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Relaxation in the Triplet Manifold of 1-Nitronaphthalene Observed by Transient Absorption Spectroscopy

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Previous phosphorescence and triplet quantum yield determinations indicate that the primary photophysical channel for 1-nitronaphthalene is the formation of its lowest energy triplet state. Also, previous direct measurements of the decay of the fluorescence from this compound indicated that the crossing between the singlet and triplet manifolds is ultrafast (sub-100 fs). In this contribution we present a sub-picosecond transient absorption study of the relaxation of photoexcited 1-nitronaphthalene in methanol and other solvents. Our measurements reveal the time scale in which the fully relaxed T_1 state is formed. We have observed that the spectral evolution associated with this process takes place in time scales from one to a few tens of picoseconds. Specifically, the appearance of the absorption spectrum of T_1 in the visible region is accompanied by the decay of transient signals at wavelengths below 400 nm. Since the fluorescence lifetime of this compound is sub-100 fs, we assigned the picoseconds decaying signals below 400 nm to an intermediate triplet state which acts as a receiver state in the intersystem crossing step and from which the T_1 population accumulates. From the details of the spectral evolution and the effects of different solvents, we also conclude that T_1 formation and vibrational cooling within this state occur in similar time scales of between 1 and 16 ps. Mainly, our results provide direct evidence in support of the participation of an upper triplet state in the mechanism for intersystem crossing in this molecule. This is considered to be common in the photophysics of several nitrated polycyclic aromatic compounds and the most determinant feature of their primary photochemistry.

Introduction

The presence of nonbonding orbitals in some substituted aromatic hydrocarbons implies the existence of upper excited states which, in several cases, substantially increase the coupling between the singlet and triplet manifolds.[1−7] As observed for example in aromatic carbonylic compounds, this has consequences in the dynamics of the S_1 states, making them short-lived due to intersystem crossing channels which become highly efficient when singlet and upper triplet states have similar energies and appropriate electronic configurations.[7−9]

In particular, the participation of upper n−π* triplets in such a role of "receiver" or intermediary states for intersystem crossing in polycyclic nitrated aromatic compounds has been suggested from the first photochemical studies on 9-nitroanthracene by Hamanoue and co-workers to explain the lack of fluorescence and the high triplet yield of this molecule.[1,2,10] More specifically, for 1-nitronaphthalene (1-NN), the early CNDO-CI calculations of Mikula et al. also indicated the existence of such type of triplet with an appropriate electronic configuration to interact through spin orbit coupling with the S_1 (π−π*) singlet of this molecule.[3]

Recently, our group made a series of direct measurements of the first singlet excited-state lifetimes of several polycyclic nitroaromatic compounds through femtosecond-resolved fluorescence techniques. Our experiments isolated and time-resolved for the first time signals from their weakly emissive singlets.[11] Those results showed that the fluorescence depletion rates are extremely large with lifetimes in the sub-picosecond and few picoseconds time scale (consistently, these compounds had been previously cataloged as "nonfluorescent"[1,2]). Besides this, more recent TD-DFT calculations on the excited states of 1-NN supported the existence of an upper triplet state with a partial n−π* character, just a few hundreds of an eV below the S_1 state.[5]

In this contribution we present a transient absorption study on 1-NN which complements our previous fluorescence experiments and allows the direct observation of the relaxation of the excited-state population within the triplet manifold. This can be done thanks to the rapid accumulation of population in the state which couples directly with the optically excited singlet in this particular molecule. Our measurements reveal the transient absorption spectral evolution leading to the system ending up in the fully relaxed first triplet excited-state T_1. We have studied 1-NN in a variety of polar and nonpolar solvents in order to determine the influence of the solvation shells in the observed triplet relaxation dynamics.

