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ARTICLES

Triplet State Mechanism for Diphenylamine Photoionization[1]

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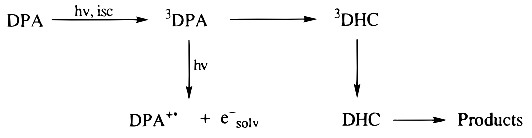
The photoionization of diphenylamine has been studied using both one- and two-laser flash photolysis in acetonitrile, alcohols, and aqueous solvent mixtures with the aim of elucidating the role of the triplet in the photoionization process. Excitation of triplet diphenylamine at 532 nm leads to irreversible triplet bleaching in all solvents, although the yields decrease by approximately an order of magnitude in comparing 1:1 aqueous acetonitrile to neat methanol or 2-propanol. Photoionization to yield the diphenylamine radical cation accounts for a substantial fraction of the triplet bleaching in all cases, demonstrating that biphotonic photoionization via an upper triplet is a viable mechanism. Triplet bleaching does not lead to either N−H bond cleavage or reverse intersystem crossing in aqueous acetonitrile. Plots of the radical cation yield as a function of laser power for one-laser (308 nm) excitation of diphenylamine are linear, consistent with monophotonic ionization under these conditions.

Photoionization is frequently observed upon high-energy UV-laser excitation of a variety of aromatic hydrocarbons in polar solvents and is an area of considerable current interest, both as a means of generating solvated electrons and radical cations for kinetic and mechanistic studies and as a cause of the damaging effects of ionizing radiation.[3−23] Photoejection of an electron can occur via several different mechanisms, depending on the available photon energy, the excited state properties of the substrate, and the solvent. Monophotonic ionization from both vibrationally excited and relaxed (fluorescent) singlet states has been observed, particularly for aromatic amines.[3] Simultaneous (nonresonant) and sequential (resonant) biphotonic ionization are also common; in the latter case absorption of a second photon by an initial singlet or triplet excited state leads to ionization. Evidence for a biphotonic mechanism involving excitation of singlet or triplet states of the molecule usually comes primarily from the observation that the solvated electron or radical cation yield depends on the square of the light intensity. However, this approach is not unequivocal, as linear yield versus intensity plots can sometimes be observed even for biphotonic processes, depending on the absorption characteristics of the species involved.[24]

A number of recent reports have demonstrated that photoionization occurs upon excitation of the triplet state of aromatic substrates. Most of these studies have utilized two-laser flash photolysis experiments in which a synthesis laser pulse is used to generate a triplet excited state, which, after a suitable time delay, is excited with a second laser pulse at a wavelength at which the initial precursor is transparent.[25,26] Examples include the ionization of upper triplets of biphenyl, phenothiazine, promazine, *N*-methylacridan, and a number of aromatic ketones in polar solvents and of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine in both polar and nonpolar solvents.[10,11,13,22,23,27−32] Although it is clear that ionization via upper excited triplet states is relatively common, previous studies have indicated that this process is solvent dependent. For example, substrates such as phenothiazine and promazine undergo ionization from their upper triplet states in acetonitrile and aqueous acetonitrile but not in alcohol solvents.[23,29] By contrast, time-resolved EPR studies have demonstrated an excited triplet mechanism for photoionization of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine in alcohols.[31,32] Also of interest is the fact that excited anthracene triplet does not photoionize in acetonitrile despite the fact that monophotonic photoionization occurs via the singlet manifold in this solvent.[33]

The photoionization of diphenylamine (DPA) provides an interesting example for studying the factors that affect biphotonic photoionization via both singlet and triplet excited states. The intensity dependence of the transient absorption behavior upon one-laser (308 nm, 16 ns) flash photolysis of diphenylamine in methanol has been examined.[34] At low laser intensity triplet amine and its cyclization product (ground state dihydrocarbazole, DHC) were observed; the cyclization was shown to be an adiabatic process leading initially to the triplet excited state of dihydrocarbazole, which was also detected in the transient absorption spectrum. In the related *N*-methyldiphenylamine, the dihydrocarbazole decays via disproportionation to yield the carbazole and tetrahydrocarbazole.[35] These low-intensity results are in good agreement with previous studies of related amines.[36,37] At high laser intensities excitation of DPA produced additional species, which were identified as the amine radical cation and the solvated electron. These results have been interpreted in terms of a two-photon ionization involving triplet DPA, with a calculated quantum yield of 0.36, based on simulations of the experimental data. These processes are summarized in reaction 1.



