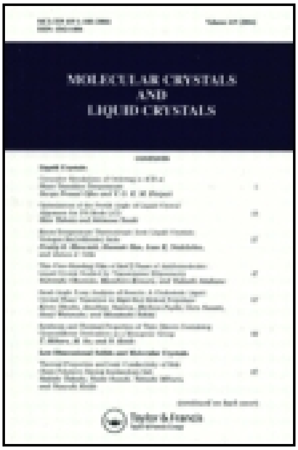

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Simulated Time Resolved Fluorescence in Ordered Phases

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SIMULATED TIME RESOLVED FLUORESCENCE IN ORDERED PHASES

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Abstract An interpretation of time resolved fluorescence emission experiments, performed on probes in isotropic and ordered polar phases, is developed. The system under scrutiny is provided by a dipolar molecule undergoing rotational diffusion, whose dipole moment is coupled to a stochastic reaction field generated by the ordered polar medium. Under quite general conditions, the fluorescence emission is defined as an integral over all possible orientations of the ground and excited states. Since the model allows to reproduce experimental results at a semi-quantitative level and a negligible computational cost, a user-friendly package with graphics utilities has been created, which can be of help to investigate interactively the dependence of the simulated spectra upon several macroscopical parameters such as the dielectric constants and the viscosity of the medium.

EXPERIMENTAL OBSERVABLE

The emission signal of a fluorescent probe is an integral over configurations $\underline{q}_0$ and $\underline{q}$ describing the ground and excited state, respectively. The set of relevant degrees of freedom of the system includes the space orientation of the molecular frame (MF) of the probe, conformational internal degrees of freedom, local solvent variables and so forth. For the case of completely depolarized light, the signal is given, neglecting constant factors depending on the instrumental apparatus, by the expression:

$$I(\omega,t) = \int d\underline{q} \int d\underline{q}_0 g[\omega - \Delta E(\underline{q})/\hbar] P^{(1)}(\underline{q}_0, \underline{q}, t) \tag{1}$$

A more complicated formulation is necessary for the case of linearly polarized light: the additional knowledge of the transition vector dipoles (both in emission *and* in absorption) would be needed[1]. However, we shall concentrate our analysis here only to depolarized light, and so an average with respect to all directions of the polarization planes can be performed. Only constant factors are generated, which can be neglected. Eq. (1) contains a band shape function $g[\omega - \Delta E(\underline{q})/\hbar]$ which depends upon the difference in energy between the two states, $\Delta E(\underline{q})$, at the configuration $\underline{q}$. A basic ingredient in Eq. (1) is the distribution at time t for the excited state population $P^{(1)}(\underline{q}_0, \underline{q}, t)$, which depends parametrically on $\underline{q}_0$ through the initial conditions, and is defined in terms of the time evolution operator $\hat{\Gamma}$:

$$P^{(1)}(\underline{q}_0, \underline{q}, t) = \int_0^t d\tau \exp\{-[\hat{\Gamma} + 1/\tau_F]\tau\}\delta(\underline{q}_0 - \underline{q})\delta(t-\tau) \tag{2}$$

A source term and a sink term have been included in Eq. (2), under some simplifying hypothesis, namely i) the sink function responsible for the decay of the population of the excited state is assimilated to the inverse of the fluorescence life-time, τ_F; ii) the source function is chosen to be the product of two Dirac delta functions in space and time: $\delta(\underline{q}_0 - \underline{q})\delta(t)$ i.e. an instantaneous, point-to-point excitation from the ground to excited state is allowed.

Our purpose is now the definition of the time evolution operator $\hat{\Gamma}$ and the calculation of the emission signal for predicting realistic experimental cases. Preliminary results (Fig. 1) concerning the time resolved fluorescence emission of coumarin 503 (C503) in the liquid crystal mixture ZLI 1167 are indeed available, which meet most of the practical requirements.

The model

A relevant set of coordinates must be chosen. First, the orientation of the probe molecule has to be included, represented by a set of Euler angles $\underline{\Omega} = \alpha, \beta, \gamma$ expressing the MF orientation with respect to the laboratory frame (LF). Given the cylindrical symmetry for all molecular properties, and the uniaxial symmetry of the anisotropic environment, the azimuthal angle γ can be factorized out in the present calculations.

