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ARTICLES

Singlet Excited-State Dynamics of Nitropolycyclic Aromatic Hydrocarbons: Direct Measurements by Femtosecond Fluorescence Up-Conversion

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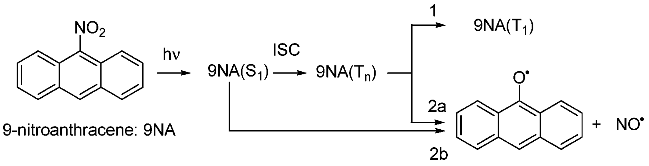
Understanding the dynamics of the electronically excited states of nitrated polycyclic aromatic hydrocarbons (NPAHs) is of great importance since photochemical reactions determine the atmospheric stability of these toxic pollutants. From previous studies, it is known that electronically excited NPAHs evolve through two parallel pathways: The formation of the first triplet state and the dissociation of nitrogen (II) oxide. In this contribution, we present the first time-resolved emission measurements of the singlet excited states which are the precursors in the aforementioned photoprocesses. We analyzed 1-nitronaphthalene, 9-nitroanthracene, 1-nitropyrene, 6-nitrochrysene, and 3-nitrofluoranthene in solution samples. Although these compounds are considered nonfluorescent, with the frequency up-conversion method it was possible to detect the emission from the S_1 states despite their femtosecond and picosecond lifetimes. Except for 1-nitronapthalene, where a single exponential is observed, for the rest of the compounds, the emission shows double-exponential decays indicating ultrafast structural changes in the excited states. From anisotropy measurements, we conclude that no significant internal conversion occurs in the singlet manifold after excitation in the first absorption band. In accord with El-Sayed rules and with previous calculations, the highly efficient intersystem crossing implied by the large triplet yields and the ultrafast S_1 decays is accounted by the $\pi-\pi^*$ nature of the S_1 and T_1 states together with the existence of higher triplet configurations which act as receiver states. Our measurements show that NPAHs have the largest intersystem crossing rates observed to date in an organic molecule.

Introduction

Nitrated polycyclic aromatic hydrocarbons (NPAHs) are important environmental pollutants formed directly during fuel combustion and indirectly by atmospheric nitration of polyaromatic hydrocarbons.[1−3] Many of them are mutagenic or carcinogenic agents and represent a potential human health risk.[4,5] The photochemistry and the photophysics of NPAHs are of great interest since their most important decay process in the atmosphere is photodegradation.[6−9] In addition, these compounds have been proposed as light-triggered NO• donors with potential applications in photodynamic therapies.[10] Finally, the evolution of the electronically excited states of nitroarenes has attracted a lot of interest due to their special nonradiative processes.[11−15] NPAHs are considered to be nonfluorescent. As we show here, this is due to the extremely short lifetime of their first singlet excited states. In the following paragraphs, we make a brief review of the current understanding about primary light-induced processes in these molecules. We then present and discuss the results of our femtosecond fluorescence up-conversion measurements on several NPAHs.

The primary photochemical pathways in NPAHs are summarized in Scheme 1 where 9-nitroanthracene (9NA) is taken as an example.[16,17] Following light absorption, NPAH molecules are known to evolve through two simultaneous pathways: The first channel is intersystem crossing (ISC) leading to the phosphorescent triplet state T_1. The second channel corresponds to a photoinduced dissociation reaction which generates nitrogen (II) oxide (NO•) and the corresponding aryloxy radical (Ar−O•). The NO• release has been proposed to occur through rearrangement to an oxaziridine type ring and/or a nitrite intermediary.[18−20] Scheme 1 considers that, in principle, the NO• dissociation can occur from unrelaxed states in the triplet manifold (pathway 2a) or directly from the excited singlet formed by light absorption (pathway 2b).[16,20]

SCHEME 1: Primary Photoprocesses in Nitrated Polycyclic Aromatic Hydrocarbons



The radical intermediaries can generate final products like anthraquinone, 10,10′-bianthrone, and anthrol depending on the conditions.[16,18] On the other hand, the NPAH triplets may undergo secondary intermolecular reactions like electron transfer or hydrogen abstraction.[21−23] The radical intermediaries of the

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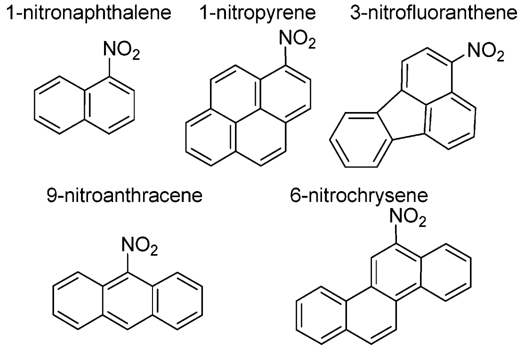
CHART 1: Molecular Structures of the Nitropolycyclic Aromatic Hydrocarbons of This Study



photodissociation channel of several NPAHs have been detected by ESR and transient absorption spectroscopy,[10,16,17,19] and the triplet states have been detected by phosphorescence, transient absorption, and Raman spectroscopy.[11−16,23−25]

