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Femtosecond studies of charge separation in photo-excited DCM in liquid solution

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Abstract

The solvatochromism of DCM in the fluorescent state has been studied using the femtosecond fluorescent up-conversion technique with a time-resolution of ~150 fs. It is shown that intramolecular charge separation is not complete within 300 fs after the excitation pulse. A significant portion of the charge separation trajectory (~30%) is controlled by the solvation process on a picosecond time scale. It is inferred that in photo-excited DCM the locally excited and charge transfer states mix in the strong adiabatic coupling limit in the inverted region.

1. Introduction

Intramolecular charge separation in liquid solution is a topic of great current interest [1-6]. Extensive studies of the dynamics of excited-state intramolecular electron transfer (ET), as e.g. manifested in organic donor-acceptor molecules [7-9], have shown that electron transfer is strongly affected by the structure and dynamics of the surrounding solvent. In descriptions of ET dynamics generally two limiting cases are considered: the non-adiabatic and adiabatic coupling limits [10-12]. In a non-adiabatic ET process, the electronic coupling between the locally excited (LE) and charge transfer (CT) states is viewed as weak and the intramolecular ET reaction is accomplished by a solvent-activated crossing from the LE to the CT state. By contrast, in the adiabatic coupling limit, a relatively strong mixing of the LE and the CT states is assumed. As a result the lowest adiabatic potential energy surface continuously changes as the reaction coordinate is changed and the concomitant changes of the wave function character from LE to CT reflect that the charge transfer is not instantaneous but shows a functional dependence on the reaction coordinate. The time dependence of the latter is often largely controlled by the dynamics of the solvation relaxation process [11,13].

A few studies of intramolecular charge separation in the adiabatic coupling limit have been reported for fluorescent organic molecules [7-9]. In these studies, analysis of the measured fluorescence transients yielded the time-dependence of the spectral Stokes shift. Moreover, since the oscillator strength of the emission from the LE state may differ appreciably from that for the emission from the CT state and since, as noted above, solvation relaxation may result in a gradual change-over of the molecular wave function from LE to CT, a significant feature of fluorescent molecules showing charge transfer in the strong adiabatic coupling case may also be that the spectral change will comprise of a change in the integrated intensity of the emission.

In this Letter, we report on a subpicosecond study of the solvatochromism of the fluorescent laser dye...
molecule, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM). The fluorescent state of DCM exhibits a large Stokes shift (for example, in methanol the absorption band is peaked at about 466 nm and the emission band maximum is about 622 nm) [14]. Furthermore, the dipole moment in the fluorescent state is very large (26.3 D) [14]. The fluorescent state has been assigned to be of charge transfer and/or twisted intramolecular charge transfer character [14-19]. Recently, time-resolved Stokes shift measurements of DCM in a few alcoholic solvents have been reported using stimulated emission as a probe [19]. Following pulsed laser excitation, the fluorescence of DCM was found to exhibit picosecond transient behaviour. It was proposed that within approximately 300 fs after photoexcitation of the DCM molecules the charge transfer state is formed. The subsequent picosecond transients are considered to be characteristic of the solvation of the charge transfer state [19].

In our experiments we have applied the fluorescent up-conversion technique. In this way we selectively monitor the population relaxation within the fluorescent state only without probing any influence of the dynamics within the electronic ground state. A major new result will be that following the pulsed excitation of the molecule, the integrated intensity of the spontaneous fluorescence becomes decreased to approximately 50% of its initial value in a few picoseconds. The results appear consistent with a model in which the lowest LE and CT states in DCM show a strong adiabatic coupling so that to a large extent the charge separation process actually occurs on a (picosecond) time scale controlled by the excited state solvation process.

2. Experimental

DCM, purchased from Exciton, was dissolved without further purification in methanol (Merck Uvasol) in a concentration of approximately 10^{-4} M. Pulses from a femtosecond Tsunami Ti:sapphire laser (80 MHz) were led through a BBO frequency doubling crystal, with a thickness of 1 mm, to produce pulses in the wavelength region 360-440 nm. Typically, pulses with a duration of about 80 fs and an energy of about 1 nJ/pulse were used for photoexcitation of the DCM samples. The emission of the sample at ambient temperature was focused onto a 1 mm thick BBO crystal, together with the gating beam, i.e. the fundamental (∼150 mW) from the Ti:sapphire laser. The sum frequency signal of the fluorescence and the gating laser beam was focused on the entrance slit of a monochromator. Photodetection was by means of a photomultiplier connected to a photon-counting system. In order to circumvent complications caused by the influence of molecular reorientation effects of the probe molecule in liquid solution on the fluorescent transient intensity [20,21], all experiments were performed maintaining the polarization direction of the probe beam at magic angle with respect to that of the polarization of the exciting laser beam. The gating pulses were scanned in steps using a variable delay line (minimum step-length ∼0.7 fs). The time resolution in our experiment is approximately 150 fs.

