Femtosecond Fluorescence and Absorption Dynamics of an Azobenzene with a Strong Push−Pull Substitution

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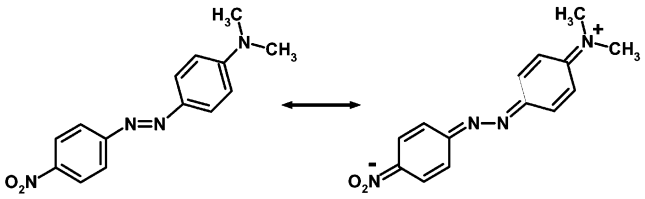
The ultrafast photoisomerization of a push−pull substituted azobenzene (4-nitro-4′-(dimethylamino)azobenzene, NA) is studied by means of femtosecond fluorescence and absorption spectroscopy. The fluorescence dynamics is biphasic. The initial fluorescence with a narrow and intense spectrum decays in ∼100 fs. This decay is accompanied by the rise of broad red-shifted and much weaker emission. The same time constants recur in the transient absorption spectra which hold additional information on the ground-state dynamics. The ground state recovers in 0.8 ps, demonstrating that only the longer time constant is associated with an internal conversion process. Small spectral changes occurring thereafter (∼5 ps) point to vibrational cooling in the ground state. The results are analyzed in comparison with the behavior of the parent compound azobenzene. Though the push−pull substitution of azobenzene strongly alters the character of its excited states, the photodynamics are surprisingly robust with respect to that substitution.

1. Introduction

trans-Azobenzenes can be interconverted to their cis isomers and vice versa by photoexcitation. Because of the prototypical character of this isomerization, azobenzene and its derivatives have become one of the "hydrogen atoms" of femtochemistry. Femtosecond absorption and more recently fluorescence studies have established the time scale of this photoreaction to be of the order of 100 fs to 1 ps (see, e.g., refs 1−4). One central issue of these studies has been the mechanism of the isomerization (inversion versus rotation). A distinction between the two mechanisms based on spectroscopic results alone is difficult if not impossible. Thus, such studies have to be supplemented by quantum chemical calculations. Results of different calculations point to either mechanism, and the subject is therefore still under debate (a very recent status report can be found in the introduction of ref 5). We recently focused on *kinetic* differences in the photodynamics of the trans → cis versus the cis → trans direction by means of femtosecond transient absorption spectroscopy and continuous wave (cw) fluorescence spectroscopy.[6] For the trans → cis reaction the transient absorption spectrum attributed to the excited state predominantly decays with time constants of 0.34 and 3.0 ps which carry nearly equal amplitudes. The opposite direction is faster (0.1 ps) and nearly single exponential. To determine the origin of the biphasic behavior of the trans form, a quantitative comparison of the cw-fluorescence of the trans form and the cis form was performed. This comparison led to the conclusion that only the 0.34 ps component contributes significantly to the fluorescence emission. A time resolved fluorescence study indeed showed that the longer component—though not completely absent—has a much weaker amplitude in the time resolved fluorescence experiment as compared to the absorption measurement.[4] The different signatures of the photodynamics of the trans form in the two spectroscopic techniques were attributed to the different radiative transitions predominantly detected by them:[6] the fluorescence experiment exclusively monitors the transition from the potential surface of the lowest excited state (nπ*) to that of the ground state S_0. For azobenzene the energy gap of this transition depends strongly on the nuclear coordinates and should strongly decrease when moving along the reaction coordinate out of the Franck−Condon range. Therefore, the motion of the photoisomerizing azobenzene has a large impact on the time resolved fluorescence spectra. Since the absorption cross sections between the S_0 and the nπ* surface are weak, the transient absorption signal is dominated by transition from the nπ* state to higher excited states. Strong excited-state absorption may happen all over the nπ* surface. Roughly speaking, the time dependence of the fluorescence emission monitors the motion of the excited molecule out of the Franck−Condon region, whereas the absorption signal reports this motion and the decay of the excited state. Apparently, in *trans*-azobenzene the motion out of the Franck−Condon range and the internal conversion to the ground state occur on different time scales; in the cis form such a partitioning of time scales does not exist.