Through a series of laser photolysis studies,[13,14,16,17,26] Hamanoue and co-workers have established that, for 9NA and other meso-substituted nitroanthracenes, the products of both channels (the anthryloxy radical and the triplet state) appear from a common precursor and that no conversion between them takes place. This has been observed both in low-temperature matrices and in room-temperature solutions.[16] In particular, in their nanosecond and picosecond transient absorption studies, they observed that the T_1 state and the anthryloxy radical are formed within their time resolution. In a latter subpicosecond transient absorption study of 9-benzoyl-10-nitroanthracene, Hamanoue et al. detected that the populations of both primary channels are established within a few picoseconds.[20]

From the triplet formation and the photoreaction yields available in the literature, it appears that ISC is the dominant primary channel for many NPAHs. For 9NA, only the photoreaction yield is known: $\Phi_{\mathrm{React}} = 0.07$,[16] suggesting that the triplet yield could be as high as 0.93. For 1-nitronaphthalene (1NN), no direct photochemical products have been detected in several solution photolysis experiments where the only intermediary state is T_1.[11,12,23,27] For this compound, the ISC yield has been estimated at 0.63 ± 0.10, indicating that the singlet state formed by light absorption evolves mainly through nonradiative processes to the lowest energy triplet and probably through rapid internal conversion to the electronic ground state.[21,28] In the case of 1-nitropyrene (1NP), the triplet yield is $\Phi_T = 0.6$.[29] For this compound, the precise photoreaction yield is unknown but the main product in a solution photolysis study (1-hydroxypyrene, 88%) is consistent with the NO• photodissociation channel.[30]

In this contribution, we report the first femtosecond resolved fluorescence measurements on several nitrated polyaromatics. Knowledge of the excited-state lifetimes of NPAHs is a relevant contribution toward a detailed description of their photochemical processes and an understanding of the factors which determine their photoreactivity.

Experimental Methods

Substances used in this study were of the highest purity available from Aldrich. The NPAHs in Chart 1 were recrystallized twice and kept isolated from light before the experiments. Solvents methanol and 1-butanol were high-performance liquid chromatography (HPLC) quality and used as received. UV−vis absorption spectra were taken in a 1 cm quartz cell with a Cary-50 spectrophotometer (Varian).

Our femtosecond fluorescence up-conversion setup is based on a Ti:Sapphire oscillator pumped by a 5 W, Verdi V5 laser (Coherent Inc.). The oscillator is tunable from 750 to 890 nm and produces sub 50 fs laser pulses at a repetition rate of 83 MHz. The femtosecond pulse train was passed through a fused silica prism compressor before it was frequency doubled in a 0.5 mm type I BBO crystal. The second harmonic was then separated from the remaining fundamental using a long-wavelength pass dichroic beamsplitter (CVI). The polarization of the second harmonic beam was adjusted with a half wave plate before it was focused into a 1 mm path length flow cell containing the NPAH solutions. The average power at the sample was 5 mW, and the focused spot was about 0.1 mm in diameter. The fluorescence from the sample was collected with a 2.5 cm focal length parabolic mirror, passed through a long wavelength pass filter to eliminate the unabsorbed pump light and refocused with a second parabolic mirror of 5 cm focal length. At the focal point, the fluorescence was crossed at an 8° angle with a focused and temporally delayed gate pulse from the remaining fundamental in another 0.5 mm BBO crystal ($\theta_{\mathrm{cut}} = 44°$). The polarization of the gate beam was adjusted to be vertical with a half wave plate, and the up-conversion crystal acceptance axis for the type I nonlinear optical interaction was adjusted to also be vertical. The resulting sum frequency mixing signal in the UV with horizontal polarization was then focused to the entrance slit of a 10 cm focal length double monochromator (Oriel) and detected with a photomultiplier tube connected to a lock-in amplifier referenced to a 200 Hz optical chopper in the path of the pump beam. The instrument response function for our apparatus was determined to be Gaussian with a 200 ± 10 fs full width at half maximum (fwhm), through a cross-correlation measurement between the gate pulses and the Raman scattering of the pump pulses in methanol.

We verified that this instrument function was consistent with the signal risetime at the blue side of the emission spectrum from a solution of anthracene in CH_2Cl_2. Small changes in the width of this function had no major effects on the time constants reported here. Signals were modeled as single- or double-exponential decays analytically convoluted with the instrument function. The 2σ errors in the exponential time constants are approximately 25% for the sub 100 fs components and approximately 15% otherwise. The NPAH concentration was adjusted to have an optical density of between 0.8 and 1.5 at the excitation wavelength. The solutions under study were frequently refreshed and repeatedly checked to verify the absence of photodegradation through UV−vis absorption spectra. Successive experiments with the same sample gave reproducible signals, indicating that photodegradation does not influence our measurements. Through runs with the solvent only and a study of the dependence of the signal with the NPAH concentration, we verified that the signals are not contaminated with up-conversion of the Raman scattering by the solvent. All experiments were performed at room temperature (20 ± 1 °C) under aerated conditions.

