

Study of the S₁ Excited State of *para*-Methoxy-3-phenyl-3-methyl Diazirine by Ultrafast Time Resolved UV–Vis and IR Spectroscopies and Theory

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Abstract: Ultrafast laser flash photolysis ($\lambda_{\text{ex}} = 375$ nm) of *para*-methoxy-3-phenyl-3-methyl diazirine ($p\text{-CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CH}_3$) produced a transient absorption band in the 400–700 nm region. The carrier of the transient absorption is assigned to the S₁ electronic excited state of this compound based on quantum chemical calculations. The strongest vibrational mode of this S₁ excited state, predicted by RI-CC2/TZVP calculations, was directly observed in the mid-infrared region and had the same lifetime as the transient absorption band detected in the visible region, confirming that the same species is responsible for both transient spectra. The S₁ state undergoes solvation within 20 ps after its formation in polar solvents. Decay of the S₁ state leads to the formation of the isomeric diazo compound and singlet carbene. With 270 nm excitation, both singlet carbene and diazo compound are formed in a much more rapid process from the initially populated diazirine S₂ state (<4 ps), in competition with internal conversion to the S₁ state. The ultrafast spectroscopy and quantum calculations presented in this study provide a rather complete and consistent understanding of the structures and the decay kinetics of the excited states of an aryldiazirine and provide some conclusive answers to the pending general mechanistic questions concerning the photoisomerization of diazirine into diazo compound and the denitrogenation into carbenes.

1. Introduction

Ultrafast time-resolved spectroscopy has been shown to be a powerful tool to probe the decay dynamics of aryl azide and diazo excited states, and the formation and decay of nitrene or carbene reactive intermediates. The singlet excited states of aryl diazo compounds,^{1–5} aryl azides,^{6–9} and an excited singlet

carbene¹⁰ have recently been detected by ultrafast time-resolved UV–vis and IR spectroscopic studies. The excited states of aryl diazo compounds typically decay within 300 fs to form singlet aryl carbenes which undergo various intra- and intermolecular reactions.^{1,2,10} These studies also suggest that the excited states of diazo compounds can undergo [1,2]-H shift in concert with nitrogen extrusion,² a carbene mimetic reaction that has been termed “Rearrangement in Excited States” or RIES by Liu et al.^{11–15} Our studies of diazo carbonyl compounds further support previous proposals that a portion of the ketene product is formed from an excited state by an RIES mechanism.^{4,16–19} These studies have provided new insights into the very fast processes that proceed on electronically excited state potential energy surfaces.

Calculations have been performed to corroborate these interpretations; however, these studies often focus only on vertical excitation energies with respect to the electronic ground

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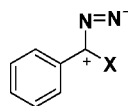
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state, without optimization of the structures of the different electronic states being considered. Unfortunately, transient UV–vis absorption experiments do not readily provide direct structural information about excited states comparable to that which can be obtained by ultrafast time-resolved infrared (IR)²⁰ or Time Resolved Resonance Raman Spectroscopy.²¹ Recent advances in electronic structure calculations (CASSCF, CC2) allow geometry optimizations of excited states and harmonic frequency calculations, analytically or numerically. Therefore, ultrafast IR spectroscopy, complemented with modern theoretical methods, appears to be a promising approach for studying excited state dynamics. Qualitative comparisons of calculated singlet electronic excited state vibrational spectra and spectroscopic data have been made previously but are not routine.^{22,23} In this study, ultrafast time-resolved UV–vis and IR spectroscopies, combined with modern quantum chemical calculations, were used to study the electronically excited states of an aryl diazirine.

Diazirines are the cyclic isomers of linear diazo compounds^{24–26} and are often employed as a preferred source of carbenes due to their greater kinetic stability and ease of handling.^{25–27} Diazirines have also found use as photoaffinity labeling reagents.^{28,29} However, the photophysics and photochemistry of diazirines are still active areas of investigation. Recently, we reported studies of arylhalodiazirine photochemistry using ultrafast time-resolved UV–vis spectroscopy (350–360 nm excitation).³⁰ A transient absorption band was formed within the laser pulse (300 fs). This transient was attributed to a ring-opened zwitterionic species.³⁰ However, the nature of this zwitterionic species as a discrete reactive intermediate or as a diazirine excited state was not determined.