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A more recent report of two-photon ionization of aromatic compounds using fluorescence-detected magnetic resonance has presented evidence that conflicts with the proposed two-photon ionization of triplet DPA.[9] Both experimental results and simulations suggest that excitation of DPA with a 12 ns, 308 nm laser pulse leads to photoionization via the singlet state at high laser intensities in 2-propanol, although at lower intensities the triplet may play a role. Plots of signal intensity versus laser power for several of the aromatics studied suggest a biphotonic singlet mechanism for ionization. Excitation of DPA with a picosecond laser pulse in either methanol or acetonitrile demonstrates unequivocally that biphotonic excitation occurs via the singlet manifold, since the amount of triplet produced during the laser pulse is negligible under these conditions.[3] It is also interesting to note that triplet bleaching of several other aromatic amines results in both photoionization and N−H bond cleavage in polar solvents.[29,30] Hydrogen abstraction reactions have also been reported.[32]

These results have prompted us to examine the behavior of diphenylamine in several polar solvents using both one- and two-laser excitation with optical and conductivity detection. Our results indicate that triplet diphenylamine is bleached upon 532 nm excitation in a variety of polar solvents, although the efficiency is almost an order of magnitude higher in 1:1 aqueous acetonitrile than in methanol. Photoionization to give radical cation contributes to the triplet bleaching in all solvents.

Experimental Section

Materials. Diphenylamine (Analar), acetonitrile (BDH, spectrograde), methanol (BDH, spectrograde), and 2-propanol (Fisher, Spectranalyzed) were used as received. 1,3-Cyclohexadiene was distilled immediately prior to use.

Laser Flash Photolysis. Either a Lumonics EX-510 excimer laser (XeCl, 308 nm, 6 ns pulses, ≤40 mJ/pulse) or a Lumonics HY750 Nd:YAG laser (532 or 266 nm; 10 ns pulses; ≤50 mJ/pulse) was used for sample excitation. Most experiments were done using a 7 × 7 mm^2 quartz flow-through cell connected with Teflon lines to a sample reservoir to minimize problems related to depletion of the starting material and buildup of fluorescent by-products. Unless otherwise stated all samples were nitrogen-purged before and during the laser experiments. The rest of the laser system is as described previously,[38] except for the use of a PC-386 computer to control the data acquisition.

Conductivity. Time-resolved changes in sample conductivity due to the formation of charged intermediates were followed using a differential approach. The solution was contained in a 10 × 10 mm^2 quartz cuvette or flow cell within which a Teflon insert, holding three platinum foil electrodes (4 × 4 mm^2) placed exactly 4 mm apart, was positioned. The arrangement of the electrodes was horizontal such that the laser beam passed through the volume between the center electrode (common) and one of the outer electrodes. The conductivity in the unirradiated volume between the other outer electrode and the common acts as a measure of the background signal. Prior to the laser pulse a dc voltage pulse was applied across the electrodes, this pulse being variable in terms of duration (1−4 ms) and amplitude (maximum 400 V). Signals were taken to a differential amplifier in order to increase the signal to noise and observe only photoinduced *changes* in conductivity of the sample. The rise time of the detection system was measured to be ~80 ns, *i.e.* significantly longer than that for the optical detection. The electrode arrangement is such that optical and conductivity detection could be carried out for the same sample, as the analyzing beam in the optical detection is also overlapped perpendicular to the laser pulse. The differential signal was passed to the digitizer and recorded, stored, and analyzed as in the laser flash photolysis setup above.