Results

Several studies have catalogued NPAHs as nonfluorescent compounds.[24,25] However, with the frequency up-conversion scheme, it is actually possible to detect emission during the extremely brief lifetime of the first singlet excited state as it decays through ISC and possibly to some extent directly through the dissociation channel (pathway 2b in Scheme 1). Figures 1 and 2 show the results from our femtosecond-resolved fluores-

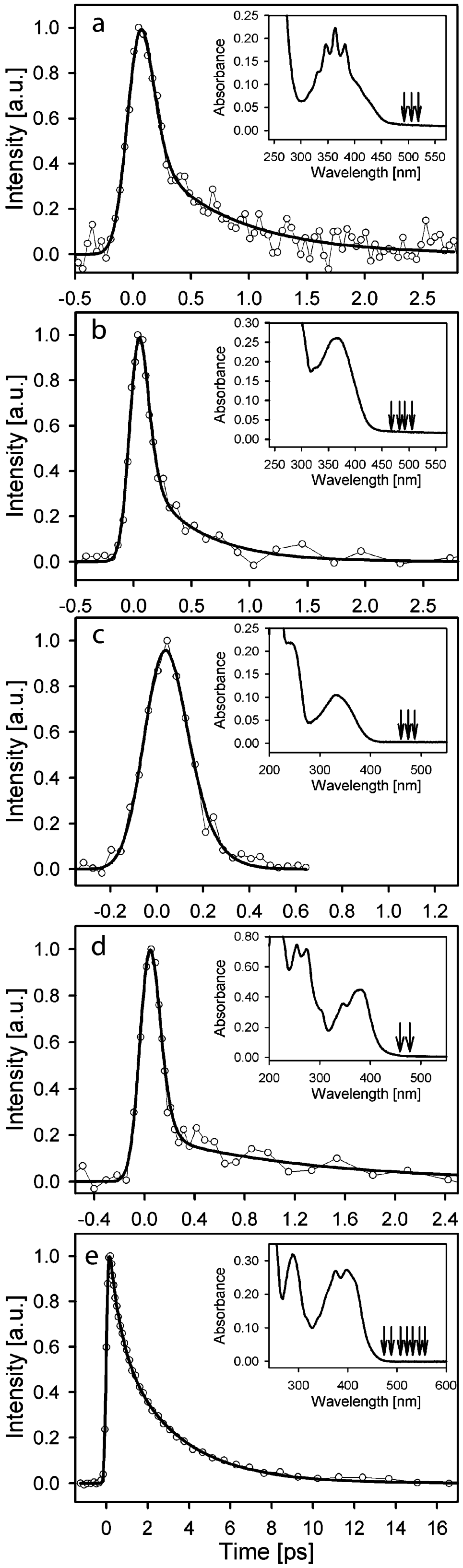


Figure 1. Femtosecond resolved fluorescence of nitropolycyclic aromatic compounds in methanol solution: (a) 9-nitroanthracene (9NA, λ_{fluor} = 505 nm), (b) 6-nitrochrysene (6NC, λ_{fluor} = 465 nm), (c) 1-nitronaphthalene (1NN, λ_{fluor} = 480 nm), (d) 3-nitrofluoranthene (3NF, λ_{fluor} = 480 nm), and (e) 1-nitropyrene (1NP, λ_{fluor} = 520 nm). In all cases, an excitation wavelength of 385 nm was used with the magic angle configuration. Solid lines are fits to the experimental data. In the insets, absorption spectra of the corresponding compound are shown where the vertical arrows are placed at the wavelengths of the fluorescence up-conversion measurements.

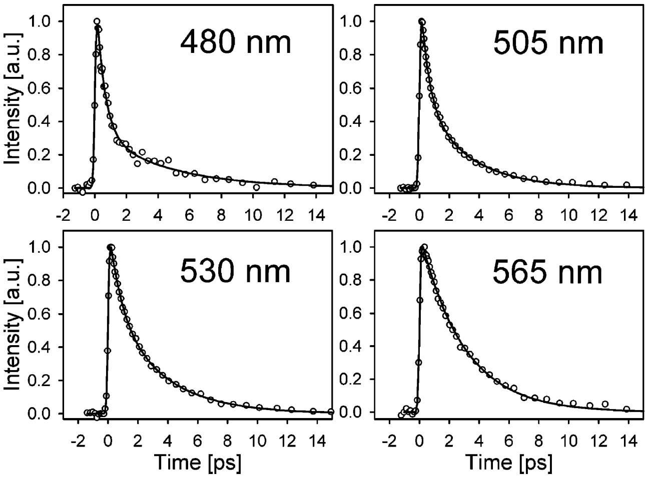


Figure 2. Fluorescence up-conversion experiments at the magic angle for 1-nitropyrene in methanol at a series of fluorescence wavelengths with an excitation wavelength of 385 nm. Solid lines are fits to the experimental data.