SCHEME 1



In an attempt to investigate whether the biphasic behavior of the trans → cis direction is rather general for azobenzenes or a peculiarity of the azobenzene parent molecule, we investigated a push−pull substituted azobenzene. Here results of a joint femtosecond absorption and fluorescence study on 4-nitro-4′-(dimethylamino)azobenzene (NA, see structure in Scheme 1) are presented. Azobenzene substituted only by a dimethylamino group has already been studied by femtosecond absorption spectroscopy[7] and has been shown to undergo internal conver-

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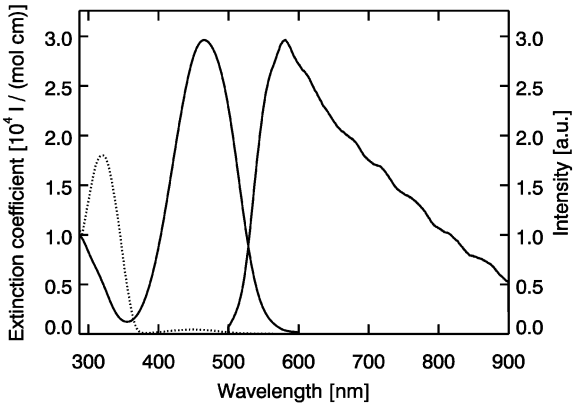

Figure 1. Steady-state absorption and emission spectra of *trans*-4-nitro-4′-(dimethylamino)azobenzene (NA) dissolved in toluene. The absorption spectrum of *trans*-azobenzene (dotted line) is included for comparison.

sion within ~1 ps. The time resolution of this study did not suffice to decide upon a biphasic behavior. The substitution pattern chosen here is expected to alter the electronic character and thereby the photodynamics more drastically than the above monosubstitution. The change of the electronic states becomes evident when comparing the absorption spectrum of NA with that of azobenzene (see Figure 1). Azobenzene has one weak electronic resonance in the visible at 440 nm which is attributed to an nπ^* excitation and stronger $\pi\pi^*$ transition in the UV around 310 nm (the spectroscopy of azobenzenes has been reviewed in ref 8). In NA these transitions nearly coincide and overlap with a charge transfer (CT) transition absent in azobenzene.[9] Even in a solvent with a polarity as moderate as benzene this CT transition dominates the visible spectrum.[9] The strong CT character of the visible transition of NA was also inferred from its resonance Raman spectrum.[10] A detailed analysis of this spectrum yielded the initial structural distortion of NA upon photoexcitation which is in line with a transition from a neutral to a zwitterionic form as shown in Scheme 1. The change of the electronic character also alters the ground-state kinetic properties. While the thermal isomerization of azobenzene occurs within hours, nitroaminoazobenzenes reform their trans isomer on the time scale of minutes or even milliseconds depending on the solvent polarity.[11]

In this paper we will (i) demonstrate the importance of a simultaneous application of femtosecond absorption and fluorescence techniques for the separation of excited- and ground-state dynamics in photoactive systems, (ii) present the influence of a strong push−pull substitution on the photoisomerization dynamics of azobenzene, and (iii) show that the biphasic nature of the reaction dynamics of *trans*-azobenzene is maintained also in push−pull substituted azobenzenes.