An additional set of variables, represented by a vector $\underline{X}$ (whose components are defined by default in the LF) is then added to the relevant set of coordinates to describe the local polarization of the solvent. A one-dimensional polarization variable was used recently to treat the solvent dynamics of an isotropic polar environment coupled to an emitting probe with an internal degree of freedom[2]. In this work we shall employ a vector description of the solvent polarization to take into account the solvent effects on the the rotational motion of the probe. The solvent dynamics is described as the dynamical behavior of the reaction field resulting by an Onsager cavity with the dielectric properties of the bulk solvent. An advantage of this phenomenological approach is the immediate relation established between the macroscopical dielectric properties of the medium, i.e. the dielectric tensor constants $\underline{\underline{\epsilon}}_0$ and $\underline{\underline{\epsilon}}_\infty$.

We define the total potential energy of the system as the sum of an orientational potential, resulting from the anisotropic interactions exerted in the liquid crystal phase acting on the probe, and of an electrostatic term, which accounts for the interaction between the electric dipole of the molecule and the reaction field. A correction due to the instantaneous relaxation of the electronic polarization and a term for the finite fluctuations of the solvent polarization are included. For a given state ($i = 0, 1$):

$$E_i(\underline{q}) = -\lambda \mathrm{P}_2(\beta) - \frac{1}{2}\underline{\mu}_i \underline{\underline{F}}_\infty \underline{\mu}_i - \underline{\mu}_i \underline{X} + \frac{1}{2}\underline{X}\underline{\underline{F}}_{\mathrm{or}}^{-1}\underline{X} + \mathcal{E}_i \tag{3}$$

The first term is a measure of the orientational effect on the i-th excited state of the molecule; $\underline{\mu}_i$ is the electric dipole moment (depending on the orientation if expressed in the LF), $\mathcal{E}_i$ is a constant (electronic) term. To simplify the treatment we assume a very simple form for the orientational potential, and we neglect any difference between orientational behavior in the two states (i.e. a unique λ parameter is needed). Also, we take both $\underline{\mu}_0$ and $\underline{\mu}_1$ as vectors aligned to the z-axis (long axis of the molecule) of the MF, i.e. $\underline{\mu}_i = \mu_i \underline{z}$. Tensors $\underline{\underline{F}}_\infty$ and

$\underline{F}_{\mathrm{or}} = \underline{F}_0 - \underline{F}_\infty$ are defined in terms of $\underline{\underline{\epsilon}}_\infty$ and $\underline{\underline{\epsilon}}_0$, which are diagonal in the LF, and of the electrostatic depolarization tensors $\underline{n}$ and $\underline{n}'$ for the cavity and in vacuo. A detailed derivation is presented elsewhere[3]. By choosing a cavity of spherical shape with radius a, (which certainly constitutes a rough approximation since C503 is somewhat elongated in shape), one can show that for a cylindrically symmetric dielectric tensor $\underline{\underline{\epsilon}}$ (i.e. $\epsilon_1 = \epsilon_2 = \epsilon_\perp$ and $\epsilon_3 = \epsilon_\parallel$), both $\underline{F}_0$ and $\underline{F}_\infty$ are diagonal in the LF. Finally, we specify the time evolution operator $\hat{\Gamma}$. We adopt a purely diffusive description for both coordinates, $\underline{\Omega}$ and $\underline{X}$. The complete time evolution operator is then:

$$\hat{\Gamma} = -\frac{1}{\tau_R}\underline{\hat{m}}P_{eq}^{(1)}(\underline{q})\underline{\hat{m}}P_{eq}^{(1)}(\underline{q})^{-1} - \underline{\hat{\nabla}}\underline{D}_S P_{eq}^{(1)}(\underline{q})\underline{\hat{\nabla}}P_{eq}^{(1)}(\underline{q})^{-1} \tag{4}$$