TABLE 1: Fluorescence Decay Times of the NPAHs Included in This Study

nitro-PAH[a]	fluorescence wavelength (nm)	τ_1 (fs)	τ_2 (ps)
1-nitronaphthalene (1NN)	480	70 (100%)	
9-nitroanthracene (9NA)	505	60 (86%)	0.73 (14%)
6-nitrochrysene (6NC)	465	50 (88%)	0.48 (12%)
3-nitrofluoranthene (3NF)	480	50 (95%)	1.3 (5%)
1-nitropyrene (1NP)	480	540 (73%)	4.4 (27%)
1-nitropyrene	505	550 (55%)	3.0 (45%)
1-nitropyrene	520	730 (48%)	3.2 (52%)
1-nitropyrene[b]	520	680 (55%)	3.2 (45%)
1-nitropyrene	530	820 (41%)	3.4 (59%)
1-nitropyrene	565		2.9 (100%)
1-nitropyrene[c]	480	200 (74%)	5.8 (26%)
1-nitropyrene[c]	550	350 (40%)	9.0(60%)

[a] Unless indicated otherwise, the excitation wavelength was 385 nm and the solvent was methanol. In parentheses, we include the percent-contribution of each exponential term. [b] Excitation wavelength: 435 nm. [c] Solvent: 1-butanol. n/a = not applicable.

cence measurements where the polarization of the 385 nm pump beam was adjusted to the magic angle (54.7°) with respect to the acceptance axis of the up-conversion crystal to avoid rotational diffusion effects. The signals decay on timescales from sub 100 fs to a few picoseconds depending on the NPAH. In Figure 1, the insets show the corresponding ground-state absorption spectra and the vertical arrows indicate wavelengths where emission signals were detected. In the case of 9NA, for the fluorescence measured at 505 nm, the signal was adjusted to a biexponential function: $I(t) = \alpha{\cdot}\exp(-t/\tau_1) + (1 - \alpha){\cdot}\exp(-t/\tau_2)$ with $\tau_1 = 60$ fs (86%), and $\tau_2 = 730$ fs (14%). For 6-nitrochrysene (6NC) at 465 nm, we observed $\tau_1 = 50$ fs (88%), and $\tau_2 = 480$ fs (12%). For 3-nitrofluoranthene (3NF) at 480 nm, we measured $\tau_1 = 50$ fs (95%), and $\tau_2 = 1.3$ ps (5%). For 1NN, we did not observe a second decay term in any region of the spectrum, and the traces were fitted to a single decay of $\tau = 70$ fs. The fluorescence decay data is summarized in Table 1. For 9NA, 6NC, 3NF, and 1NN, we did not observe significant deviations from these numbers at other emission wavelengths. However, for 1NP where the decays are biexponential and overall slower, there is a clear trend across the emission spectrum; this is shown in detail in Figure 2. For 1NP at 480 nm, we measured: $\tau_1 = 540$ fs (73%) and $\tau_2 = 4.4$ ps (27%); while at 505 nm the decay times are $\tau_1 = 550$ fs (55%),

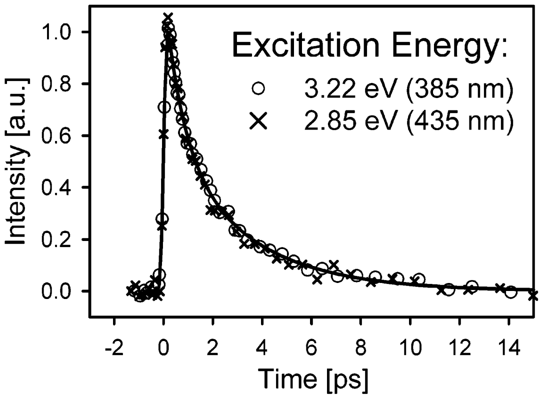


Figure 3. Femtosecond resolved fluorescence for 1-nitropyrene in methanol taken at a wavelength of 520 nm. The open circles correspond to an experiment with an excitation wavelength of 385 nm and the crosses to an excitation wavelength of 435 nm. The solid line corresponds to a biexponential fit of the 385 nm excitation data.

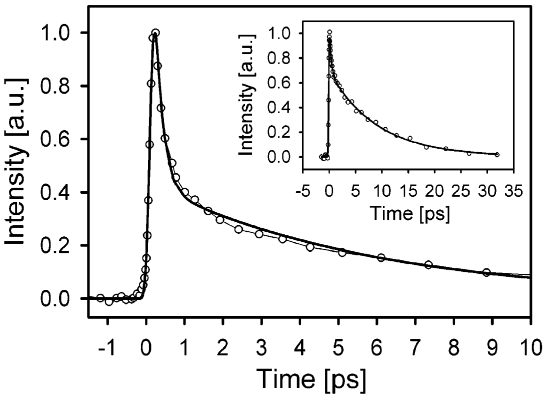


Figure 4. Femtosecond resolved fluorescence for 1-nitropyrene in butanol taken at the magic angle configuration after excitation with 385 nm pulses. Fluorescence wavelengths are 480 nm (main graph) and 550 nm (inset).

and $\tau_2 = 3.0$ ps (45%). At the red side of the emission spectrum, the data can be fitted to a single-exponential decay of 2.9 ps at 565 nm. In summary, for 1NP, we observed the presence of a fast (subpicosecond) component in the decay whose amplitude decreases at the red side of the spectrum. Such a component is essentially absent at the longest wavelength detected (565 nm). To test whether such a trend in 1NP is related to the excess vibrational energy placed in the molecule by the pump pulse, we measured the emission decay at 520 nm using two different excitation wavelengths: 385 nm (3.22 eV) and 435 nm (2.85 eV). As can be seen in Figure 3, there is no effect from changing the pump photon energy as the two decay traces overlap at all delay times. The parameters obtained from biexponential fits are included in Table 1. Both experiments give decay times and amplitudes which are within the uncertainty of each other.

