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Subpicosecond solvation relaxation of DASPI in polar liquids

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Abstract

The solvation dynamics of 2-(p-dimethylaminostyryl)pyridylmethyl iodide (DASPI) dissolved in the solvents methanol, ethylene glycol, ethanol and acetonitrile, has been studied using the fluorescent up-conversion technique with a time resolution of about 100 fs. A bimodal solvent response function is obtained for DASPI dissolved in the polar solvents. In the bimodal response function the ultrafast initial decay component, a Gaussian term with a characteristic frequency of $\omega_G \approx 10 \text{ ps}^{-1}$, is attributed to inertial free streaming motions of the solvent molecules. In addition, for all solutions slower decay components with time constants of several picoseconds typical of rotational and translational diffusional motions of the solvent molecules have been found.

1. Introduction

Solvation dynamics is a topic of great current interest [1–22]. For fluorescent probe molecules, the experimental information concerning the solvation dynamics is commonly obtained from dynamic Stokes shift measurements [3–5]. In such experiments, pulsed photo-excitation of the probe molecules is applied to induce an abrupt and substantial change in the electronic charge distribution within the solute molecules. After the excitation, the configurations of the solvent molecules in the solvent layers around the solute molecules no longer correspond to a minimum in the free energy of the system. Rotational and translational motions of the solvent molecules effectively lead to the dynamic relaxation of the solvation energy. This relaxation will experimentally manifest itself as a dynamic (red) Stokes shift of the emission of the solute. The solvation response function, $C(t)$,

characteristic of the dynamics of the Stokes shift, is given by

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

where $\nu(0)$, $\nu(\infty)$, and $\nu(t)$ are the optical frequencies corresponding to the first moment of the emission band of the solute at time zero, infinite and intermediate times. $C(t)$ provides a direct measure of the solvent dynamic response.

In early experimental and theoretical studies, solvation relaxation was considered to originate mainly from overdamped diffusional motions of the solvent molecules. Recent molecular dynamics simulations of water [6], acetonitrile [7,8], methanol [9,10] and methyl chloride [11–14], however, revealed a bimodal behavior of the solvent response relaxation function. A large amplitude (> 50%) initial component, with a time constant of about 100 fs, was

simulated [15] in addition to the longer component at the picosecond time scale. The 100 fs decay component was attributed to the influence of ‘inertial free streaming motions’. The latter motions characterize the rapid collisionless rotational motions of the solvent molecules in the solvent cages in the solvation layers. Surprisingly, small-angle orientational changes of the solvent molecules around the solute molecules are sufficient to account for a large part of the free-energy relaxation [9,16]. The second (picosecond) component in the bimodal solvation response function was attributed to the effects of rotational and translational diffusion of the solvent molecules [17]. Using high-time resolution techniques, for several systems the existence of an ultrafast decay component within the initial few hundred femtoseconds has recently been experimentally established [1,16,18–20].

In this paper we report on an investigation of the solvation dynamics of the polar styryl dye 2-(p-dimethylaminostyryl)pyridylmethyl iodide (DASPI), see inset Fig. 1. DASPI shows an appreciable static Stokes shift as exemplified by the positions of the band maxima in the absorption and emission spectra in methanol at about 460 and 635 nm, respectively, thus enabling us to apply the fluorescence up-conversion method. Recently, a time-resolved study of the solvation dynamics of DASPI dissolved in methanol and acetonitrile was reported by Bingenmann and Ernsting [20]. Transient absorption and stimulated emission spectra were obtained with an experimental resolution of 100 fs. The analysis of the time-dependence of the first, second and third central moments of the $S_0 \rightarrow S_1$ band transition of DASPI [20] in methanol was accomplished on the basis of a multiple-Debye continuum model, i.e. without invoking inertial motions to contribute to the solvation dynamics. The ultrafast relaxation component ($\omega_G = 10 \text{ ps}^{-1}$) in the data obtained for DASPI in acetonitrile was interpreted in terms of the Brownian oscillator model [21].