We recently studied the photochemistry of phenyldiazirine (and the phenylchlorodiazirine analogue) by ultrafast infrared spectroscopy (270 nm excitation)³¹ and found that singlet

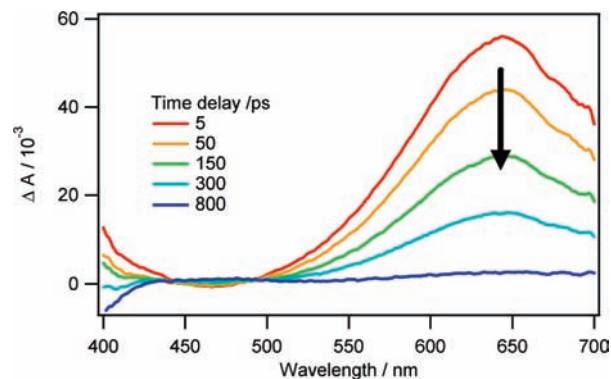


Figure 1. Transient UV–vis spectra produced by ultrafast photolysis of *p*-methoxy-3-phenyl-3-methyl diazirine (*p*-CH₃OC₆H₄CN₂CH₃) in acetonitrile. The spectra were generated by ultrafast LFP ($\lambda_{\text{ex}} = 375$ nm) with a time window of 5–800 ps.

Table 1. Amplitudes and Lifetimes of Transient Absorptions Produced by Ultrafast UV–Vis ($\lambda_{\text{ex}} = 375$ nm) of *p*-Methoxy-3-phenyl-3-methyl Diazirine (*p*-CH₃OC₆H₄CN₂CH₃) in Selected Solvents^a

Solvent	λ_{max} (nm)	A	τ (ps)
acetonitrile	650	0.0516	267 ± 19
chloroform	650	0.0680	271 ± 5
cyclohexane	620	0.0337	58 ± 1
methanol	650	0.0370	424 ± 4
methanol- <i>O-d</i>	650	0.0381	390 ± 10
2,2,2-trifluoroethanol	700	0.0331	846 ± 58

^a Lifetimes are obtained by fitting the kinetic traces to an exponential function.

phenylcarbene and phenyldiazomethane were both formed in less than 1 ps upon excitation, but the excited states responsible for zwitterion formation were not characterized.

Herein, we are pleased to report a continuation of our studies, the first direct observation of the singlet excited state (S₁) of *para*-methoxy-3-phenyl-3-methyl diazirine (*p*-CH₃OC₆H₄CN₂CH₃) and the formation of the carbene and diazo compound derived from it, using ultrafast time-resolved IR and UV–vis spectroscopies. This diazirine was chosen for detailed study because of its favorable ground state absorption at 400 nm, which allows ready promotion to the S₁ state, and second the dipolar nature of the S₁ leads this excited state to a rather long lifetime which facilitates detection.

2. Results

2.1. Ultrafast UV–Vis Spectroscopy With 375 nm Excitation.

Ultrafast laser flash photolysis (LFP) ($\lambda_{\text{ex}} = 375$ nm) of *p*-methoxy-3-phenyl-3-methyl diazirine (*p*-CH₃OC₆H₄CN₂CH₃) in acetonitrile produces the transient spectra shown in Figure 1.

A broadly absorbing transient with maximum absorption near 650 nm is formed within the laser pulse (300 fs), and decays with a lifetime of 267 ps (Table 1, Figure S2, Supporting Information). The lifetime of this transient in chloroform is almost the same ($\tau = 271$ ps) as in acetonitrile but is significantly shortened ($\tau = 58$ ps) in cyclohexane (Table 1). This observation is consistent with the prior conclusion³⁰ that a very polar intermediate is formed upon photolysis of aryl-diazirines. The extended lifetimes of the transient in methanol (424 ps) and 2,2,2-trifluoroethanol (846 ps) suggest that the

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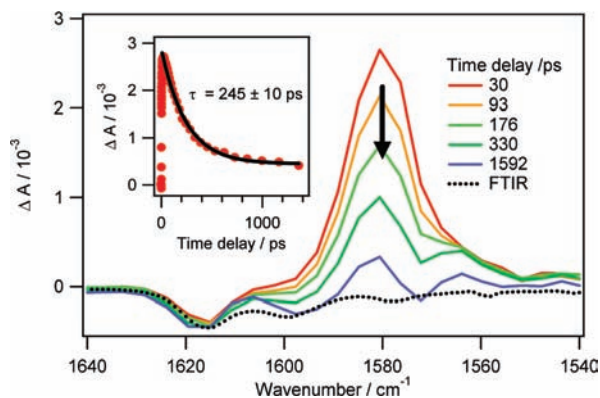


