

Figure 1. Structural model and atom numbering of 1-(2-chloroethyl)-3-cyclohexyl-1-nitrosourea (CCNU). The numbers in parentheses are the atomic electronic charges calculated in this work.

tivity than CCNU. Thus the charge distribution state on the atoms of antitumor agents may contribute to the antitumor activity of molecules. Therefore, studying the antitumor activity not only on the aspect of structure but also on the aspect of charge distribution will give more comprehensive and profound understanding about the activity of antitumor agents.

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Dynamics of Polar Solvation for the Electronic Excited State of Coumarin 481 with Excess Vibrational Energy

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The dipolar interaction between the electronically excited solute molecule and the surrounding solvents is expected to be important in determining the kinetics of chemical reaction such as the excited state charge transfer. Over the past decade the dynamic nature of solute-solvent interaction has been the focus of many solution dynamics studies¹⁻⁵ and widely investigated using various kinds of ultrafast spectroscopic techniques.⁶

Time-resolved Stokes shift experiments have provided fairly detailed picture of the polar solvation dynamics. The und-

erlying concept of the dynamic Stokes shift experiment relies on the presumption that there is significant change in the magnitude and/or direction of dipole moment upon electronic excitation. The electronic charge distribution of the probe is strongly perturbed upon excitation with a ultrashort laser pulse and nonequilibrium configuration between the probe and solvents is instantaneously formed. Subsequently the solvent molecules start to reorganize in order to lower the free energy of solvation. The process of lowering the free energy of solvation results in the red shift of emission

spectrum with time. The spectral evolution contains information about the solvent response to the perturbation of electronic charge distribution. For these studies coumarin derivatives were successfully employed as a nearly ideal probe and the characteristic solvation times for a variety of solvents were determined.^{4,7}

Fluorescence up-conversion technique is convenient in studying ultrafast excited state dynamics occurring in molecular systems since its time resolution is only limited by the laser pulse width.⁸ Transient absorption measurements are also widely employed. But interpretation of absorption data is sometimes more complicated than the emission ones. In this work, 7-diethylaminocoumarin (coumarin 481) was used as a solvation probe and the probe molecule was excited to a high-lying electronic state which contains much larger vibrational excess energy compared to former works.⁴ While recent experiments by Elsaesser *et al.* on vibronic relaxation for high-lying electronic state of large molecules in solution dealt with the intramolecular processes,⁹ this work is primarily concerned with the effect of larger vibrational excess energy on solvation dynamics.

Experimental

The fundamental output pulse of a self mode locked Ti:sapphire laser (Spectra Physics Tsunami) was frequency doubled first, then the doubled output and the remaining fundamental were recombined to produce pulses of 267 nm photons. This third harmonic generation is achieved in an Inrad Tripler (Model 5-050). The pulse width was broadened more than twice after the frequency tripling. The third harmonic of Ti:sapphire laser with an average power of 50 mW was routinely generated at 100 MHz repetition rate. The femtosecond uv pulse of the third harmonic was used to excite the coumarin molecules to high lying singlet states and the investigation of the ultrafast fluorescence dynamics was followed by a fluorescence upconversion technique. Fluorescence upconversion was done in a type I phase matched BBO crystal (thickness 500 μm). The cross correlation between pump and gate pulse was measured by difference frequency generation technique. The cross correlation trace was well represented by a Gaussian function with the Gaussian width of 240 fs. It is estimated that the decay time constants of about 100 fs or smaller can be extracted from deconvolution procedure. The polarization direction of pump with respect to gate beam was adjusted to the magic angle with a half wave plate. The upconverted fluorescence signal was effectively discriminated from the background by the spatial and optical filters and further wavelength-resolved by a small grating monochromator, then detected by a photon counting system. The signal level is usually more than a few hundred counts/second with a detection bandwidth of about 400 cm^{-1} . When the signal intensity is low, a number of scans are averaged for the data analysis.

The concentration of coumarin solution was adjusted to give the absorbance value of approximately one at the absorption maximum. The solution was circulated using a flow cell to avoid any long time thermal effect. The absorption spectra of coumarin solution was checked after measurements to ensure that no photodegradation had occurred.

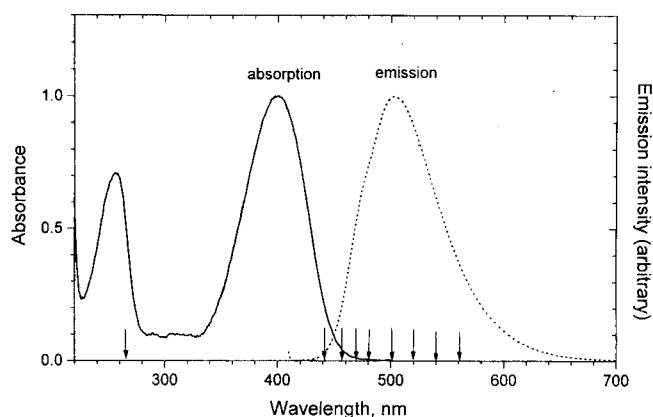


Figure 1. Steady state absorption and emission spectra of coumarin 481 in acetonitrile. Excitation wavelength (267 nm) and emission wavelengths (440 nm, 455 nm, 467 nm, 480 nm, 501 nm, 520 nm, 540 nm, 559 nm) are marked with arrows.

