Direct Observation of the 4-Methoxyphenylnitrene Intersystem Crossing from S_1 to T_1 Using Picosecond Kerr-Gated Time-Resolved Resonance Raman Spectroscopy

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A picosecond Kerr-gated time-resolved resonance Raman (ps-KTR^3) study of the singlet 4-methoxyphenylnitrene intersystem crossing to produce the triplet 4-methoxyphenylnitrene species is reported. The experimental resonance Raman vibrational band frequencies observed for the singlet and triplet 4-methoxylphenylnitrene species in the time-resolved Raman experiments are compared to each other and to predictions from previously published density functional theory calculations. The structure, properties, and chemical reactivity of the singlet and triplet states of the 4-methoxyphenylnitrenes are briefly discussed.

Introduction

The photochemistry of aryl azides have been particularly well investigated, and the use of laser flash photolysis to directly probe their reaction intermediates and photoproducts has led to a greater understanding of their reaction mechanisms.[1−60] Photolysis of aryl azides in room temperature solutions typically leads to formation of a singlet arylnitrene species and a nitrogen molecule. In some cases, the singlet arylnitrene can do a very rapid ring expansion reaction to produce ketenimines (dehydroazepines) that can then be trapped by nucleophiles. In other cases, molecules like 2-pyrimidylnitrene decay mainly by intersystem crossing (ISC) to form the triplet arylnitrene species.[55] The chemistry and reaction mechanisms of singlet phenylnitrene have been a very well investigated prototype for arylnitrenes and their reactions.[7,8,18,20,21,42−46,52−54] While the singlet phenylnitrene has a short lifetime of about 1 ns in room temperature solutions because of its very fast ring expansion reaction, the lifetimes of singlet phenylnitrenes may be significantly longer when various substituents are added to the phenyl ring.[16−18,22−25,29,40,55,57] These longer lived singlet arylnitrene intermediates are able to be trapped more easily by nucleophiles such as diethylamine or pyridine, and some are able to react with water to form arylnitrenium ions.[26,28,31−37,40,47,48,61] A great deal has been learned about the chemistry and reaction mechanisms of arylnitrenes from these studies.

While there have been many spectroscopic investigations of arylnitrenes and their reactions, there are relatively few studies that have made use of direct time-resolved vibrational spectroscopic characterization of these species and their reactions in room temperature solutions. Time-resolved infrared spectroscopy has been used by several groups to study the ring expansion reactions of several arylnitrenes as well as to probe several arylnitrenium ions in organic solvents.[14,41,48,56,62] We have recently reported the first time-resolved resonance Raman spectra of an arylnitrene and its ring expansion reaction as well as of a triplet arylnitrene and its dimerization reaction in room temperature solutions.[60]

In this paper, we present a picosecond Kerr-gated time-resolved resonance Raman study of the singlet 4-methoxyphenylnitrene intersystem crossing (ISC) to produce the triplet 4-methoxyphenylnitrene species. To our knowledge, this is the first direct time-resolved vibrational spectroscopic observation of an arylnitrene intersystem crossing in room temperature solutions. Picosecond Kerr-gated time-resolved resonance Raman spectroscopy (ps-KTR^3) experiments observed that a 4-methoxyphenylnitrene species was produced promptly after 267 nm photolysis of 4-methoxyphenyl azide in acetonitrile and water/acetonitrile solvents. The first 4-methoxyphenylnitrene species observed in the ps-KTR^3 experiments decayed and produced the triplet 4-methoxyphenylnitrene species in acetonitrile solution that has been previously observed in nanosecond time-resolved resonance Raman spectroscopy (ns-TR^3) experiments.[60c] However, in the water/acetonitrile solvents the first 4-methoxyphenylnitrene species observed in the ps-KTR^3 experiments decayed and produced the 4-methoxyphenylnitrenium ion that has been previously observed in ns-TR^3 experiments.[61d,e] Based on the expected chemical reactivity of singlet arylnitrenes substituted with electron-donating groups toward water to form arylnitrenium ions, the first species observed in the ps-KTR^3 experiments is assigned to the singlet 4-methoxyphenylnitrene species and its decay in the acetonitrile solvent to the triplet 4-methoxyphenylnitrene species to the ISC reaction. The experimental resonance Raman vibrational band frequencies observed for the singlet and triplet 4-methoxylphenylnitrene species in the time-resolved Raman experiments are compared to each other and to predictions from previously published density functional theory calculations.[61e]

Experimental Methods

Preparation of 4-Methoxyphenyl Azide Precursor Compound. Samples of 4-methoxyphenyl azide were synthesized based on previously described methods,[63] and further details of the synthesis and characterization are given in the supporting information of ref 60c. The 4-methoxyphenyl azide samples were prepared with concentrations of ∼1 mM using spectroscopic grade acetonitrile and deionized water solvents. These sample solutions were used in the ps-KTR^3 experiments described in the next subsection.

