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Time resolved fluorescence spectroscopy

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Abstract. Time correlated single photon counting was used to investigate solvent dynamics of laser dyes in a polar, viscous solvent. The resolved total luminescence spectra of oxazine 4 in 2-methyltetrahydrofuran (2-MTHF) have been measured and solvent relaxation observed.

Keywords. Fluorescence spectroscopy; fluorescence decay; oxazine 4; solvent dynamics; total luminescence spectra.

1. Introduction

Time resolved fluorescence spectroscopy (Lakowiz 1986) is a widely used technique to investigate dynamical processes such as solvation dynamics in chemical systems (Simon 1988) and to characterize the interaction of the fluorescent probe molecule with its chemical environment (Burkhalter *et al* 1987). The aim of this paper is to show how the measured decay curves can be analysed and what kind of information can be obtained from time resolved emission and total luminescence spectroscopy.

2. Experimental

In these experiments a typical arrangement for time correlated single photon counting (TCSPC) was used (Canonica *et al* 1985). The excitation source consists of a mode-locked Coherent Innova 1–15 argon ion laser and a synchronously pumped extended rhodamine 6G dye laser equipped with a Coherent 7200 cavity dumper. The output was a periodic train of 10 ps fwhm pulses with a separation of 13·22 ns and an average power of about 50 mW. Emission from the sample was analysed by a Spex 1400 double monochromator, which was modified for subtractive dispersion, and imaged on the photocathode of a selected Hamamatsu R928 photomultiplier (Meister *et al* 1987). The timing reference signal was taken from a Spectra Physics 403B fast photodiode. Two- and three-dimensional spectra were obtained by sequentially measuring the fluorescence decay, $I(t)$, at different emission and excitation/emission wavelength settings, respectively.

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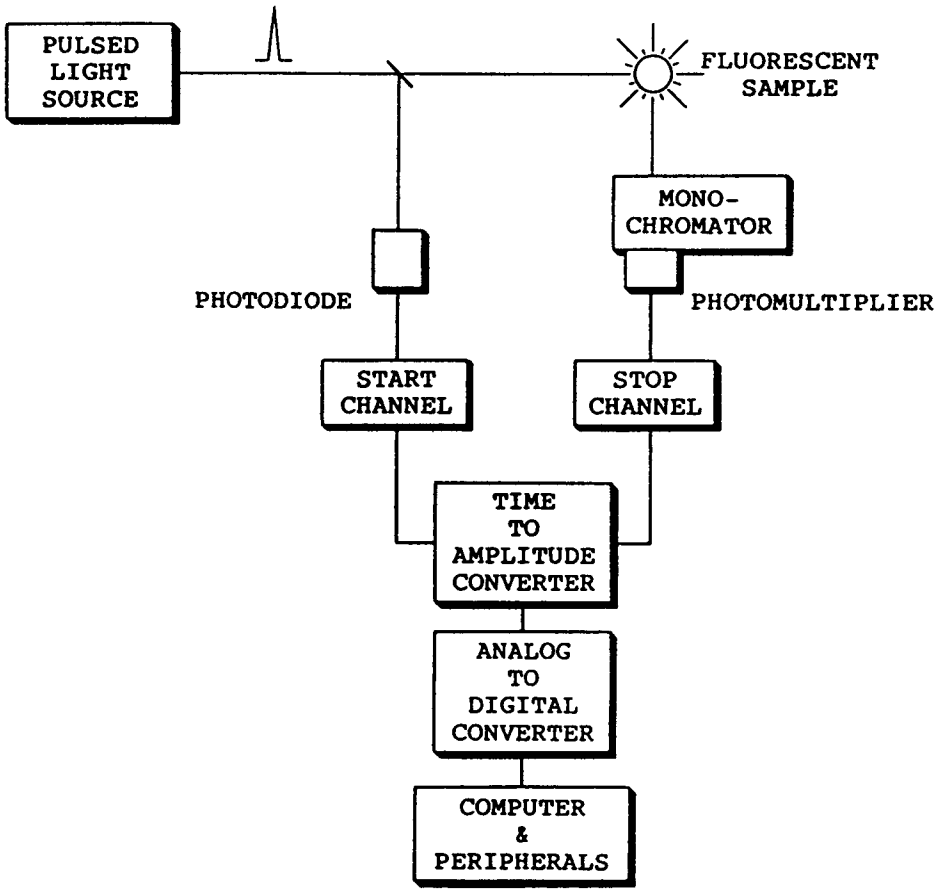

