COLLISIONAL ALIGNMENT OF MOLECULES IN HIGH PRESSURE FLUID JETS

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INTRODUCTION

Ordered molecular arrays and the mechanisms by which they are produced is an area of considerable scientific and technological interest. Both the linear and nonlinear optical responses of a

medium are strongly influenced by the degree of ordering of its component parts. Second order nonlinear optical responses for instance are forbidden in centrosymmetric media[1] whilst the coupling between optical fields via $\chi^{(3)}$ in degenerate four-wave mixing and transient grating phenomena can be significantly enhanced by the presence of molecular ordering[2].

The imposition of order in an otherwise isotropic fluid is achieved by the application of external forces which act in opposition to the randomising effects of Brownian motion. The application of an external electric field to produce bulk orientation and alignment via dipole and induced dipole interactions is well known and forms the basis of Electric Field Induced Second Harmonic Generation (EFISH) technique[3] and electric dichroism and birefringence phenomena (Electro Optic Kerr Effect)[4]. The degree of anisotropy induced in these instances is small, the orientational distribution function for the dipolar array in polar coordinates being given by

$$P(\theta,\phi) = \frac{\exp(-\mu E / kT)\cos\theta}{\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta .\exp(-\mu E / kT)\cos\theta} \quad (1)$$

where θ is the angle between the applied electric field and the permanent molecular dipole moment μ. Even for highly polar molecules ($\mu \sim 20$ Debye) practible values of ($\mu E/kT$) are small (c.a. 0.06) resulting in only weakly anisotropic arrays and as such (with the exception of liquid crystals) the technique has limited application.

An alternative approach is to generate molecular alignment via the shear (collisional) forces generated by laminar fluid flow, the observation of induced birefringence in flowing canada balsam by Maxwell in 1873 being the first experimental observation of the coupling between molecular ordering and the linear optical properties of a medium. Until recently the only application of these principles to fluid media has been the Couette technique in which a velocity gradient is used to align anisotropic solute molecules in a solution confined between counter rotating concentric cylinders[5-8]. The torques generated by such mechanical means are weak and consequently Couette flow has only been successfully applied to the alignment of macromolecules such as DNA.