Picosecond Kerr-Gated Time-Resolved Resonance Raman (ps-KTR^3) Experiments. The experimental apparatus and

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methods used for the ps-KTR^3 experiments have been detailed in refs 64 and 65, so only a brief description is given here. The Kerr-gated fluorescence rejection variation of the ps-TR^3 experiments is described in ref 61e and is based on the technique developed at Rutherford Appleton Laboratory that is described in detail in refs 66 and 67. The Ti:sapphire regenerative amplifier laser system was used in the picosecond mode to produce a 800 nm, ~1 ps, and 1 kHz output, and the third harmonic (267 nm) of this output was employed as the pump excitation wavelength. The second harmonic (400 nm) was utilized to pump an OPA whose output was mixed with some residual 800 nm light to generate a 320 nm probe excitation wavelength. The durations of the pump and probe pulses were both about 1.5 ps, and the pulse energies at the sample were about 10 and 2 μJ, respectively, focused to a spot size of about 200 μm. These probe and pump beams were focused onto a 0.5 mm thick flowing liquid stream of sample placed at one focus of an ellipsoidal mirror. The emitted/scattered light from the sample was collected by the ellipsoidal mirror and then passed through a Glan Taylor polarizer. This collected light was then focused into the Kerr medium (a 2 mm UV cell containing benzene) placed at the other focus point of the ellipsoid between a crossed polarizer pair with an extinction ratio of $\sim 10^5$. The gating 800 nm beam was polarized at 45° and focused into the Kerr medium. The gating pulse intensity was adjusted to act as a half-wave plate that rotates the polarization of the scattered/emitted light of the sample to enable it to be transmitted through a Glan Taylor polarizer for the duration of the induced anisotropy created by the picosecond gating pulse. The scattered/emitted light that passed through the second polarizer was focused into a monochromator and detected by a liquid nitrogen cooled CCD detector. The Raman scattered light was acquired at varying time delays following the pump pulse by using a computer-controlled optical delay line, and the polarization of the pump and probe pulses was set at the magic angle in the ps-KTR^3 experiments. The time zero delay between the pump and probe laser beams was found by using fluorescence depletion of *trans*-stilbene. The time resolution for the ps-KTR^3 measurements was determined to be ~2 ps.

Results and Discussion

Picosecond Kerr-Gated Time-Resolved Resonance Raman (ps-KTR^3) Observation of the S$_1$ to T$_1$ Intersystem Crossing of 4-Methoxyphenylnitrene. Figure 1 presents an overview of selected ps-KTR^3 spectra obtained after 267 nm photolysis of 4-methoxyphenyl azide in acetonitrile solvent using a 320 nm probe excitation wavelength. A more comprehensive overview of the ps-KTR^3 spectra collected at all the delay times used is given in the Supporting Information (Figure S1). The ps-KTR^3 spectra in Figure 1 have broader Raman bands than the previous ns-TR^3 spectra due to the larger spectral bandwidth of the ~1.5 ps pulses used in the ps-KTR^3 experiments, and this leads to some Raman bands not being very well resolved from one another. The ps-KTR^3 spectra in Figure 1 shows that the first species observed appears within about 1 ps, becomes more intense up to about 20 ps, and then starts to decay into a second species within several hundred picoseconds.

