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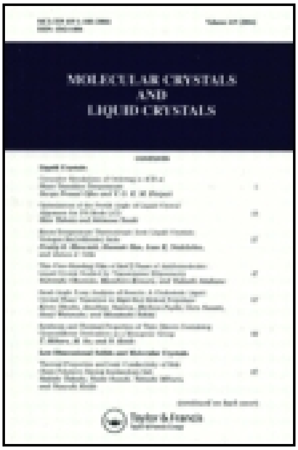

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ULTRAFAST SOLVATION OF POLAR PHOTOCHROMIC REACTION PRODUCTS

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Abstract A first part reports on the time-resolved dynamic Stokes shift of fluorescence for a solvatochromic dye in a dielectric solvent. This serves to introduce techniques, observables, and analysis in pump-probe spectroscopy with a fs white-light probe. A second part deals with the photodissociation of an aromatic disulfide into two polar radical fragments. The solvatochromism of the fragments is examined both statically as well as by fs spectroscopy. The solvation process is simulated by molecular dynamics calculations.

INTRODUCTION

In this paper we are considering what happens when we perturb a molecular solute, that is the solvation dynamics of a polar solute in a dielectric liquid. In order to follow the photophysics by optical means the molecular solute should absorb strongly in the visible range.

The experimental section of this paper consists of two parts. The first part is concerned with the time-resolved measurement of the dynamic Stokes shift which is observed after the dipole moment of a rigid, fluorescing molecule is changed upon optical excitation.[1] This serves to introduce concepts and limitations of fs pump-probe spectroscopy using a white-light continuum probe. The second part deals with a much more complicated case, namely the photodissociation of a weakly polar molecule into two polar radical fragments and their subsequent solvation. As reported in a third part, we try to understand the observations by molecular dynamics calculations of a qualitative nature.

TIME-RESOLVED DYNAMIC STOKES SHIFT

As solvatochromic probe molecule consider the compound 2-(p-Dimethyl Amino Styryl) Pyridylmethyl Iodide (DASPI), which is also known in dye laser physics as a saturable absorber dye for wavelengths around 480 nm. Figure 1 gives the molecular structure as well as the absorption and fluorescence spectra of DASPI in ethanol and acetonitrile. We excite this dye with 80 fs pulses at 470 nm.. A transient absorption spectrum recorded

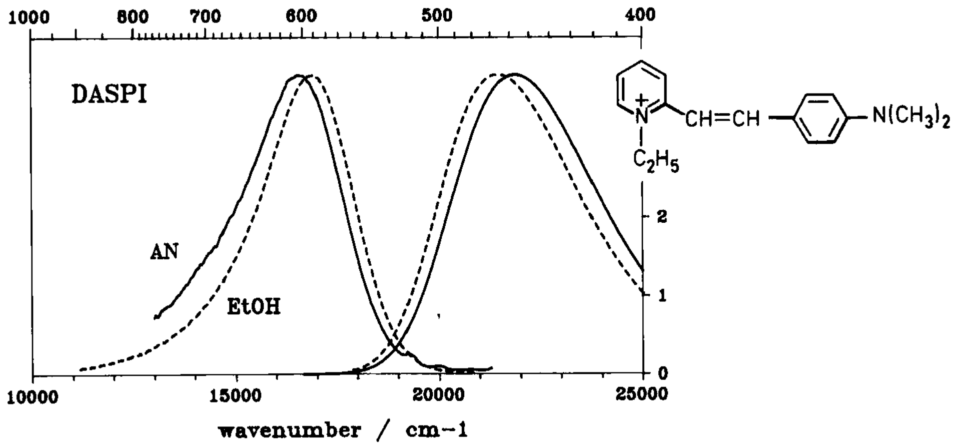

FIGURE 1 Structure and spectra of DASPI in methanol.

right afterwards registers changes to this absorption spectrum. The spectral contributions to such a transient absorption - and gain - spectrum are indicated schematically in figure 2. Immediately after the pump pulse one observes excited-state absorption (ESA) from the primary excited state S1. This may depend on the excess internal vibrational energy remaining in the molecule. Molecules are also removed from the ground state, and this shows up as a bleached absorption band (ABS). One also observes stimulated emission - or gain - in the fluorescence band of the molecule (FLS). As the dielectric solvation of the excited solute progresses, the external stabilization of the excited state and the ground state changes. As a result, the gain band experiences a spectral sweep.