Here $\underline{\hat{m}}$ is the infinitesimal rotation vector operator for a particle in α, β. $\underline{\hat{\nabla}}$ is the gradient in $\underline{X}$; $P_{eq}^{(1)}(\underline{q})$ is the Boltzmann equilibrium distribution of the excited state population, defined with respect to $E_1(\underline{q})$. Tensor $\underline{D}_S$ is diagonal in the LF, and its principal values depend on the solvent relaxation times $\tau_S^{\perp,\parallel}$, according to the relation

$$\frac{D_S^{\perp,\parallel}}{k_B T} = \frac{F_{\mathrm{or}}^{\perp,\parallel}}{\tau_S^{\perp,\parallel}} \tag{5}$$

All parameters are, at least in principle, known or measurable: λ can be obtained by experimental information on solute ordering, μ_0 can be evaluated by standard semi-empirical calculations; μ_1 can be derived from measures of stationary solvatochromic effects using the Lippert-Mataga relation; $\mathcal{E}_1 - \mathcal{E}_0$ can be evaluated once and for all from the absorption spectrum in gas phase. The dynamical parameters are also, in principle, measurable or approximately known: τ_R from the Stokes-Einstein relation and the viscosity, $\tau_S^{\perp,\parallel}$ from dielectric relaxation experiments. In practice, many of these quantities are ill-defined or difficult to measure, but an estimate of the order of magnitude can be reasonably given.

Although dynamical and static properties of the system can be predicted once a small number of macroscopical parameters is defined, the numerical implementation of the model, is not, by any means, a trivial problem. We shall describe in the remaining Sections an approximate but accurate computational approach based on a complete separation of time scales between rotational and solvent degrees of freedom. It is useful to choose rescaled quantities to represent both the potential functions and the time evolution operator:

$$\underline{X} \leftarrow (k_B T)^{-1/2}\underline{F}_{\mathrm{or}}^{-1/2}\underline{X} \tag{6}$$

$$\mu_{0,1}^{\perp,\parallel} \leftarrow \mu_{0,1}\left(F_{\mathrm{or}}^{\perp,\parallel}/k_B T\right)^{1/2} \tag{7}$$

In the rescaled representation, the principal values of $\underline{D}_S$ are simply the inverse values of the solvent relaxation times; the dipole vector for the i-th state has components $(\mu_i^\perp, \mu_i^\perp, \mu_i^\parallel)^{\mathrm{tr}}$ in the MF; the potential energy, in $k_B T$ units, is obtained simply as:

$$E_i(\underline{q}) = \mathcal{F}_i - \lambda \mathrm{P}_2(\cos\beta) - \frac{1}{2}(\underline{X} - \underline{\mu}_i)^2 \tag{8}$$

where $\mathcal{F}_i$, λ are now expressed in k_BT units and contain corrections terms depending on the anisotropy of the dielectric tensors, the magnitude of the electric dipole moments and so on. By substituting reasonable numerical values for these quantities one always finds that the corrections to the orientational distribution resulting from static dielectric effects are generally small. Thus, the Boltzmann distribution functions in the i–th state can be simply written as $P_{eq}^{(i)}(\underline{q}) = P(\underline{\Omega})G(\underline{X} - \underline{\mu}_i)$, where $P(\underline{\Omega})$ is the equilibrium distribution with respect to the orientational term $\lambda P_2(cos\beta)$ only and $G(\underline{X} - \underline{\mu}_i)$ is a Gaussian distribution of the solvent polarization centered on the rescaled dipole.

Let us consider as main object of our investigation the frequency of the intensity maximum of the fluorescence emission, $\omega_{\max}(t)$, whose shift in time define the transient Stokes shift correlation function[4]:

$$C(t) = \frac{\omega_{\max}(t) - \omega_{\max}(\infty)}{\omega_{\max}(0) - \omega_{\max}(\infty)} \tag{9}$$

By neglecting any change in the width of the spectrum with time, we may identify the frequency of the maximum with the average of the frequency of transition $\Delta\omega(\underline{q})$, given by the difference of energy between the states. After some algebra [and identifying the band shape function $g(\omega)$ with a simple known Gaussian function, for convenience sake], one finds a simple enough expression for the Stokes shift function, in terms of rescaled dipole vectors in the two states

$$C(t) = \frac{\overline{\Delta\underline{\mu}\underline{\mu}_1} - \langle \Delta\underline{\mu}\underline{X} | \exp(-\hat{\Gamma}t) | P_{eq}^{(0)} \rangle}{\overline{\Delta\underline{\mu}^2}} \tag{10}$$

where $\Delta\underline{\mu} = \underline{\mu}_1 - \underline{\mu}_0$ and $\overline{f}$ stands for the average of $f(\underline{\Omega})$ with respect to $P(\underline{\Omega})$.