2. Experimental Section

The setup for femtosecond fluorescence experiments has been described before in detail in ref 12. In brief: The experiment is based on recording the fluorescence emission by a Kerr gate driven by femtosecond NIR pulses. Excitation pulses were generated from the output (~200 μJ) of a femtosecond laser/amplifier system (Clark CPA 2001 running at 775 nm with a repetition rate of 1 kHz) via a two-stage noncollinear optical parametric amplifier (NOPA) tuned to 480 nm. Compressed NOPA pulses with an energy of $\lesssim$1 μJ were focused onto the sample cell. The emission generated by this excitation was collected with reflective optics and imaged onto the Kerr medium (a fused silica plate) placed between two wire grid polarizers. The Kerr gate is operated by a femtosecond NIR laser pulse obtained from a two-stage optical parametric amplifier again pumped by a portion (250 μJ) of the amplifier output. Employing the NIR pulses at 1100 nm instead of the amplifier output has the advantage of opening the spectral region from 700 to 950 nm for fluorescence measurements and improving the temporal resolution. After passing the Kerr gate the fluorescence light is dispersed by a $f = 300$ nm spectrometer (Acton Research, Spectra Pro 300i) equipped with a 150 lines/mm grating blazed at 800 nm and detected with a liquid nitrogen cooled CCD camera (Princeton Instruments, Spec-10:400B). The recorded spectra were corrected for spectral sensitivity using a blackbody radiator as a reference. The duration of the instrumental response function of the setup is 130−150 fs (fwhm). The spectral dependence of time zero induced by the group velocity dispersion of the optical components was derived by recording the spectrotemporal behavior of a white light continuum generated at the sample location. When correcting for this dependence, the contribution of the solvent was added using tabulated values of the linear dispersion of the solvent. For the data presented here at every setting of the delay line the signal was accumulated for 5 s or 5000 laser shots; then signal traces of 20 scans of the delay line were averaged. To record steady-state fluorescence spectra this same setup was used where the gate pulses were blocked and the analyzer of the Kerr shutter turned to a parallel alignment.

The absorption experiments were performed using a setup based on a home-built Ti−sapphire laser chirped pulse amplifier (CPA) system operated at 800 nm.[13] A single-stage NOPA pumped by the Ti:Sa amplifier (1 kHz) provided excitation pulses at 490 nm. These pulses were compressed to a duration of 40 fs by a prism compressor and focused onto the sample cell (optical path length 1 mm). At the sample location the excitation light had a diameter of 50 μm and an energy of 0.5 μJ. For the probing of the induced absorption changes, a white light continuum was generated by focusing a small portion of the amplifier output onto a 2 mm sapphire plate monitoring the absorption changes. The white light was split into a probe and a reference beam which both crossed the excitation beam at the sample location. The reference pulses arrived at the sample prior to the excitation pulse; the arrival of the probe pulses was adjusted by a delay stage. Probe and reference pulses were detected by a multichannel setup allowing the simultaneous acquisition of the transient absorption in a spectral range from 470 to 730 nm with a resolution of 6 nm. The time resolution of the setup was determined by analyzing the coherent artifact of the neat solvents[14] to be 100 fs. This artifact, which is somewhat smaller than the actual signal, was properly scaled (considering the absorption of the solute) and subtracted from the raw signal to to obtain the pure response of the solute. For the data presented here at every delay setting the signals of 100 laser shots were accumulated and the results of three scans were averaged. For special absorption experiments with higher time resolution the white light probe setup was replaced by a single-stage NOPA identical to the one used in the pump branch. That NOPA was tuned to 650 nm, and its output was compressed to 28 fs (fwhm). For the NOPA/NOPA pump probe experiments 100 laser shots were accumulated and five scans were averaged. The temporal resolution of this experiment was better than 40 fs.

4-Nitro-4′-(dimethylamino)azobenzene was synthesized according to ref 15, purified by recrystallization, and characterized by NMR. Concentrations of NA in the toluene solutions were chosen to reach an optical density (OD) in the 1 mm sample

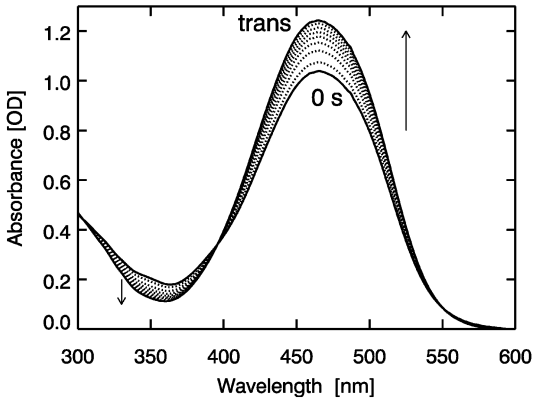

Figure 2. Absorption spectra of NA in toluene recorded after steady-state illumination at time intervals of 10 s indicating the reformation of the trans isomer.

cell of ~2 OD and ~1 OD for the fluorescence and the absorption experiments, respectively. Sample solutions were circulated rapidly through the sample cell to ensure a replacement of the sample after each laser shot. Large volumes of the sample solutions of ~10−100 mL were chosen to avoid accumulation of the cis photoproduct. (The cis isomer thermally reforms the trans isomer in ~70 s; therefore, the photostationary concentration of the cis isomer is negligible here.)

