

# Reconstructing the Solvation Time Correlation Function from the Time-Dependent Fluorescence Stokes Shift

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A new method is presented to obtain the solvation time correlation function from the time dependence of the fluorescence Stokes shift. The fluorescence band is reconstructed by using the steady-state fluorescence band and the time profiles of the fluorescence collected at some discrete values of the wavenumber  $\tilde{\nu}$ . The time profiles are described as a sum of three exponentials. The time constants and amplitudes for the discrete values of  $\tilde{\nu}$  are used to generate a crude approximation to the true band at time  $t$ . A procedure is given to refine the crude band and to obtain the band at any time between the preparation of the fluorescent solute and the time at which its solvation has reached the final stage. The method produces accurate, method-independent time-resolved fluorescence spectra and solvation time correlation functions. In this paper it is applied to the excited state kinetics of 4-aminophthalimide in tetrahydrofuran and *n*-undecanol.

Microscopic solvation dynamics, i.e. solvent relaxation, has a key role in the dynamics of polar solutions, especially in charge transfer and proton transfer reactions.<sup>1–4</sup> Time-resolved fluorescence spectroscopy is frequently used to probe the dynamics of the microscopic solvation of a non-equilibrium state prepared by optical excitation with an ultrashort laser pulse.<sup>5–9</sup> In this manner one may generate the electronically excited state of a solute with an electric dipole moment or an electric charge quite different from that in the ground state at a sharply defined time. The solution is in a non-equilibrium state immediately after the laser pulse excitation. The non-equilibrium state relaxes through solvent rearrangements in the first few solvent shells around the excited solute. The time-dependent red-shift of the fluorescence spectrum is associated with the relaxation. To observe the time-dependent Stokes shift of the fluorescence, the excitation process must be much faster than the relaxation, and the rate of relaxation should be comparable to or faster than the rate of fluorescence decay. The former condition can be achieved by using a picosecond laser pulse for the excitation. The fulfilment of the latter condition requires a proper choice of solute and solvent.

Rate constants that describe solvation dynamics are obtained from the time-resolved fluorescence spectra. The time-dependent Stokes shift, which is observed in the

time-resolved fluorescence spectra, is frequently presented with solvation time correlation function  $C(t)$ , which is defined as

$$C(t) = \frac{\tilde{\nu}_m(t) - \tilde{\nu}_m(\infty)}{\tilde{\nu}_m(0) - \tilde{\nu}_m(\infty)} \quad (1)$$

where  $\tilde{\nu}_m$  is the wavenumber corresponding to the maximum intensity of the time-resolved fluorescence spectrum. In this paper we focus on the problem of how to compute accurately the solvation time correlation function from the time-dependences of the intensity at different wavelengths in the fluorescence spectrum. The major task is to find the function describing the motion of the peak of the fluorescence band along the wavenumber scale as a function of time. The time-dependence of the fluorescence spectrum can be obtained either directly by recording the whole spectrum at a number of delay times, or indirectly by measuring the time-dependence of the fluorescence at several wavelengths in the spectrum. In the direct method the fluorescence spectrum is recorded in a narrow time window between  $t$  and  $t + \Delta t$ . The single-photon-counting technique has been adapted for this purpose to measure the intensity of the fluorescence transmitted through a scanning monochromator within the selected time window.<sup>10</sup> In the indirect method the fluorescence spectrum at a selected delay time is reconstructed on the basis of the accurate observations of the

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time-dependent fluorescence at a number of coarsely spaced wavelengths in the spectrum. The new approach presented here is based on the indirect method.

The usual approach in the indirect method starts by fitting an appropriate mathematical function to the observed time-dependence at each of the selected wavelengths. The fitting is followed by a procedure in which crude fluorescence spectra are reconstructed at chosen time delays by using the obtained analytical functions of time and the steady-state fluorescence spectrum. The crude spectrum consists of a band characterised by the intensity at a small number, say ten, of wavelengths. The crude spectrum is subsequently refined by fitting a log-normal bandshape function<sup>11</sup> to the small number of available points in this spectrum. The deviations of the true bandshape from the asymmetric gaussian shape of the log-normal function cannot be accounted for in this manner. The alternative indirect method which is presented here does not rely on the assumption of a log-normal bandshape, but is instead based on a procedure to obtain the actual bandshape by interpolating between experimental data points. The method overcomes the problem of determining accurately the spectral shape and the wavenumber of the maximum of the fluorescence band.