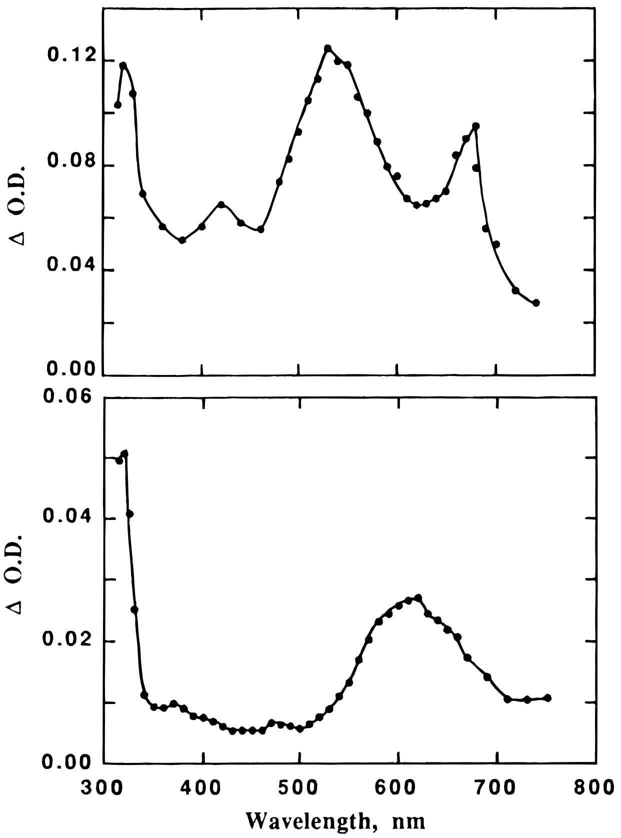

Figure 1. Transient absorption spectra at two delays following 308 nm laser excitation of diphenylamine in nitrogen-saturated 1:1 aqueous acetonitrile (top, 0.3 μs; bottom, 2.5 μs).

Results

One-Laser Experiments. Most of the one-laser (308 nm) transient experiments were carried out in aqueous acetonitrile since this was found to be the most convenient solvent for studying the photoionization of triplet DPA. The observed transient phenomena in 1:1 aqueous acetonitrile were similar to those reported previously in methanol.[34] Figure 1 shows transient absorption spectra recorded at two time delays after laser excitation. The early spectrum (Figure 1, top) shows primarily triplet (520 nm) with a small amount of radical cation (670 nm); both species are formed within the laser pulse. There is also a weak maximum at 430 nm, which is consistent with the triplet excited state of DHC, formed via adiabatic cyclization of triplet DPA.[34] The lifetime of triplet DPA is ~1 μs in well-degassed aqueous acetonitrile. The radical cation is somewhat shorter lived, with a lifetime of 0.5 μs. The late spectrum in Figure 1 (bottom) shows ground state DHC, which has λ_{max} at ~610 nm and decays by second-order kinetics, in agreement with the earlier observation of the decay of a similar dihydrocarbazole by disproportionation.[35] The spectra in Figure 1 were recorded over a wider wavelength range than those in the earlier methanol study and show that there is substantial absorption below 350 nm on all time scales. Kinetic traces recorded at 315 nm indicate that a fraction of this signal is produced within the laser pulse while the remainder grows in with a lifetime of approximately 0.5 μs. The decay kinetics at this wavelength are similar to those of DHC at 630 nm, but there is obviously also a contribution from a longer lived species. This was confirmed by a recording a spectrum after the complete decay of DHC, which still shows a long-lived species at 320 nm with some weak absorption at longer wavelengths. The

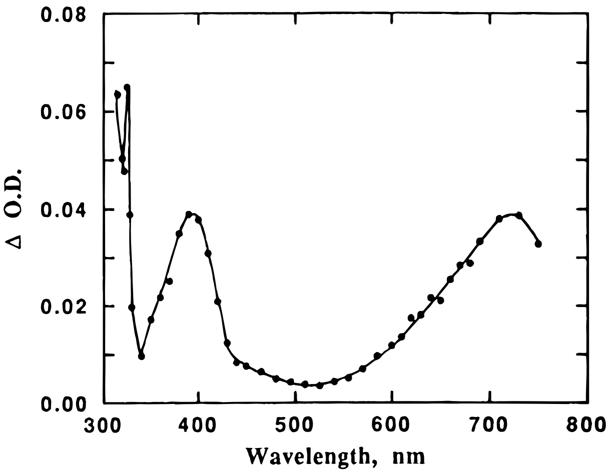

Figure 2. Transient absorption spectrum recorded 2 μs after 308 nm laser excitation of diphenylamine in oxygen-saturated 1:1 aqueous acetonitrile.