We have performed fluorescence up-conversion experiments for DASPI dissolved in several polar solvents with a time resolution of approximately 100 fs. We find that the solvation relaxation around DASPI in the polar solvents shows a bimodal character. We discuss that the fastest decay component is due to inertial free streaming motions of the solvent

Fig. 1. Representative fluorescence transients of DASPI dissolved in methanol recorded at sum frequencies of 305, 340 and 365 nm, corresponding to fluorescence emitted at 478, 571 and 645 nm, respectively. The experimental response function is shown in the lower left corner.

molecules, whereas the slower (picosecond) decay components are related to reorientational diffusional motions.

2. Experimental

DASPI was purchased from Exciton and used without further purification. Solutions of DASPI in methanol (Merck Uvasol), ethylene glycol (Aldrich), ethanol (Nedalco), and acetonitrile (Merck Uvasol) were prepared. The dye concentrations had typically an optical density of 0.6 at the excitation wavelength of 420 nm, which corresponds to a concentration of approximately $2 \times 10^{-4} \text{ M}$. The solvents were used as purchased. Steady-state fluorescence spectra were measured on a calibrated emission spectrometer out-fitted with time-correlated single-photon counting detection [22].

A femtosecond up-conversion set-up was used to measure the solvation dynamics. Details are described elsewhere [18,19]. Briefly, a cw Ar^+ laser is used to pump a femtosecond Tsunami Ti:sapphire laser. Typically, the laser produces pulses of a dura-

tion of 80 fs at a repetition rate of 82 MHz. The pulses were focused onto a 1 mm β -barium borate (BBO) crystal for frequency doubling. The frequency-doubled excitation pulses were separated from the fundamental-frequency beam with a dichroic beamsplitter. The fundamental-frequency beam (central wavelength: 840 nm) was used as a gating beam and the frequency-doubled part of the beam is used as the pump beam. The time interval between the excitation pulse and the gating pulse could be varied using an optical delay line. In our apparatus, the pump beam (≈ 1 nJ/pulse) passed a stepping motor-driven translational stage. To avoid effects due to rotational motions of the probe molecule, all data were taken under magic angle conditions. To this end the polarization of the pump beam with respect to the gate beam was controlled by a quartz half-wave plate, set at 54.7° , in the pump arm. The pump beam was focused onto a flow cell, with an optical path length of 1 mm, containing the sample solution. The photo-induced fluorescence was focused together with the gating pulse onto a 1 mm BBO crystal (type I phase matching) yielding light at the sum frequency, i.e. the sum of the frequency of the fluorescence and the fundamental frequency of the Ti:sapphire laser. The up-converted emission was led through an UG11 band-pass filter and a Zeiss M20 monochromator. The sum frequencies were selected by tuning the angle of the BBO crystal as well as the monochromator wavelength. Finally, photo-detection was by means of a photomultiplier coupled to a photon-counting system. The output of the photon counter was fed into a personal computer. Typically, the up-conversion signal was averaged for 1 s at each delay time. A decay measurement was performed using typical scan step sizes of 6.6 and 66 fs, resulting in time windows of 3.3 and 33 ps, respectively. The cross-correlation between the excitation and gating pulses is measured to be 150 fs (FWHM of the sech^2 -shaped response function) indicating that after deconvolution our experimental time resolution amounts to about 100 fs.

3. Results

Typical fluorescence transients for DASPI dissolved in methanol at different detection wave-

lengths are displayed in Fig. 1. The figure illustrates that the fluorescence transients detected at the blue side of the fluorescence spectrum of DASPI show an instantaneous rise and a decay component on a (sub)picosecond time scale. Transients detected more to the red of the fluorescence spectrum show a (sub)picosecond rise instead of the (sub)ps decay. For DASPI dissolved in ethylene glycol, ethanol or acetonitrile similar results were obtained.

The fluorescence spectra at different times after the excitation pulse were reconstructed following the method given by Maroncelli and Fleming [23]. Fluorescent transients were recorded in the wavelength range from 480 up to 650 nm with an interval of 15 nm. The transients were deconvoluted with the instrument response function and fit to a multiexponential decay function. After calibrating the integrated intensity of each individual fitted transient to the corresponding intensity of the calibrated steady-state emission spectrum, the time-resolved emission spectra could be reconstructed. The time-dependent fluorescence spectra were fitted to a log-normal line shape function [23]. Log-normal functional fits for DASPI dissolved in various solvents are displayed in

Fig. 2. Time dependence of the reconstructed fluorescence spectra of DASPI dissolved in (a) methanol, (b) ethylene glycol, (c) ethanol and (d) acetonitrile.