Experimental Section

Our transient absorption spectrometer is based on a chirped pulse, regeneratively amplified femtosecond laser system which produces a 1 kHz train of approximately 150 fs, 0.3 mJ pulses, centered at 800 nm. Excitation light at 400 nm was generated in a 0.5 mm β-BBO crystal and separated from the remaining fundamental with a dichroic mirror (CVI). After passing through a half-wave plate to adjust for magic angle conditions, the excitation pulses were focused at the sample with a 15 cm fused silica lens. In order to reduce the excitation intensity, the sample was placed about 6 cm in front of the focal point so that the beam diameter at the sample was 0.8 mm as measured by the knife-edge method. A portion of the fundamental was used to

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produce a white light continuum either in a 1 cm path-length quartz cell filled with water or in a 1 mm Z-cut sapphire plate. For experiments measuring transient absorbance at wavelengths below 400 nm, the probe pulses were formed by second harmonic generation of a section of a continuum between 760 and 780 nm. In these cases, a half-wave plate was placed before the continuum generation in order to maintain magic angle alignment due to the type I wave mixing at the β-BBO crystal used to generate 380 to 390 nm light. The probe beam was sent through a delay stage before it was focused at the sample to a beam radius of between 20 and 200 μm. The relative spot sizes of the pump and the probe beams ensured that the focused probe light was homogeneously overlapped with the excitation pulses for the full spectral range of our experiment (see Results and Discussion).

The solutions were circulated either in a 1 mm path length quartz flow cell or in a free flowing jet with an optical path of 0.45 ± 0.05 mm. For both these methods to handle the sample, we found consistent results. After traveling through the sample, the probe beam was focused on the entrance slit of a 10 cm double monochromator and detected with a silicon photodiode or a photomultiplier tube connected to a lock-in amplifier (Stanford Research Systems). The amplifier was referenced to a phase-locked optical chopper (New Focus) which synchronously blocked two of every three excitation pulses. The pulse energy for the experiments in most solvents was 70 μJ to 85 μJ, except for benzene, where the pulse energy was reduced with the aid of neutral density filters to 25 μJ or less, in order to minimize the two-photon excitation of the solvent.

At most wavelengths, the signal around $t = 0$ is obscured by signals from the coherent interaction between the pump and probe pulses (coherent spike). This effect is mainly due to cross-phase modulation in the solvent and the flow-cell walls,[12,13] as verified by back to back experiments performed for every single wavelength where the sample was replaced by the solvent alone. The analysis of the transient absorption traces did not include the time interval where the solvent-only experiments showed these modulations: In methanol this effect influenced typically the −300 to 300 fs time interval (corresponds to the time range where the solvent alone signals have not fully recovered to the baseline). In benzene we observed that it takes even longer times for these modulations to be fully over (up to 0.7 ps above $t = 0$).

Transient absorption spectra at long delay times (150 ps) were obtained by scanning the monocromator's wavelength at a fixed delay position while measuring the transmission change at the sample.[14] With the 150 ps spectra, it was possible to scale the relative ΔOD signals of single-wavelength time scans to correct for small changes in excitation energy and alignment conditions which occur from day to day. It should be noted that these transient spectra were acquired at delay times where the transients have completely ceased to evolve, and therefore corrections for the white light dispersion are unnecessary.[14] The spectral precision of this method was verified by checking that the transient absorption spectrum of the T_1 state of 1-NN taken at 150 ps was accurately reproduced from previous measurements in the nanosecond time scale (see Results and Discussion).[3,15−17]

1-NN was purchased from Aldrich and recrystallized from methanol before use. HPLC grade methanol, CCl_4, $CHCl_3$, $CDCl_3$, and anhydrous benzene were purchased from Aldrich and used as received. All experiments were made at room temperature (20 ± 1 °C) under aerated conditions. The 1-NN concentrations were adjusted to have an optical absorption of 1.5 or 0.4 in a 1 mm path length at the excitation wavelength for probe wavelengths above and below 400 nm, respectively.