We have previously observed the triplet 4-methoxyphenylnitrene species in acetonitrile solvent using ns-TR^3 spectroscopy and a 320 nm probe wavelength following ultraviolet photolysis of 4-methoxyphenyl azide.[60c] The second species observed in the ps-KTR^3 spectra of Figure 1 appears similar to the ns-TR^3 spectra previously reported for the triplet state of the 4-methoxyphenylnitrene species.[60c] Figure 2 presents a comparison between the 10 ns spectrum of the ns-TR^3 spectra previously reported in ref 60c and the ps-KTR^3 spectrum obtained at 400 ps, 850 ps, and 4 ns in Figure 1 of this study. Inspection of Figure 2 shows there is good agreement between the nanosecond and picosecond spectra considering the lower spectral resolution of the ps-KTR^3 spectra, and this identifies the second species as probably being due to triplet 4-methoxyphenylnitrene.

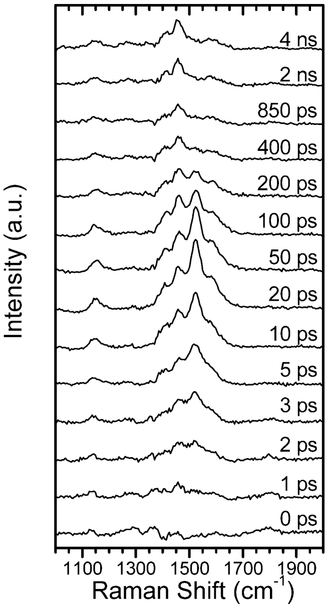


Figure 1. Overview of selected ps-KTR^3 spectra obtained after 267 nm photolysis of 4-methoxyphenyl azide in acetonitrile solvent using a 320 nm probe excitation wavelength. The time delays are indicated to the right of each spectrum.

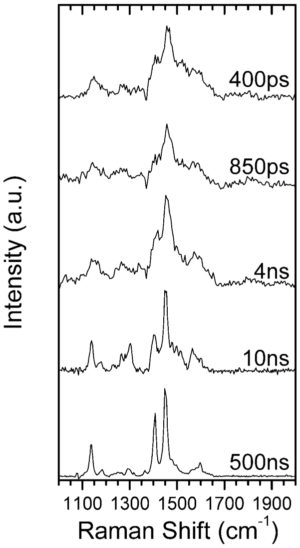


Figure 2. Comparison of 320 nm ps-KTR^3 spectra obtained at 400 ps, 850 ps, and 4 ns (this work) to 320 nm ns-TR^3 spectrum obtained at 10 ns and 500 ns (from ref 60c) in acetonitrile solvent.

In previous ns-TR^3 experiments, the decay of the triplet 4-methoxyphenylnitrene led to the growth of its azo dimerization product on the hundreds of nanoseconds time scale.[60c] Since the triplet 4-methoxyphenylnitrene and its dimerization product have common structural features such as the methoxy phenyl moiety, many of their vibrational frequencies and resonance Raman bands are very similar to one another with only a handful of vibrations associated mainly with the nitrene or azo moieties being diagnostic or characteristic of each species. This made it difficult to elucidate how many of the resonance Raman bands

TABLE 1: Experimental Raman Vibrational Frequencies Observed in the 10 ps and 10 ns Time-Resolved Resonance Raman Spectra of the 4-Methoxyphenylnitrenes Shown in Figures 1 and 2[a]

