

Picosecond time-resolved laser emission of coumarin 102: Solvent relaxation

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Abstract. The time-resolved laser emission of coumarin 102 was investigated in various aprotic and protic solvents at picosecond resolution by frequency upconversion technique. The spectral shift of the transient emission spectrum is attributed to solvent reorientation and the results are discussed.

Keywords. Frequency upconversion; phase matching; solvent-relaxation.

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1. Introduction

Following the original experiment of Halliday and Topp [1], the frequency conversion technique has been applied by a number of workers to the investigation of charge transfer processes, energy transfer processes, isomerization reactions, vibrational relaxations and solvent relaxations [2]. As demonstrated by Moore *et al* [3] the use of multichannel detection with upconversion technique can provide more spectral information which cannot be obtained by other standard techniques such as streak camera and time correlated single photon-counting. This technique is attractive because the time-resolution achievable by this method is determined solely by the duration of the excitation pulse and not by the sample lifetimes and also the upconverted emission is free from background noise. As a part of our programme on picosecond processes in aminocoumarins, we present the preliminary investigation of solvation dynamics in protic and aprotic solvents using C 102 as a probe molecule and the frequency upconversion technique developed in our laboratory. Although the experimental and theoretical studies in solvation dynamics in solution has undergone a dramatic revolution in the past decade, yet the situation is not very clear as witnessed by discrepancies between theoretical and experimental results [4, 5].

When a molecule is excited to higher electronic state, several processes compete to deactivate the excited state during its lifetime. These processes can arise from either Franck–Condon state or relaxed excited state. The evolution of the excited state is controlled by the relative rates of different deactivation processes. The main processes which usually compete with the radiative deactivation of Franck–Condon excited state are vibrational relaxation, solvent relaxation, formation of charge transfer complexes, isomerization, energy transfer between like molecules and inter-system crossing (ISC) to the triplet state. For large molecules such as C 102, we expect

vibrational relaxation in S_1 state to be a very fast process which escapes our instrumental resolution. For coumarins, the ISC yields by triplet counting technique have been reported to be less than 0.05 for ethanol [6] at room temperature. The rate constant for ISC calculated using $\tau(S_1) = 4.36$ ns is so low that the process takes place on a time scale much longer than the time delay. Intermolecular energy transfer processes between like molecules via Forster mechanism are relatively fast at high concentrations and slow at normal concentrations. In the present system this process was minimized by keeping the concentration of the solute at $1 \times 10^{-3} \text{ mol dm}^{-3}$. Our probe molecule is a rigid one and structural considerations show that isomerization is quite unlikely. Although, discrete charge transfer complex via hydrogen transfer has been reported for C 102 in water [7], protonation of C 102 is not possible in protic and aprotic solvents. Our previous studies [8] have shown that dipole moment of C 102 changes from 5.016 D to 6.849 D upon excitation from S_0 to S_1 state. Also, our luminescence studies of C 102 as function of temperature reveals that the fluorescence of C 102 at room temperature (293 K) occurs at longer wavelength ($\lambda_{\text{max}} = 468$ nm) than the one obtained at 77 K ($\lambda_{\text{max}} = 456$ nm). There is no broadening of the emission at intermediate temperatures and no spectral shift is observed below 77 K (figure 1). Such characteristics of dye solution are generally the reflections of solvent-relaxation [9].

Immediately after laser excitation, the probe molecule will be in a 'Franck-Condon' (FC) excited state (a transitory excited state), possessing an altered electron distribution