The decay part of the deconvoluted up-conversion transients as obtained for a series of detection wavelengths, was fitted to a tri-exponential function, $I_s(\lambda, t)$. To construct the time-resolved spectra, the latter function first had to be properly scaled. Scaling of $I_s(\lambda, t)$ was to its calibrated value at 30 ps, where, in turn, these calibrated values were determined in a separate experiment using our picosecond fluorescence set-up [22] which gives more accurate information on the longer time scale. The variation in the sensitivity as a function of the detection wavelength of the picosecond fluorescence set-up was calibrated using a variety of standard fluorescing materials [23]. Subsequently, the emission spectrum of DCM corrected for instrumental sensitivity could be determined. The decay traces recorded with the picosecond fluorescence set-up were normalized to the corrected cw emission spectrum of DCM following the method described by Maroncelli and Fleming [24]. Finally, from the scaled decays, $I_s(\lambda, t)$, the time-resolved spectra were reconstructed.

3. Results

Fig. 1 shows fluorescent decays observed for DCM dissolved in methanol at a few detection wavelengths. Applying the iterative deconvolution procedure mentioned in Section 2, using the instrumental
Fig. 1. Normalized fluorescence decays of DCM in methanol observed at 335, 355, and 365 nm, corresponding to fluorescence emitted at 560, 610, and 645 nm, respectively. The datapoints displayed in (a) have been recorded using a stepsize of 6 fs/point to allow for a detailed investigation of the behaviour of the fluorescence intensity within 3 ps after photoexcitation, while the datapoints presented in (b) have been obtained employing a stepsize of 60 fs/point, thereby expanding the delay range to 30 ps and thus a study of the slower components of the solvation process could be carried out. The experimental response function is included in (a).

Fig. 2. Experimental time-dependent Stokes shift, $C(t)$ (X), and integrated fluorescence intensity (I) of DCM in methanol. Drawn curves represent computer simulated results.
Table 1 Experimentally observed solvent relaxation times for methanol at ambient temperature

<table>
<thead>
<tr>
<th>( \tau_1 ) (ps)</th>
<th>( \tau_2 ) (ps)</th>
<th>( \tau_3 ) (ps)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 ( \pm 0.1 ) (75%)</td>
<td>4.3 ( \pm 1.0 ) (25%)</td>
<td>1.5</td>
<td>this work</td>
</tr>
<tr>
<td>3.3 (100%)</td>
<td>-</td>
<td>3.3</td>
<td>[27]</td>
</tr>
<tr>
<td>1.16 (40%)</td>
<td>9.57 (60%)</td>
<td>6.21</td>
<td>[28]</td>
</tr>
<tr>
<td>1.26 (60%)</td>
<td>8.35 (40%)</td>
<td>4.10</td>
<td>[28]</td>
</tr>
<tr>
<td>1.0 (21%)</td>
<td>10.3 (79%)</td>
<td>8.3</td>
<td>[29]</td>
</tr>
<tr>
<td>0.075 (57%)</td>
<td>0.580 (43%)</td>
<td>0.292</td>
<td>[30]</td>
</tr>
<tr>
<td>2.7 ( \pm 0.6 ) (100%)</td>
<td>-</td>
<td>2.7</td>
<td>[19]</td>
</tr>
<tr>
<td>( \approx 0.1 ) (60%)</td>
<td>( \approx 1.0 ) (40%)</td>
<td>0.5</td>
<td>[31]</td>
</tr>
</tbody>
</table>

* Average solvent relaxation time.

fluorescent state as follows from the initial rapid increase of the fluorescence occurs faster than 150 fs. Secondly, the integrated intensity shows a rapid decrease to about 50\% of its maximum value on the (picosecond) time scale of the solvation process. It should be recalled that the experimental set-up is such that detection is at magic angle so that possible rapid changes in the orientation of the transition dipole moment and their effect on the integrated emission intensity are not detected. Finally, the line width (fwhm) of the simulated log-normal functions for DCM in methanol shows some subpicosecond transient behaviour: the line width is about 3800 cm\(^{-1}\) at 500 fs and it attains a constant value of approximately 2300 cm\(^{-1}\) after a few ps.

4. Discussion

Recently, time-resolved Stokes shift experiments of DCM in a few alcoholic solvents have been reported by Easter and Baronavski [19] using stimulated emission as a probe. From these experiments it was concluded that DCM behaves as expected when it is assumed to be chemically indifferent to its surrounding medium, i.e. the time-dependence of the Stokes shift completely follows the solvation dynamics in the charge transfer state. This conclusion basically also implies that the charge transfer process is considered to be completed within 300 fs after the DCM has been excited [19]. Also the data of our work as manifested by the fact that the time behaviour of the \( C(t) \) functions of Fig. 2 is determined by the known solvation times of the solvents, seem to justify the idea that for DCM in polar alcoholic solvents one probes on a picosecond time scale simply the relaxation along a single (unperturbed) parabolic potential energy surface characteristic of the CT state. Thus in this respect the Stokes relaxation of the DCM molecule in the excited state behaves as expected for a perfect solvation probe molecule, as for example coumarine 152 [2].