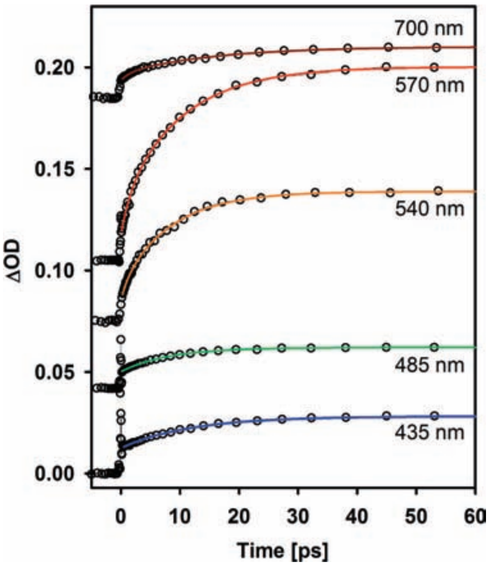


Figure 1. Transient absorption results for 1-nitronaphthalene in methanol at several wavelengths in the visible region. Colored solid lines indicate fits to single- (λ < 515 nm) or double ($\lambda \geq$ 515 nm)-rising terms to a constant level. The fast features at $t = 0$ are due to the coherent interaction between the pump and probe pulses and are not included in the data analysis.

Results and Discussion

Our previous up-conversion measurements on 1-NN in diverse solvents showed that for excitation in the first electronic band, the fluorescence lifetime of this compound is extremely short, of less than 100 fs.[5,11] This rapid S_1 decay is considered to be mainly determined by a highly efficient intersystem crossing since the yield for triplet formation has been estimated at about 0.63.[18,19] Moreover, it has been suggested that upon some considerations for the data analysis, the actual yield might approach unity.[16] Taking into account the results of the TD-DFT and previous CNDO-CI calculations already mentioned, the rapid fluorescence decay is consistent with the coupling to a particular upper triplet state that is nearly isoenergetic with the first singlet, and which also has a partial n−π* character.[3,5] The previous up-conversion results simplify the interpretation of the present transient absorption experiments since they isolated the dynamics of the originally excited-state, indicating that it disappears within the first 100 fs, which is below the instrumental resolution for the present transient absorption experiments.

Figure 1 shows a set of transient absorption measurements as a function of time for methanol solutions of 1-NN (visible wavelengths). As can be seen, the transient signals in this region appear within the time resolution of our experiments and are followed by an additional rise to a constant level (420 to 700 nm). For wavelengths from 420 to 500 nm, the increase in absorbance is accurately described by a single-exponential rise to a constant. The time constants in this spectral interval go from 11.6 ps at 420 nm to 6.6 ps at 500 nm. For the spectral region above 500 nm, the traces are clearly better described by two rising terms to a constant level since we observed up to a factor of 10 improvement in the root mean squared error of the fits in going from one to two exponential terms. Such differences between single- and double-exponential fits are emphasized in Figure 2 (experiment with a jet) and in the Supporting

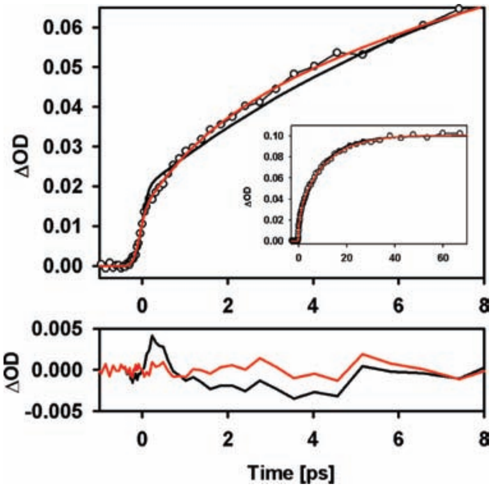


Figure 2. Transient absorption trace for 1-nitronaphthalene in methanol for a probe wavelength of 590 nm. The black and red solid lines indicate, respectively, fits to single- or double-exponential rising terms to a constant level convoluted with a Gaussian instrument response time of 280 fs. This trace was taken with a free flowing jet where, at this particular wavelength, the solvent-alone modulations near $t = 0$ are practically absent. The inset shows the same data in a larger time interval. The lower graph shows the differences between the fits and the data points for the respective functions.

Information (experiment with a flow-cell), where we show the trace at the center of the main band in the visible region (590 nm, see below). The graph includes nonlinear least-squares fits to both types of functions. In this region (515−700 nm), the first rise occurs with a time constant of around 1.5 ps and is followed by a slower signal increment with time constants between 8.4 ps at 540 nm and 15.7 ps at 700 nm.