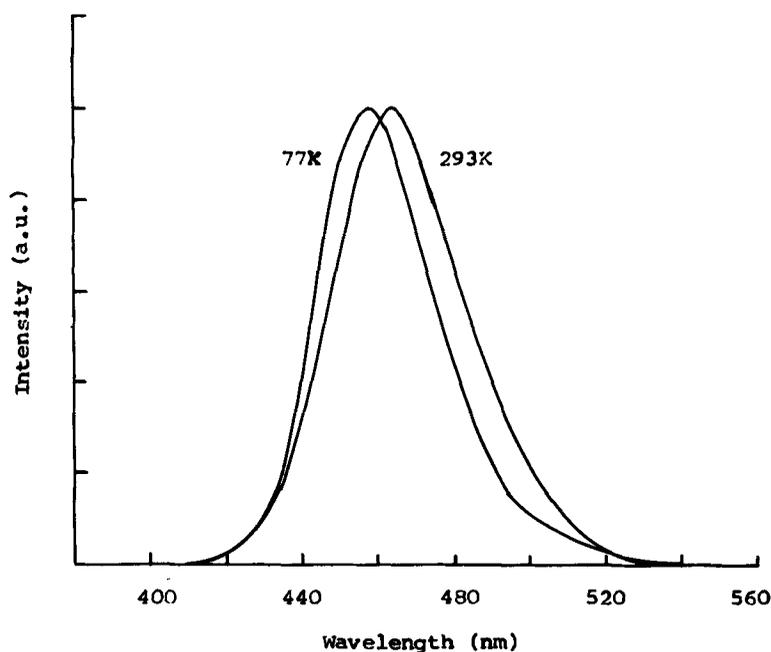


Figure 1. Normalized fluorescence spectra of C 102 ($1 \times 10^{-3} \text{ mol dm}^{-3}$) at 77 K and 293 K.

but the ground state geometry. The excited molecule is initially surrounded by equilibrium ground state solvent cage. During the lifetime of the excited state (S_1), the solvent cage adopts orientation consistent with the new excited state charge distribution of the probe molecule. As the solvent orientation changes continuously with time, the energy of the solute-solvent configuration changes correspondingly leading to the time-dependent spectral shift in the emission peak of the probe molecule. The solvation dynamics of C102 in non-associating solvents such as acetonitrile has been investigated earlier by Kahlow *et al* [10] from sub-picosecond fluorescence spectroscopy and the measured solvent-relaxation time was reported to be 0.9 ps. However, the time scale of solvation process at room temperature is expected to be in the picosecond domain for the associating solvents such as alcohols. In the present work, we focus our attention on the measurements of time-dependent superradiant laser emission on picosecond time scale in both polar aprotic and protic (alcohols) solvents to evaluate solvent-relaxation and compare its time scale relative to orientational relaxation time of solute molecule determined previously [8] in the ps time domain. The superradiant laser emission is nothing but amplified spontaneous emission (ASE) which shortens the S_1 state lifetime from τ_f to τ_{ASE} . According to the relation derived by Penzkofer and Blau [11] for the ratio of these two lifetimes, for a given dye, the lifetime of S_1 in the presence of ASE can be altered by suitably adjusting the solid angle of effective ASE and the position of maximum gain. Therefore, when the conversion efficiency of the mixing crystal is very poor to upconvert the fluorescence, one can use the superradiant emission as a probe by adjusting the excitation conditions properly. This study is also important in view of the current interest [12] on the influence of rotational motions of solvent and probe molecules on the dye laser performance.

2. Theoretical description

When two optical fields of frequencies ω_1 and ω_2 are mixed in a phase matched non-linear crystal, the output optical field with frequencies $\omega_1 + \omega_2$ and $\omega_1 - \omega_2$ is generated. The time-resolved spectra can be measured at a given time after excitation either by tuning the laser frequency or by tuning the crystal at a fixed laser frequency to select the fluorescence wavelength. The phase matching condition for frequency conversion is that $k_3 = k_1 + k_2$, where k_1 , k_2 and k_3 are the fluorescence, gating laser and output signal wave vectors, respectively. The conversion efficiency of the crystal is proportional to the intensity of the gating pulse:

$$\frac{I(\omega_1 + \omega_2)}{I(\omega_1)} \propto I(\omega_2). \quad (1)$$

The instantaneous power of the sum-frequency in a crystal of length L is given approximately by [13]

$$P_\omega(L) = L^2 P_1 P_2 \omega_3 / \omega_1 \quad (2)$$

where subscripts on the frequency ω and the power/unit area P refer to the fluorescence, gating pulse, and the sum-frequency respectively. If the power of the laser remains constant to within a few per cent, the upconverted signal at a particular delay is proportional to the fluorescence intensity.

3. Experimental

The schematic of the upconversion experiment is shown in figure 2. The laser system was passively and actively mode-locked Nd:YAG laser (Continuum, USA) which provided 1064 nm pulse of 35 ps duration at a repetition rate of 10 Hz with energy of 70 mJ. It was frequency doubled to 532 nm in a KDP crystal. Subsequently, mixing up of 1064 nm and 532 nm lights in another KDP crystal provided a sum-frequency at 355 nm (35 ps, 15 mJ).