assignment of the species absorbing at short wavelengths was more readily established after consideration of the transient phenomena in oxygen-saturated solutions, as outlined below. It should also be noted that, in contrast to the results in methanol, the solvated electron is not readily detected in aqueous acetonitrile. In this solvent the electron is trapped to give an acetonitrile dimer radical anion that has only very weak absorption below 750 nm.[3]

Oxygen quenches triplet DPA with a measured rate constant of $4 \times 10^9\ M^{-1}\ s^{-1}$ in aqueous acetonitrile and prevents the formation of most of the signals due to triplet and ground state DHC. However, under these conditions the radical cation is still produced, and there is a residual long-lived signal that remains after the radical cation has decayed and has maxima at 325, 400, and 730 nm (Figure 2). Similar results are also observed when triplet DPA is quenched with 1,3-cyclohexadiene. In the presence of sufficient diene (5 mM) to quench >95% of the triplet the transient absorption shows only radical cation and a longer lived species identical to that observed at long time delays under an oxygen atmosphere. The spectrum of this residual absorption is consistent with the formation of the diphenylaminyl radical, which has been previously generated by hydrogen abstraction from DPA by *tert*-butoxyl radical and by irradiation of DPA in glasses.[39,40] We have confirmed this by generating the radical via hydrogen abstraction from DPA by *tert*-butoxyl radical produced by 355 nm excitation of di-*tert*-butyl peroxide in 4:1 peroxide/benzene. Under these conditions the long wavelength absorptions (400 and 700 nm) are the same as those observed from DPA alone at long times, and the radical lifetime is not appreciably shortened by oxygen-purging of the solution. Diphenylaminyl radicals have been shown to be unaffected by oxygen, at least on the time scale of nanosecond laser flash photolysis experiments.[41]

For oxygen-purged samples there is clearly a two-component growth at 315 nm, consisting of instantaneous and 0.5 μs components. Similarly, the signal at 330 nm shows a rapid 0.5 μs decay as well as a much longer lived residual absorption. These results are consistent with a second radical cation band in the 330 nm region (instantaneous jump at 315 nm, 0.5 μs decay at 330 nm), as has also been observed by generating the same radical cation from an alternate precursor.[41] The radical cation then decays by deprotonation to give the long-lived diphenylaminyl radical, in agreement with earlier results for other amine radical cations.[10,29] Further, we cannot exclude the possibility that some radical is produced by direct photohomolysis, as has been observed for some other amines.[29,30,42] Under a nitrogen atmosphere (where both triplet DPA and DHC are formed) some of the short wavelength signal is also due to DHC since the decay kinetics in the long time regime (≤20 μs) are the same as those at 630 nm. It is also possible that triplet DPA absorbs in this region, although the complex mixture of transients makes it difficult to establish this with any certainty.

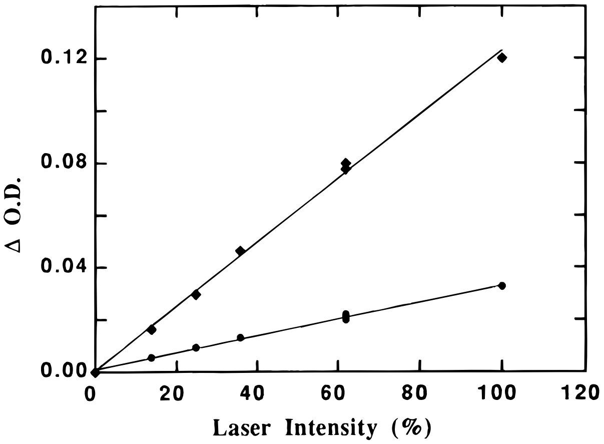

Figure 3. Plots of transient absorption intensity at 670 nm as a function of laser intensity for 308 nm excitation of diphenylamine in 1:1 aqueous acetonitrile (◆) and methanol (●).