3. Results

3.1. Steady-State Spectroscopy. When the visible absorption band of NA in toluene peaking at 464 nm is excited with a NOPA pulse centered at 480 nm, a very weak fluorescence emission is recorded (Figure 1). The emission spectrum features a rather sharp rise to a maximum at 590 nm and a long tail extending to the NIR. Illumination of NA in toluene leads to a reduction of the absorption in the visible due to the cis formation (note that for azobenzene itself an increase of the visible absorption is observed). This reduction relaxes with a time constant of 70 s, the time constant of the cis → trans reaction (Figure 2).

3.2. Femtosecond Fluorescence Spectroscopy. An overview of the fluorescence spectra recorded as a function of time is given in Figure 3a. As expected for a chromophore with a small fluorescence quantum yield, the fluorescence of NA decays very fast, within less than a few hundred femtoseconds (Figure 3). A closer inspection of this decay at two wavelengths (Figure 3b) shows the emission dynamics depends on the detection wavelength. At the blue edge of the emission spectrum (530 nm) the time trace is nearly symmetric, indicating that the fluorescence decay time is on the order of or below the instrumental response time which is equal to 150 fs (fwhm). In the red wing of the emission (800 nm) a significantly slower decay with a characteristic time of ~1 ps is observed. This wavelength dependence of the fluorescence lifetime is equivalent to a change of the emission spectra with time (Figure 3c). Immediately after photoexcitation the emission spectrum features the sharp peak also present in the steady-state spectrum (broken curve). However, the tail in the NIR is by far less pronounced. As the spectrum with the sharp peak decreases in amplitude, a very broad spectrum centered around 700 nm emerges which then decays in ~1 ps, thereby retaining its shape. This biphasic decay of the fluorescence emission is the origin of the peculiar shape of the cw spectrum of NA (see Figure 3c). The peak stems from a strongly emitting but very short lived species, and the tail is caused by the weak but longer lived emission centered at 700 nm. Prior to a numerical analysis of these results, a note