EXPERIMENTAL

A recent series of pilot experiments by us at RAL has demonstrated that it is possible to produce highly ordered arrays of small to medium sized molecules (Resorufin and R6-G) at the exit face of $100\mu m$ and $500\mu m$ sapphire nozzles using ethylene glycol and polyethylene glycol jets[9,10]. Using a novel polarisation resolved picosecond time correlated single photon counting technique (TCSPC) we have been able to measure the intrinsic alignment of these arrays and to determine the nature of the angle dependent intermolecular potential responsible for the alignment (fig 2). Well depths as large as 0.7 kT have been measured yielding intrinsic alignment factors that are over an order of magnitude greater than those achievable by the imposition of strong DC electric fields. A further refinement of the technique involves variable excitation polarisation, enabling the photoselection of a range of non-equilibrium orientational
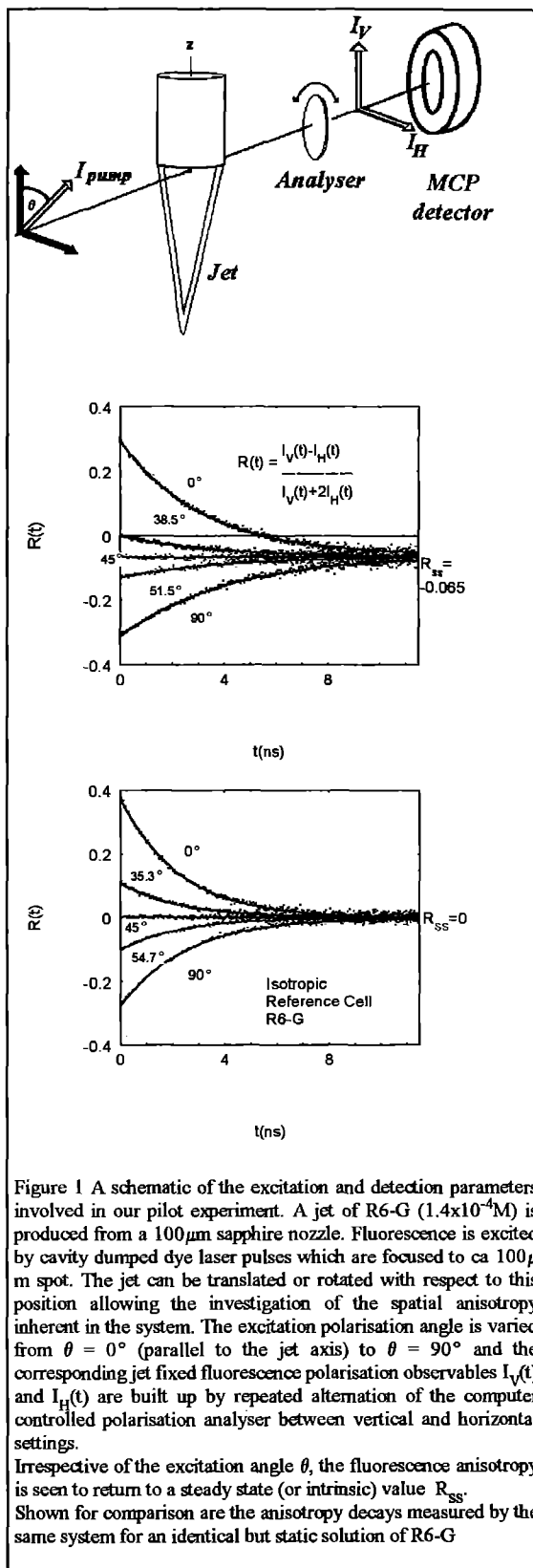

Figure 1 A schematic of the excitation and detection parameters involved in our pilot experiment. A jet of R6-G ($1.4\times10^{-4}M$) is produced from a $100\mu m$ sapphire nozzle. Fluorescence is excited by cavity dumped dye laser pulses which are focused to ca 100μ m spot. The jet can be translated or rotated with respect to this position allowing the investigation of the spatial anisotropy inherent in the system. The excitation polarisation angle is varied from $\theta = 0°$ (parallel to the jet axis) to $\theta = 90°$ and the corresponding jet fixed fluorescence polarisation observables $I_V(t)$ and $I_H(t)$ are built up by repeated alternation of the computer controlled polarisation analyser between vertical and horizontal settings.

Irrespective of the excitation angle θ, the fluorescence anisotropy is seen to return to a steady state (or intrinsic) value R_{SS}.

Shown for comparison are the anisotropy decays measured by the same system for an identical but static solution of R6-G

distributions and the subsequent relaxation back to the equilibrium configuration (fig 1). The symmetry breaking presence of the aligning potential permits the observation of orientational processes forbidden in isotropic media (figs. 1 and 3).

The fundamental rate constants obtainable from these measurements together with those from an otherwise identical but isotropic system and the angle dependent potential surface, constitute the most complete picture now available of the directional nature of molecular collisions and the role of frictional forces at the molecular level.

ANALYSIS

The orientational probability distribution function for an ordered assembly of oriented molecules is most conveniently expressed as an expansion of spherical harmonics.

$$P(\theta,\phi,t) = \frac{1}{4\pi}\left(1 + \sum_{K>0,Q} Y_{KQ}(\theta,\phi)\langle\alpha_{KQ}(t)\rangle\right) \qquad (2)$$