Figure 1. Principle of TCSPC measurement.

3. The analysis of fluorescence decay, $I(t)$

In the following a summary of the deconvolution method used in given. The experimental data are Fourier transformed and the parameter fit is performed in Fourier space, taking the statistical properties of the measured data into account. Full details are given elsewhere (Wild *et al* 1977). The observed decay curves obtained from a fluorescent system excited by a short light pulse are distorted by the finite duration of the excitation pulse and by the limited frequency response of the detection system. Assuming the response to be linear, however, the measured decay, $f(t)$, is given by the convolution integral

$$f(t) = p(t) \times h(t) \times a(t), \tag{1}$$

where $p(t)$ is the pulse shape of the excitation pulse, $h(t)$ the response function of the fluorescent system and $a(t)$ the apparatus function. The measured pulse shape $e(t)$ is given by

$$e(t) = p(t) \times a(t). \tag{2}$$

The apparatus function is assumed to be independent of wavelength and so, since convolution is commutative, the observed fluorescence decay may be written as

$$f(t) = e(t) \times h(t). \tag{3}$$

The true luminescence decay function of many photochemical systems can be represented by a model function $h_m(t)$, composed of the sum of M exponentials,

$$h_m(t) = \sum_s^M a_s \exp[-(t+b)/\tau_s], \tag{4}$$

where b is the experimental time shift. The analytical Fourier transform $H_m(v)$ is given by

$$H_m(v) = \sum_s^M a_s \tau_s \frac{1 - i2\pi v\tau_s}{1 + (2\pi v\tau_s)^2} e^{2\pi i b v}. \tag{5}$$

The amplitudes a_s, τ_s and b can be considered to be adjustable parameters. They are calculated from a least-squares fit in Fourier space.

As an example, figure 2 shows the time dependent emission of oxazine 4 in 2-MTHF at room temperature together with the prompt response $e(t)$ of the arrangement (taken