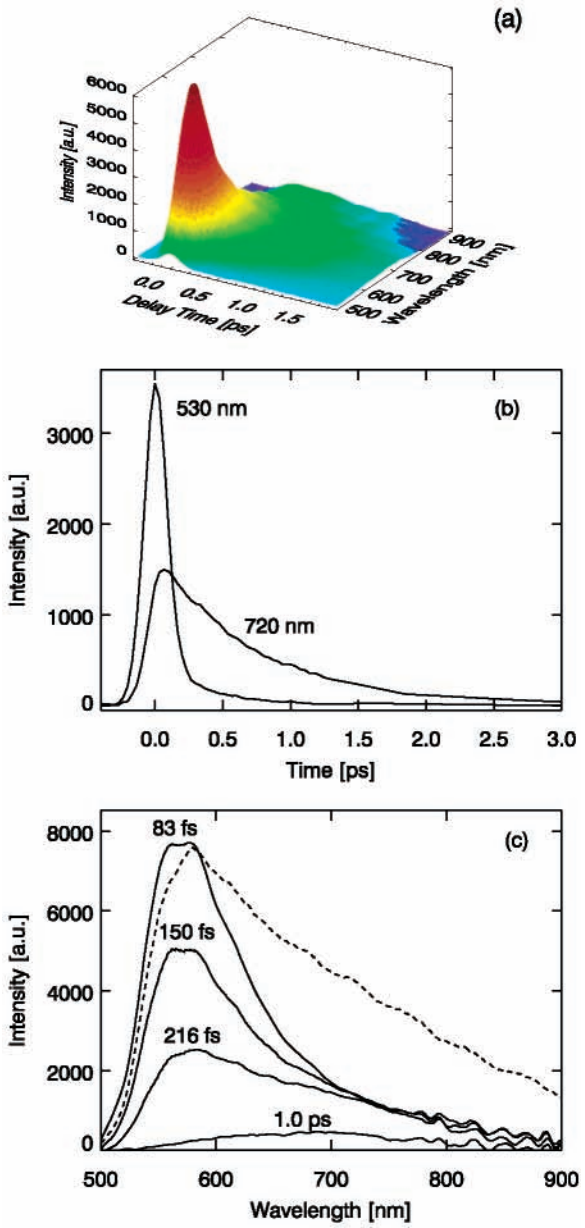

Figure 3. Time resolved fluorescence spectra of NA in toluene. (a) Overview. (b) Time traces at different wavelengths. (c) Time-dependent spectra at the delay times given in the figure. The steady-state fluorescence spectrum is plotted as a dashed line.

concerning inner filter effects is in place. The fluorescence light which is generated close to the front window of the sample cell has to pass that cell before it is detected. Thereby, it could be attenuated by either the static absorption of the sample (static inner filter) or its transient absorption (dynamic inner filter). The shape of the fluorescence spectrum does not change upon dilution; therefore, the static inner filter effect is not of importance here. As will be shown in the next section, the fluorescence emission overlaps spectrally with a transient absorption band which might distort the fluorescence signal (dynamic inner filter). However, by normalizing the fluorescence experiments to the excitation conditions of the absorption experiments, it can be shown that this effect does not surmount 10%. Therefore, considerations of dynamic inner filter effects will be disregarded in the discussion of the fluorescence decay.

To extract dynamic parameters on the fluorescence decay, the data were fitted globally using a multiexponential trial function convoluted with a Gaussian. The Gaussian represents

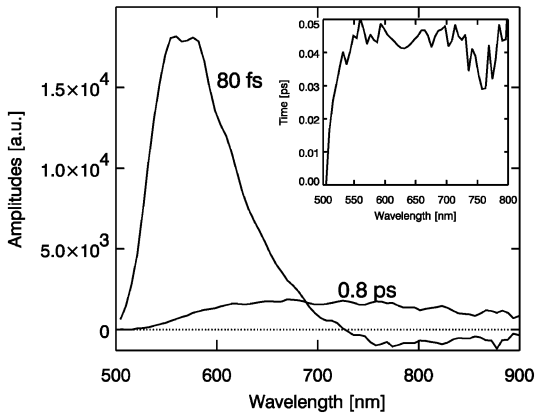

Figure 4. Decay associated spectra obtained by global analysis of the time resolved fluorescene data presented in Figure 3. The insert gives the time dependence of the "numerical" delay zero.

the experimental response function; its width was determined in an independent experiment on β-carotene to be 150 fs (fwhm). The decay traces at all wavelengths >550 nm are nicely reproduced by a biexponential trial function using two time constants. At the blue edge of the emission spectrum (λ < 550 nm) the global fit was only successful if the delay zero was treated as a free-fitting parameter (insert in Figure 4). This time zero shift is attributed to a molecular process occurring on a time scale of ~50 fs which is not accounted for in further discussion since its dynamics are faster than the instrumental response function of the emission experiment. The global fit yielded time constants of 80 fs and 0.8 ps. Most of the emission intensity decays with the 80 fs component, its amplitude being ~10 times higher than that of the 0.8 ps component. The spectrum associated with the 80 fs time peaks at 570 nm and features the sharp maximum around time zero in the time resolved spectra. Beyond 700 nm the spectrum of the 80 fs component is negative, indicating a delayed rise of the long-wavelength emission. The signal that emerges during that rise is strongly red shifted as compared to the 80 fs spectrum and extends to 900 nm. The decay of this spectral signature with a time constant of 0.8 ps terminates the emission of NA in toluene.