singlet 4-methoxyphenylnitrene			triplet 4-methoxyphenylnitrene		
vibrational mode, possible description	UBPW91/cc-PVDZ calcd value (cm^{-1})	expt 10 ps ps-KTR^3 freq shift (cm^{-1})	vibrational mode, possible description	UBPW91/cc-PVDZ calcd value (cm^{-1})	expt 10 ns ns-TR^3 freq shift (cm^{-1})
ν_{29}, C−H bend	758		ν_{29}, C−H bend	768	
ν_{28}, C−H bend	808		ν_{28}, C−H bend	810	
ν_{27}, CCC bend	810		ν_{27}, CCC bend	824	824
ν_{26}, C−H bend	911		ν_{26}, C−H bend	914	
ν_{25}, C−H bend	937		ν_{25}, C−H bend	938	
ν_{24}, CCC bend	951		ν_{24}, CCC bend	958	
ν_{23}, CCC bend + C−O str	1025		ν_{23}, CCC bend + C−O str	1027	
ν_{22}, C−C str + C−H bend	1077		ν_{22}, C−C str + C−H bend	1081	
ν_{21}, CH_3 bend	1116		ν_{21}, CH_3 bend	1117	
ν_{20}, C−H bend	1133		ν_{20}, C−H bend	1131	1139
ν_{19}, C−H bend + CH_3 bend	1155	1148	ν_{19}, CH_3 bend	1156	
ν_{18}, C−C str	1222		ν_{18}, C−C str	1235	1232
ν_{17}, C−C str + C−O str	1257	1265	ν_{17}, C−C str + C−O str	1256	1265
ν_{16}, C−C str + C−O str	1283		ν_{16}, C−C str + C−O str	1291	1301
ν_{15}, C−C str + C−N str	1379		ν_{15}, C−C str + C−N str	1322	
ν_{14}, C−C str + C−N str	1412	1405	ν_{14}, CH_3 bend + C−N str	1403	1401
ν_{13}, CH_3 bend	1420		ν_{13}, CH_3 bend	1420	
ν_{12}, C−C str + C−N str	1424		ν_{12}, C−C str + CH_3 bend	1422	
ν_{11}, C−C str + CH_3 bend	1432		ν_{11}, C−C str + CH_3 bend	1433	
ν_{10}, C−C str + CH_3 bend + C−N str	1446	1458	ν_{10}, C−C str + C−N str + C−O str	1445	1448
ν_{9}, C−C str	1485	1523	ν_{9}, C−C str	1499	1499
ν_{8}, C−O str + C−C str + C−N str	1584	1584	ν_{8}, C−N str + C−C str + C−O str	1585	1575

[a] The experimental vibrational frequencies are compared to those from UBPW91/cc-PVDZ computations from ref 60c for the singlet and triplet States of 4-methoxyphenylnitrenes. See text for more details.

in the 10 ns ns-TR^3 spectrum were mostly due to the triplet species and which ones had noticeable contributions from the azo-dimer product. The comparison of the 10 ns ns-TR^3 spectrum in Figure 2 with 400 ps, 850 ps, and 4 ns ps-KTR^3 spectra enable this ambiguity to be resolved. Since the triplet 4-methoxyphenylnitrene species decays on the hundreds of nanoseconds time scale into its azo-dimer product, one would expect negligible amounts of the azo-dimer product to be found in the 400 and 850 ps ps-KTR^3 spectra. Therefore, these 400 and 850 ps spectra should be almost entirely due to the triplet 4-methoxyphenylnitrene species. The 400 and 850 ps ps-KTR^3 spectra are essentially the same as those obtained at 4 and 10 ns (taking into account the higher resolution of the 10 ns spectrum). This indicates that the 4 and 10 ns spectra are also due mostly to the triplet 4-methoxyphenylnitrene species. There is apparently little discernible contribution of the azo-dimer product resonance Raman spectrum to the spectra obtained up to 10 ns. This allows us to assign most of the Raman bands observed in the higher resolution 10 ns TR^3 spectrum to the triplet 4-methoxyophenylnitrene species. The Raman band vibrational frequencies of the ns-TR^3 spectra along with their tentative assignments are shown in Table 1 and compared to previously reported results from density functional theory calculations.[60c] Inspection of Table 1 shows the Raman vibrational frequencies observed in the 10 ns ns-TR^3 spectra of Figure 2 are in reasonable agreement with those predicted from the density functional theory calculations with an average difference of about 5 cm^{-1} between the experimental and calculated values.

It is useful to compare the 400 ps and 4 ns ps-KTR^3 spectra and the 10 ns ns-TR^3 spectrum to that at 500 ns, and this comparison is also presented in Figure 2. Examination of Figure 2 shows that the resonance Raman intensity pattern of the 500 ns spectrum is noticeably different from those of the 400 ps, 4 ns, and 10 ns spectra. This is consistent with the 400 ps, 4 ns, and 10 ns spectra being mainly due to the triplet 4-methoxyphenylnitrene, while the 500 ns spectrum is mainly due to the azo-dimer species formed from the triplet 4-methoxyphenylnitrene dimerization reaction. In addition, the 500 ns spectrum shows significant intensity in its overtones and combination bands in the 2400−3200 cm^{-1} region while the 10 ns spectrum does not (see Figure 1 of ref 60c), also suggesting that these spectra are mainly due to two distinctly different species. We note that the 500 ns spectrum was found to be essentially identical to that observed for the resonance Raman spectrum of an authentic sample of the azo-dimer product that was synthesized by another method.[60c] This clearly confirmed the identity of the azo-dimer product species being responsible for the 500 ns TR^3 spectrum.[60c] Although both the triplet 4-methoxyphenylnitrene and its azo-dimer product have very similar vibrational frequencies for many of their Raman bands due to their similar 4-methoxyphenyl moieties, their resonance Raman spectra can be clearly distinguished from one another by their different resonance Raman intensities and their appearance at distinctly different times after photolysis of the parent 4-methoxyphenyl azide. This points out one of the advantages of using TR^3 spectroscopy for following a chemical reaction and identifying intermediates at different times during the reaction. This is also why the first species observed in the ps-KTR^3 spectra shown in Figure 1 can be distinguished clearly from the second species (their resonance Raman intensity patterns differ and are associated with different times after photolysis of the parent compound).