The solutions of C 102 (Eastman Kodak and Exciton, USA) prepared at $1 \times 10^{-3} \text{ mol dm}^{-3}$ in various solvents were contained in a 10 mm pathlength quartz cell and excited by a 355 nm pulse. The unwanted feedback from the cell walls was avoided by careful alignment of the pump beam and the cell. A typical dye laser output for ethanolic solution of C 102 had nearly 5 mrad divergence and bandwidth of 13 nm (fwhm) as compared with 43 nm (fwhm) for fluorescence (figure 3). The thermal effects in the solution were minimized by circulating the dye solution. The superradiant laser emission collected by the lens was focussed onto the KDP type II crystal (4 mm path length) where it was mixed collinearly with the 1064 nm gating pulse. Our attempts to upconvert the fluorescence were in vain probably due to low conversion efficiency of the crystal used. The arrival time of the excitation pulse on the mixing crystal was controlled by adjusting the distance travelled by pump pulse using variable optical delay. By angle-tuning the crystal and adjusting the relative convergence of the input pulses in the crystal, we were able to upconvert the laser emission from 455–485 nm (spectral coverage: 30 nm; fwhm: 13 nm) to 318–333 nm (spectral coverage: 15 nm; fwhm: 5 nm). In addition to the upconverted signal, the output from the crystal consisted of the fundamental and its second harmonic which were cut off by using appropriate filters.

The upconverted signal was collected by the optical fibre and measured with a 0.5 m polychromator (Spectroscopy Instruments, Germany, 600 g/mm) and double intensified photodiode array which were controlled by a microcomputer. The signal was recorded as a function of delay. The spectral data were averaged over multiple measurements. The time-resolved spectra were obtained with no/little distortion.

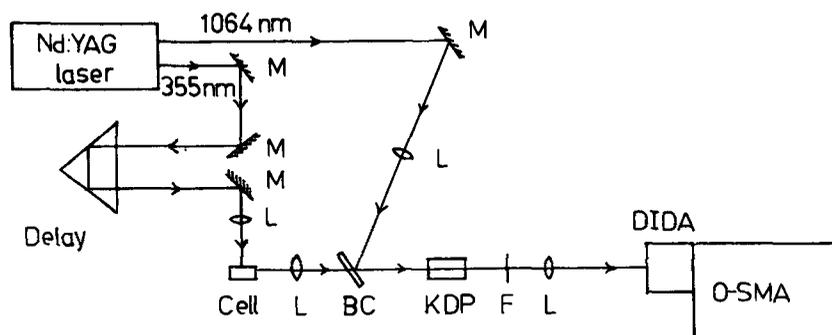


Figure 2. Schematic of upconversion experiment:
M: Mirror; L: Lens; BC: Beam combiner; F: Filter.

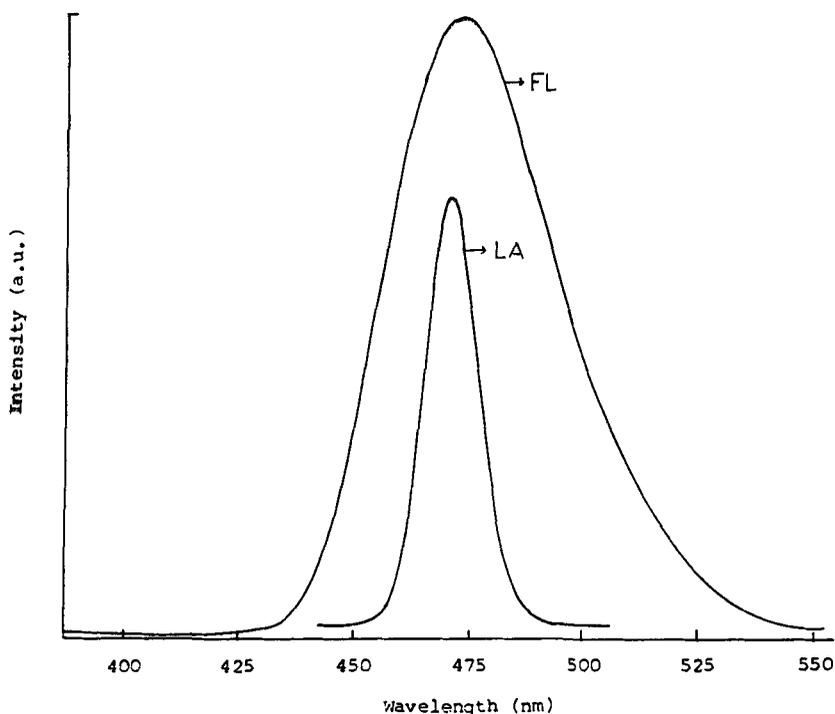


Figure 3. Static fluorescence (FL) and dye laser spectra (LA) of C 102 in ethanol at $1 \times 10^{-3} \text{ Mol dm}^{-3}$