However, the picosecond transient behaviour of the integrated intensity is not compatible with the view of a dynamical solvation taking place in a pure CT state. As illustrated in Fig. 2, the integrated intensity of the fluorescence is decreased by about 50\% of its maximum value after the pulsed excitation of the DCM molecules. In time-resolved studies of DCM, the picosecond transient decay of the integrated intensity has not been reported previously. A transient change in the integrated intensity related to the solvation kinetics is not unexpected: since the radiative decay rate of an emissive state changes as \( \nu^3 \) [32], and since solvation gives rise to a decrease of \( \nu(t) \) of the emissive state, one expects that the integrated intensity of the emission from CT will decrease as solvation progresses. However, it is readily verified that the \( \nu^3 \) effect on the emission intensity should be less than 25\%.

As has been discussed in a few recent papers [7–9], the picosecond temporal behaviour of the integrated intensity is relevant for understanding the time-dependence of the charge separation process itself. In the limit of strong adiabatic coupling of the LE and CT states, solvation will appreciably affect the electronic structure, and concomitantly, the radiative character of the excited state will also be changed as time develops. In an attempt to quantitatively simulate the dynamical effects of solvation, we have followed the computational procedure outlined...
in Refs. [7-9] for the calculation of the time evolution of the emission spectrum. Details will be given elsewhere [25]. Reasonable agreement between the simulated and the experimental results was obtained. Assuming (i) linear coupling of the electronic states with the surrounding dielectric medium with a reorganization energy around 1300 cm⁻¹ (comparable to the value obtained from Ref. [14]), (ii) an electronic coupling between the LC and CT states of about 550 cm⁻¹, (iii) a ratio of the electronic transition dipole moments of the LE and CT states of approximately 3, and numerically solving the generalized Smoluchowski equation for the excited state population density distribution \( p(t) \), we simulate time dependences for the function, \( C(t) \), and the integrated intensity for the spontaneous emission, as represented by the plotted curves in Fig. 2. Comparison with the experimental data shows that the intramolecular ET process for DCM in polar solvents is satisfactorily discussed within the strong adiabatic coupling model.

A schematic representation of the computed functional dependence of the adiabatic potential energy surfaces on the solvation coordinate using the parameter values mentioned above is depicted in Fig. 3. A remarkable feature of the resulting energy scheme (in which the energy gap (\( \Delta G \)) between the LE state and the CT state is 1770 cm⁻¹ and the reorganization energy (\( \lambda \)) is around 1300 cm⁻¹, so that \( \lambda < \Delta G \)) is that apparently the charge separation in photo-excited DCM occurs in the inverted region. The evolution of the population distribution function at various times after the exciting laser pulse is included in Fig. 3. When it is recalled that in the adiabatic coupling limit the CT character of the excited state wave function increases as solvation progresses, Fig. 3 also illustrates that the charge separation of DCM in the excited state in polar solvents is closely connected to its solvation and occurs on a picosecond time scale rather than a femtosecond time scale. It should be added however, that a salient feature of the simulations is that shortly after photo-excitation of the DCM molecule, i.e. before solvation has even started so that \( z \) in Fig. 3 is still zero, the molecule is already in a state which is characterized by a 3:7 ratio of LE and CT zeroth-order wave functions. This situation is similar to that reported elsewhere for the 4-(9-anthryl)-N,N'-dimethylaniline (ADMA) molecule for which also a mixture of LE and CT states was produced within 150 fs after photo-excitation [2,7-9]. Thus within about 300 fs after photo-excitation, the DCM molecules are prepared in the excited \( S_1 \) state (cf. Fig. 3), which is significantly charge transfer in character. This state acts as a trap of the excitation and the effect of solvation is merely to produce an increase in the amount of charge transfer character, from about 70% to 100%.

The dynamics immediately preceding the feeding of the \( S_1 \) state comprises of fluorescent decay, internal conversion and radiationless intramolecular vibrational redistribution. Most likely, within a time span of tens of femtoseconds after the laser pulse is turned on, the molecular excitations are spread out in energy from the excitation energy (at 24000 cm⁻¹) to the emission detected at the shortest wavelength (at 19230 cm⁻¹). Due to the dynamical wide spread of the excitation energy the spontaneous fluorescence from the initially higher excited states is too weak to be observed. Further details concerning the intramolecular relaxation dynamics within 150 fs after the photo-excitation of the higher lying electronic levels of DCM in liquid solution are currently under study in this laboratory.

Finally, we briefly comment on the characteristic decay times as deduced from the computer simulations of the \( C(t) \) transients in Fig. 2. As already noted above, the obtained decay times correspond to the
known solvation times of methanol [19,27–31]. Evidently, this result implies that as far as the time-de-
pendence of the Stokes shift is concerned the DCM probe molecule behaves as an almost ideal probe for
the study of solvation dynamics [2]. This feature is in agreement with the scheme of Fig. 3 which illus-
trates that indeed there is only a slight deviation from a parabolic shape function for \( z < 0 \) (inverted region).

In summary, for photo-excited DCM the influence of the solvation dynamics in methanol on the intra-
molecular charge separation process has been stud-
ied by means ultrafast fluorescence upconversion
measurements. The fluorescence decay kinetics as
well as the transient behaviour of the integrated
emission intensity are accounted for assuming a
strong adiabatic coupling between the LE and CT
states in the inverted region.

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