)$ and $I_H(t)$ as a function of excitation polarisation. In all cases the system is seen to return to a constant final anisotropy (within experimental error), independent of the

to final orientation distribution is, however, a complex function of the excitation polarisation relative to the jet axis, and significant departures from isotropic fluorescence observables, measured with the same polarisation geometry, are seen. Figure 4 shows the results for excitation polarised at 45° to the jet axis. In an isotropic system this produces identical $I_V(t)$ and $I_H(t)$ curves, as shown in Figure 2. The jet dynamics in this situation are quite distinct, with $R(t)$ remaining constant at $\sim 3\%$. It was not possible to obtain identical $I_V(t)$ and $I_H(t)$ curves under any excitation polarisation conditions.

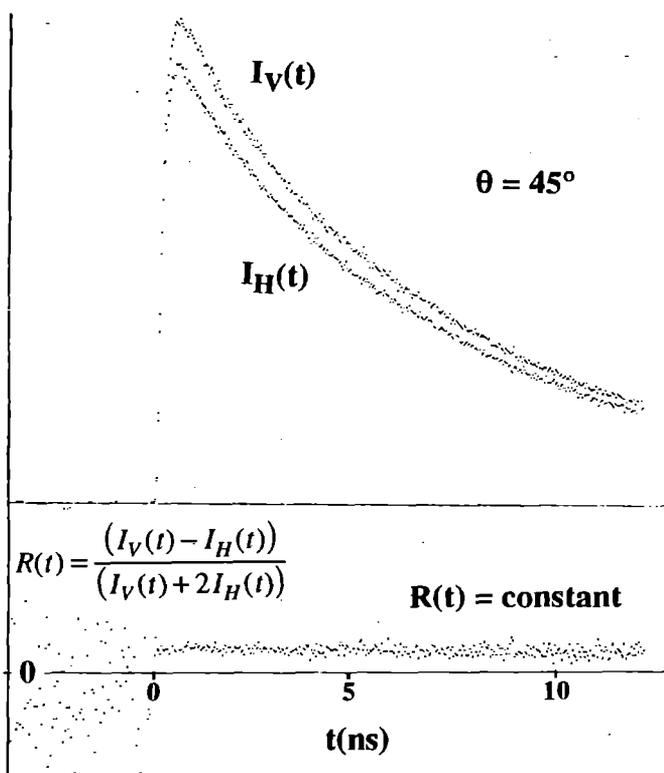


Figure 4 jet with excitation polarisation at 45° to the jet axis.

The coupling between the ground and initial excited state orientational distribution functions is, however, sensitive to the excitation polarisation ⁽⁴⁾ ⁽⁵⁾ ⁽⁹⁾ and it is possible to find a "magic angle" excitation polarisation for a given ground state orientational distribution which gives rise to, an initially isotropic excited state ⁽⁹⁾ (in terms of the polarisation observables allowed in single photon electric dipole transitions). It is then possible to observe the evolution of this isotropic array of molecules under the anisotropic collisional conditions of the jet. For the R6G ethylene glycol / polyethylene glycol system studied, the magic excitation angle was found to be at $\theta = 49^\circ$ from the jet axis; the $I_V(t)$, $I_H(t)$ and $R(t)$ curves are shown in figure 5. The anisotropy is seen to reach its equilibrium value with an exponential growth in time of $\tau = 1.25$ ns.

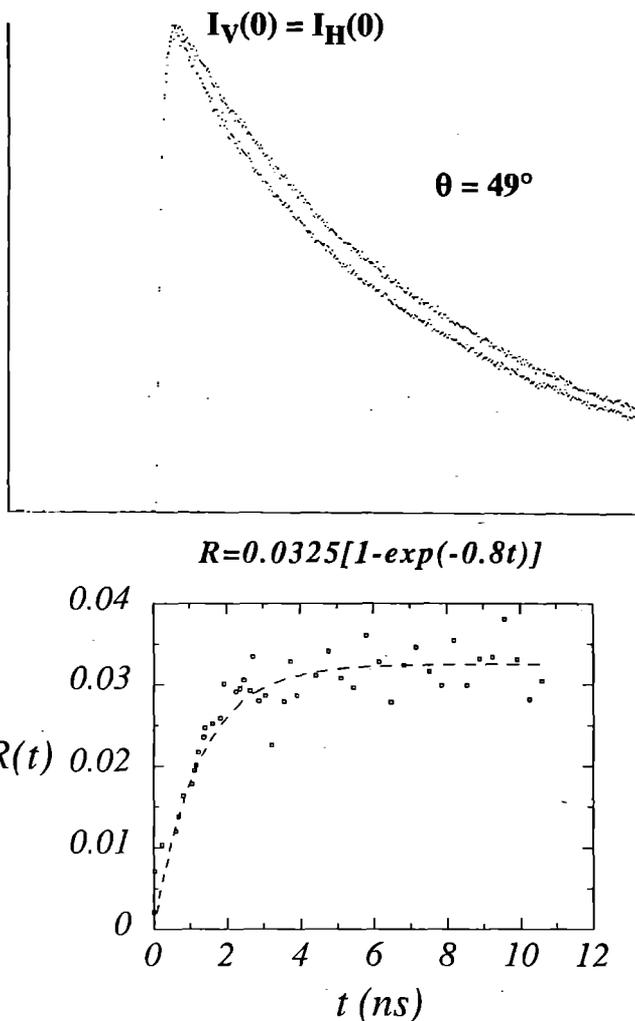


Figure 5 magic angle excitation at $\theta = 49^\circ$ to the jet axis. The $R(t)$ curve shows the growth of collisional induced alignment with an exponential rise time of 1.25 ns

These results clearly indicate the presence of dynamic molecular ordering mechanisms within the jet. We believe that these are the first real-time measurements of such processes. Further polarised TCSPC experiments at RAL are planned, to investigate these new and intriguing phenomena.

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