SIMULATED TIME RESOLVED EMISSION

At time $t = 0$ the system is prepared in the equilibrium configuration of the ground state; after the exciting pulse the solvent polarization readjusts itself to the larger dipole moment of the excited state, until equilibrium is reached at $t = \infty$. The measurable effect is a shift towards the red in the frequency of the maximum intensity of the fluorescence band.

The numerical solution of the dynamical problem can be achieved by representing the time evolution operator in matrix form in a suitable set of basis functions in $\underline{q}$. The linear algebraic problem is then reduced in the usual way to the diagonalization of the matrix, to find the eigenvalues (i.e. the decay modes) of the problem. The correlation function represented by Eq. (10) is then resolved in a sum of exponentials. This approach is in principle exact, and has to be ultimately followed when the time scales of the various processes involved (rotation and solvent relaxation) are relatively close. Serious difficulties arise from the relatively high dimensionality of the problem and from its algebraic complexity. For these reasons, we postpone the exact treatment of the dynamical problem to a future work. Here we present an approximate treatment of different dynamical regimes, and we compare theoretical predictions to preliminary experimental results. To this purpose, we assume a time scale separation between the solute and solvent motions and we use the analogue of a Born-Oppenheimer approximation[5]. We analyze two distinct possibilities. In the first case, very slow solute tumbling is allowed; in the second case very fast solute tumbling is considered.

In the case of slow tumbling motion $\tau_R >> \tau_S^{\perp,\parallel}$. After averaging out the fast solvent dynamics the following expression for the Stokes shift is recovered:

$$C(t) = \frac{\overline{\Delta\underline{\mu}\Delta\underline{\mu}(t)}}{\overline{\Delta\underline{\mu}^2}} \tag{11}$$

where $\Delta\underline{\mu}(t)$ has the meaning of a (rescaled) dipole at time t, obtained from the straightforward expression:

$$\Delta\underline{\mu}(t) = \exp(-\underline{D}_S t)\Delta\underline{\mu} \tag{12}$$

In this limit, the solvent distribution of the excited state is essentially a Gaussian whose center moves from $\underline{\mu}_1$ to $\underline{\mu}_0$, The Stokes shift follows the time evolution of the rescaled dipole and the decay times are given exactly by the relaxation times of the solvent. A revised version of Eq. (11) which takes into account corrections due to the slow tumbling motion is the following:

$$C(t) = \frac{\overline{\Delta\underline{\mu}\exp(-\overline{\Gamma}_R t)\Delta\underline{\mu}(t)}}{\overline{\Delta\underline{\mu}^2}} \tag{13}$$

here $\overline{\Gamma}_R$ is the rotational operator, averaged with respect to the fast relaxing solvent variables. Eq. (13) can be solved numerically.

Next, we analyze the case of very fast tumbling. The separation of time scales is now indicated by the condition $\tau_R \ll \tau_S^{\perp,\parallel}$. The calculation of the Stokes shift follows closely the methodology presented in ref. 5, where the slow set of coordinates (the solvent variables in the present case) is treated by defining an averaged operator with respect to the fast relaxing coordinates (i.e. the solute orientation angles). A slow decaying contribution to the overall correlation function is then calculated, whereas a residual term is found to account for the rapid fluctuations of the fast cooordinates for each fixed configuration of the slow coordinates.

In the case under investigation an additional complication is given by the fact that, for large values of λ, the solute tumbling motion is affected by the kinetic process associated to the change of preferential orientation with respect to the director (i.e. the activated jump motion between the minima at $\beta = 0$ and $\beta = \pi$). Thus the time scale separation between slow solvent modes and fast solute modes would seem not complete. This is not the case, however, since the Stokes shift correlation function *does not* depend, by symmetry reasons, upon the eigenfunction of the complete operator $\hat{\Gamma}$ which is associated to the jump motion: or, in other terms, the motional regimes monitored by the Stokes shift observable are related only to librations of the already aligned solute molecule, and not to large readjustments in orientation.