Results and Discussion

The steady-state absorption and emission spectra of coumarin 481 in acetonitrile are shown in Figure 1. Excitation and fluorescence detection wavelengths are also marked as arrows in the figure. It is noted that Stokes shift between

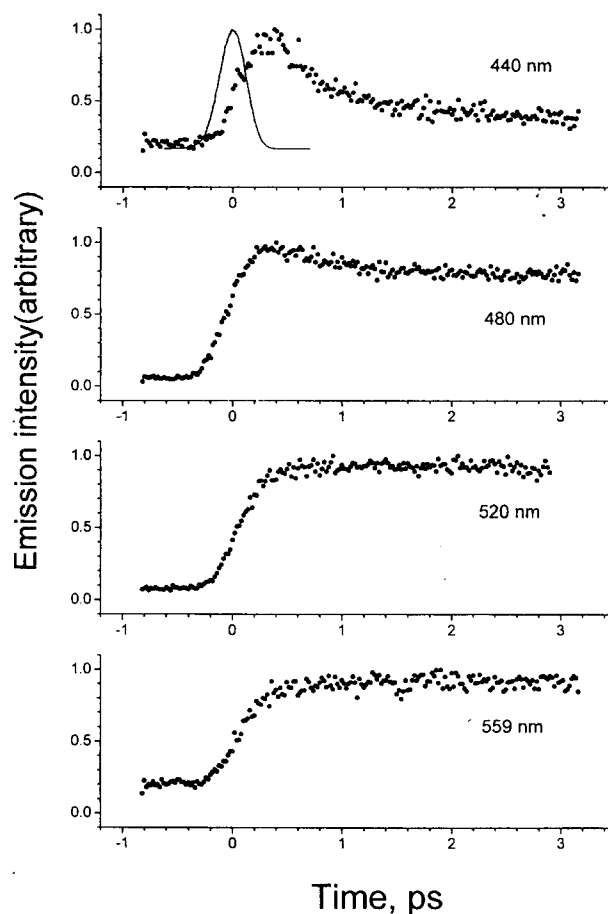


Figure 2. Fluorescence rise and decay dynamics of coumarin 481 in acetonitrile measured at four different wavelengths. Instrument response function is shown along with the emission transient at 440 nm.

the absorption and emission band maxima amounts to about 4500 cm^{-1} . Large Stokes shift is related to a big change in the dipole moment upon excitation of the electronic state.

The dipole moment change provides a driving force for the solvent relaxation. The excitation of the coumarin 481 with a laser pulse of 267 nm light results in the deposition of excess vibrational energy of about 13000 cm^{-1} from the 0-0 electronic transition energy. Fluorescence intensity change over a few picoseconds time scale is recorded and displayed in Figure 2 for several selected wavelengths. A couple of points can be noted in the figure. First, the emission intensity rises rapidly with a time constant of 130-190 fs at all wavelengths, which is slow enough to be resolved by the instrument response function. This time constant may be attributed to the internal conversion from S_0 to S_1 or the intramolecular vibrational redistribution.¹⁰ If the vibrational redistribution is occurring in a time scale comparable to or slower than the time resolution of our apparatus, we would expect that the time-resolved emission spectrum is somewhat different (for instance, more pronounced vibronic feature in early time spectra) from the steady-state emission spectrum. But the absence of any significant change in the shape of time-resolved emission spectra suggests that the vibrational energy redistribution occurs faster than we can resolve. In addition to the fast rise, fluorescence intensity quickly decays to some level in the blue edge (440 nm) of the emission band and further rise is observed at the red edge (559 nm). The fast decay of fluorescence intensity at the blue edge and further rise at the red edge corresponds to the spectral evolution from a higher energy configuration to a lower energy configuration with time. This dynamic Stokes shift is closely correlated to the solvation dynamics in polar environment.^{11,12}

Time-resolved emission spectra can be obtained from the fluorescence transients at different wavelengths and are shown in Figure 3. The time-resolved emission spectra are fitted with a log-normal function to obtain the spectral peak shift.¹³ Figure 4 shows the peak position of the time-resolved emission spectra as a function of time. The peak shift is well modeled by a biexponential function of two time constants (150 fs and 670 fs). These values can be compared to Maroncelli's results in which 89 fs and 630 fs time constants are obtained.⁴ There may be some uncertainty for the