We also tested the effect of using a longer linear alcohol as the solvent in the 1NP experiments. In Figure 4, we show the up-conversion measurements of 1NP in 1-butanol at two fluorescence wavelengths. In both cases, the data shows biexponential behavior. For $\lambda_{\text{fluor}} = 480$ nm, we observed $\tau_1 = 200$ fs (74%) and $\tau_2 = 5.8$ ps (26%), and for $\lambda_{\text{fluor}} = 550$ nm (inset), we observed $\tau_1 = 350$ fs (40%) and $\tau_2 = 9.0$ ps (60%). Similar to the experiments in methanol, the contribution of the fast component gets smaller at the longer fluorescence wavelengths. However, here the fast components are shorter while the picosecond decay time constants are longer in comparison with the methanol case.

We now turn to the fluorescence anisotropy experiments made at selected emission wavelengths for 1NN, 9NA, and 1NP. For these measurements, the polarization of the pump beam was adjusted to determine the fluorescence's parallel and perpendicular components with respect to the excitation axis. Ultrafast anisotropy measurements are useful to determine the relative orientation of the transition dipoles involved in the excitation and fluorescence events. The results are presented in Figure 5 where for all cases an excitation wavelength of 385 nm was used and the solvent was methanol. In the figure, we show two emission wavelengths for 1NP and single ones for 9NA and 1NN. As can be seen, there is no difference in the shape of the traces taken with parallel or perpendicular excitation/detection configurations for any of the three compounds. Furthermore, the anisotropy values near $t = 0$ are between 0.3 and 0.4 as expected when the singlet excited state formed in the initial transition is the emitting state for a solution sample. For 1NP where the fluorescence signal is a bit longer lived, a slow anisotropy decay was detected. This feature was attributed to rotational diffusion with an exponential decay time constant of 13.5 ps. In 1NN, the $r(t)$ values have larger fluctuations due to the low signal-to-noise ratio and the short lifetimes, however, in all cases, the $r(t \cong 0)$ values are consistent with nearly parallel transition dipole vectors.

Discussion

In summary, we have detected the ultrafast emission from the singlet excited states of several NPAHs. The rapid decays should be due mainly to an extremely fast ISC process although it is likely that the direct reactive channel also contributes to deplete the excited singlet population in some of the compounds (pathway 2b in Scheme 1). We first examine the case of 1NN where the signal is single exponential and where no direct decomposition has been observed in previous studies. The spectroscopic assignment of 1NN absorption and phosphorescence spectra has been performed by Mikula et al. through comparisons of spectroscopic data to molecular orbital calculations at the CNDO−CI level.[27] The authors determined that the first two excited singlets in 1NN are similar to naphthalene's first two excited $\pi-\pi^*$ singlets, $^1B_{3u}$ and $^1B_{2u}$, with some ring to nitro group charge-transfer character added in. Also, in agreement with an analysis of the phosphorescence's vibronic structure,[31] and with more recent triplet−triplet energy transfer studies,[21] it was concluded that the lowest energy triplet has $\pi-\pi^*$ character and is similar to napthalene's T_1 state: $^3B_{2u}$. With their CNDO−CI calculation, the authors localized several upper triplet states one of which is nearly isoenergetic with the lowest excited singlet (T_4 in Mikula's study). This upper triplet was calculated to have 50% $\sigma-\pi^*$ character and was considered the most probable receiver state in the ISC according to El-Sayed's rules.[32] The present study shows that the depletion of the emitting state in 1NN occurs with a total rate of about 1.4×10^{13} s^{-1}, and the anisotropy measurements show that no significant internal conversion between singlets of different transition moment orientations takes place. Our excitation wavelength of 385 nm is at the red edge of the first absorption band of 1NN whose maximum is 333 nm in methanol. Mikula's calculations locate the short axis polarized $^1B_{2u}$ type state as the lowest energy singlet below the $^1B_{3u}$ type state (CNDO−CI energies: 4.12 and 4.19 eV, respectively). The latter state was also calculated to have a much smaller oscillator strength. Although a confirmation of the assignment of the first absorption band of 1NN and of the upper triplets responsible for the rapid ISC requires a new analysis using today's higher level com-