The radical cation yield at 670 nm was measured as a function of the laser intensity for oxygen-saturated solutions of 1:1 aqueous acetonitrile and methanol; overlap of the radical cation signal with both the triplet amine and the dihydrocarbazole makes it difficult to quantify the triplet yield for nitrogen-saturated solutions. The resulting plots (shown in Figure 3) are linear over the range of laser intensities employed and do not show any hint of the positive curvature that would be expected for a two-photon process.

Two-Laser Experiments. Triplet DPA generated by 308 nm laser irradiation in aqueous acetonitrile was excited after a 300 ns delay with a 532 nm pulse. The second laser results in efficient and permanent bleaching of the triplet at 520 nm (Figure 4, top) with concomitant formation of additional radical cation at 670 nm (Figure 4, bottom). Similar traces recorded at 315 nm indicate the formation of a substantial fraction of additional signal as a result of the triplet bleaching, again consistent with a second absorption band of $DPA^{+\bullet}$ at this wavelength. The two-laser results are somewhat complicated by the fact that there is also a small amount of absorption due to DHC at 532 nm. If the two-laser pulses are delayed by sufficient time to allow the triplet to decay completely, efficient bleaching of the dihydrocarbazole is also observed at 630 nm. This is not surprising in view of the fact that a light-induced ring-opening reaction of the dihydrocarbazole of *N*-methylcarbazole to regenerate *N*-methyldiphenylamine has been reported.[35,36] In our experiments selective excitation of DHC leads to bleaching but does not lead to production of amine radical cation. Further, monitoring at 315 nm in a two-laser experiment shows neither bleaching of the initial signal nor formation of additional species. This suggests that DHC and its photochemical product have similar molar absorption coefficients at this wavelength.

Two-laser excitation of DPA with conductivity detection confirms that ionic species are produced upon excitation of triplet DPA in aqueous acetonitrile. The conductivity traces show a large increase in conductance as a result of the second laser pulse; complex decay kinetics that reflect the combined effects of the generation of solvated electrons, radical ions, and protons in the one- and two-laser experiments are observed. Excitation of the dihydrocarbazole alone at a sufficient delay to allow for complete triplet decay does not lead to any net increase in conductance, confirming that this reaction does not

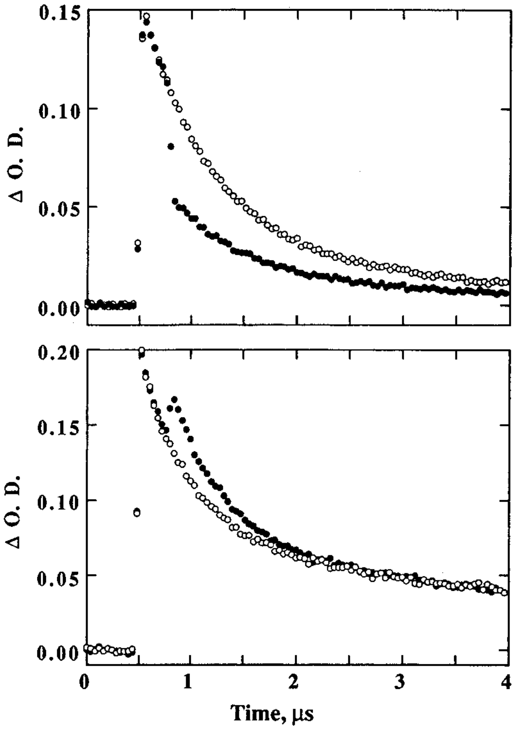

Figure 4. Decay of diphenylamine triplet at 520 nm (top) and radical cation at 670 nm (bottom) in 1:1 aqueous acetonitrile in one-laser (○, 308 nm) and two-laser (●, 308 + 532 nm) experiments.

lead to ionic species and consistent with electrocyclic ring-opening to give DPA.