The total Stokes shift function in the regime of fast tumbling can then be written as

$$C(t) = C_S(t) + C_R(t) \tag{14}$$

where the slow decaying term is given as a normalized correlation function calculated in the solvent coordinates space only:

$$C_S(t) = \frac{\overline{\Delta\underline{\mu}\,\underline{\mu}_1} - \langle \mathcal{E}(\underline{X})|\exp(-\bar{\hat{\Gamma}}_S t)|P_0(\underline{X})\rangle_S}{\overline{\Delta\underline{\mu}^2}} \tag{15}$$

Here $\bar{\hat{\Gamma}}_S$ is the time evolution operator averaged with respect to the fast set of coordinates $\underline{\Omega}$, which has an equilibrium solution $P_1(\underline{X})$, obtained averaging the excited state total equilibrium distribution; the corresponding quantity for the ground state is $P_0(\underline{X})$. Finally $\mathcal{E}(\underline{X})$ is defined as the average of the dipole-field interaction energy divided by $P_1(\underline{X})$, i.e.:

$$\mathcal{E}(\underline{X}) = \frac{\langle \Delta\underline{\mu}\underline{X} P_1(\underline{\Omega}, \underline{X})\rangle_R}{P_1(\underline{X})} \tag{16}$$

Functions $\mathcal{E}(\underline{X})$, $P_{0,1}(\underline{X})$ and operator $\bar{\hat{\Gamma}}_S$ can be written explicitly in terms of simple integrals involving Bessel functions whose arguments depend upon λ, the dipole components and β. A numerical treatment of Eq. (15) is relatively simple, using a matrix representation of $\bar{\hat{\Gamma}}_S$ upon a suitable basis set of functions spanning the solvent space $\underline{X}$ only. Following again closely ref. 5, the fast decaying contribution can also be written in the form:

$$C_R(t) = -\frac{\langle \Delta\underline{\mu}\underline{X} - \mathcal{E}(\underline{X})|\exp(-\hat{\Gamma}_R t)|P_0(\underline{\Omega}, \underline{X})\rangle}{\overline{\Delta\underline{\mu}^2}}, \tag{17}$$

where $\hat{\Gamma}_R$ is that part of the initial complete operator acting on $\underline{\Omega}$ only. Again a numerical solution is easily found, since the solvent coordinates act now as parameters and the actual dynamical problem is defined with respect to $\underline{\Omega}$ only.

Remarks

In order to attempt a comparison of the theoretical predictions with experiments, it is necessary to assign reasonable values to all physical parameters involved in the model. First one may estimate the quantities entering the potential. Typical values for $\epsilon_0^{\perp}$ and $\epsilon_0^{\parallel}$ for the nematic phase of ZLI 1167 are 8 and 4, while $\epsilon_\infty^{\perp}$ and $\epsilon_\infty^{\parallel}$ are both close to 1.5[1]. The magnitude of the dipole moment μ_0 of the ground state of C503 can be calculated; a semiempirical PM3 calculation gives a value around 5 D,and it confirms that the dipole lies mainly along the principal axis[6]. The magnitude of the dipole moment μ_1 of the excited state can be estimated by means of the Lippert-Mataga relation. From a series of measures of the static Stokes shift in several solvents, one can estimate μ_1 to be around 6.5 D, the Onsager cavity radius having being chosen close to 3.5 Å. Finally, the orientational potential parameter λ is roughly given as 1×10^{-20} J, and so it is close to 2 k_BT units at $T = 330$ K. Next one can attempt an estimate of the dynamical parameters τ_R and $\tau_S^{\perp,\parallel}$. It is rather difficult to evaluate these quantities since systematic measures of rotational diffusion and dielectric relaxation data are lacking; nevertheless, we may say that τ_R should be of the order of fractions of nanoseconds (say 0.5 ns at $T = 307$ K close to the nematic-smectic A transition); the solvent times being *longer*, $\tau_S^{\perp} \approx 0.5$ ns and $\tau_S^{\parallel} \approx$ 2-3 ns.