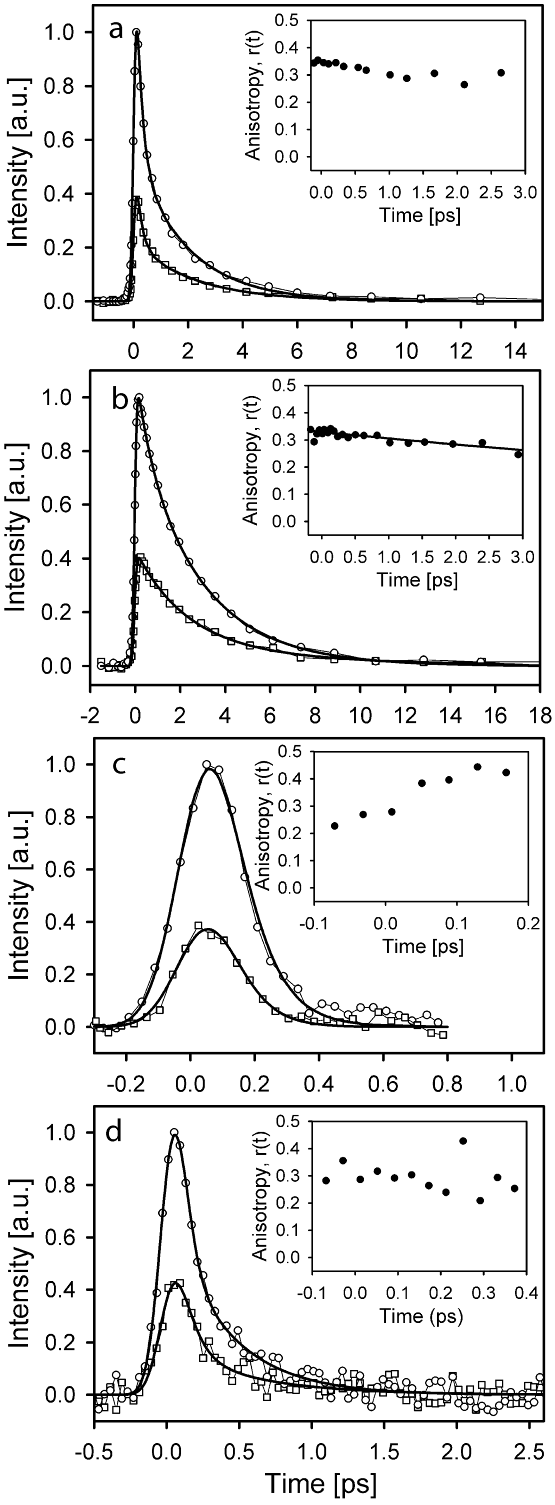


Figure 5. Ultrafast anisotropy measurements of nitropolycyclic aromatic compounds in methanol after 385 nm excitation: (a) 1-nitropyrene ($\lambda_{\mathrm{fluor}} = 480$ nm), (b) 1-nitropyrene ($\lambda_{\mathrm{fluor}} = 550$ nm), (c) 1-nitronaphthalene ($\lambda_{\mathrm{fluor}} = 480$ nm), and (d) 9-nitroanthracene ($\lambda_{\mathrm{fluor}} = 505$ nm). Circles denote experiments where the fluorescence component parallel to the excitation polarization is detected, and squares, to the component perpendicular to the excitation pulses. The insets show the anisotropy values calculated from the two experimental traces. In the inset of Figure 5b, we include a single-exponential fit to the anisotropy decay (decay time: 13.5 ps, solid line).

putational methods, our results clearly show that the emitting state is formed directly in the vertical excitation and that this state undergoes sub 100 fs ISC to the triplet manifold of 1NN.

Likewise, our anisotropy measurements for 9NA and for 1NP indicate that there is negligible internal conversion in the singlet manifold during the fluorescence decay. From the first studies by Chapman et al.,[18] and from the spectroscopic studies of Hamanoune et al.,[16] it has been established that the lowest energy triplet and singlet states of 9NA are also $\pi-\pi^*$ character and that an upper $n-\pi^*$ triplet state should be involved in the photophysics. 9NA is more photolabile than 1NN. However, the T_1 detection in previous studies and the sub 10% photoreaction yield indicate that ISC is the predominant primary channel of 9NA.[16]

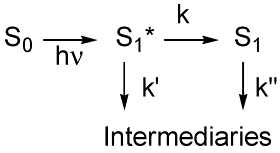
With the exception of 1NN, the nitroaromatics of our study have double-exponential decays. This indicates that some kind of molecular rearrangement takes place so that at early times the total decay of the excited singlet is faster and it slows down after this first period. It should be noted that for 1NP the relative contribution of the fast component of the decay (subpicosecond) becomes smaller at longer fluorescence wavelengths with a concomitant reshaping and red shifting of the spectrum. On the other hand, for 9NA, 6NC, and 3NF, the time constants and the relative contributions of the two exponentials are within our uncertainty for all the detected wavelengths. Subpicosecond components in an emission spectrum are frequently assigned to relaxation processes like internal conversion, vibrational redistribution, cooling, and solvation.[33,34] From our anisotropy measurements, we can conclude that internal conversion between the two lowest excited singlets (of perpendicular transition dipole moments) does not occur during the fluorescence decay. Also, in our experiments on 1NP, we observed that a change of 0.38 eV in the excitation energy has no effect on the biexponential decay at 520 nm, showing that the fast component is not due to a simple vibrational redistribution and cooling in S_1.