The new method will be applied to obtain the solvation time correlation function  $C(t)$  for the fluorescent state of 4-aminophthalimide in tetrahydrofuran and in *n*-undecanol.

## Experimental

4-Aminophthalimide (4AP) was purchased from Eastman Kodak and purified by recrystallization from ethanol. Purity was checked by HPLC. Tetrahydrofuran was distilled and passed through a 30-cm long column of silica gel. The absorption and emission spectra of the solvent and samples were measured to check their purity and to adjust the concentration to  $1.0 \times 10^{-4}$  M. Oxygen was removed from the samples by three successive freeze-pump-thaw cycles.

In order to measure the temperature of the sample, a narrow glass tube extending to just above the light path was inserted inside the cuvette. The tube contained a small amount of pentane or ethanol to achieve thermal contact between the sample and the thermoelement Pt-100. The required temperatures were accomplished with a home-made optical cryostat equipped with a Cryoson TRL-6 temperature control unit.

The fluorescence was collected at right angles to the direction of the laser beam. To avoid reflected laser light from entering the streak camera, the sample cuvette was oriented at an angle of  $45^\circ$ , and the fluorescence was then collected from the back of the cuvette. The influence of the rotational reorientation of 4AP on the result was avoided by collecting the fluorescence through a polarizer oriented at the magic angle ( $54.7^\circ$ ) with respect to the

vertical polarisation of the excitation light. The scattered excitation light was filtered by using cut-off filters, transmitting only wavelengths longer than 305 nm. The fluorescence wavelength of interest was selected either with interference filters of 10 nm bandpass or with cut-off filters transmitting only above 550 nm.

Static fluorescence spectra were recorded on a Perkin-Elmer MPF 66 fluorescence spectrophotometer and are corrected for instrumental distortions. Absorption spectra were recorded on a Perkin-Elmer Lambda 2 UV/VIS absorption spectrophotometer.

Fluorescence decays were studied by exciting with a picosecond 295 nm pulse and by recording the time profiles with a streak camera (Hadland, Imacon 500). The methods used to correct the image distortions of the streak camera and to calibrate its time axis are described elsewhere.<sup>12</sup> The excitation pulses were produced by a laser system, in which a dual-jet dye laser (Coherent 702) was pumped synchronously by the second harmonic of a CW actively mode-locked Nd:YAG laser (Coherent Antares). The remaining 1064 nm pulses of the Antares were amplified at 10 Hz repetition rate in a flashlamp-pumped regenerative amplifier (Quantel Int. RGA 60). The second harmonic of these pulses was used to pump the dye laser amplifier (Quantel Int. PTA 10). Without a saturable absorber in the dye laser oscillator, the laser system produced 1 ps FWHM and 2 mJ pulses at 590 nm at 10 Hz repetition rate, and 400  $\mu$ J at the second harmonic of these pulses. A saturable absorber shortened the dye laser pulse down to 600 fs. The time-resolution of the set-up was limited by the streak camera to 5 ps.