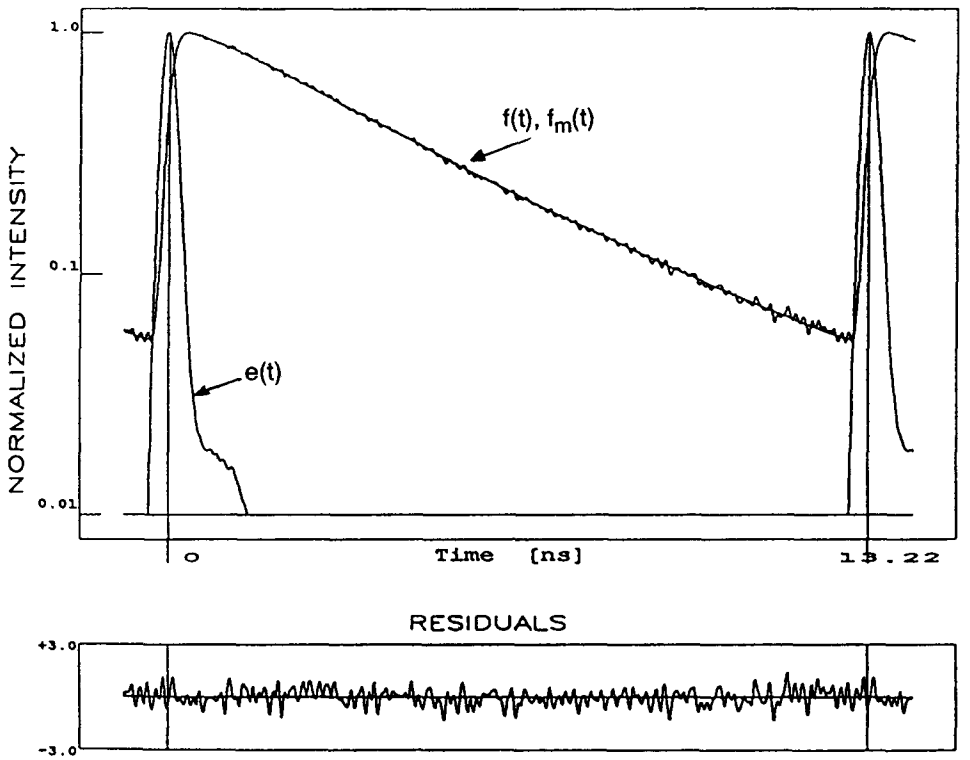

Figure 2. Fluorescence decay of oxazine 4 in 2-MTHF at room temperature. Shown are the mapped decay curve $f(t)$, prompt response $e(t)$, fitted curve $f_m(t)$ on a log-linear plot and the residuals.

from a scattering sample) and the fit curve $f_m(t) = e(t) \times h_m(t)$. The fit to the data yields a single exponential decay with a lifetime of $\tau_f = 3{\cdot}56(2)$ ns.

4. Solvent relaxation of oxazine 4 in 2-methyltetrahydrofuran

4·1 *Time resolved emission spectra* $I(t, \bar{\nu}_{em})$

The permanent electric dipole moment of the dye molecule changes upon excitation to the S_1 electronic state. As the optical transition is fast compared to possible relaxation processes in the solute–solvent system, a non-equilibrium state is reached and a relaxation on a generalized solvation coordinate starts to take place. The fluorescence, emitted after rearrangement of the surrounding solvent molecules, is shifted to the red by an amount $\Delta\bar{\nu}_{ss} := \bar{\nu}_{ex} - \bar{\nu}_{em}$, where $\bar{\nu}_{ex}$ and $\bar{\nu}_{em}$ mean the wave number of maximum absorption and emission, respectively. If the relaxation time, τ_r, is comparable to the fluorescence lifetime, τ_f, of the solute the variation of the emission spectrum with time can be followed (figure 3). As 2-MTHF is a glass-forming solvent, its viscosity and consequently the relaxation time can be controlled over several orders of magnitude by choosing the appropriate temperature.

Assuming a single exponential temporal behavior of this dynamic Stokes shift $\Delta\bar{\nu}(t) := \bar{\nu}_{ex} - \bar{\nu}_{em}(t)$,

$$\Delta\bar{\nu}(t) = \Delta\bar{\nu}_{ss} \cdot (1 - \exp\{-t/\tau_r\}), \tag{6}$$

the temperature dependence of the relaxation time τ_r can be described by an Arrhenius law,

$$\tau_r^{-1}(T) = \tau_{r0}^{-1} \cdot \exp\{-E_A/kT\}, \tag{7}$$

where E_A denotes the activation energy, k the Boltzmann constant and T the temperature (cf. figure 4). The analysis yields an activation energy of $E_A = 3{\cdot}6(2)$ kcal/mol $= 0{\cdot}16(1)$ eV.