Comparing the measurements of 1NP in methanol and 1-butanol, we can see that the solvent does play a role in determining the fluorescence decay rates. Such an effect could be due to an influence of the solvent's polarity on the relative energies of S_1 and the triplet manifold, which would change the degree of spin orbit coupling and the Frank Condon factors. Also, the solvent response times (solvation times) could have an effect on the rate in which the potential energy surface of the system is explored and therefore on the S_1 decay times.[33] Both of these aspects should result in the differences observed in methanol vs 1-butanol. To underline this idea, we note that the solvent response times of methanol are overall faster than those in 1-butanol. However, the subpicosecond component in 1-butanol is actually faster (about 300 vs 550 fs), indicating that the solvent reorganization dynamics alone do not determine the observed decays.

In the nitroaromatic *p*-nitroaniline, subpicosecond decays in the stimulated emission spectrum have been associated with changes in the NO_2 group orientation to form an intramolecular charge-transfer state.[35] Since the S_1 states of our nitroaromatics also have significant charge-transfer character,[27] we believe that the fast time constants (τ_1) in our study could be related to a rapid equilibration of the orientation of the nitro group which occurs simultaneously with the decay of the fluorescent state. The orientation of the nitro group in NPAHs has been found to be rotated out of the aromatic ring plane due to a balance between π-bonding and steric interactions with adjacent H atoms.[36,37] It is expected that such a balance will be altered upon electronic excitation, inducing therefore a new NO_2 equilibrium orientation.

The changes in the fluorescence decay rate before and after this type of rearrangement can be modeled with the kinetic

SCHEME 2: Kinetic Scheme for the First Singlet Excited State of Nitrated Polycyclic Aromatics with Biexponential Emission Decay



sequence of Scheme 2 where S_1* and S_1 represent the fluorescent state before and after molecular relaxation, *k* is the rate of this rearrangement, and k' and k'' are the respective singlet decay rates.

In principle, the rates k' and k'' can include terms due to ISC and terms associated with the NO• release channel. Solution of the kinetic equations predicts the following time dependence of the populations

$$S^*{}_1(t) = S^*{}_1(t_0)\,\mathrm{e}^{-(k+k')t} \tag{1}$$

$$S_1(t) = \frac{S^*{}_1(t_0)k}{k''-k'-k}\left(\mathrm{e}^{-(k+k')t} - \mathrm{e}^{-k''\cdot t}\right) \tag{2}$$

which are similar to the case of consecutive unimolecular reactions and where $S_1*(t_0)$ is the initial excited-state population. Considering that at any wavelength the emission from both S_1* and S_1 is detected, the scheme predicts biexponential fluorescence decays with $(k + k')^{-1}$ as the fast time constant and $(k'')^{-1}$ as the slower time constant. It should be noticed that the absence of rise components is consistent with an overlap (at least partially) of the emission spectra of both populations.

Conclusions

Measurements of the transient fluorescence from several NPAHs yielded important new information about their excited-state dynamics. The decay of the S_1 states occurs on time scales as short as a few tens of femtoseconds. The results support an ultrafast ISC to an upper triplet state as the main channel for S_1. Such a process represents one of the fastest nonradiative singlet−triplet transitions measured to date in a molecule. In fact, the only sub 50 fs ISC times we know of correspond to metallic complexes.[38] The rapid depletion of the fluorescent state should play a determinant role on the photochemistry of all NPAHs. As has been pointed out before,[27] the $\pi-\pi^*$ nature of the S_1 and T_1 states together with the presence of upper $n-\pi^*$ triplet states nearly isoenergetic to S_1 appears to be a common feature in NPAHs. At this point, it is uncertain whether rearrangement and NO• dissociation occurs exclusively from S_1 or to some extent from the T_n states. If this transformation occurs exclusively from the S_1 state, then it is precisely a competition between the photochemical and the ISC channel from S_1 that determines the degree of photoreactivity of the NPAHs. Our studies represent an important case-study of molecules with very large spin orbit coupling, leading to ISC rates which are large enough to compete with vibrational motion and fast molecular rearrangements.

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References and Notes

(1) MacCrehan, W. A.; May, W. E.; Yang, S. D.; Benner, B. A., Jr. *Anal. Chem.* **1988**, *60*, 194.

(2) Paputa-Peck, M. C.; Marano, R. S.; Schuetzle, D.; Riley, T. L.; Hampton, C. V.; Prater, T. J.; Skewes, L. M.; Jensen, T. E.; Ruehle, P. H.; Bosch, L. C.; Duncan, W. P. *Anal. Chem.* **1983**, *55*, 1946.

(3) Kamens, R. M.; Zhi-Hua, F.; Yao, Y.; Chen, D.; Chen, S.; Vartiainen, M. *Chemosphere* **1994**, *28*, 1623.

(4) Ohgaki, H.; Negishi, C.; Wakabayashi, K.; Kusama, K.; Sato, S.; Sugimura, T. *Carcinogenesis* **1984**, *5*, 583.