## Principles

The new method involves a numerical procedure for interpolating experimental data points. The spectral relaxation of the fluorescence may be considered the transition from the initial state of solvation to the final state of solvation. The whole population in the excited state is assumed to decay mono-exponentially with time constant  $\tau_2$ . Theoretically the description of the spectral relaxation should involve a continuous distribution of relaxation times. A mathematical form which proved suitable for the accurate phenomenological description of the time-dependence of the fluorescence over the whole spectral range is given by

$$I(t, \tilde{\nu}) = A_1(\tilde{\nu}) \exp[-t/\tau_1(\tilde{\nu})] + A_2 \{ \exp[-t/\tau_2(\tilde{\nu})] - \exp[-t/\tau_3(\tilde{\nu})] \} \quad (2)$$

The integration of eqn. (2) from  $t = 0$  to  $t = \infty$  yields the total intensity at wavenumber  $\tilde{\nu}$ :

$$\int_0^\infty I(t, \tilde{\nu}) dt = A_1(\tilde{\nu}) \tau_1(\tilde{\nu}) + A_2(\tilde{\nu}) [\tau_2(\tilde{\nu}) - \tau_3(\tilde{\nu})] \quad (3a)$$

Applying eqn. (3a), the relative contributions of the first term  $I_{\text{rel},i}(\tilde{\nu})$  and of the second term  $I_{\text{rel},f}(\tilde{\nu})$  in eqn. (2) to the total intensity at wavenumber  $\tilde{\nu}$  are calculated to be

$$I_{\text{rel},i}(\tilde{\nu}) = \frac{A_1(\tilde{\nu})\tau_1(\tilde{\nu})}{A_1(\tilde{\nu})\tau_1(\tilde{\nu}) + A_2(\tilde{\nu})[\tau_2(\tilde{\nu}) - \tau_3(\tilde{\nu})]} \quad (3b)$$

and

$$I_{\text{rel},f}(\tilde{\nu}) = \frac{A_2(\tilde{\nu})[\tau_2(\tilde{\nu}) - \tau_3(\tilde{\nu})]}{A_1(\tilde{\nu})\tau_1(\tilde{\nu}) + A_2(\tilde{\nu})[\tau_2(\tilde{\nu}) - \tau_3(\tilde{\nu})]} \quad (3c)$$

A crude approximation to the initial spectrum,  $I'_i(\tilde{\nu})$ , and the final spectrum,  $I'_f(\tilde{\nu})$ , can be obtained by normalising the relative intensities with respect to the intensity of the steady-state spectrum  $I_{\text{fl}}(\tilde{\nu})$ . In this manner eqn. (4a) and (4b) are obtained:

$$I'_i(\tilde{\nu}) = I_{\text{rel},i}(\tilde{\nu}) I_{\text{fl}}(\tilde{\nu}) \quad (4a)$$

$$I'_f(\tilde{\nu}) = I_{\text{rel},f}(\tilde{\nu}) I_{\text{fl}}(\tilde{\nu}) \quad (4b)$$

The next stage is to find an appropriate function to describe the crude initial spectrum  $I'_i(\tilde{\nu})$ . From eqn. (2) it is evident that the initial spectrum corresponds to the fluorescence spectrum at time zero. Since the initial spectrum also equals the non-equilibrium state, it is fair to assume that the fluorescence spectrum of the glassy solution of 4AP provides us a good assumption about the initial spectrum. The broadening of the liquid-state spectrum is not taken into account here, since the analytical function that is used in this work fits the initial spectrum of 4AP very well in every solvent. The steady-state fluorescence band of the glassy solution of 4AP in *n*-propanol is fitted to the crude initial band  $I'_i(\tilde{\nu})$ . The fitted band is then the refined initial band  $I_i(\tilde{\nu})$  in the solvation process. The fluorescence band corresponding to the final stage of solvation  $I_f(\tilde{\nu})$  is obtained by subtracting the initial band  $I_i(\tilde{\nu})$  from the steady-state fluorescence band. Since the steady-state fluorescence spectra are recorded as a function of wavelength  $\lambda$  with a constant resolution on the wavelength scale, the variation of the resolution on the wavenumber scale has to be taken into account in the transformation of the original band to a band as a function of wavenumber  $\tilde{\nu}$ . The appropriate transformation is

$$I(\tilde{\nu}) \approx I(\lambda)\lambda^2 \quad (5)$$

The fitting of eqn. (2) to the observed time profile for the fluorescence at wavenumber  $\tilde{\nu}$  yields experimental values for the time constants  $\tau_1(\tilde{\nu})$ ,  $\tau_2(\tilde{\nu})$  and  $\tau_3(\tilde{\nu})$  at a number of discrete values of  $\tilde{\nu}$ . The polynomials in eqn. (6) may be used for the interpolation of the  $\tau_k(\tilde{\nu})$  values at the intermediate values of  $\tilde{\nu}$ :

$$\tau_k(\lambda) = a_k + b_k\lambda + c_k\lambda^2 \quad (k = 1,2,3) \quad (6)$$