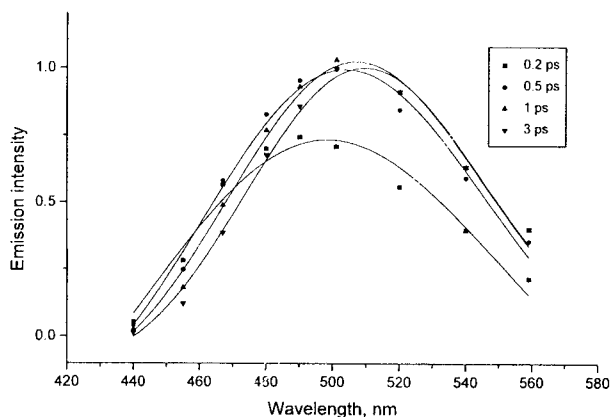


Figure 3. Time-resolved emission spectra of coumarin 481 in acetonitrile at 0.2 ps, 0.5 ps, 1 ps, and 3 ps after excitation. Curves represent the best fit with a log-normal function.

faster time constant of our data due to limitation on the time resolution of the apparatus. In addition, the measured fluorescence shift corresponds to only a portion of the total Stokes shift, which may suggest the early part of relaxation dynamics is too fast to be measured with our apparatus. The slower time constant is very close to their value even though the probe structure is somewhat different (Coumarin 481 vs Coumarin 153) and the quite different amount of excitation energy is employed in the two experiments. The similar time constant obtained for two different probes in the same solvent may be in consistency with the fact that we are measuring the solvent dynamics in general. The amplitude weighted average solvation time (410 fs) is obtained and compared to the predictions of theoretical models. The average solvation time lies between the Debye relaxation time (4.3 ps) and the longitudinal relaxation time (200 fs) of acetonitrile. This result is in accord with the prediction of the mean spherical approximation for polar solvent dynamics. According to this theory, solvent relaxation proceeds nonexponentially with an average time constant greater than the longitudinal relaxation time.^{14,15}

It is observed that similar solvent relaxation times are obtained despite a large difference in excess vibrational energy. The large excess vibrational energy deposited into a probe molecule eventually spreads out to surrounding solvents resulting in local heating of the system. The energy transfer to surrounding solvents causes temperature rise and viscosity change which would affect the solvent dynamics. It seems in our experiment that local heating is irrelevant to the solvent response to the electronic charge redistribution of a probe. In case of acetonitrile, the solvent response to sudden change in the dipole moment of a solute molecule seems to occur much faster than the vibrational cooling of the solute molecule. A recent study on vibrational relaxation of trans-stilbene indicates that vibrational cooling rate is well correlated with the thermal diffusivity of solvent.¹⁶

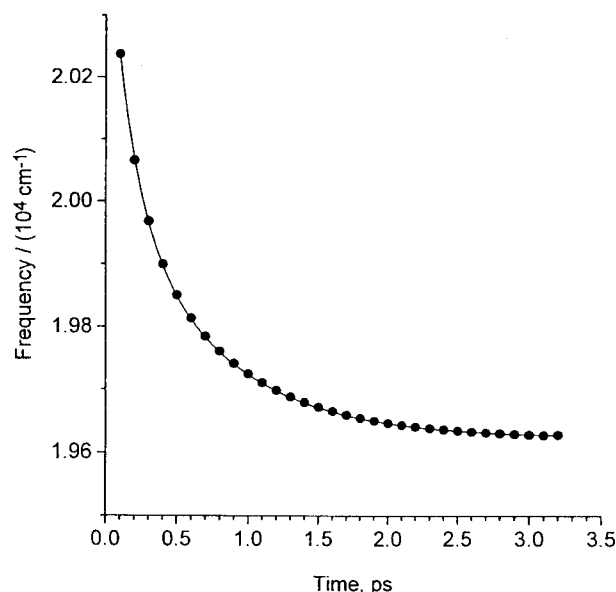


Figure 4. Time dependence of the emission peak frequency measured for coumarin 481 in acetonitrile. The best fit is obtained when a biexponential function ($\tau_1=150\text{ fs}$ and $\tau_2=670\text{ fs}$) is employed.

Considering the thermal diffusivity of acetonitrile, the time scale of vibrational cooling in acetonitrile would fall in a few picoseconds time scale. Therefore the solvation dynamics in acetonitrile is well separated from the vibrational relaxation process and not affected by the presence of excess vibrational energy. In summary, the excited state dynamics of 7-diethylaminocoumarin laser dye in acetonitrile were studied by the femtosecond fluorescence up-conversion method. Dye molecules are pumped with 240 fs excitation pulses of 267 nm light resonant to S_0 - S_n transitions, which results in very high excess energy from the 0-0 transition of the molecule. Fluorescence dynamics was interpreted using a simple free energy of solvation model. Polar solvation times are extracted from the time-dependent Stokes shift measurements and compared with the dielectric relaxation time of the solvent. Solvation dynamics is well modelled by a biexponential function of two time constants. The results indicate that the excess vibrational energy which is deposited in the probe molecule after the electronic redistribution does not seem to alter the solvation dynamics. In addition, the rapid rise of fluorescence intensity which was observed at all detected wavelength with a time constant of 130-190 fs is attributed to the internal conversion from S_n to S_1 electronic state.

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