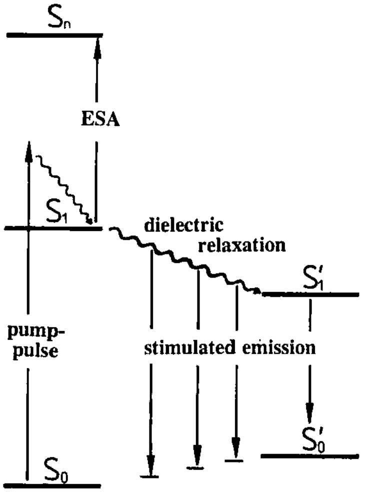

FIGURE 2 Spectral contributions to fs transient absorption and gain.

This process can be followed by pump-and-probe spectroscopy with a white-light probe pulse. The time resolution (fwhm of the spectral cross correlation function) in our case is better than 200 fs. Figure 3 shows a transient spectrum at the relatively late time of 3.3 ps after excitation (solid, noisy line). Note that there is increased absorption, for example at 420 nm, as well as decreased absorption or bleaching at 480 nm and indeed gain in the fluorecence region at 600 nm. The shape of the gain band (dashed line labelled FLS) can be obtained from the fluorescence spectrum. Its amplitude is related to that for the bleached absorption spectrum (dashed line labelled ABS). The excited-state absorption spectrum was obtained from a fitting procedure of all components to the observed transient spectrum; the resultant ESA spectrum is also shown as a dashed line in figure 3.

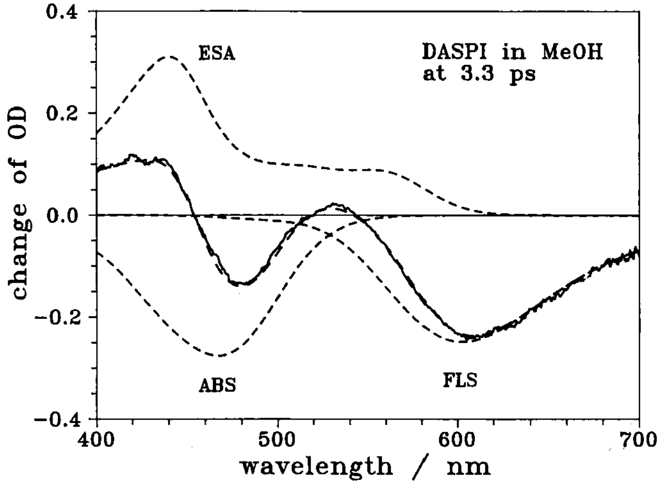

FIGURE 3 Transient absorption and gain for DASPI in methanol after 3.3 ps.

Next we discuss spectral evolution. Clearly the bleached absorption does not depend on time. It can also be argued that the ESA band does not depend significantly on time. Any temporal change must therefore be assigned to a change in the gain band. Figure 4 shows the temporal evolution of the gain band up to 3.8 ps after excitation. One observes a shift of the gain band to lower energies due to solvation. However there is also a subtle change of form because vibrational relaxation is occurring on the same time-scale as solvation. This observation is only possible if the entire spectrum is recorded. It will therefore be missed if only fluorescence-upconversion techniques at a single wavelength are employed. We are currently measuring this photophysical reaction with a better signal/noise and time resolution for a global analysis.

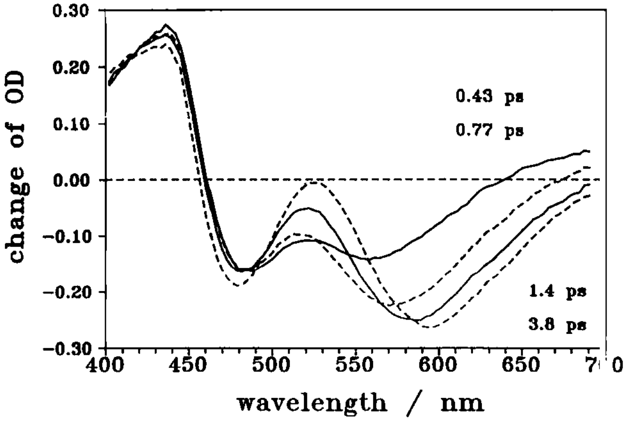

FIGURE 4 Temporal evolution of the DASPI gain band (in methanol).