We recently reported 320 nm ps-KTR^3 spectra obtained after 267 nm photolysis of 4-methoxyphenyl azide in a 60% water/40% acetonitrile solvent system.[61e] Figure 3 shows a comparison of an overview of selected ps-TR^3 spectra acquired in the 60% water/40% acetonitrile solvent system from ref 61e and the ps-KTR^3 spectra reported here in pure acetonitrile solvent. Examination of the 3 ps ps-TR^3 spectra obtained in both solvent systems shows that they are almost the same, taking into account the somewhat broader bands in the 60% water/40% acetonitrile solvent. The first species in both solvent systems in Figure 3 appear within the 1−2 ps time resolution of the ps-KTR^3 experiments. Since ultraviolet photolysis of aryl azides leads directly to a nitrogen bond cleavage to produce the singlet arylnitrene and a nitrogen molecule, it is reasonable to assign

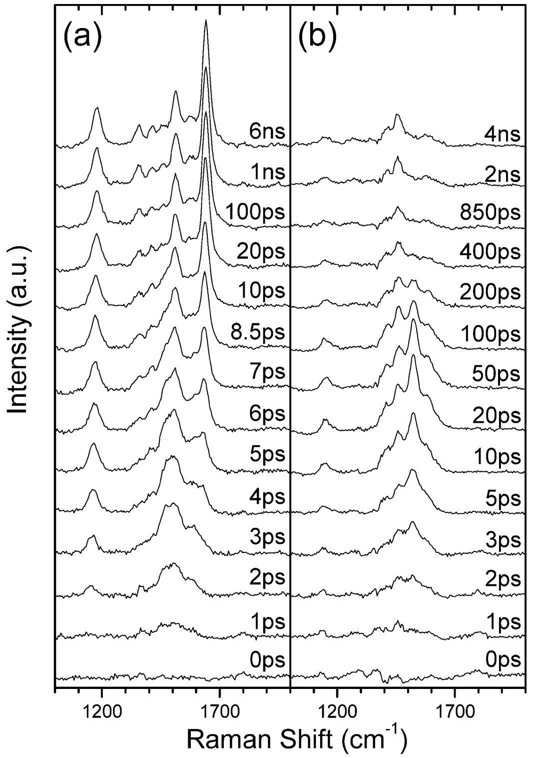


Figure 3. Comparison of overview of selected ps-KTR^3 spectra acquired in the 60% water/40% acetonitrile solvent system (a) from ref 61e and selected ps-KTR^3 spectra reported here in pure acetonitrile solvent (b). The time delays are indicated to the right of each spectrum.

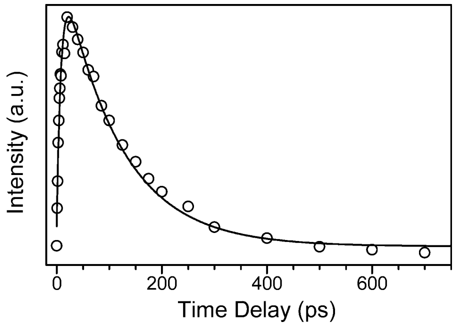
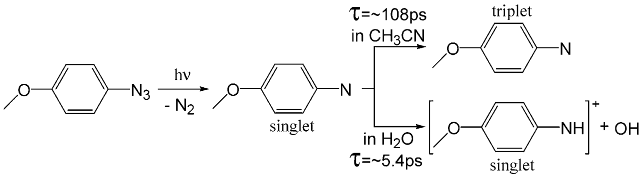


Figure 4. Integrated intensity of the strong 1523 cm^{-1} Raman band of the singlet 4-methoxyphenylnitrene species as a function of time (open circles). The line presents a best-fit exponential decay and growth curve to the data.