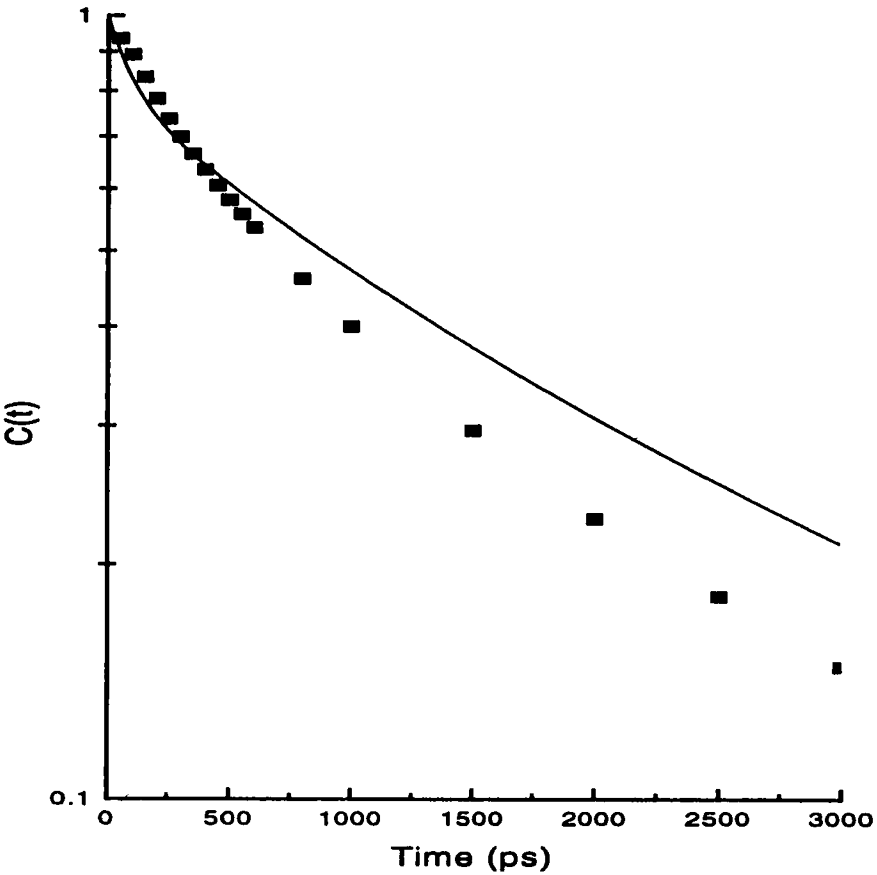

FIGURE 1: Experimental Stokes shift $C(t)$ of C503 in ZLI 1167 at $T = 307$ K (from ref. 6) (squares), and a theoretical prediction obtained in the limit of fast tumbling (solid line).

We choose then to reproduce the available experimental data using the fast solute tumbling motion model [Eqns. (15) and (17)]. An effective *slow* correlation timeof 2.3 ns is calculated solving numerically Eq. (15). From numerical calculation of the fast relaxing correlation function expressed in Eq. (17), one gets an effective *fast* correlation time of about 0.3 ns. The fast and slow component enter the total Stokes shift correlation function with weight respectively close to 0.4 and 0.6. A comparison with the two-exponential fit of the experimental Stokes shift function for C503 in ZLI 1167 reported in Fig. 1, is encouraging: the best fit is obtained with a fast decay time of 0.4 ns (and 0.4 amplitude), and a slow decay time of 2.4 ns (and 0.6 amplitude). The approximate treatment summarized in the previous paragraphs allows a simple and fast calculation of the time resolved emission fluorescence spectrum. The only minor complication is given by the diagonalization of the Smoluchowski operator for the rotator in the case of fast tumbling motion, which can be performed by well-known linear algebra algorithm, after representing the operator on a basis set of spherical harmonic functions, and by the numerical solutions required to evaluate both the fast and slow decaying terms if the case is assumed, as we did in this example, of fast solute tumbling motion.