Figure 2. Transient IR spectra produced by ultrafast photolysis of *p*-methoxy-3-phenyl-3-methyl diazirine in chloroform. The spectra were generated by ultrafast LFP ($\lambda_{\text{ex}} = 400$ nm) with a time window of 30–1600 ps. (Inset) Kinetics decay at 1580 cm^{-1} by fitting to an exponential function.

carrier of this transient is not a singlet carbene, because alcohols are well-known singlet carbene quenchers.^{5,24}

A bathochromic shift of the maximum absorption of the transient spectra in polar and protic solvents (Figure S1, Supporting Information) is also observed. A similar observation has been reported for singlet aryl carbenes and has been attributed to specific solvation of the reactive intermediate by heteroatoms present in solvent molecules.³ This result is again consistent with the production of a polar intermediate, a species which is more readily solvated by polar or protic solvents than nonpolar solvents. A triplet carbene has biradical rather than zwitterionic character, and a triplet carbene's lifetime should not be significantly affected by solvent polarity.

2.2. Ultrafast IR Spectroscopy with 400 nm Excitation.

Ultrafast LFP of *p*-CH₃OC₆H₄CN₂CH₃ (400 nm) produces the transient IR spectra shown in Figure 2.

A transient vibrational band that absorbs strongly at 1580 cm^{-1} was observed immediately after the laser pulse (300 fs). This transient species decays with a lifetime of 245 ps in chloroform (inset in Figure 2), in good agreement with the decay of the transient absorption ($\tau = 271$ ps) observed at 650 nm in the same solvent (Table 1). Parent singlet phenylcarbene has also been detected by ultrafast IR spectroscopy (270 nm excitation) and it has a C=C vibration at 1580 cm^{-1} in chloroform.³¹ However, the fact that the 1580 cm^{-1} band decays with a time constant of 408 ps in methanol-*d*₄ (Figure S3, Supporting Information), much longer than the decay times recorded in acetonitrile and in chloroform, argues against assigning singlet *p*-CH₃OC₆H₄CCH₃ carbene as the carrier of this band. Furthermore, the decay time constant is consistent with the decay of the transient observed by ultrafast UV-vis spectroscopy in methanol-*O*-*d* (Figure S2e, Supporting Information, $\tau = 390$ ps). This convinces us that we have detected the same polar species in both the transient UV-vis and IR experiments. Indeed, the transient 1580 cm^{-1} IR band decays with a much shorter time constant in cyclohexane ($\tau = 66$ ps, Figure S3b, Supporting Information), which again is in perfect agreement with the decay of the transient ($\tau = 63$ ps) observed by ultrafast UV-vis spectroscopy (Figure S2a, Supporting Information, and Table 1). This further supports our conclusion that the transients observed at 640 nm and the IR band at 1580 cm^{-1} originate from the same intermediate.

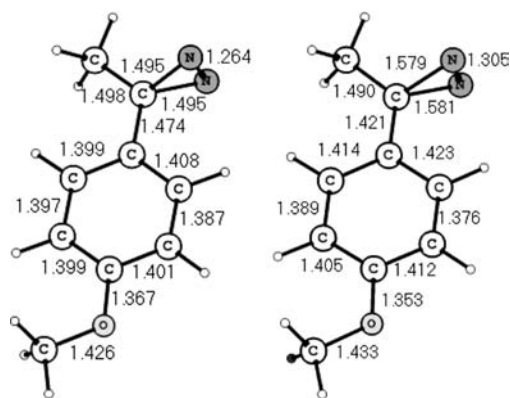


Figure 3. Optimized geometries of S_0 (left) and S_1 (right) states of *p*-CH₃OC₆H₄CN₂CH₃ at the RI-CC2/TZVP level of theory (the bond lengths are in Angstroms).