SCHEME 1



the first species in the ps-KTR^3 spectra in Figures 1 and 3 to the singlet 4-methoxyphenylnitrene. Further support for this assignment is found in the fate of the first species in the 60% water/40% acetonitrile solvent. Our recent study in ref 61e found that the first species decayed with a time constant of 5.4 ps to directly form the singlet 4-methoxyphenylnitrenium ion. This assignment was confirmed by comparison of the second species ps-KTR^3 spectra in the largely aqueous solvent to those previously observed for the ns-TR^3 spectrum of the singlet 4-methoxyphenylnitrenium ion.[61d,e] Because the second species observed in the largely aqueous solvent is due to the singlet 4-methoxyphenylnitrenium ion and the first species appears within the 1−2 ps time resolution of the ps-KTR^3 experiments of Figure 3, we assign the first species in both solvent systems as being due to singlet 4-methoxyphenylnitrene. This is consistent with the known chemical reactivity of singlet arylnitrenes substituted with electron-donating groups reacting very quickly with water to produce their corresponding singlet arylnitrenium ion and the known photochemistry of aryl azides such as 4-methoxyphenyl azide. The Raman band vibrational frequencies of the singlet 4-methoxyphenylnitrene species observed in the 10 ps-KTR^3 spectrum along with their tentative assignments are shown in Table 1 and compared to previously reported results from density functional theory calculations.[60c] Inspection of Table 1 shows that the Raman vibrational frequencies observed in the 10 ps-KTR^3 spectra of Figures 1 and 3 appear to be in reasonable agreement with those predicted from the density functional theory calculations with an average difference of about 12 cm^{-1} between the experimental and calculated values.

By elucidation of the fates of the two species observed in Figure 1 after photolysis of 4-methoxyphenyl azide in acetonitrile and in the 60% water/40% acetonitrile solvents, the first species was assigned to the singlet 4-methoxyphenylnitrene and the second species to the triplet 4-methoxyphenylnitrene. Thus, the evolution of the first species into the second species in Figure 1 in acetonitrile solvent is the direct time-resolved vibrational spectroscopic observation of the S_1 to T_1 intersystem crossing (ISC) reaction for 4-methoxyphenylnitrene. The integrated intensity of the strong 1523 cm^{-1} Raman band of the singlet 4-methoxyphenylnitrene species as a function of time can be used to follow the S_1 to T_1 ISC reaction, and this is shown in Figure 4. The growth and decay times of the integrated intensity of the strong 1523 cm^{-1} Raman band of the singlet 4-methoxyphenylnitrene species as a function of time in Figure 4 were fit to simple exponential growth and decay functions (shown by the solid line in Figure 4). The best fit to the data of Figure 4 found a 8.5 ps time constant for the rise time and a 108 ps time constant for the decay time. This indicates that the S_1 to T_1 ISC reaction has a time constant of 108 ps for the 4-methoxyphenylnitrenes at room temperature in acetonitrile solvent.

Scheme 1 can be referred to in subsequent discussion of the ISC reaction and the reaction of the singlet 4-methoxyphenylnitrene with water.