Absorption spectra at various concentrations for all the solvents were recorded using Hitachi (Model 3200) UV/Vis spectrophotometer and steady-state fluorescence emissions were measured using a 400 Watt Hg lamp, a scanning monochromator (Oriel), a photomultiplier (RCA 931A) and an X-Y recorder (Riken Denshi). Low temperature luminescence studies were made using closed cycle refrigerator (RMC Cryosystems, USA).

4. Results and discussion

Steady-state spectral characteristics of C 102 in various solvents at optimum concentrations along with the properties of the solvents are shown in table 1. We find that compared to dioxane solution, all other selected solutions exhibit red-shift both in absorption and fluorescence maxima which correlate reasonably with solvent polarity calculated according to Lippert [14]. Such spectral shifts are generally the reflections of solute-solvent interactions which may be of general or specific type such as hydrogen bonding. The C 102 is a planar molecule in the ground state and its dipole moment as stated earlier changes after excitation, indicating that C 102 should be solvated relatively larger in S_1 compared to ground state. In the general type of solvent effect, the Stokes shift depends on dielectric constant and refractive index of solvents, while

specific effects are associated with n-donor, π -donor and hydrogen bonding abilities of the solvents. For polar solutes like C 102, the interaction with non-polar solvents like dioxane depends on the dipole-induced-dipole forces, while with aprotic (polar but non-hydrogen bonding) solvents, the solute-solvent interaction depends on the stronger dipole-dipole forces. In protic solvents (alcohols), in addition to dipole-dipole

Table 1. Steady-state absorption and fluorescence characteristics of C 102 in various solvents and calculated values of polarity functions of solvents using Lippert's expression (1957).

Solvent	Dielectric constant (ϵ)	Refractive index (n)	Solvent polarity* (Δf)	λ_{ab} nm	λ_{fl} nm
Dioxane	02.21	1.4200	0.0215	372	427
DMSO	48.90	1.4770	0.2645	380	440
Acetonitrile	38.80	1.3442	0.3053	382	441
DMF	37.06	1.4305	0.2746	384	443
Ethanol	23.40	1.3611	0.2885	388	463
Methanol	32.04	1.3288	0.3080	391	471

$$*\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$$

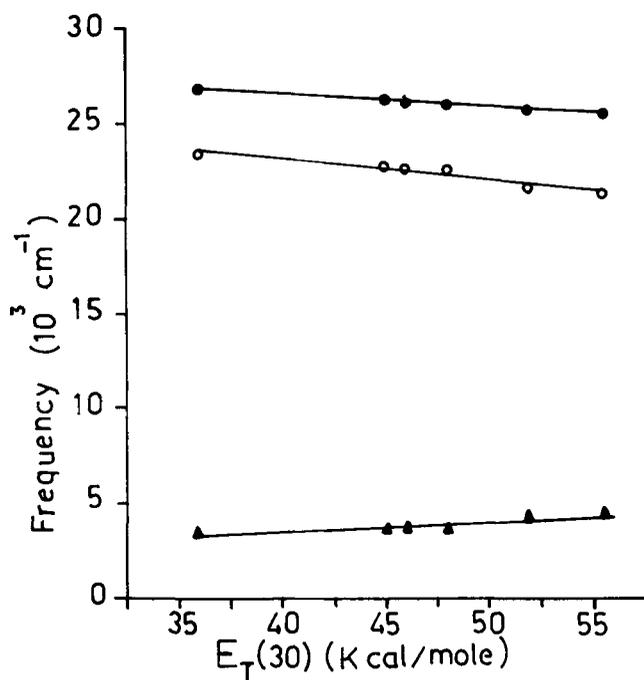


Figure 4. Absorption maxima (●), Static emission maxima (○) and Stokes shift (▲) as a function of $E_T(30)$.

