TWO DISTINCT SOLVATED STRUCTURES OF PARA-NITROANILINE IN ACETONITRILE AND THEIR DISSOCIATION AND REASSOCIATION DYNAMICS

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(Received 12 May 1997)

We have measured the femtosecond time-resolved absorption spectra of para-nitroaniline in acetonitrile just after the photoexcitation to the lowest excited singlet state. The Singular Value Decomposition (SVD) analysis shows that two temporal evolutions follow the photoexcitation. The fast component (0.7 ps time constant) describes the dissociation of the 1:2 associated form to generate the 1:0 form followed by its reassociation with AN molecules. A slower temporal evolution of 10 ps is most likely to represent the cooling down process of the whole system.

Keywords: Femtosecond spectra; para-nitroaniline; dissociation dynamics

In previous two papers [1, 2], we showed that para-nitroaniline (pNA) exists in two distinct solvated forms in acetonitrile (AN). In the first paper, we carried out a Singular Value Decomposition (SVD) analysis of a set of ultraviolet absorption spectra of pNA in AN/CCl4 mixed solvents and found that the large bathochromic shift of the pNA

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absorption with increasing AN concentration is due to the change of the solvation structure of pNA. In pure CCl₄, pNA exists in the free form (1:0), and in AN it exists as 1:1 and 1:2 solvated forms. In the second paper [2], we used Raman spectroscopy to elucidate the structure of these two solvated species. We concluded that in the 1:1 form, the AN molecule is attached to the amino part of pNA and that, in the 1:2 form, the second AN molecule is attached to the nitro part of pNA.

The difference in the absorption spectra of the 1:1 and 1:2 associated forms of pNA/AN (as shown in Fig. 1) makes it feasible to photoexcite selectively one of the two distinct solvated structures and examine the subsequent dissociation/solvation dynamics by ultrafast time-resolved spectroscopy. In this paper, we present the femtosecond time-resolved

![Intrinsic absorption spectra of the 1:0 (free form, in pure CCl₄), 1:1 and 1:2 associated forms of pNA in AN.](image)

**FIGURE 1** Intrinsic absorption spectra of the 1:0 (free form, in pure CCl₄), 1:1 and 1:2 associated forms of pNA in AN.
absorption dynamics of the solvated structures of pNA/AN following
the photoexcitation at 400 nm.

The sample of pNA was purchased from Wako Chemicals and
purified by vacuum sublimation. Acetonitrile used was of HPLC grade
(Wako) and used as received. The femtosecond laser system used in the
present study has been described in detail earlier [3]. The ultraviolet
continuum probe (310–390 nm) was generated by focusing femtose-
cond pulses (400 nm, 300 fs) into water and was used with suitable
filters. The femtosecond time-resolved absorption spectra were
measured using 400 nm pump (300 fs, 1 kHz, 4 µJ) pulses, which
selectively photoexcite the 1:2 species.

The femtosecond time-resolved absorption spectra of pNA/AN at
various time delays between the pump and probe pulses are shown in
Figure 2. In addition to the broad bleaching features, the observed
spectra also exhibits positive absorption at very early times. Also, it is
noticeable that the bleach recovery is faster at longer wavelengths than
that at shorter wavelengths. This means that more than one transient
species are involved in the time-resolved spectra. In order to extract
more detailed dynamical information following the photoexcitation,
we have made use of an SVD analysis [5]. The analysis reveals the
presence of two large singular values indicating that there are two
distinct components involved. The temporal evolutions and their
corresponding spectral components were obtained then by using
standard curve fitting procedures [6]. The first component thus
obtained represents a very fast process with a time constant of
0.7 ps, whose spectral component exhibits positive and negative
absorption features (Fig. 3). The second component has a time
constant of 10 ps (not shown). In order to understand the spectral
features derived from the SVD analysis, we calculated the difference
absorption spectra of the 1:0 and 1:2 forms. The calculated difference
spectra matches fairly well with the spectra of the fast component as
shown in Figure 3. The fast component thus represents the
dissociation of the 1:2 solvated structure immediately after the
photoexcitation to produce the 1:0 form which then reassociates with
two acetonitrile molecules to produce the 1:2 solvated form with a time
constant of 0.7 ps. The slower component with a time constant of 10 ps
most probably represents the cooling down process of the whole
system.
The SVD analysis of the femtosecond time-resolved absorption spectra shows that the dissociation of the 1:2 form to 1:0 and the reassociation of the 1:0 form with AN molecule to be very fast (0.7 ps). It seems that the dissociation is even faster than 0.7 ps and is too fast to be observed with the present time-resolution (300 fs).
FIGURE 3  The recomposed temporal evolution (a, filled circle) and spectra of the fast component (b, dotted line). The solid line in (b) is the difference spectra between the 1:0 and 1:2 forms (see text for details).

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