Comparison of the TR^3 spectra of Singlet and Triplet 4-Methoxyphenylnitrenes and Their Reactions. Examination of the ps-KTR^3 spectra for the singlet and triplet 4-methoxyphenylnitrenes in Figure 1 reveals that most of the resonance Raman enhancement for the singlet 4-methoxyphenylnitrene ps-KTR^3 spectra appears in the ν_{14} (C−C str + C−N str), ν_{10} (C−C str + CH_3 bend + C−N str), ν_9 (C−C str), and ν_8 (C−O str + C−C str + C−N str) Raman bands with the largest enhancement occurring in the ν_9 (C−C str) Raman band. This indicates that the $S_1 \rightarrow S_n$ transition associated with the KTR^3 spectra involves mainly changes in the structure of the phenyl ring accompanied by some changes in the C−O and C−N bonds. The triplet 4-methoxyphenylnitrene nanosecond and picosecond TR^3 spectra exhibit the strongest enhancement in the ν_{10} (C−C str + C−N + C−O) Raman band accompanied by appreciable enhancement of the ν_{14} (CH_3 bend + C−N str), ν_9 (C−C str), and ν_8 (C−N str + C−C str + C−O str) Raman bands. This indicates that the $T_1 \rightarrow T_n$ associated with the TR^3 spectra of the triplet 4-methoxyphenylnitrene involves mainly changes in the structure of the C−C, C−N, and C−O bonds accompanied by a moderate amount of the nominal CH_3 bend motion. The different spin density in the S_1 and T_1 states and their relevant S_n and T_n states appears to lead the resonance Raman enhancement of the $S_1 \rightarrow S_n$ transition and $T_1 \rightarrow T_n$ transition to have noticeably different intensity patterns in their TR^3 spectra. The experimental Raman vibrational frequencies of the ν_{10}, ν_9, and ν_8 Raman bands are consistently higher for the singlet 4-methoyxphenylnitrene than for the triplet 4-methoxyphenylnitrene (1458, 1523, and 1584 cm^{-1}, respectively, for the singlet compared to 1448, 1499, and 1575 cm^{-1} for the triplet). This suggests that the singlet charge distribution and/or spin density may be more localized than in the triplet state.

We note that the density functional theory (DFT) UBPW91/cc-PVDZ calculations agreed noticeably better for the triplet state Raman vibrational frequencies than those for the singlet state. The differences were only 5 cm^{-1} on average between the experimental and computed values for the triplet state compared to corresponding differences of 12 cm^{-1} for the singlet state. The UBPW91/cc-PVDZ calculations for the triplet state of 4-methoxyphenylnitrene had no appreciable spin contamination as deduced from their $\langle S^2 \rangle$ values.[60c] However, the UBPW91/cc-PVDZ calculations for the singlet state of 4-methoxyphenylnitrene had some spin contamination as discerned from their $\langle S^2 \rangle$ values.[60c] This may be the main reason for the UBPW91/cc-PVDZ computed vibrational frequencies having worse agreement with the experimental TR^3 spectra vibrational frequencies for the singlet compared to the triplet. This is consistent with the largest disagreement between the DFT calculations and the experimental Raman frequencies being observed for the ν_{10}, ν_9, and ν_8 vibrational modes of the singlet state, which would be expected to be more affected by any spin contamination effects. The ps-KTR^3 spectra and their experimental vibrational frequencies for the S_1 state may provide a useful experimental benchmark for testing how well different ab initio and DFT calculations are able to calculate the structure, vibrational frequencies, and properties of an open shell singlet arylnitrene in room temperature solutions. We hope this experimental data may be useful for theoretical groups to test and assess what ab initio and DFT methods can more accurately calculate the structures and vibrational frequencies for singlet open shell arylnitrenes that can be difficult to calculate very accurately due to spin contamination effects.