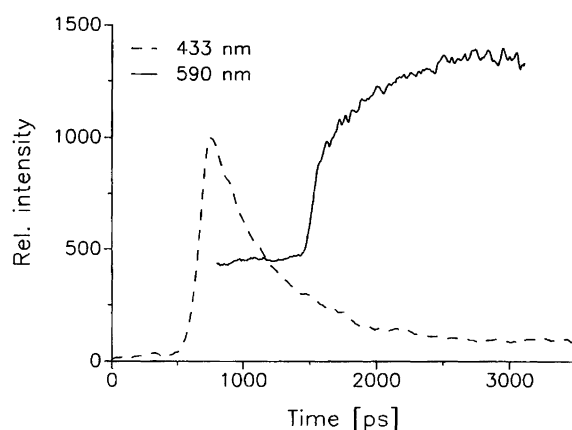


Fig. 1. Typical fluorescence decays of 4AP. The fast decay is collected at 433 nm and the slow decay with finite formation time at 590 nm.

In practice the second-order term in eqn. (6) could be neglected. The pre-exponential factors in eqn. (2) are obtained as follows:

$$A_1(\tilde{\nu}) = \frac{I_i(\tilde{\nu})}{\tau_1(\tilde{\nu})} \quad (7a)$$

$$A_2(\tilde{\nu}) = \frac{I_f(\tilde{\nu})}{\tau_2(\tilde{\nu}) - \tau_3(\tilde{\nu})} \quad (7b)$$

Using values for the  $\tau_k(\tilde{\nu})$  from eqn. (6) and for  $A_1(\tilde{\nu})$  and  $A_2(\tilde{\nu})$  from eqns. (7a) and (7b), respectively, fluorescence bands  $I(t, \tilde{\nu})$  can be reconstructed for any time  $t$  between the time of preparation of the fluorescent state and the time when the solvation has reached its final stage. The maximum of the band  $I(t, \tilde{\nu})$  will be denoted by  $\tilde{\nu}_m(t)$ . The value of  $\tilde{\nu}_m(t)$  is obtained through the linear least-squares fit to the plot of the partial derivative  $dI(t, \tilde{\nu})/d\tilde{\nu}$  in the neighbourhood of the band maximum. Then  $\tilde{\nu}_m(t)$  is

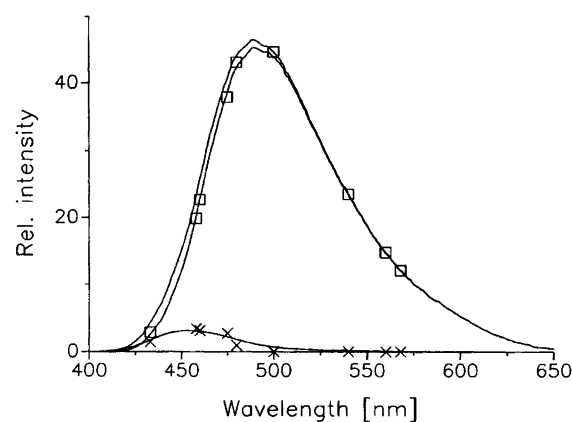


Fig. 2. Steady-state fluorescence spectrum of 4AP in tetrahydrofuran at  $-40^\circ\text{C}$ . The cross denotes the spectrum of the initial state and open square cube the spectrum of the final state.

taken as the value where the linear function is zero. The fitting range can be, e.g.,  $\pm 10$  nm from the approximate band maximum.