Table 1
Solvent correlation function $S_p(t)$ ^a

Solvent	a_G	ω_G (ps ⁻¹)	a_1	τ_1 (ps)	a_2	τ_2 (ps)	$\Delta\nu$ ^b (cm ⁻¹)	τ_c ^c (ps)
methanol	0.14 ± 0.05	6.0 ± 1.0	0.75 ± 0.05	1.3 ± 0.5	0.11 ± 0.05	12.4 ± 1.0	3500	1.0 ± 0.5
ethylene glycol	0.19 ± 0.05	3.6 ± 1.0	0.38 ± 0.05	2.8 ± 0.5	0.43 ± 0.05	17.5 ± 1.0	3300	5.0 ± 1.0
ethanol	0.23 ± 0.05	9.8 ± 1.0	0.32 ± 0.05	1.0 ± 0.5	0.45 ± 0.05	11.9 ± 1.0	2800	4.0 ± 1.0
acetonitrile	0.53 ± 0.05	11.0 ± 1.0	0.47 ± 0.05	0.8 ± 0.1			2000	0.3 ± 0.2

^a $S_p(t)$ is fitted to a function of the form: $S_p(t) = a_G \exp(-\omega_G^2 t^2/2) + \sum a_i \exp(-t/\tau_i)$.

^b The total shift is calculated by adding the pre-exponential factors.

^c τ_c is the time required for $C(t)$ to decay to e^{-1} ; it represents an average solvation time.

Fig. 2. Clearly, the emission band maximum shows a red shift as time after the excitation pulse progresses. For DASPI in methanol, for example, the peak frequency of the emission spectrum shifts from 19.3 kK at about 100 fs after the pulsed excitation to about 15.8 kK at 30 ps. For DASPI in ethylene glycol, the peak frequency of the emission spectrum at 100 fs after excitation starts at about 19.3 kK, whereas at 30 ps the peak position has shifted to 16.4 kK. Similar

phenomena were also observed for DASPI dissolved in ethanol and acetonitrile (Fig. 2c and d).

4. Discussion

To obtain the relaxation behavior of $C(t)$ for DASPI dissolved in the different solvents, we need to plot the first moment ($\bar{\nu}(t)$) as a function of time. On the other hand, $\bar{\nu}(t)$ and the peak frequency, $\nu_p(t)$, are likely to exhibit similar time-dependencies [16] and since, from a practical point of view $\nu_p(t)$ of the log-normal fits of the reconstructed emission spectra can be determined with a higher accuracy (better reproducibility) than $\bar{\nu}(t)$, we restrict the discussion to the time-dependence of the peak frequency $\nu_p(t)$. Fig. 3 shows $\nu_p(t)$ as function of t as deduced from the log-normal fits to the reconstructed emission spectra. In the insets the early time behavior of $\nu_p(t)$ is shown.

The experimental data points as represented by the dots in Fig. 3 were fitted to a function of the form

$$C(t) = a_G \exp(-\omega_G^2 t^2/2) + \sum_{i=1}^2 a_i \exp(-t/\tau_i). \quad (2)$$

Eq. (2) is appropriate when the solvation relaxation dynamics of DASPI in the investigated solutions is determined by inertial free streaming motions and a multiple-Debye term characteristic of rotational diffusional motions [9,17]. More specifically, the Gaussian term on the right-hand side is representative of the inertial solvation decay, with ω_G as the solvation frequency, whereas the exponential terms

Fig. 3. Plot of the frequency of the fluorescence band maximum versus time for DASPI dissolved in (a) methanol, (b) ethylene glycol, (c) ethanol and (d) acetonitrile. Experimental data points are drawn as squares whereas the fits to Eq. (2) are represented by drawn curves. Insets show behavior up to 1 ps on enlarged scale. In (a) error bars are included, the magnitude of the error bars for (b)–(d) is similar.

characterize the decay resulting from Debye-type relaxation. The results of the fits of the data to Eq. (2) for the various solvents are given by the drawn curves in Fig. 3, whereas the best-fit parameter values have been collected in Table 1.