For the 1-NN/methanol system we also performed transient absorption measurements at three wavelengths below 400 nm, and the results are included in Figure 3. For this region, at 390 nm we observed a decay in the early part of the trace which is followed by an increase in the absorbance. At 385 nm, we observed a single-exponential decay while for the 380 nm experiments, the transient signal undergoes a biexponential decay to a constant level. At 390 nm, the time constant for the decaying exponential term is 2.5 ps, and the signal increase is due to a term with a 10.7 ps time constant. The single decay at 385 nm has a time constant of 3.7 ps, and for the 380 nm traces, the biexponential decay has time constants of 3 and 9.9 ps, respectively. In this spectral region, it is clear that the ~10 ps contribution goes from positive (decay) to negative (rise) at precisely 385 nm, which translates into an apparent isosbestic behavior for times above a few picoseconds. This last explains the fairly good description of the data at 385 nm with a single-exponential decay function to a constant level.

Table 1 contains a sample of the time constants and amplitudes across the spectrum, and the full set of parameters is included in the Supporting Information. It should be noted that although global fitting was attempted to describe the traces with fewer parameters (obtaining global time constants), using a fitting procedure with all freely varying parameters gives a significant improvement, with 1 order of magnitude better root mean squared error for several of the wavelengths. As we detail below, we consider that this is due to the fact that together with the overall increase of the absorbance in the visible region, the broad central band at 590 nm (see below), appears to undergo some changes in its width and shape in multiple time scales, the accounting of which requires freely varying parameters in the fits.

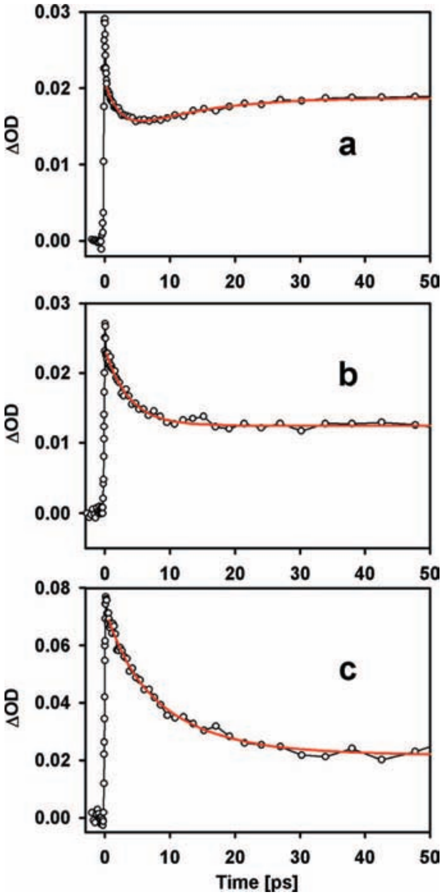


Figure 3. Transient absorption results for 1-nitronaphthalene in methanol for probe wavelengths of (a) 390 nm, (b) 385 nm, and (c) 380 nm. The red solid lines correspond to fits to double- and single-exponential functions plus a constant term; see text. The fast features at $t = 0$ are due to the coherent interaction between the pump and probe pulses and are not considered for the fits.

TABLE 1: Curve-Fitting Parameters for Some Selected Transient Absorption Traces of 1-Nitronaphthalene in Various Solvents[a]

solvent	λ_{det} [nm]	a	b [ps]	c	d [ps]	e
methanol	380	0.011	3.0	0.04	9.9	0.022
methanol	385	0.011	3.7	–	–	0.012
methanol	390	0.009	2.5	−0.007	10.7	0.019
methanol	435	–	–	−0.016	11.8	0.028
methanol	540	−0.007	1.1	−0.046	8.4	0.064
methanol	590	−0.018	1.1	−0.071	11.5	0.101
methanol	700	−0.003	1.5	−0.013	15.7	0.025
benzene	420	–	–	−0.006	10.4	0.009
benzene	540	−0.005	2.0	−0.012	11.1	0.018
benzene	700	–	–	−0.002	8.8	0.005
$CHCl_3$	540	−0.002	2.0	−0.010	9.7	0.014
$CDCl_3$	540	−0.003	2.3	−0.008	10.6	0.013
CCl_4	540	−0.002	1.3	−0.011	10.7	0.015