3.3. Femtosecond Absorption Spectroscopy. The results of the femtosecond absorption experiments on NA covering a broad spectral region from 470 to 730 nm are depicted in Figure 5a. The time resolution in these experiments (fwhm of the cross-correlation function) was equal to 100 fs. Immediately after photoexcitation at 490 nm the bleach of the ground-state absorption results in a negative difference absorption (bleach of the NA absorption) for wavelengths smaller than 530 nm. Toward longer wavelength a positive difference absorption spectrum is detected with a maximum at 650 nm and a shoulder at 580 nm. This transient absorption signal decays on the picosecond time scale, leaving a tiny offset at long delay times. In a second set of experiments the rise of the transient absorption is investigated at 645 nm (solid curve in Figure 5b). In these experiments the time resolution (fwhm of the cross correlation function) was equal to 37 fs. The rise of the transient absorption of NA is fast but slower than the experimental limit, which is represented by the convolution of the correlation function with an instantaneous rise (broken curve). A control experiment on the stimulated emission of the laser dye rhodamine 6G reproduces qualitatively the broken curve (data not shown). Apparently the signal rise in NA is delayed relative to the instantaneous response; i.e., a molecular relaxation process with

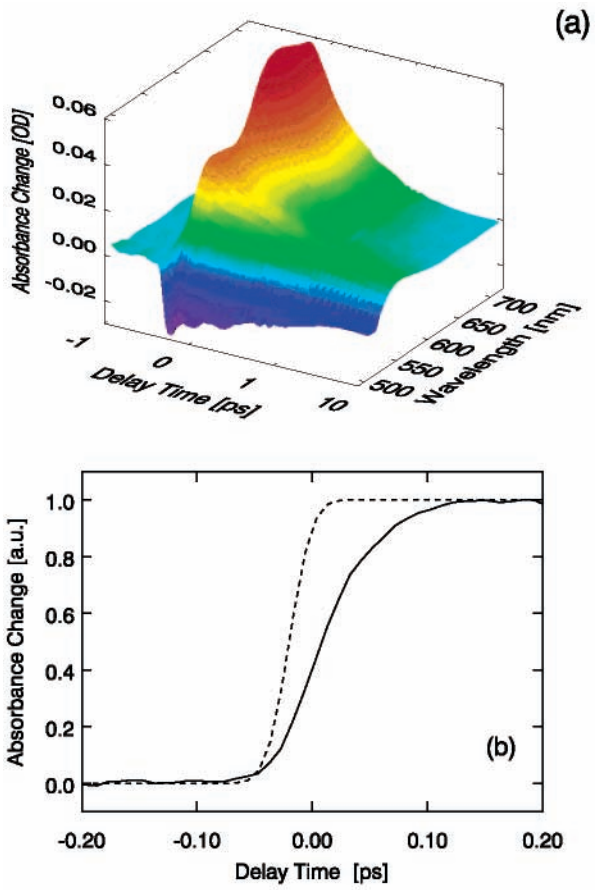

Figure 5. Transient absorption measurements on NA in toluene. (a) Overview. (b) Rise behavior of the transient absorption of NA at 645 nm (solid line) in comparison with the experimental rise determined from the measured cross correlation function (dashed line).

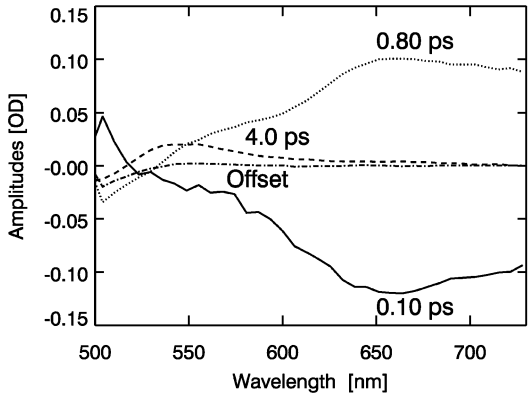

Figure 6. Decay associated spectra derived from the toluene absorption data. The corresponding time constants are given in the figure.

a fast time constant of 70 fs exists (obtained by fitting the time trace in Figure 5b) and determines the buildup of the absorption at 645 nm.

This delayed rise is more difficult to identify in the transient absorption spectra due to the limited time resolution of this experiment. A global fit procedure exerted on the transient spectra, however, recovers a time constant of the same order (100 fs versus the 70 fs determined above). The resulting decay associated spectra are depicted in Figure 6; the respective time constants are 100 fs, 0.8 ps, 4 ps, and infinity. The shortest time constant of ~100 fs is related to a negative difference spectrum representing the delayed rise of the long-wavelength absorption. The dominant part of the positive signal (increased

absorption) decays within ~0.8 ps. This decay is accompanied by a partial recovery of the ground-state absorption spectrum. The remaining part of the signal decays in some picoseconds (4 ps) and changes sign around 520 nm. A very small offset (absorption changes at late times) follows the steady state cis−trans difference spectrum.