In principle it should be possible to use the relative yields of triplet bleaching and radical cation production and the reported estimates of 15 000 and 27 000 M^{-1} cm^{-1} for the molar absorption coefficients (in methanol) of the triplet and radical cation, respectively, to estimate the fraction of bleaching that leads to photoionization.[34] Although the relatively short lifetime of the radical cation makes it difficult to quantify its yield in the two-laser experiment, our data, in combination with the published molar absorption coefficients, suggest that the yield of triplet bleaching is not fully accounted for by radical cation production. However, there is no additional transient evidence for other products in the two-laser experiments in aqueous acetonitrile. In particular, one- and two-laser traces at 720 nm, a region where only the diphenylaminyl radical absorbs, are identical. Similarly, there is no evidence for increased production of ground state DHC at the time of the second laser pulse. Reverse intersystem crossing to the singlet manifold is another potential mechanism for triplet bleaching. This would result in DPA fluorescence ($\Phi_F = 0.11$)[34] at 340 nm at the time of the 532 nm laser pulse. The fact that two-laser fluorescence was not observed indicates that the reverse intersystem crossing mechanism is unlikely to account for a significant fraction of the observed triplet bleaching. Based on the fluorescence quantum yield and the intensity of the one-laser (308 nm) DPA fluorescence signal, we estimate that two-laser fluorescence would have been observed if ≥10% of the triplet bleaching had occurred via reverse intersystem crossing to give singlet DPA.

The amoung of bleaching at 520 nm was measured under matched conditions (same laser power and experimental conditions) for triplet DPA in several solvents. The relative efficiencies are reported in Table 1 as the fraction of total triplets bleached by the 532 nm laser pulse at 0.3 μs after the initial 308 nm synthesis laser pulse. The relative triplet yields produced by 308 nm excitation of DPA under matched conditions are also given for comparison. The triplet bleaching was corrected for the contribution due to bleaching of the small amount of residual DHC absorption at 520 nm. This was done by measuring the amount of bleaching 5.5 μs after the laser pulse, at which time all of the triplets have decayed and the remaining bleaching arises only from DHC. In each case, the bleaching of the triplet was accompanied by formation of additional radical cation at 670 nm. Given the small yields of triplet bleaching and radical cation production in some cases, it is not possible to draw any quantitative conclusions as to whether the fraction of bleaching that leads to photoionization changes significantly in the various solvents.

TABLE 1: Relative Triplet Yields (One Laser, 308 nm) and Fraction of Triplet DPA Bleached at a Fixed 532 nm Laser Intensity for Various Solvents

solvent	relative triplet yields	fraction bleached (%)
1:1 aqueous acetonitrile	0.1	46
acetonitrile	0.07	23
1:1 aqueous methanol	0.085	10
1:1 aqueous 2-propanol	0.06	9
methanol	0.04	5
2-propanol	0.028	4

Discussion

The above results confirm that excitation of triplet DPA does lead to photoionization in both acetonitrile and alcohols. For example, efficient triplet bleaching is observed upon 532 nm excitation of triplet DPA in aqueous acetonitrile, and the combination of optical and conductivity measurements confirms that a significant fraction of triplet bleaching leads to photoionization to give $DPA^{+\bullet}$. These results are consistent with previous work on DPA in an ethanol glass at 77 K, in which case a biphotonic reaction via the triplet was suggested to lead to $DPA^{+\bullet}$.[43] Although attempts to quantify the relative triplet bleaching and radical cation yields in the two-laser experiments suggest that pathways other than photoionization may also occur, there is no evidence for cyclization, N−H bond cleavage to generate the diphenylaminyl radical, or reverse intersystem crossing to regenerate singlet DPA in aqueous acetonitrile. This suggests that errors in the extinction coefficients used to estimate the relative yields may account for some or all of the discrepancy. The lack of N−H bond cleavage for the upper triplet of DPA is in contrast to results for other aromatic amines such as iminodibenzyl and phenothiazine, for which triplet bleaching resulted in both photoionization and N−H bond cleavage in acetonitrile.[29,30] The differences in chemistry of the upper triplet states may be related to a combination of changes in solvent and the fact that additional decay pathways are available to diphenylamine as compared to the more rigid cyclic analogs.