[a] The data are described by two-exponential functions plus a constant term (fitting function: $a \exp(-t/b) + c \exp(-t/d) + e$) or in some cases, by one-exponential functions plus a constant term (fitting function: $c \exp(-t/d) + e$); see text. Data for 1NN/MeOH in the 420 to 700 nm range as well as all acquired data for 1NN/benzene has been scaled with the transient absorption spectra obtained at long delay times.

A sample of the transient data for benzene solutions of 1-NN in the visible region is included in Figure 4. For this solvent, wavelengths from 540 to 600 nm required fits to a double-exponential rise to a constant while in the rest of the spectrum

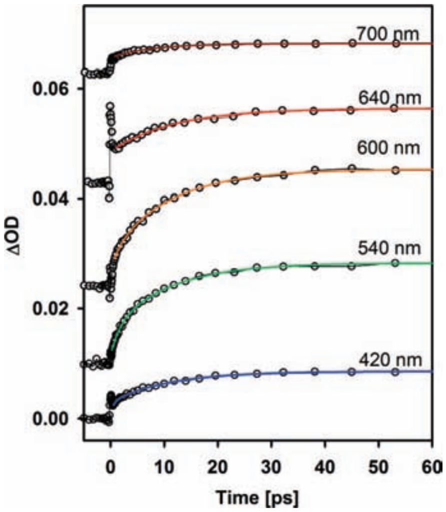


Figure 4. Transient absorption results for 1-nitronaphthalene in benzene at several wavelengths in the visible region. Colored solid lines indicate fits to single- or double (540 and 600 nm)-exponential rising terms to a constant level. The fast features at $t = 0$ are due to the coherent interaction between the pump and probe pulses and are not included in the data analysis.

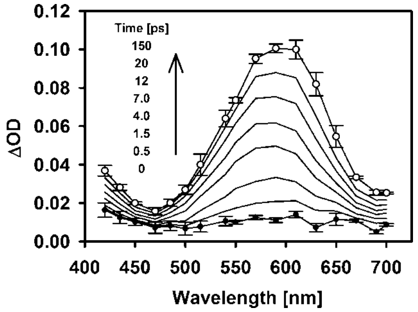


Figure 5. Transient absorption spectral evolution of methanol solutions of 1-nitronaphthalene in the visible region from 0 ps (black circles) to 150 ps (empty circles). The error bars at 150 ps correspond to ±1 standard deviation calculated from three independent measurements of the transient spectrum. The $t = 0$ spectrum has been estimated from an extrapolation of the fits to single-wavelength traces. Here, the error bars consider errors from the individual time scans at times near zero.

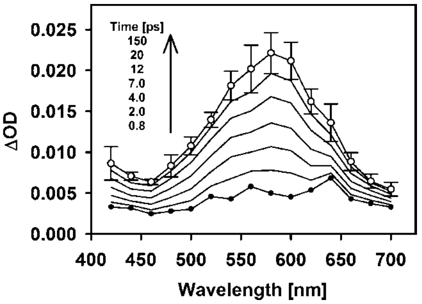


Figure 6. Transient absorption spectral evolution of benzene solutions of 1-nitronaphthalene in the visible region from 0.8 ps (black circles) to 150 ps (empty circles). The error bars at 150 ps correspond to ±1 standard deviation calculated from four independent measurements of the transient spectrum.

no significant improvement was seen when going from one to two exponentials. For this system, similar time constants describe the absorption increments in the visible region in comparison with the methanol case (see Table 1 and Supporting Information).

Figures 5 and 6 show the spectral evolution in the visible region for 1-NN in methanol and benzene solutions, respectively. For times longer than about 50 ps, the transient absorption has ceased to evolve, leaving a constant signal level in the entire spectral region. The spectra at long times (see 150 ps) match very well with the absorption spectra of the phosphorescent triplet state of 1-NN, which has been measured by several researchers in nanosecond experiments.[3,15,17] Since for both solvents at wavelengths above 400 nm the transient absorption increases with time, it can be concluded that the final state (phosphorescent T_1 state) has a larger absorption coefficient than its precursor in this spectral region.