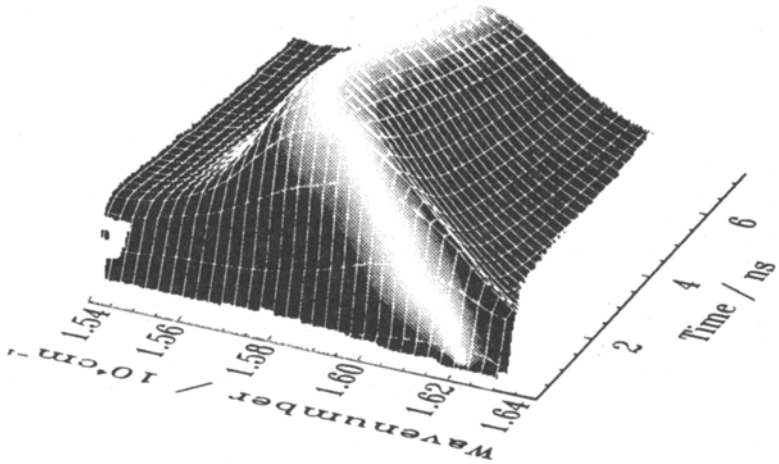

Figure 3. Emission intensity of oxazine 4 in 2-MTHF versus emission wavenumber and time at $T = 140$ K after excitation at $\bar{\nu}_{ex} = 1{\cdot}639{\cdot}10^5\,\mathrm{cm}^{-1}$.

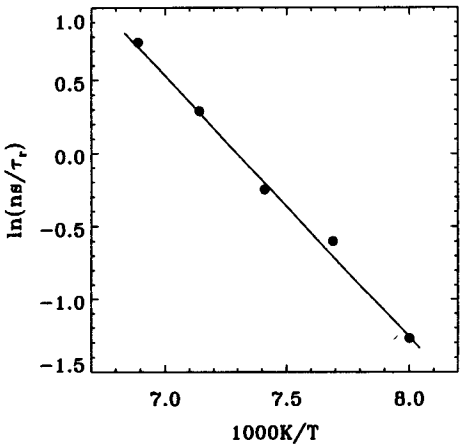

Figure 4. Arrhenius plot of the extracted relaxation times. The slope yields an activation energy of $E_a = 3{\cdot}6(2)$ kcal/mol $= 0{\cdot}16(1)$ eV. No correction for prompt response has been made.

4.2 *Time resolved total luminescence spectra* $I(t, \bar{\nu}_{em}, \bar{\nu}_{ex})$

In general the representation of the steady state emission intensity as a function of excitation and detection wavenumber is referred to as the total luminescence spectrum (TLS). In this case two extreme regimes of spectroscopy of a dye molecule in solution can be considered, namely $\tau_r \ll \tau_f$ or $\tau_r \gg \tau_f$. In the first case, normally at elevated temperatures, the emission is independent of excitation. Hence for each allowed $S_1 \rightarrow S_0$ transition in the TLS the line connecting the emission maxima is parallel to the excitation axis. In the second regime, at low temperature, no relaxation prior to emission is possible and a maximum correlation between excitation and emission is observed. This results in a diagonal pattern parallel to $\bar{\nu}_{ex} = \bar{\nu}_{em}$ in the TLS and can be seen as an extreme case of the so-called edge excitation redshift (EERS).

Here we present a time resolved TLS. The additional time axis allows the recording of a TLS without stray light (e.g. figures 5c, d) and the study of changes in the TLS during the relaxation process. In the appropriate temperature regime, where $\tau_r \approx \tau_f$, the time resolved TLS shows the time evolution between both of the cases discussed above (figure 5).

At an early time there is an obvious linear correlation between the emission and excitation wave number (figure 5b). Here the line connecting the emission maxima (in the center of the contour labelled "Max") has already moved out of the straylight region (cf. figure 5a), but is still skewed with respect to the excitation axis and intersects the line $\bar{\nu}_{ex} = \bar{\nu}_{em}$ at $\bar{\nu}_{em}(t \rightarrow \infty)$. This manifestation of an EERS diminishes about 1 ns later (figure 5c) and has vanished 5 ns after excitation (figure 5d): the relaxation was complete before emission took place and consequently the "maximum-line" for each emission spot in the TLS is parallel to the excitation axis at $\bar{\nu}_{em} = \bar{\nu}_{em}(t \rightarrow \infty)$.