interaction, specific interaction such as H-bonding may be effective as the intramolecular charge transfer (ICT) character of C 102 is favourable for H-bonding with hydroxy group in alcohols. The dependence of Stokes shift, $\nu_a - \nu_f$ (cm^{-1}), on solvent polarity according to Lippert's expression seems to be less regular within polar solvents. This trend may perhaps be due to the fact that the Lippert's relation ignores the molecular aspect of solvation. It is therefore useful as pointed out by others also [15, 10] to use E_T (30) function, the empirical measure of solvent polarity [16] for understanding the polarization dependence of spectral characteristics. Figure 3 shows the steady-state absorption and emission maxima and Stokes shift as a function of E_T (30). As seen from figure 4, the absorption and static emission maxima are linearly related to E_T (30), the slope of the plot for emission being greater than that for absorption, implying that the solvation in S_1 is consistent with the finding that $\mu_e > \mu_g$. The linear E_T (30) dependence of Stokes shift indicates the existence of general type of solute-solvent interaction.

Transient emission spectra recorded in protic solvents (ethanol and n-butanol) were found to be red-shifted almost continuously on longer time scales available with the set up, while in aprotic solvents (AN and DMSO), the shift though being continuous is

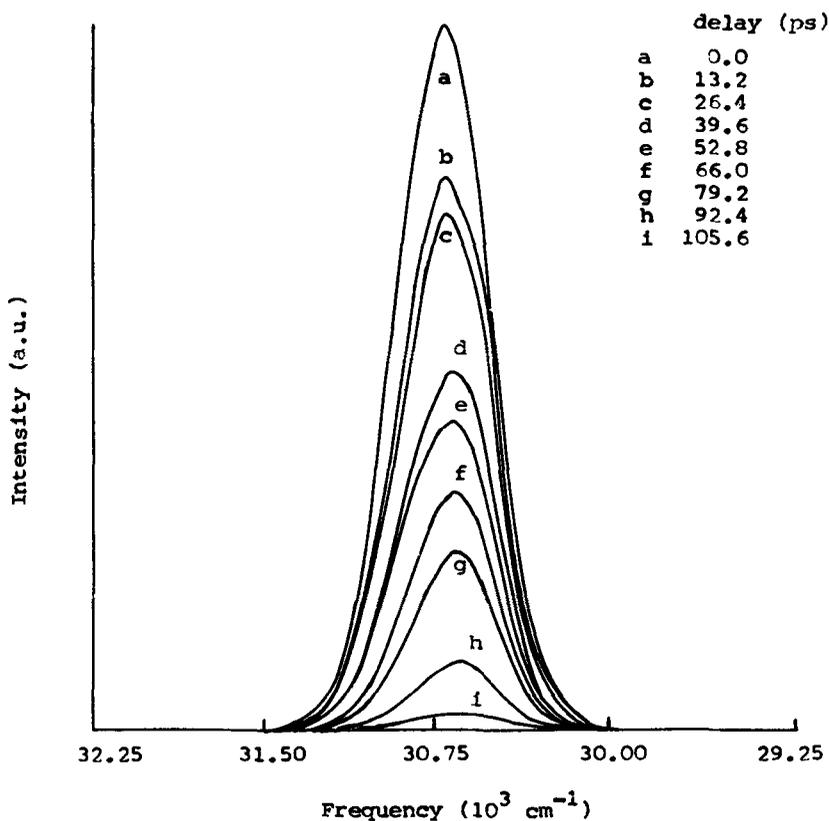


Figure 5. Time resolved spectra of C 102 at 20°C.

complete at early times (nearly 45 ps), indicating that solvent relaxation in aprotic solvents is very fast and falls within the time-resolution of the instrument. The observed continuous red-shift can be ascribed to a continuously evolving solvent-relaxation. The FC (S_1) state is a quasi-continuum state consisting of discrete orientational levels corresponding to solute-solvent configurations. The transient spectra thus correspond to an elementary emission (almost continuous) originating from all possible orientational levels located between non-relaxed FC state and equilibrated excited state. Typical time-resolved spectra for ethanolic solutions is given in figure 5. The temporal profiles obtained from plots of intensity of the upconverted signal versus time (figure 6) yielded $1/e$ times (τ_{ASE}) of 45 ps and 60 ps respectively for n-butanol and ethanol which were found to be independent of wavelength. Consequently, the transient solvation phenomena is not apparent in the intensity decay profiles. The wavelength independence of decay in the present time-resolved experiment may be due to the narrow spectral coverage of the upconverted signal. Such a behaviour has been reported earlier [17]. For AN and DMSO the decay falls within the time response of the system. The τ_{ASE} values correspond to reduced lifetimes of S_1 state by amplified spontaneous emission via stimulated emission. Since lifetimes of S_1 are very much reduced, we believe that other non-radiative process probably that involving rearrangement of solute molecules hindered by solvent may be operative since these lifetimes approximately correlate with the viscosity of the solvent. During the course of solvation the degree of charge transfer in S_1 state may change continuously and the interconversion