SOLVATION OF POLAR RADICAL REACTION PRODUCTS

In order to obtain data on the solvent dynamics from such measurements, the molecular solvatochromic probe must fulfill a number of requirements. It has to have a change of dipole moment upon optical excitation, and there must be no isomerisation or photochemical reaction. In this second part we discuss the completely different case of photodissociation and solvatochromism of radical reaction products.

Let us consider the parent compound bis-(p-aminophenyl) disulfide. It may be weakly polar because of deviations from inversion symmetry. Excitation at 310 nm yields polar p-aminophyenyl-thiyl radicals.[2] Their structure and absorption spectra several μs after excitation and in different solvents - all of them polar aprotic - are shown in figure 5; the "static" solvatochromism of the radical reaction products is evident. The absorption spectrum of the thiyl radicals in solution can be fitted quite well by an asymmetrized Gaussian function (a "log-normal" distribution[3] over wavenumbers) as is also shown in the figure.

Right after dissociation, the two fragments should be located head-to-head. The corresponding dipole moments should oppose each other and the charge distribution should be that of a *real quadrupole*. The following question arises: is there a different solvent resonse now, as compared to that in a sudden *dipole* field? We have recorded the spectral evolution of the thiyl absorption band with 180 fs time resolution. Figure 6

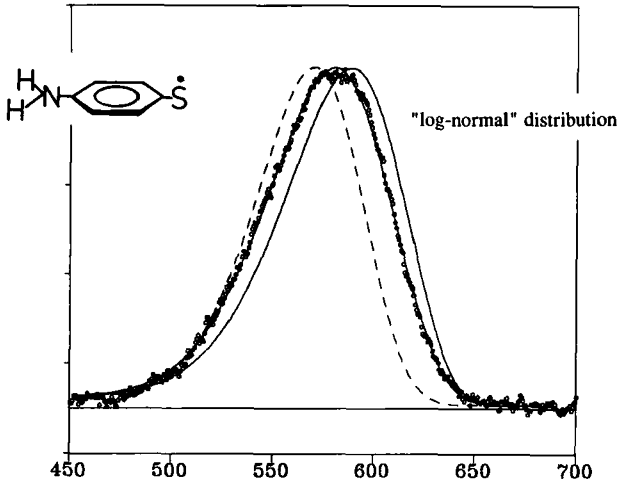

FIGURE 5 Static solvatochromism of thiyl absorption in polar aprotic solvents.

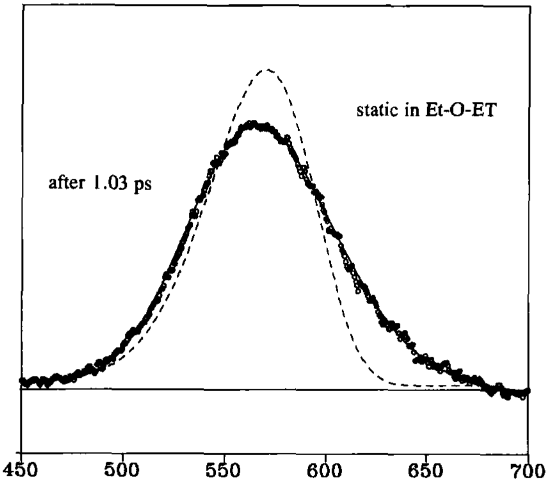

FIGURE 6 Transient thiyl absorption spectrum after after 1.03 ps in methanol.

shows a typical transient absorption spectrum 1.03 ps after excitation for a solution in methanol dots). It is compared to a "static" - *ie.* μs spectrum - in diethyl ether (dashed line). By comparison, the red band edge in the ps spectrum is extended, possibly indicating hot molecules. An analysis in terms of log-normal distributions allows us to calculate the median band wavenumber (*i.e.* the spectral centre for the absorption band).

It is found that the spectral shift in methanol, as a function of time, is biexponential with time constants of 0.4 ps (55%) and 2.4 ps (45%) at 43 °C. This is consistent with data obtained from the Stokes shift of fluorescence for rigid dyes.