5. Conclusions

Dynamical processes of a dye molecule in a polar solvent have been investigated measuring spectrally resolved decays with TCSPC.

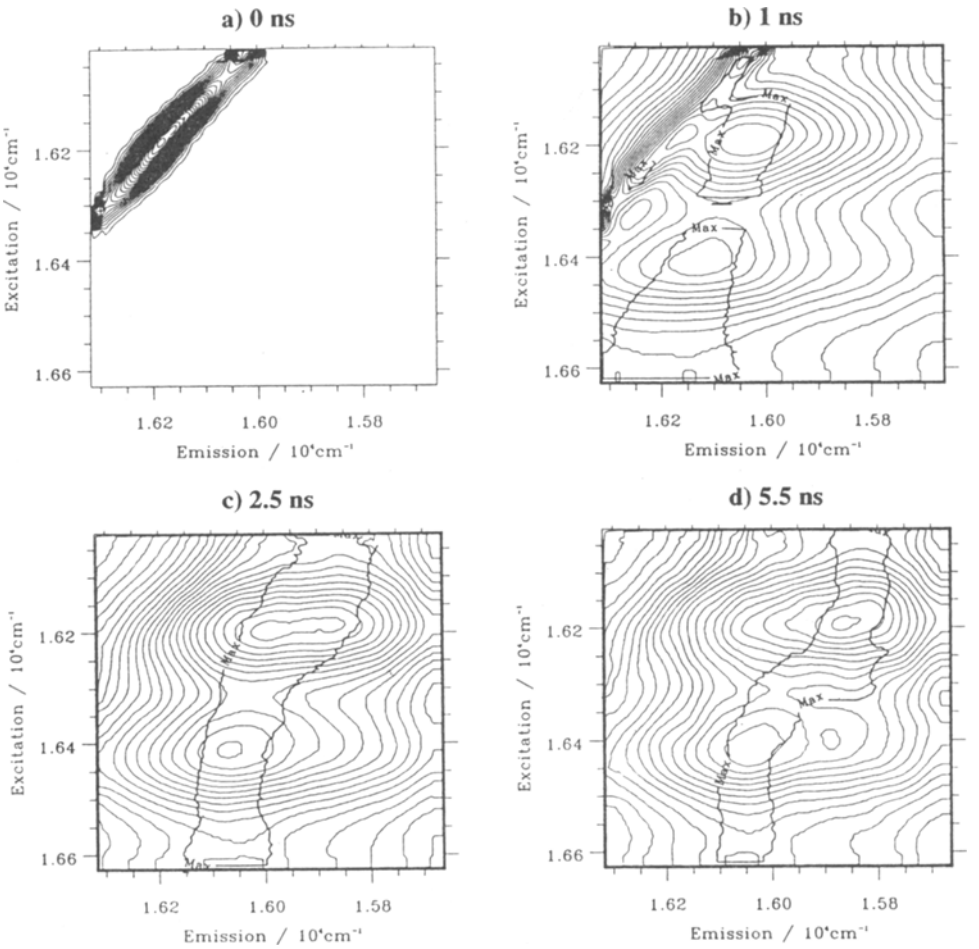

Figure 5. Time resolved TLS of oxazine 4 in 2-MTHF at $T = 132$ K integrated over approximately 0·4 ns; (**a**) during excitation, (**b**) 1 ns after excitation, (**c**) 2·5 ns after excitation, (**d**) 5·5 ns after excitation. The thin contours show the recorded emission intensity, whereas the thick ones, marked with "Max", connect the points of 96% emission intensity for each excitation wavenumber. The structure at $\bar{\nu}_{ex} = \bar{\nu}_{em}$ in the upper left of (**b**) originates from the stray light due to the finite temporal response of the apparatus.

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