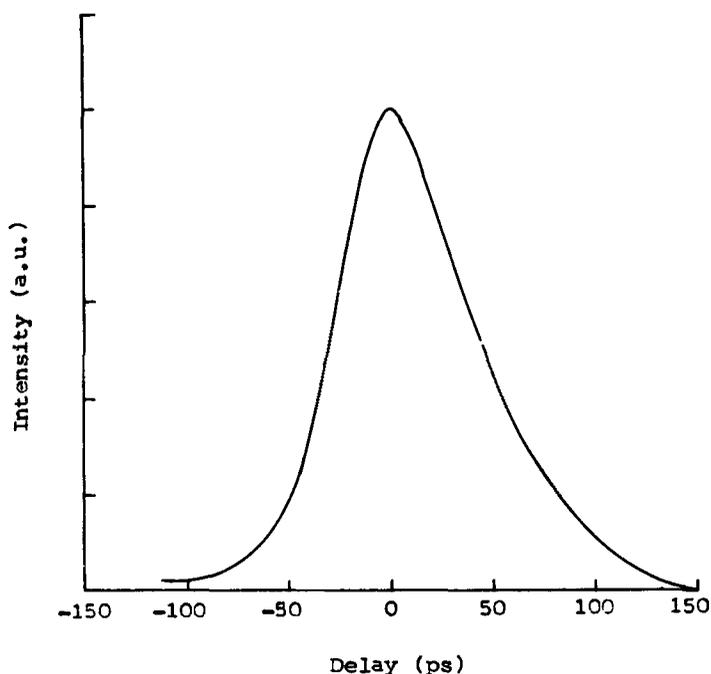


Figure 6. Decay profile of the upconverted signal of C 102 in ethanol.

kinetics of charge transfer transient species is modulated by solvent motion. We also notice that these lifetimes are in reasonable agreement with τ_S values derived from Stokes shift correlation functions. However, it is important to note that τ_{ASE} obtained from $I(t)$ decay curve is concentration dependent while τ_S derived from $C(t)$ decay curve is concentration independent.

Solvation dynamics in polar liquids with a variety of probe/solvents combinations have been examined by different workers to experimentally verify the prediction, from dielectric continuum theory [18, 19] that the solvent orientational relaxation time, τ_S , as measured by the fluorescence spectral shift of a probe solute, should proceed exponentially in time equal to solvent's longitudinal relaxation time, τ_l , defined as

$$\tau_l = (\epsilon_\infty/\epsilon_0)\tau_d \quad (3)$$

where ϵ_∞ and ϵ_0 are infinite frequency and static dielectric constants, respectively and τ_d is the bulk dielectric relaxation time. The time evolution of the solvent-relaxation is usually quantified by the correlation function $C(t)$ [20] defined as

$$C(t) = \frac{\nu_{\max}(t) - \nu_{\max}(\infty)}{\nu_{\max}(0) - \nu_{\max}(\infty)} \quad (4)$$

in which $\nu_{\max}(0)$, $\nu_{\max}(\infty)$ and $\nu_{\max}(t)$ are the optical frequencies that correspond respectively, to the wavelength maxima of emission spectrum of the probe at times zero, infinity (when the solute solvent system is at equilibrium), and at intermediate time t (during the relaxation). In the absence of specific interactions $C(t)$ provides a solute-independent measure of solvation dynamics as described by Castener and Fleming [19]. If the solvent orientation is described by continuum model, $C(t) = \exp(-t/\tau_S)$, i.e., $C(t)$ decays exponentially with a time constant equal to τ_S .