A complete package has been prepared, which uses home-made Fortran routines for the computational part and available free software for the graphical representation, input of physical parameters and output of different kinds of results (complete fluorescence spectrum, Stokes-shift function, effective decay times and so on). The graphical interface uses a simple menu-driven scheme based on the library TCL/TK (a system for developing and using a graphical user interface - GUI - available as freeware). The package has been written for and is currently running on a DEC 3000/500 Alpha processor, under OSF/1 3.2c, but it is easily adaptable to other systems.

An example of the graphical outcome of the program is shown in Fig. 2. The program may be of help in providing a quick understanding of effects due to polarity and order on the complex multi-exponential decay observed in experimental time-resolved fluorescence in isotropic and ordered fluids.

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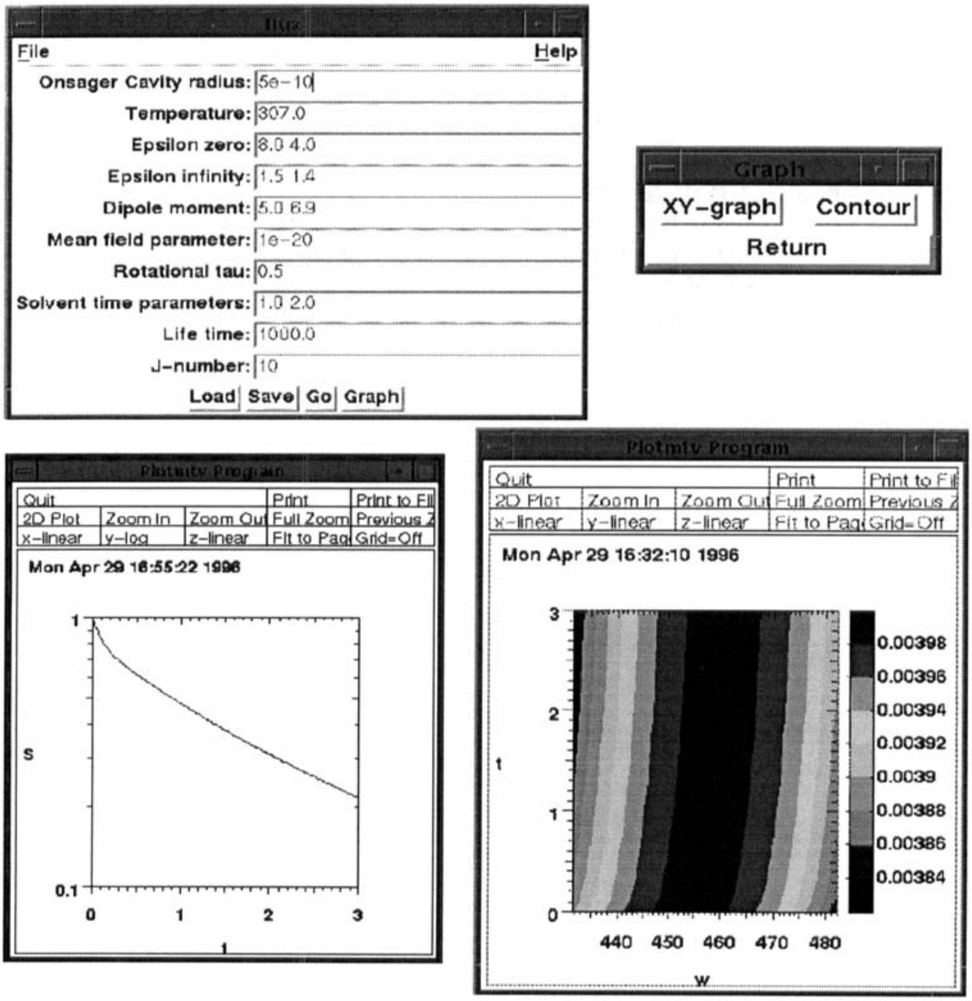

Onsager Cavity radius: 5e-10
Temperature: 307.0
Epsilon zero: 8.0 4.0
Epsilon infinity: 1.5 1.4
Dipole moment: 5.0 6.9
Mean field parameter: 1e-20
Rotational tau: 0.5
Solvent time parameters: 1.0 2.0
Life time: 1000.0
J-number: 10

Mon Apr 29 16:55:22 1996

Mon Apr 29 16:32:10 1996

FIGURE 2: Graphical front-end for the simulation and prediction of time-resolved spectra.

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