4. Discussion

The most prominent experimental observations are the following: (i) Fluorescence emission has a strong contribution decaying with $\tau = 100$ fs. (ii) This fluorescence emission is strongly red shifted and shows a narrow peak at 575 nm. (iii) A weaker emission at still longer wavelengths (broad peak at 700 nm) decays with $\tau = 0.8$ ps. (iv) The transient absorption changes display the same time constants. (v) The longer time constant is related to the decay of strong absorption changes. (vi) The short time constant is mainly connected with the rise of absorption changes.

We now want to present a molecular model which is able to describe the experimental observations. The existence of fluorescence emission decaying with the two time constants of 100 fs and 0.8 ps indicates that these processes must be connected to reactions in the excited electronic state or to internal conversion to the ground state. A very striking feature which has to be explained first is the strong red shifted fluorescence spectrum of NA observed immediately after photoexcitation (Figure 3) peaking at 575 nm. The peak wavelength corresponds to a Stokes shift $\Delta\nu_s$ of 4200 cm^{-1}. This Stokes shift between absorption and fluorescence should be related to the reorganization energy λ associated with the optical transition. If the excited-state lifetime is longer than the vibrational and solvent relaxation times, the shift $\Delta\nu_s$ should be equal to 2λ. A resonance Raman study on NA in benzene[9] yielded a total reorganization energy of 2429 cm^{-1}. This energy was partitioned into a high-frequency intramolecular contribution λ_v of 1004 cm^{-1} and a solvent portion λ_s of 1425 cm^{-1}. The solvent reorganization energy λ_s was subdivided into a fast inertial part λ_i of 630 cm^{-1} and slow diffusive part λ_r of 795 cm^{-1}. The Stokes shift $\Delta\nu_s$ observed here corresponds to an effective reorganization energy of 2100 cm^{-1}, which indicates that the relaxation of the high-frequency contribution λ_v and of a major part of the solvent contribution λ_s has occurred within the instrumental response time of the femtosecond experiment, i.e., within ~100 fs. A residual dynamic signature of the buildup of the Stokes shift is the time dependence of delay zero depicted in Figure 4, insert, which is equivalent to a red shift of the early emission spectrum with time. This red shift presumably stems from the slower contributions to the solvent reorganization energy. An analysis of this dynamic Stokes shift is not possible since its initial parts are extremely fast and since the slower parts are truncated by the decay of the emission after 100 fs. These observations are in line with the resonance Raman results. The distortions of NA upon photoexcitation derived from this Raman study can be completely assigned to the transition from the neutral form of NA to the zwitterionic structure (see Scheme 1); no signature of a distortion due to the trans → cis isomerization was detected.

The onset of this isomerization may be connected to the ~100 fs decay of the intense fluorescence signal centered around 575 nm. This decay is most likely not associated with a transition between different excited states. As shown by analysis of the absorption spectrum of NA,[9] the primarily excited state (the CT state) is lowest in energy; thus a transition between this state and for instance the nπ^* state cannot occur. We, therefore, assign this decay to a large amplitude motion on the excited-state surface along the isomerization coordinate. This motion brings the excited molecule closer to a conical intersection with the ground state. This 100 fs process is not associated with the decay of the excited state: The disappearance of the intense emission around 575 nm goes along with the rise of a weak and broad emission spectrum at 700 nm which demonstrates that NA is still in its excited state after the 100 fs process. A partial decay to the electronic ground state with 100 fs is excluded by the absorption experiments. The time traces in the spectral region of the ground-state absorption lack the 100 fs contribution (see Figure 6); i.e., the ground state is not partially recovered with 100 fs. The strong decrease of the emission intensity within 100 fs is thus not a consequence of the depletion of the excited state but is due to the change (decrease) of the emission probability. The ground-state absorption only recovers with a time constant of 0.8 ps as can be seen from the transient absorption traces in Figure 5. The broad emission spectrum associated with the 0.8 ps might be an indication that the localized vibrational wave packet generated by the photoexcitation gets spread over the potential energy surface and does not immediately find the conical intersection to the ground state.