For extracting accurate $C(t)$ functions one should use the correct shapes of the transient emission spectra and the peak frequencies. The description of the method of analysis has appeared in many references [15, 10, 19]. The method of measurement in the present system was simplified by measuring the peak frequencies $\nu(t)$ directly from the normalized transient spectra (figure 7) and $\nu(\infty)$ was taken to be the limiting frequency beyond which spectral shift did not occur. Typical normalized time evolving spectra for ethanolic solutions is displayed in figure 6. In case of alcohols, $C(t)$ functions determined from relation (4) were found to decay non-exponentially. Nevertheless, the decays were fitted well by a single exponential dependency with time constants of $\tau_S = 55$ ps for ethanol and 65 ps for n-butanol (figure 8). In order to test the validity of dielectric continuum model (DCM) the longitudinal relaxation times from relation (3) were calculated using the available dielectric parameters at 293 K [$\epsilon_0 = 26.00$; $\epsilon_\infty = 1.85$; $\tau_d = 130$ ps, $n_0 = 1.359$ for ethanol [21], $\epsilon_0 = 17.8$; $\epsilon_\infty = 3.5$; $\tau_d = 613$ ps, $n_0 = 1.399$ for n-butanol [19] and the values are collected in table 2. In case of n-butanol agreement between τ_S (65 ps) and τ_l (110 ps) is sensible, while in case of ethanol τ_S (55 ps) is about six times greater than τ_l (9 ps) are agrees with the value of $\tau_S = 40$ ps reported earlier by Struve *et al* [22] who used DMABN as a probe molecule. As argued by Sumi and Marcus [23] the better relation for evaluating the longitudinal relaxation time for alcohols should be $\tau_l = (n_0^2/\epsilon_0)\tau_d$ where n_0 is the refractive index of the solvent and this relation yields $\tau_l = 65$ ps which is in excellent agreement with our experimental value. Interestingly, our experimental value of τ_S is in close agreement