The moments $\langle\alpha_{KQ}(t)\rangle$ of the distribution contain all the information on the time dependent orientational dynamics of the system following laser excitation. Single photon electric dipole selection rules restrict the polarisation observables of any excited state distribution to the cylindrically symmetric $\langle\alpha_{20}\rangle$ and cylindrically asymmetric $\{\langle\alpha_{22}\rangle + \langle\alpha_{2-2}\rangle\}$ alignment moments[11]. The time dependent fluorescence anisotropy measured in the jet fixed axis system, R(t) is

$$R(t) = \frac{I_V(t) - I_H(t)}{I_V(t) + 2I_H(t)} = \frac{\frac{\langle\alpha_{20}(t)\rangle}{\sqrt{5}} - \frac{1}{\sqrt{30}}\{\langle\alpha_{22}(t)\rangle + \langle\alpha_{2-2}(t)\rangle\}}{1 + \frac{2}{\sqrt{30}}\{\langle\alpha_{22}(t)\rangle + \langle\alpha_{2-2}(t)\rangle\}} \qquad (3)$$

For excitation polarised at $\theta=45°$ to the jet axis the subsequent photoselection yields an excited array for which $\langle\alpha_{20}(0)\rangle,\langle\alpha_{22}(0)\rangle$ and $\langle\alpha_{2-2}(0)\rangle$ are extremely close to their equilibrium values. R(t) is constant (R_{ss}), yielding the intrinsic anisotropy of the system which can be measured downstream from the nozzle exit (fig 2). ϕ dependent R(t) data for $\theta = 0°$ and $90°$ are used to investigate the cylindrical ordering of the array. All the arrays so far produced are cylindrically symmetric and the R_{ss} data is then used to construct the angle dependent potential energy surface (E(θ)) for the equilibrium distribution. Variation of θ permits the photoselection of a range of non-equilibrium orientational distributions by changing the initial values of the excited state alignment moments. The relaxation of these distributions strongly depends on E(θ). One of the most striking features of the symmetry breaking due to the E(θ) is the direct observation of the collisional ordering of an initially "isotropic" array (fig 3).

The relaxation dynamics of the individual moments of the system are observed to be linear i.e.

$$\frac{\partial}{\partial t}\left[\langle\alpha_{KQ}(t)\rangle - \langle\alpha_{KQ}(ss)\rangle\right] = -\gamma_{KQ}\left[\langle\alpha_{KQ}(t)\rangle - \langle\alpha_{KQ}(ss)\rangle\right]$$

$$\left[\langle\alpha_{KQ}(t)\rangle - \langle\alpha_{KQ}(ss)\rangle\right] = \left[\langle\alpha_{KQ}(0)\rangle - \langle\alpha_{KQ}(ss)\rangle\right]\exp\left(-\gamma_{KQ}t\right) \qquad (4)$$

Under isotropic conditions each moment $\langle\alpha_{KQ}\rangle$ relaxes independently and the rate constants γ_{KQ} are related by simple symmetry factors[12]. An obvious consequence is that $\gamma_{20} = \gamma_{2Q}$. The effect of E($\theta$) is to break this restriction. Our primary results following a self-consistent R(t), θ analysis indicate that