From the transient absorption data we learn that optical excitation initially populates a state, which shows very small absorption changes. It is only with the decay of this state (within 80−100 fs) that the strong transient absorption of the excited state (see Figure 5) is built up. Apparently the molecular configuration of NA is changed with the 100 fs process in a way to yield the broad increased absorption between 550 and 750 nm. The molecule has moved along the reaction coordinate away from the Franck−Condon region.

The strong excited-state absorption decays with the 0.8 ps time constant. Very little absorption change is left afterward. Thus the absorption of the ground-state NA molecules is essentially reformed. This observation together with the transient fluorescence emission signal clearly proves that the 0.8 ps process is connected to the decay of the excited state and the formation of a ground-state molecule (in the cis or the initial trans form). The subsequent 4 ps dynamic process has a spectral signature—absorption decrease on the long-wavelength side of the NA absorption and an increase toward the absorption peak—indicative for vibrational cooling. This behavior is well expected since most of the excitation energy is still stored in the vibrations of the NA molecule. The time scale for this cooling process is typical for molecules of that size[16] and is comparable with values obtained for azobenzene (see below).[2] The weak absorbance change remaining at later delay times shows the signature for the formation of *cis*-NA and can be assigned to the isomerized molecules.

The absorption dynamics of NA are surprisingly similar to those of the parent molecule azobenzene. Differences originate mainly from the changed character of the initially excited state: an nπ^* character for azobenzene and a CT character for NA. Transient absorption measurements on *trans*-azobenzene in ethanol yielded biphasic time traces for the excited-state dynamics with time constants of 0.32 and 2 ps.[2] This compares with the values of 0.1 and 0.8 ps reported here; i.e., a moderate acceleration is observed in NA. The femtosecond fluorescence signatures are again very similar. The *trans*-azobenzene fluorescence decay (in hexane) can be described biexponentially.[4] A fast 200 fs component carries most of the amplitude and is most dominant in the blue part of the fluorescence spectrum. When moving to the red a longer lived contribution gains some amplitude. This—apart from the numerical values of the time

constants—exactly mirrors the temporal behavior found in NA. Thus the interpretation put forward for the behavior of fluorescence of azobenzene also seems to apply to NA. After photoexcitation a steep slope of the excited-state surface drives the vibrational wave packet out of the Franck−Condon vicinity. This movement occurring in ∼100 fs in NA reduces the fluorescence emission probability drastically. After that rapid initial motion the wave packet "meanders" on the excited-state surface searching of the conical intersection to the ground state, resulting in a strongly red shifted and broad emission. The internal conversion to the ground state in ∼0.8 ps partially replenishes the trans ground state and forms the cis isomer. The cooling of these nascent ground states seems to be somewhat faster in NA than in azobenzene, for which values of 12 ps in DMSO[6] and ∼10 ps in ethanol[2] were reported. The faster cooling rate can be attributed to the polar character of NA which might increase the solute solvent coupling and the larger number of degrees of freedom due to the dimethylamino group and the nitro group.

In conclusion, the combination of femtosecond fluorescence and absorption techniques allowed obtaining a detailed picture of the excited-state dynamics of 4-nitro-4′-(dimethylamino)-azobenzene. Three stages could be separated: (i) Inter- and intramolecular modes adapt extremely rapidly (<100 fs) to the new charge distribution caused by the CT excitation. (ii) Within 100 fs a large amplitude motion on the excited-state potential away from the Franck−Condon region takes place. (iii) A "search" of the conical intersection to the ground state taking ∼1 ps terminates the excited-state dynamics. The last two stages are very similar to what is observed in the parent compound azobenzene, indicating that a push−pull substitution of azobenzene has little impact on the photoisomerization dynamics. Based on the spectroscopic results presented here, a distinction between an inversion or rotation mechanism is not possible yet. However, the detailed time resolved fluorescence data should be much more accessible to a comparison with quantum chemical calculations than absorption data, since only the ground-state surface and *one* excited-state surface have to be determined.

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