(5) Tokiwa, H.; Ohnishi, Y. *Crit. Rev. Toxicol.* **1986**, *17*, 23.

(6) Gerasimov, G. Y. *High Energy Chem.* **2004**, *38*, 161.

(7) Fan, Z.; Chen, D.; Birla, P.; Kamens, R. M. *Atmos. Environ.* **1995**, *29*, 1171.

(8) Fan, Z.; Kamens, R. M.; Hu, J.; Zhang, J.; McDow, S. *Environ. Sci. Technol.* **1996**, *30*, 1358.

(9) Warner, S. D.; Farant, J.-P.; Butler, I. S. *Chemosphere* **2004**, *54*, 1207.

(10) Fukuhara, K.; Kurihara, M.; Miyata, N. *J. Am. Chem. Soc.* **2001**, *123*, 8662.

(11) Anderson, R. W., Jr.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *Chem. Phys. Lett.* **1974**, *28*, 153.

(12) Capellos, C.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1159.

(13) Hamanoue, K.; Hirayama, S.; Nakayama, T.; Teranishi, H. *Chem. Lett.* **1980**, 407.

(14) Hamanoue, K.; Hirayama, S.; Nakayama, T.; Teranishi, H. *J. Phys. Chem.* **1980**, *84*, 2074.

(15) Ohtani, H.; Kobayashi, T.; Suzuki, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 43.

(16) Hamanoue, K.; Nakayama, T.; Kajiwara, K.; Yamanaka, S.; Ushida, K. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3145.

(17) Hamanoue, K.; Amano, M.; Kimoto, M.; Kajiwara, Y.; Nakayama, T.; Teranishi, H. *J. Am. Chem. Soc.* **1984**, *106*, 5993.

(18) Chapman, O. L.; Heckert, D. C.; Reasoner, J. W.; Thackaberry, S. P. *J. Am. Chem. Soc.* **1966**, *88*, 5550.

(19) Ioki, Y. *J. Chem. Soc., Perkin Trans. 2* **1977**, *10*, 1240.

(20) Hamanoue, K.; Nakayama, T.; Amijima, Y.; Ibuki, K. *Chem. Phys. Lett.* **1997**, *267*, 165.

(21) Hurley, R.; Testa, A. C. *J. Am. Chem. Soc.* **1968**, *90*, 1949.

(22) Goerner, H. *J. Chem. Soc., Perkin Trans. 2* **2002**, *10*, 1778.

(23) Fournier, T.; Tavender, S. M.; Parker, A. W. *J. Phys. Chem. A* **1997**, *101*, 5320.

(24) Rusakowicz, R.; Testa, A. C. *Spectrochim. Acta, Part A* **1971**, *27*, 787.

(25) Wolfbeis, O. S.; Posch, W.; Gübitz, G.; Tritthart, P. *Anal. Chim. Acta* **1983**, *147*, 405.

(26) Hamanoue, K.; Nakayama, T.; Ushida, K.; Kajiwara, K.; Yamanaka, S. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3365.

(27) Mikula, J. J.; Anderson, R. W.; Harris, L. E.; Stuebing, E. W. *J. Mol. Spectrosc.* **1972**, *42*, 350.

(28) The triplet yield in 1-nitronaphthalene was measured by an energy-transfer technique using *cis*-piperylene (ref 21). It has been mentioned before by Anderson et al. (ref 11) that a small reduction in the value considered as the fraction of piperylene triplets which produce the trans isomer would make the 1-nitonapthalene triplet yield close to unity.

(29) Scheerer, R.; Henglein, A. *Ber. Bunsen-Ges.* **1977**, *81*, 1234.

(30) Van den Braken-Van Leersum, A. M.; Tintel, C.; Van 't Zelfde, M.; Cornelisse, J.; Lugtenburg, J. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 120.

(31) Lim, E. C.; Stanislaus, J. *Chem. Phys. Lett.* **1970**, *6*, 195.

(32) El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834. Lower, S. K.; El-Sayed, M. A. *Chem. Rev.* **1966**, *66*, 199.

(33) Stratt, R. M.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 12981.

(34) Kasajima, T.; Akimoto, S.; Sato, S.; Yamazaki, I. *J. Phys. Chem. A* **2004**, *108*, 3268.

(35) Kovalenko, S. A.; Schanz, R.; Farztdinov, V. M.; Henning, H.; Ernsting, N. P. *Chem. Phys. Lett.* **2000**, *323*, 312.

(36) Li, Y. S.; Fu, P. P.; Church, J. S. *J. Mol. Struct.* **2000**, *217*, 550−551.

(37) Onchoke, K. K.; Hadad, C. M.; Dutta, P. K. *Polycyclic Aromat. Compd.* **2004**, *24*, 37.

(38) Cannizzo, A.; van Mourik, F.; Gawelda, W.; Zgrablic, G.: Bressler, C.; Chergui, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3174.

(39) Druzhinin, S. I.; Ernsting, N. P.; Kovalenko, S. A.; Lustres, L. P.; Senyushkina, T. A.; Zachariasse, K. A. *J. Phys. Chem. A* **2006**, *110*, 2955.