γ_{20}(isotropic) = 4.5 x 10^{8}s^{-1} > $\gamma_{2\pm2}$ (jet) = 3.8 x 10^{8}s^{-1} > γ_{20} (jet) = 3.2 x 10^{8}s^{-1}
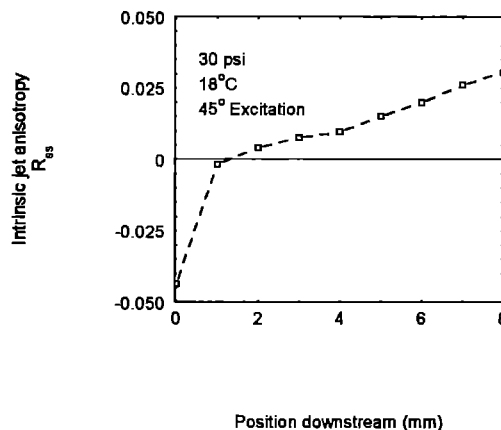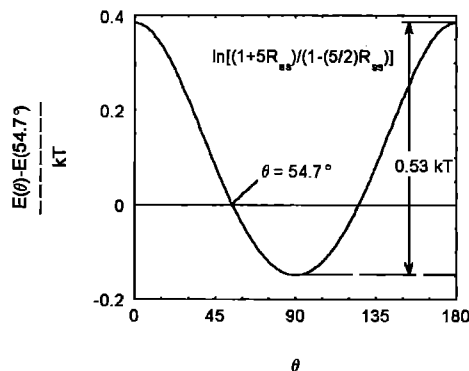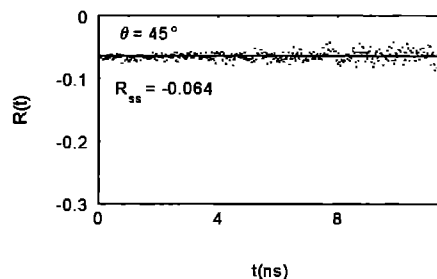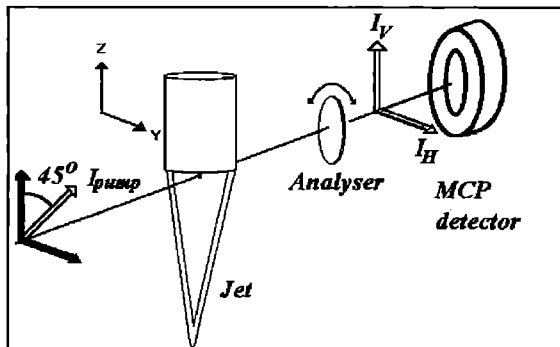

Figure 2 For the excitation polarised at $\theta = 45°$ to the jet axis, the excited state orientational distribution function suffers little disturbance from its intrinsic or steady state form. The fluorescence anisotropy R(t) is (to within experimental error) a constant R_{ss}. The R_{ss} date can be inverted to yield the angle dependent intermolecular potential generated by the shear flow. Translation of the jet with respect to the laser axis enables a picture of the spatial dependence of R_{ss} and hence E(θ) to be built up.

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The physical reason for this behaviour is that different torques are exerted on the $\langle \alpha_{20}(0) \rangle$ and $\langle \alpha_{2\pm2}(0) \rangle$ moments. In addition, off diagonal relaxation due to the interconversion of photoselected but non-optically active moments (K'>2; Q'$\neq$ 0,2) of the distribution is also possible.This can easily be seen from a simple treatment of Debye-type orientational relaxation in the presence of an external potential E(θ). In such instances, the time dependent orientational probability distribution function is given by P(θ,ϕ,t)[13]

$$\frac{\partial}{\partial t}\left[P(\theta,\phi,t) - P(\theta,\phi,ss) \right] = -\hat{H}\left[P(\theta,\phi,t) - P(\theta,\phi,ss) \right] \quad (5)$$

where P(θ,ϕ,ss) is the steady state or equilibrium distribution function and $\hat{H}$ is a Markovian relaxation operator of the form[14]

$$\hat{H} = -D\nabla^2 - D\nabla^2\left(\nabla E(\theta) / kT \right) \quad (6)$$

where D is the molecular diffusion coeffecient for rotational motion perpendicular to the symmetry axis.
Expanding P(θ,ϕ,t) in terms of spherical harmonics as above, the time dependent moments $\langle \alpha_{LQ}(t) \rangle$ are given by[15]

$$\langle \alpha_{KQ}(t) \rangle - \langle \alpha_{KQ}(ss) \rangle =$$

$$(\exp - K(K+1)Dt) \sum_{K'}\langle KQ|\exp\left\{ -D\nabla^2\left(\frac{\nabla E(\theta)}{kT} \right)t \right\}| K'Q\rangle$$

$$\times\left\{ \langle \alpha_{K'Q}(t) \rangle - \langle \alpha_{K'Q}(ss) \rangle \right\} \quad (7)$$

The ∇E(θ) term represents the gradient, or torque generated by the effective intermolecular potential E(θ) and plays the role of coupling the otherwise orthogonal moments of P(θ,ϕ,t).