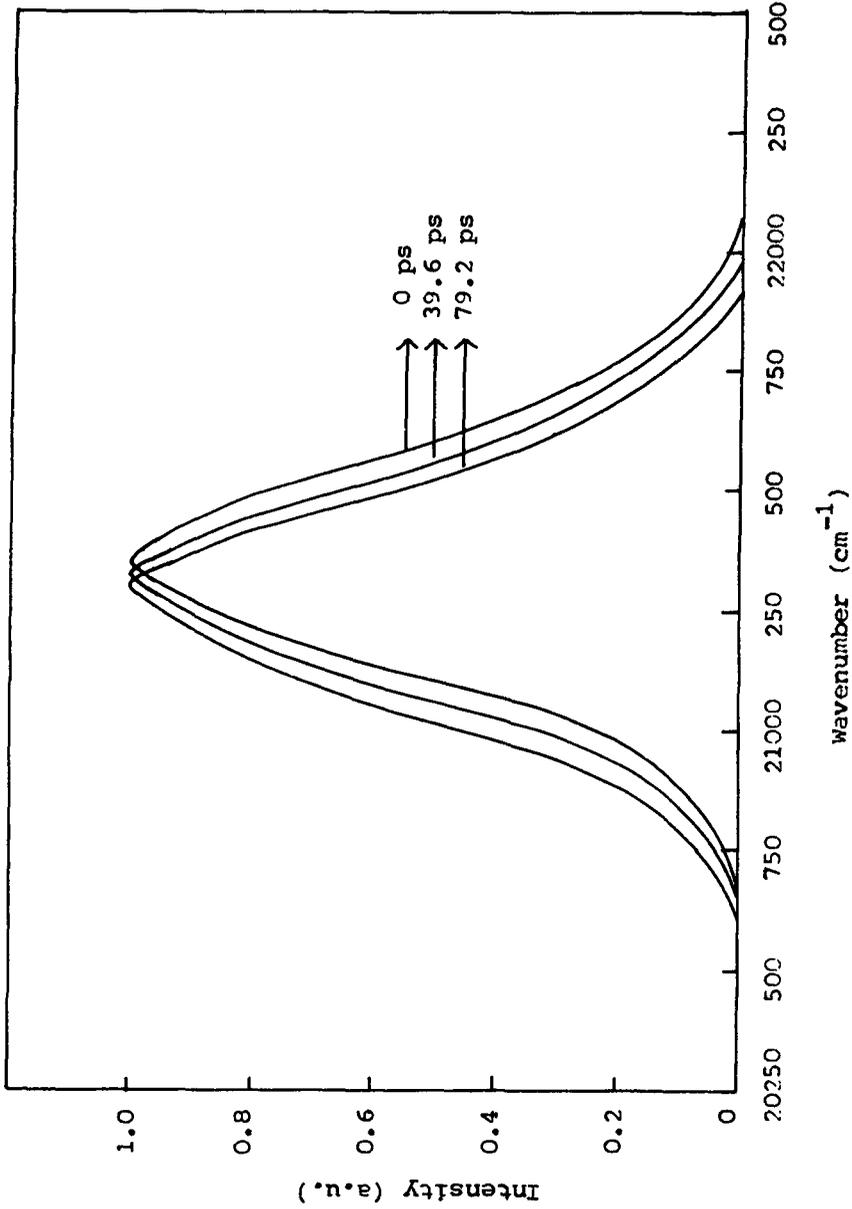


Figure 7. Normalized time-evolving spectra of C 102 in ethanol.

Picosecond time-resolved laser emission of coumarin

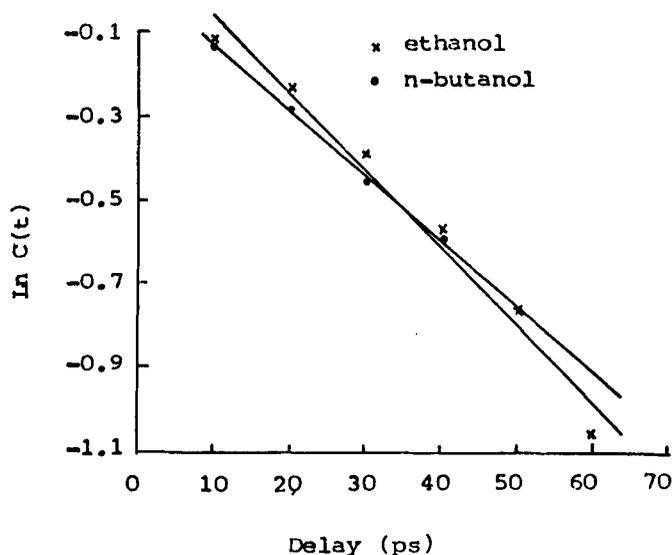


Figure 8. Stokes shift correlation function $C(t)$ for ethanol and n-butanol.

Table 2. Dielectric parameters and solvation times.

Solvent	τ_d (ps)	$\tau_i = (\epsilon_\infty/\epsilon_0)\tau_d$ (ps)	$\tau_i = (n_0^2/\epsilon_0)\tau_d$ (ps)	$\tau_s(\text{obs})$ (ps)
n-butanol	613	120	67	65(66 ^a)
ethanol	130	9	9	55(40 ^b)

^aCastener *et al* 1987; ^bStruve *et al* 1973

with earlier reported values of $\tau_s = 66$ ps for n-butanol with LDS-750 as a probe molecule [19]. We therefore feel confident that our simplified extraction of $C(t)$ function from transient laser emission spectra are good enough for the description of solvation dynamics in n-butanol except the non-exponential behaviour of $C(t)$. However, with regard to ethanol, the agreement between experimental and theoretical results is obviously not good. These findings show that the continuum approach is not sufficient for the description of actual dynamics in the present systems. As pointed out by previous workers [24, 25, 26] the overall solvation dynamics according to molecular based models should show continuous range of times between τ_i and τ_d , with the shortest being τ_i and the longest τ_d . It is, therefore, concluded that the observed deviation from DCM model particularly for ethanol may result from the molecular aspect of solvents which is not included in the continuum description. In actual situation, the solute-solvent interaction becomes complicated due to the change in the intramolecular charge transfer and μ_e of S_1 state during solvation process. The basic difference in the two solvents may be associated with the importance of time-dependent changes in effective dipole moments and varying degree of polarization dependence of

dipole moments. Further studies are planned for better understanding of solvation dynamics on time scales ranging from sub-picoseconds to few hundred picoseconds applying refined theoretical models. As it is well-known, each time scale has a significance in the upconversion technique. However, the present system utilizing the superradiant laser emission as a probe can reveal the solvation dynamics and is better suited for selecting dyes as luminescence probes required for many applications [27].

Oriental relaxation time of 78 ps for C 102 in ethanol obtained from induced dichroism technique is greater than the solvent-relaxation time of 55 ps. This shows that rotational motion of the solute does not influence greatly that of the solvent.

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