A previous time-resolved transient absorption and time-resolved infrared investigation of the photolysis of 4-methoxyphenyl azide observed that photolysis in cyclohexane solvent led to an 80% yield of the azo-dimer product while photolysis in the presence of diethylamine resulted in a 27% yield of the ketenimine adduct.[15] Since the azo-dimer product is associated with the triplet 4-methoxyphenylnitrene species and the ketenimine adduct is associated with a reaction of the singlet 4-methoxyphenylnitrene species, this implies that both the singlet and triplet 4-methoxyphenylnitrenes are formed in the solution phase consistent with our present observation of both species and their ISC in the ps-KTR^3 experiments. A more recent study using laser flash photolysis and product analysis observed that the photolysis of 4-methoxyphenyl azide in pentane solution formed a transient absorption spectrum of the triplet 4-methoxyphenylnitrene and the ketenimine products over a 100 ns window immediately following the photolysis laser pulse.[54] The singlet 4-methoxyphenylnitrene ISC to the triplet was estimated to have a rate constant $>500 \times 10^6$ s^{-1} with $\tau < 1$ ns.[54] Our direct ps-KTR^3 observation of the ISC reaction in acetonitrile solvent and measured $\tau = 108$ ps is consistent with the previous upper limit found in the previous work of ref 54. The demonstration of ps-KTR^3 in clearly distinguishing the singlet and triplet states of arylnitrenes and direct observation of their ISC reaction in our present work opens the possibility of doing very detailed studies of the relative reactivity of singlet and triplet arylnitrenes toward a range of substrates and different environments. For example, in the presence of water, the singlet 4-methoxyphenylnitrene was found to react with a time constant of about 5.4 ps to produce the singlet 4-methoxyphenylnitrenium ion,[61e] while in acetonitrile solvent the singlet 4-methoxyphenylnitrene undergoes ISC to produce the triplet 4-methoxyphenylnitrene (this work) and subsequently produces the azo-dimer product.[60c] In the presence of diethylamine, photolysis of 4-methoxyphenyl azide in cyclohexane solvent produced 27% ketenimine adducts, indicating this reaction is in competition with the fast ISC reaction.[54] Future studies are planned to investigate the reaction of diethylamine and other selected substrates to directly probe their reactivity toward the singlet and triplet 4-methoxyphenylnitrenes. In addition, it will be interesting to explore substituent and environment effects on the relative chemical reactivity of the very-short-lived singlet arylnitrenes. Our recent study showed that the reaction of the singlet 4-methoxyphenlnitrene with water was about 30 times faster than that of the singlet 2-fluorenylnitrene with water to produce their respective singlet arylnitrenium ions.[61e] This indicates substituent effects can be very important for the chemical reactivity of the singlet nitrene moiety. The shifts in the Raman band vibrational frequencies and intensity patterns are very sensitive probes of substituent and solvent or environmental effects on the structures of reactive intermediates. Thus, the ps-KTR^3 experiments will allow one to examine in detail how the structure and chemical reactivity of the short-lived singlet and triplet arylnitrenes change for different substituents and in differing environments. This should prove an interesting area to explore in the future.

Conclusions

A picosecond Kerr-gated time-resolved resonance Raman (ps-KTR^3) study of the S_1 to T_1 ISC reaction for 4-methoxyphenylnitrenes in room temperature acetonitrile solution was presented. ps-KTR^3 experiments observed that a 4-methoxyphenylnitrene species was formed immediately upon 267 nm photolysis of 4-methoxyphenyl azide in acetonitrile and water/acetonitrile solvents. This first species decayed to form the triplet 4-methoxyphenylnitrene species in acetonitrile solution that has been observed in previously published ns-TR^3 experiments. In the water/acetonitrile solvent, the first species observed in the ps-KTR^3 experiments decayed and produced the 4-methoxyphenylnitrenium ion that has been previously observed in ns-TR^3 experiments. The expected chemical reactivity of singlet arylnitrenes substituted with electron-donating groups (such as methoxy, hydroxy, thio, and amino) toward water is to form arylnitrenium ions. Thus, the first species observed in the ps-KTR^3 experiments was assigned to the singlet 4-methoxyphenylnitrene species and its decay in the acetonitrile solvent to the triplet 4-methoxyphenylnitrene species to the ISC reaction. The S_1 to T_1 ISC reaction was found to have a time constant of about 108 ps for the 4-methoxyphenylnitrenes at room temperature in acetonitrile solvent. The results from UBPW91/cc-PVDZ DFT calculations agreed noticeably better for the triplet state Raman vibrational frequencies than those for the singlet state. This could be due to some spin contamination in the calculations done for the singlet state. The experimental Raman vibrational frequencies of the ν_{10}, ν_9, and ν_8 Raman bands are higher for the singlet 4-methoyxphenylnitrene than for the triplet 4-methoxyphenylnitrene: 1458, 1523, and 1584 cm^{-1}, respectively, for the singlet compared to 1448, 1499, and 1575 cm^{-1} for the triplet. This may suggest that the singlet charge distribution and/or spin density may be more localized on the nitrene moiety than in the triplet state, where it may be more delocalized into the phenyl ring. We briefly discussed the potential utility of ps-KTR^3 spectroscopy to probe the structure, properties, and chemical reactivity of singlet and triplet arylnitrenes in room temperature solutions at the vibrational spectroscopic level of detail so as to elucidate substituent and environmental effects on their structure and chemical reactivity.

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Supporting Information Available: Figure S1 shows the ps-KTR^3 spectra obtained after 267 nm photolysis of 4-methoxyphenyl azide in acetonitrile solvent using a 320 nm probe wavelength. This material is available free of charge via the Internet at http://pubs.acs.org.

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