As noted in the Introduction, molecular dynamics calculations have demonstrated that the solvent response function for small polar solvents can be bimodal, i.e. the response function contains a large-amplitude component, typical of underdamped solvent motions, which decays on a 100 fs time scale followed by a much slower component, typical of reorientational and translational motions of the solvent molecules that are diffusive in nature, decaying on a picosecond time scale. From Table 1 it is seen that a bimodal solvation relaxation behavior is found indeed for all investigated solvents. In fact, the results for DASPI in acetonitrile are compatible with the results obtained by Bingemann and Ernsting [20], who reported $\omega_G = 10 \text{ ps}^{-1}$ (48%) and $\tau_1 = 1.0 \text{ ps}$ (52%). Following the interpretation of these authors, we attribute the bimodal solvation relaxation of DASPI in acetonitrile to the influence of inertial solvent motions (Gaussian component) and the diffusional Debye-type solvent molecular motions on the longer time scale.

Similarly, for DASPI in methanol, ethylene glycol and ethanol both inertial and diffusional components are found to contribute to the solvation response function. Previously, the solvation relaxation dynamics in methanol has been studied for probe molecules such as coumarin 152 [24], coumarin 153 [16] and DCM [18,19,25,26], which exhibit fluorescence from a charge-transfer state. An ultrafast Gaussian decay component, with $\omega_G = 6.0\text{--}12.0 \text{ ps}^{-1}$ (30–40%), has been found for the solvation of these solute molecules dissolved in methanol. For DASPI in methanol we find $\omega_G = 6 \text{ ps}^{-1}$ (see Table 1). It thus seems that the different solute molecules show similar solvation behavior and that their solvation dynamics is not significantly influenced by the details of the solute–solvent interactions. It should be added, however, that from transient absorption experiments performed elsewhere [20] for DASPI in methanol, unlike in the up-conversion experiments of this work, a Gaussian component could not be discerned in the fits for the solvation response function. Instead, Bingemann and Ernsting found an ultrashort expo-

nential decay component with a characteristic decay time of 100 fs. Taking into account the uncertainty of the fitting procedures we still consider this ultrafast decay component to be indicative of the presence of inertial motions contributing to the solvation dynamics.

It is of interest to note that the magnitude of the time constants τ_1 and τ_2 as deduced here for the various solvents (see Table 1) are in agreement with the picosecond components of the solvent relaxation reported for other solute molecules elsewhere [16]. The exponential terms in Eq. (2) in the multiple-Debye continuum model derived from the solvent molecular motions in the bulk and are assumed to be not so sensitive to the details of the molecular interactions between the solute and solvent molecules in nearby solvation layers. It is to be expected, therefore, that values for τ_i ($i = 1\text{--}2$) are typical of the nature of the solvent and will change little with the nature of the solute.

In view of the high-time resolution of our experiments, the possible effects of vibrational relaxation as the cause for the observed time-dependent spectral changes needs some comment. With an optical excitation near 420 nm, the DASPI molecules have about 5000 cm^{-1} excess vibrational energy in the first excited singlet state. Earlier studies of vibrational relaxation in Nile Blue and oxazine in liquid solution [27,28] showed that in these large molecules the excess vibrational energy relaxed with typical decay times less than 50 fs. Furthermore, Horng et al. [16] found, by comparing experimental data with simulated data for large-sized molecules with excess energy on the order of 3500 cm^{-1} and high-lying Franck–Condon active modes, that the emission spectra measured after 50 fs are those for the vibrationally relaxed molecule. Similarly, it is believed that for DASPI intramolecular vibrational relaxation is completed within the duration time of the applied laser pulses.

In conclusion, we have studied the solvation dynamics of the solute DASPI in several polar solvents at room temperature. A bimodal solvent response function was found for all the investigated solvents. The ultrafast, initial component is attributed to inertial free streaming motions of the solvent molecules, whereas the slower component on the picosecond time scale is due to the diffusional and rotational

motions of the solvents. From the obtained dynamic solvation times it seems that the solvation dynamics is not significantly influenced by the solute–solvent interactions.

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