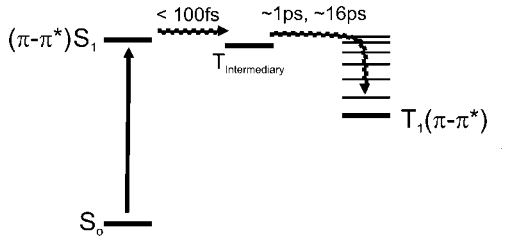
Considering that our previous up-conversion results show that the initially excited singlet state decays with a 60 ± 10 fs time constant,[5] the ~1 to ~16 ps growth of the fully relaxed T_1 state, together with the decay seen at wavelengths below 400 nm indicate that the phosphorescent state accumulates from an upper vibronic state in the triplet manifold which is the one that directly couples with the vertically excited singlet, thereby acting as an intermediary between the fluorescent state (lifetime <100 fs) and the final phosphorescent triplet of $\pi-\pi^*$ character.[3,18,19] Our fitting procedure at the different wavelengths allows an estimate of the visible spectrum of this state (preceding the $t >$ 1 ps signal evolution in the visible region). This spectrum was obtained by setting the time in the single- or double-exponential terms to zero in the fitting functions. Note that this does not necessarily correspond to the signal near $t = 0$ which is masked by the coherent spike at most wavelengths. Rather, it is the estimated spectrum of the intermediary before any of the picosecond-scale spectral evolution from extrapolation of the exponential fits. We only performed this exercise for 1-NN/methanol where we have a better signal-to-noise ratio.

As can be seen in Figure 5, the $t = 0$ spectrum is appreciably different from the one at long times. It is significantly broad and featureless in this region, and in particular, the absorbance from 450 to 700 nm is smaller than at 420−430 nm (contrary to the T_1 spectrum at 150 ps). The signals observed below 400 nm are also indicative of the depletion of the intermediate state, as the time scales for the decays in that region roughly match the time constants for the signal accumulation times observed in the visible region. As can be inferred from the spectral evolution, transients below 400 nm clearly point out that the absorption coefficients of both the S_1-coupled intermediary state and T_1 become comparable on this short wavelength range. In addition, the absence of negative signals due to the S_0 bleaching at these wavelengths indicates the predominance of the molar absorption coefficients of the triplet states (the ground-state absorption gradually increases for wavelengths below 400 nm; see ref 5).

In spite of the matching between time constants, from the observation of the wavelength-dependent double-exponential dynamics, it is clear that the accumulation of transient absorption in the visible region does not obey simple one-to-one kinetics from the intermediate state. Instead, the overall spectral evolution occurs in multiple time scales and is completed in a few tens of picoseconds. As we further discuss below, we consider that this is due to the fact that in the formation of the fully relaxed T_1 state, the system actually needs to transit through a series of upper vibronic states.

It is important to mention that for our excitation wavelength at the red edge of the first absorption band (excitation energy: 3.099 eV), the system has an excess energy of about 0.719 eV with respect to the T_1 state of which the first phosphorescence band (0−0 transition) is at about 19 200 cm^{-1} (2.38 eV) in ethanol.[3,19] Also, our previous TD-DFT calculations showed that

SCHEME 1: Diagram of the Primary Photoprocesses in 1-Nitronaphthalene[a]



[a] The sub-100 fs decay of the initially excited singlet state is concluded from previous fluorescence up-conversion experiments, and the picoseconds accumulation of the T_1 state is observed in the present transient absorption experiments.

there is a near 1 eV difference between the calculated S_1 energy (3.3279 eV) and the calculated T_1 energy (2.3326 eV) in methanol.[5] Therefore, as the system transits from the initially excited singlet to the state to which it couples (intermediary state) and down to the fully relaxed T_1 state, this energy must be released to the solvent, a process known to occur in the picoseconds time scale.[20,21] A simplified diagram of the overall process is included in Scheme 1. Further evidence of such cooling comes from the observed spectral reshaping implied by the different time constants at different wavelengths. In effect, a narrowing of the main band centered at 590 nm is evident, where in methanol, the width goes from 4900 cm^{-1} at 1 ps to only 3780 cm^{-1} at 150 ps. According to these observations, the visible-region spectra (shown in Figures 5 and 6) at intermediate times should correspond to the overlap of the spectrum of relaxed T_1 molecules with that of its precursor and also including other upper vibrationally hot intermediaries transited by the system as it progresses downward in energy due to the interactions with the solvent (vibrational cooling).