It is concluded that the spectral evolution for thiyl radicals is caused by dielectric relaxation of the surrounding solvent.

MOLECULAR DYNAMICS SIMULATIONS OF DISULFIDE SOLVATION

Molecular dynamic simulations were performed in order to obtain a comprehensible picture for the thiyl radical generation and the subsequent solvation. Lack of structural and energetic data forces us to adopt a very simple model of the molecular solute, which is shown in figure 7. The aminophenyl thiyl radical is represented by a three-site flexible structure indicated N-Ph-S. Structural parameters for this generic model are also indicated in the figure. The parent molecule bis-(p-aminophenyl) disulfide is taken as composite N-Ph-S-S-Ph-N. The solvent methanol is also represented by a flexible three-site model.[4] In a first step, we want to obtain the dynamic response of the methanol solvent shell when the initial charge distribution on the parent N-Ph-S-S-Ph-N is changed. The assumed charge distribution before and after the ultrafast photochemical reaction are also given in figure 7. We start from a random configuration of one parent molecule surrounded by 198 methanol molecules in an appropriate cubic box at 18° C. The charge distribution is altered at time zero and the equations of motion are integrated (in steps of 1/4 fs) up to 15 ps to yield the corresponding trajectory. From an analysis of the potential energy of the solute one obtains its dielectric stabilisation as a function of time. The first 1.5 ps of the normalized spectral relaxation function are shown in figure 8 for an average of 10 trajectories. A fast initial stabilisation occurs within 250 fs. This is consistent with

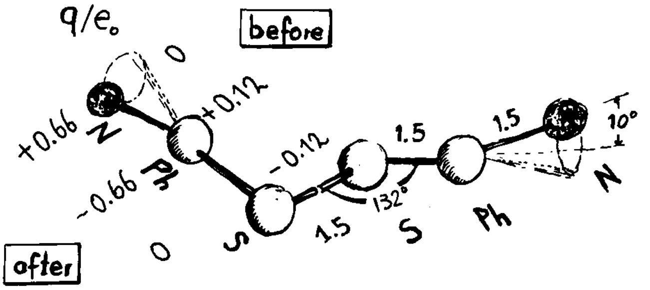

FIGURE 7 Simplified, qualitative model for molecular dynamics simulations.

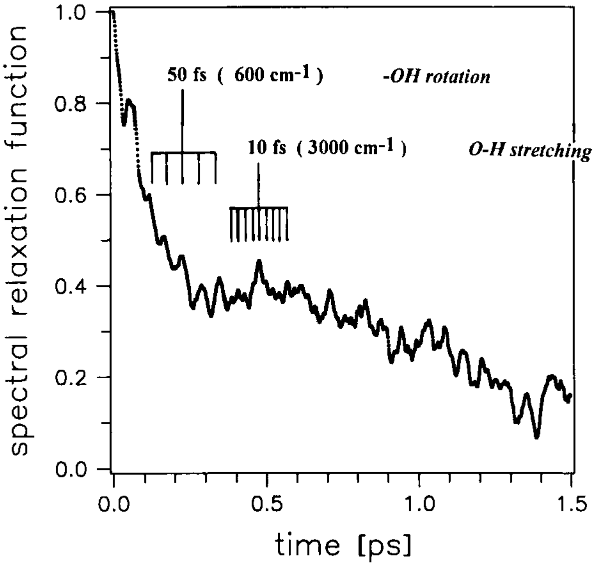

FIGURE 8 Spectral relaxation from molecular dynamics simulations.

MD simulations of dipole solvation.[5] Following the initial response, the simulated solvation then has an effective time constant of 1.7 ps, similar to the observed spectral evolution. Residual structure may be assigned to -OH rotation of the model methanol (50 fs) and O-H stretching activity in the first solvent shell.

In our experiments, the early time window up to 250 fs is probably obscured due to the overlying process of photodissociation of the parent bis(p-aminophyenyl) disulfide. The experimental time resolution is not sufficient to resolve the residual vibrational structure.

In conclusion, experiments and simulations give a consistent view of the transient absorption spectra after UV photolysis of an aromatic disulfide in solution, as indicating dielectric relaxation of polar photochromic reaction products.

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