Steady state, R_{ss}, and initial anisotropy measurements, R(0), can be used to determine the quadrupolar (K=2) and hexadecapolar (K=4) contributions to E(θ). The diffusion equation can then be numerically solved with this input to yield predicted γ_{KQ} values which can be directly compared with the experimental data obtained from our R(t) vs. θ measurements. This approach allows a test of fundamental theory in a manner not permitted by conventional time resolved fluorescence anisotropy and four wave mixing studies, which invariably observe molecular motion averaged over an isotropic collisional background[11].

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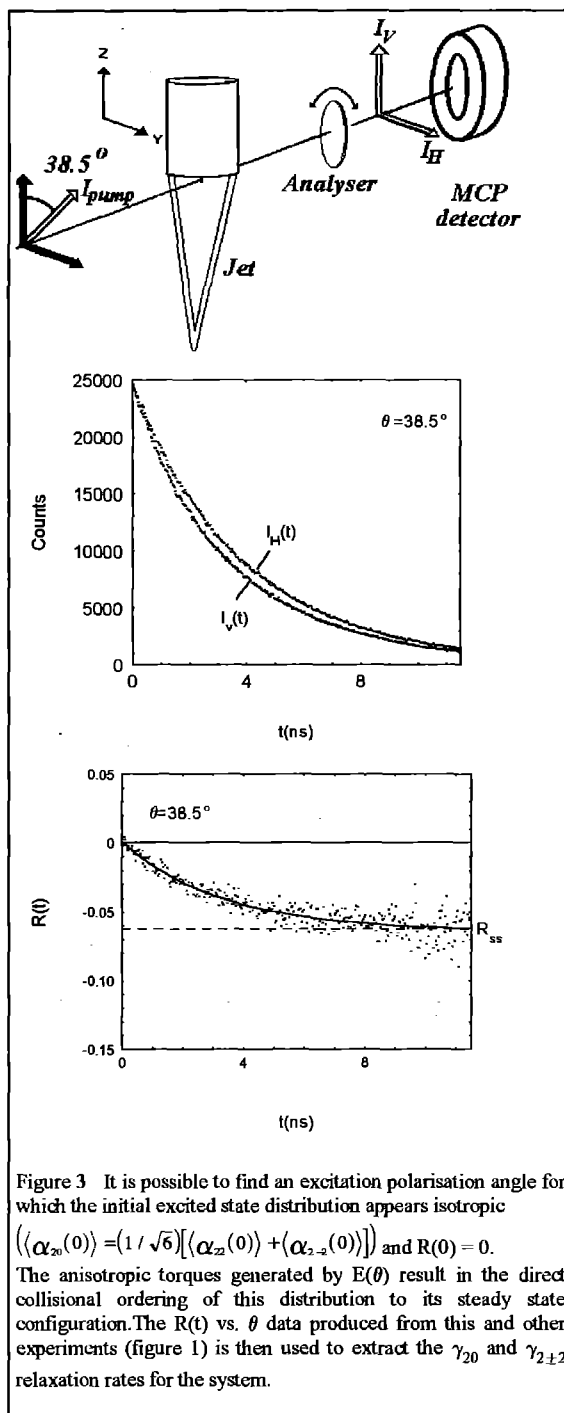12. B.Berne and R.Pecora, Dynamic Light Scattering, Wiley, New York, (1976).

Figure 3 It is possible to find an excitation polarisation angle for which the initial excited state distribution appears isotropic

$\left(\langle \alpha_{20}(0) \rangle = (1/\sqrt{6})[\langle \alpha_{22}(0) \rangle + \langle \alpha_{2-2}(0) \rangle] \right)$ and R(0) = 0.
The anisotropic torques generated by E(θ) result in the direct collisional ordering of this distribution to its steady state configuration.The R(t) vs. θ data produced from this and other experiments (figure 1) is then used to extract the γ_{20} and $\gamma_{2\pm2}$ relaxation rates for the system.

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