The solvation time correlation function  $C(t)$  presented in eqn. (1) may be written in the bi-exponential form

$$C(t) = A_1 \exp(-t/\tau_{S1}) + A_2 \exp(-t/\tau_{S2}) \quad (8)$$

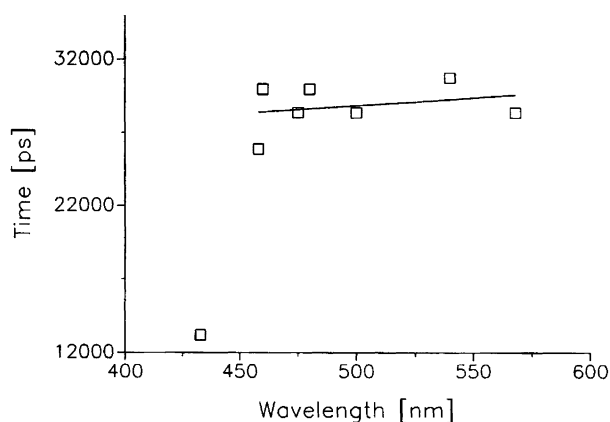
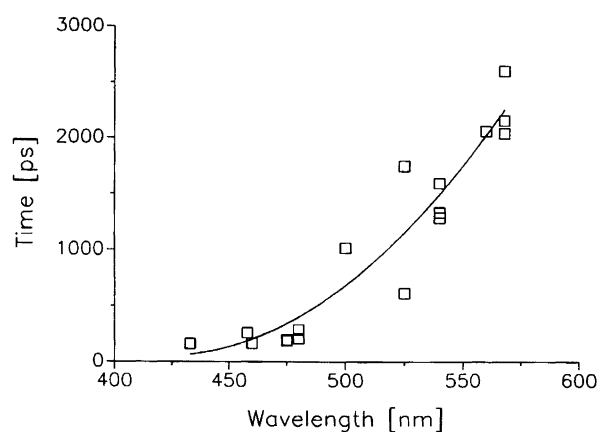
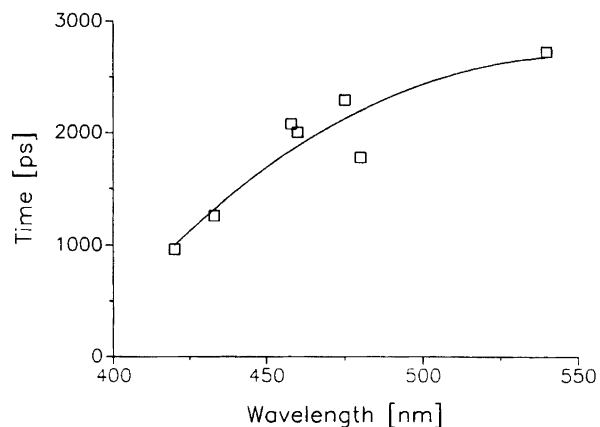


Fig. 3. Wavelength-dependence of the fluorescence decay time and formation of 4AP in tetrahydrofuran at  $-40^\circ\text{C}$ : (a) the decay of the initial state, (b) the formation time of the final state and (c) the decay of the final state.

where  $\tau_{S1}$  and  $\tau_{S2}$  are solvation time constants and  $A_1$  and  $A_2$  are amplitudes. Alternatively, an average solvation time constant  $\langle\tau_S\rangle$  can be calculated. It is defined as  $\langle\tau_S\rangle = \int C(t)dt$ .

## Results and discussion

In this work we used 4-aminophthalimide (4AP) to probe the solvation dynamics in tetrahydrofuran and in *n*-undecanol. Typical data for obtaining solvation time correlation functions are shown in Figs. 1–5. Fluorescence decays at two wavelengths, collected at 433 and 590 nm by using streak camera equipment, are shown in Fig. 1. Note the fast decay at the blue side and formation time at the red side of the spectrum. The steady-state spectrum of 4AP in tetrahydrofuran at  $-40^\circ\text{C}$  is shown in Fig. 2, where the cross denotes the spectrum of the initial state and the open square the spectrum of the final state. The wavelength-dependence of time-constants in Figs. 3a–3c are fitted to second-order polynomials. In spite of a rather high noise level in this particular example, the resulting correlation function  $C(t)$  is single-exponential, smooth and produces physically acceptable solvation time-constant.