The data in Table 1 demonstrate that the triplet bleaching yields vary by approximately an order of magnitude for the various solvent mixtures. The triplet bleaching is most efficient in aqueous acetonitrile and lowest in methanol and 2-propanol; in most cases the bleaching yield in a 1:1 aqueous solvent mixture is twice that in the neat solvent. In all cases the triplet bleaching is accompanied by the formation of additional radical cation at 670 nm. The relative bleaching yields do not appear to show any trend with respect to either solvent polarity or viscosity. The variations in yields may be related to changes in the rates of chemical versus nonchemical decay mechanisms for the upper excited states populated by the 532 nm laser pulse. The available information on the photophysics and photochemistry of DPA indicates that quantum yields for formation of the lowest energy triplet and for photocyclization show substantial solvent dependence.[34,40] These results have been rationalized on the basis of the formation of hydrogen-bonded complexes between the excited singlet of DPA and the hydrogen bond donor.[34] Similar effects may be responsible for the solvent effects on the triplet bleaching yields. To the extent that the relative bleaching yields reflect relative photoionization yields in the different solvents, it is interesting to compare the present results to literature data on the effect of solvent on photoionization yields. For example, photoionization of 2,7-bis(dimethylamino)-4,5,9,10-tetrahydropyrene is observed in acetonitrile but not in dimethylformamide, despite the large dielectric constant of the latter.[3] These results have been rationalized in terms of the importance of specific interactions between the solvent and excited solute in determining the photoionization efficiency. Photoionization yields of triplet promazine as a function of the water content in aqueous methanol mixtures have also been reported.[23] In this case the photoionization yield increases linearly with the percentage of water and has been explained on the basis of a lower solvation energy for the electron in methanol as compared to water.

Although the two-laser results clearly demonstrate that photoionization can occur from an upper triplet state, they do not require that this be the mechanism for radical cation formation in the one-laser (308 nm) flash photolysis experiments. In both methanol and aqueous acetonitrile, plots of laser intensity versus radical cation yield appear to be linear over the range of laser intensities used in our experiments, which suggests (although it does not prove)[24] that photoionization is monophotonic. Note that although these experiments were done under an oxygen atmosphere, the triplet lifetime was still substantially longer than the 6 ns laser pulse. The linear dose dependence is in contrast to the reported production of $DPA^{+\bullet}$ via formation and excitation of the triplet using a single 308 nm laser pulse.[34] This conclusion was based on differences in the intensity dependences of the radical cation and solvated electron signals as compared to those for triplet DPA and DPA fluorescence. Although the latter signals show very pronounced negative curvature at high laser intensity, the curvature is much less pronounced for $DPA^{+\bullet}$ or the solvated electron. Furthermore, the laser pulse duration in the previous experiments was 16 ns, as compared to 6 ns in our experiments. Given the reported singlet lifetime of DPA of 3 ns, the possibility of triplet excitation within a single laser pulse will certainly be higher for the longer pulse duration. However, it is also interesting to note that our experiments demonstrate that the transient phenomena in the 300−330 nm region are complex and absorption of a second 308 nm photon by species other than either singlet or triplet DPA (e.g. $DPA^{+\bullet}$) could also contribute to the laser intensity results in the previous work.

It is clear from the above discussion that it is difficult to distinguish between the possible mechanisms for the one-laser photoionization of DPA, as has frequently been observed for other substrates.[3−23,27−32] In fact, it is likely that both monophotonic and sequential biphotonic mechanisms from either the singlet or triplet can occur, with the contributions from each route varying with the solvent and the laser wavelength, intensity, and pulse duration. Our results have demonstrated the feasibility of triplet photoionization using 532 nm excitation. Although the yields are relatively low in pure alcohol solutions, it is possible that a biphotonic process involving a second 308 nm photon would give a higher yield for electron photoejection. Unfortunately, in this case we were unable to test directly whether or not there are differences in photoionization yields for 308 versus 532 nm excitation of the triplet in a two-laser experiment. This is a result of the fact that there is no convenient way to generate triplet DPA under conditions such that the ground state amine does not absorb substantially at 308 nm. Therefore, there is always substantial production of additional triplet and radical cation by the second 308 nm laser pulse. The question of wavelength dependence of excited triplet photoionization yields can probably be better investigated for a system where the one-photon chemistry is less complex and where selective excitation of the triplet can be accomplished over a relatively wide range of excitation energies.

Supporting Information Available: One- and two-laser conductivity traces (1 page). Ordering information is given on any current masthead page.

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