Taking into account the aforementioned relative energies, the T_1 formation dynamics should have a vibrational cooling component; therefore, we further investigated the influence of the solvent environment in the signal growth at 540 nm. We picked this wavelength because it is off center of the main T_1 band where the effects of vibrational relaxation are frequently large due to band narrowing and/or blue-shifting of the band.[20−25] Results are included in Figure 7. As this figure shows, the main behavior of a one to tens of picoseconds signal growth is maintained in every solvent. There are clear but moderate differences in the biexponential rise times observed in the different solvents (see Table 1). For example, the second time constant goes from 8.4 ps in methanol to 10.7 ps in CCl_4. However, it is obvious that the changes are not as remarkable as those seen in other systems where the signal evolution is known to be exclusively due to vibrational relaxation. In such cases, there are examples where the solvent without hydrogen atoms (CCl_4) produces substantially slower relaxation. In those systems it has also been seen that the cooling dynamics are accelerated by a factor of about 1.4 when going from $CHCl_3$ to $CDCl_3$.[20] From the moderate solvent effects in our experiments, and since the main feature of the spectral evolution in Figures 5 and 6 is the growth of transient absorption signals, we consider that the process of formation of the fully relaxed T_1 state involves state conversion from the intermediate or receiver state and also, to some extent, vibrational cooling as evidenced by the band narrowing, biexponential behavior, and wavelength dependent time constants. That is, the accumulation of population in the phosphorescent T_1 state due to internal conversion steps cannot be completely differentiated from the vibrational relaxation within this electronic state as both processes appear to be occurring in similar time scales.

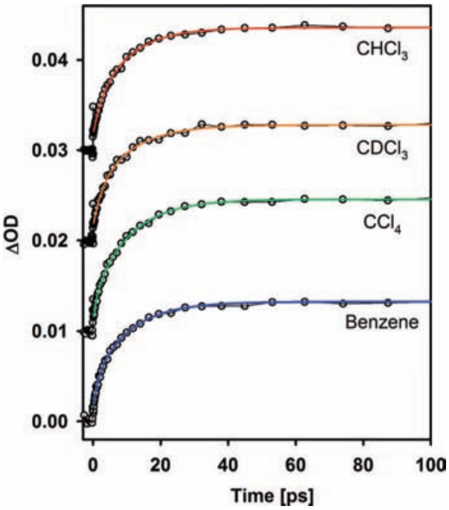


Figure 7. Transient absorption results for 1-nitronaphthalene in several solvents at 540 nm. Colored solid lines indicate fits to double-exponential rising terms to a constant level. The fast features at $t = 0$ are due to the coherent interaction between the pump and probe pulses and are not included in the data analysis.

Considering that the intermediate observed here acts as a receiver state in the triplet manifold, the ~1 to ~16 ps accumulation of T_1 population ($T_n \rightarrow T_1$) appears to be significantly slower in comparison with what is most commonly observed for internal conversion to the lowest energy singlet excited-state of a molecule when it is optically excited into an upper singlet.[23,24,26−32] There are, however, examples of $S_n \rightarrow S_1$ processes, even in alternating aromatic compounds, which occur in a slower time scale of a few picoseconds.[28,33−35] It has been concluded that such slow internal conversion in the singlet manifold occurs in cases of weak coupling between states with a somewhat large energy gap (~1 eV).[33]