The time-resolved fluorescence spectra of 4AP in tetrahydrofuran at  $-40^\circ\text{C}$  are portrayed in Fig. 4. The corresponding solvation time correlation function is shown in Fig. 5 together with the correlation function of 4AP obtained in *n*-undecanol at  $20^\circ\text{C}$ . The average solvation time constants  $\langle\tau_S\rangle$  in tetrahydrofuran and in *n*-undecanol are 1320 and 630 ps, respectively. The total spectral shift is ca.  $2000\text{ cm}^{-1}$ . The result of *n*-undecanol may be compared to the solvent longitudinal relaxation time  $\tau_L$  of 670 ps, which should be equal to the solvation time constant. The correlation function in *n*-undecanol is strongly bi-exponential, which is typical for correlation functions measured in hydrogen-bonding solvents.<sup>13</sup> The fast component of the correlation function, which has the main

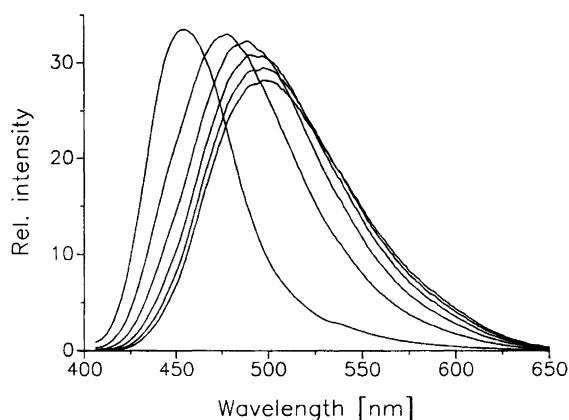


Fig. 4. Time-resolved fluorescence spectra of 4AP in tetrahydrofuran at  $-40^\circ\text{C}$ . The spectra correspond to time delays from 0 to 5 ns.

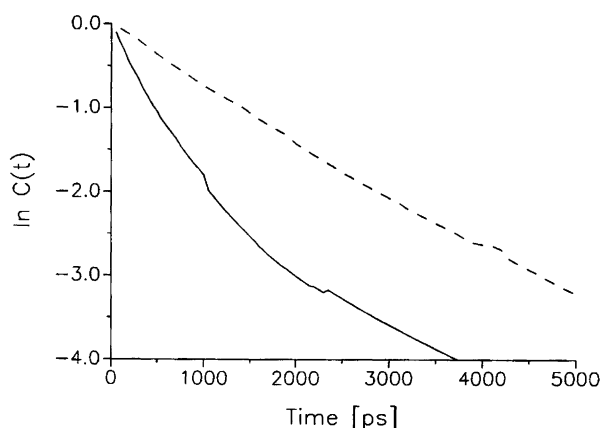


Fig. 5. Solvation time correlation function of 4AP in tetrahydrofuran at  $-40^{\circ}\text{C}$  (the dashed line) and in *n*-undecanol at  $20^{\circ}\text{C}$  (the solid line) as a function of time. See text for details.

contribution to  $\langle \tau_s \rangle$ , is proportional to the longitudinal relaxation time of the solvent. It is assigned to the small-amplitude inertial rotational motion of solvent molecules in the first solvation shell, while the slow component is supposed to arise from the diffuse restructuring of the first solvation shell.<sup>14</sup>

The jumps seen in correlation functions are caused by the noise in the steady-state spectrum. This problem can be solved by choosing an appropriate fitting range, say 15 nm, when calculating the  $\tilde{\nu}_m(t)$  from the first derivative of a time-resolved spectrum. Too large a fitting range causes an artificial spectral shift arising from the asymmetry of the spectrum, while too small a value introduces jumps to  $C(t)$ .

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