Concerning the triplet manifold, there are several reports in the literature of long-lived (picoseconds) upper vibronic triplet states, including carotenoids,[36] oligo(*p*-phenylenevinilydene)s,[37] aromatic carbonylic compounds,[9,38] and nitrobenzaldehydes.[39] Particularly relevant for the present experiments, measurements of the decay of upper triplet states (T_n) formed through direct $T_1 \rightarrow T_n$ optical excitation of several substituted naphthalenes indicate that the lifetime of the upper triplet states lie in the ~10 to ~60 ps time range.[40,41] We consider that the time scales observed in our measurements are fully consistent with those determinations, and that such slow relaxation into the T_1 state is probably related to a weak coupling between the phosphorescent state the and the intermediate triplet state.[37]

As already mentioned, our previous calculations at the TD-DFT level of theory do suggest the existence of a nearly S_1-isoenergetic triplet state with a partial n−π* character (third triplet state at the DFT level of theory).[5] With the currently available theoretical results, this state should be considered as a candidate to account for the rapid singlet to triplet crossing and also as the intermediate state observed in the present experiments at wavelengths below 400 nm. It is clear however, that more sophisticated excited-state calculations are necessary to fully understand the photophysics of nitroaromatic compounds. Particularly interesting would be searches for state crossings in the potential energy surfaces, theoretical estimates of the spin-orbit coupling matrix elements, and also accurate predictions of the most stable geometries for the excited states of 1-NN.

The TD-DFT calculations included in a recent experimental and theoretical study of 1-nitropyrene by Crespo-Hernández and co-workers also point toward the participation of the third triplet state in the intersystem crossing of this molecule.[4] Agreeing with our previous up-conversion measurements,[11] in the case of 1-nitropyrene, the decay of the first singlet excited-state was observed to be biexponential, occurring in the one to a few picoseconds time scale. Such a slower first step ($\sim$7 ps) makes the population of any intermediary state stay in the steady-state regime without significant accumulation of population. Consistently, for 1-nitropyrene, the T_1 state was observed to be formed in a similar time scale as the S_1 decays.

Other experiments which shed light into the photophysics of nitroaromatic compounds were recently completed by Vauthey et al.[42] In those studies it was shown that when the size of the aromatic system is increased, going from 1-nitropyrene to 3-nitroperylene, the lifetime of the S_1 state is increased significantly (from a few picoseconds in the former, up to several hundreds of picoseconds for the latter). As the authors indicate, a probable explanation of this dramatic change is related to the stabilization of the S_1 state in 3-nitroperylene in comparison with 1-nitropyrene. In this logic, a significant stabilization with respect to the $n-\pi^*$ triplet would then impede or significantly reduce the coupling to this state, making the S_1 state longer-lived. Such indirect evidence is consistent with the participation of upper triplet states in the photophysics of several of the smaller polycyclic nitroaromatic molecules.[1−4,42]

Conclusions

The most relevant result of this study is the observation that the ultrafast fluorescence decay and the formation of the relaxed T_1 state occur in distinctly different time scales, where the former one takes place within 100 fs while the latter one takes a few tens of picoseconds to be completed. These results support the notion that in the transit from the optically excited-state to the lowest vibroelectronic state of the triplet manifold, an intermediate state mediates the population transfer between the singlet and triplet manifolds. Although the involvement of this type of state in the photophysics of nitroaromatics has been suggested previously on the basis of their high triplet yield and some theoretical results, this is the first direct observation of the participation of an intermediary state. In addition, from the details of the spectral evolution which includes some typical signatures of a vibrational relaxation processes, it appears that during the triplet manifold relaxation both the cooling and the [intermediary] $\rightarrow T_1$ state crossing occur in similar time scales between $\sim$1 and $\sim$16 ps. Such slow conversion is different from what is most commonly observed in the singlet manifolds where the singlet to singlet internal conversion is typically ultrafast. We consider that this is due to a large energy gap, of about 1 eV, between the postulated receiver state and the phosphorescent triplet.

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Supporting Information Available: 1NN/methanol 590 nm single-wavelength scan with a flow cell as well as coefficients and time constants for all the single-wavelength ΔOD vs delay traces for the methanol and benzene systems of this contribution. This material is available free of charge via the Internet at http://pubs.acs.org.

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