Time-dependent density functional theory^{32–35} calculations with the B3LYP functional (TD-B3LYP) and RI-CC2/TZVP calculations predict that the S_1 electronic excited state of this diazirine is initially populated with 350–400 nm excitations (Table S1, Supporting Information). This calculation is in good agreement with the steady state absorption spectra (Figure S4, Supporting Information). Therefore, we propose that the polar transient observed by both ultrafast UV-vis and IR spectroscopies can be assigned to the S_1 excited state of *p*-CH₃OC₆H₄CN₂CH₃. To further support this proposition, optimization of the S_1 excited state of *p*-CH₃OC₆H₄CN₂CH₃ at the RI-CC2/TZVP level of theory predicts that the S_1 state has a quinoidal structure in the phenyl group, and the vibrational mode with the strongest intensity is due to aromatic C=C stretches at 1618 cm^{-1} (Figure 3, Supporting Information, Table S2). Unpublished computational data on parent phenyldiazirine also indicate that this aromatic C=C vibrational band at $\sim 1600\text{ cm}^{-1}$ can be used as an IR marker for the S_1 state, and interestingly, the S_2 and S_3 excited states and the S_0 ground state are not expected to have a significant band in this region (Figure S5, Supporting Information). The reasonable agreement between the experimental data (1580 cm^{-1}) and the predicted value (1618 cm^{-1}) convinces us that the S_1 excited state of *p*-CH₃OC₆H₄CN₂CH₃ is observed directly in this study.

The complementary experimental and theoretical studies in this work allow us to obtain detailed structural information of the excited states dynamics. For example, the initial S_1 state formed within the laser pulse (300 fs) absorbs at the same frequency at 1572 cm^{-1} in chloroform, methanol-*d*₄ (CD₃OD) and cyclohexane; then within 20 ps after the laser pulse, the peak undergoes a blue shift of 8 cm^{-1} in CHCl₃, 12 cm^{-1} in CD₃OD, while in cyclohexane, no shift is observed (Figure S6, Supporting Information). The blue-shifting and band narrowing of the newly born transient vibrational absorption is usually observed by ultrafast time-resolved IR spectroscopy and assigned to vibrational cooling.³⁶ However, in this case, since blue-shifting is not observed in cyclohexane, we instead assign this change to solvation³⁷ of the S_1 excited state by polar solvents.

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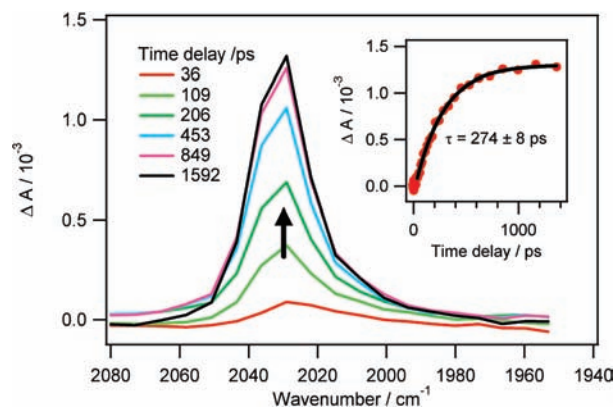


Figure 4. Transient IR spectra produced by ultrafast photolysis of *p*-methoxy-3-phenyl-3-methyl diazirine in chloroform. The spectra were generated by ultrafast LFP ($\lambda_{\text{ex}} = 400$ nm) with a time window of 30–1600 ps. (Inset) Kinetics of growth at 2030 cm^{-1} by fitting to an exponential function.

This is consistent with the observation of solvation of the polar intermediate monitored by ultrafast time-resolved UV–vis spectroscopy (Figure S1, Supporting Information). Thus, the S₁ state of the diazirine is weakly solvated in nonpolar solvent (cyclohexane), and more strongly solvated in polar and protic solvents (chloroform, methanol and TFE). This observation is consistent with the polar nature and the quinoidal structure of the S₁ excited state. Hence we deduce that there is more double-bond character in the S₁ state in the more polar solvent. Moreover, from the RI-CC2/TZVP calculations, the S₀ state along with the vertically excited S₁ and S₂ excited states have dipole moments of 3.51, 6.85, and 3.92 D respectively. The exceedingly large dipole moment of the S₁ state is consistent with a polar intermediate, as expected. The significantly longer lifetime (Table 1) and the large bathochromic shift of the transient visible band (Figure S1c, Supporting Information) in TFE, relative to methanol indicates that the S₁ state experiences some specific stabilization by hydrogen bonding with solvent.

This study also allows us to clearly monitor the photoreactions of the S₁ state. Ultrafast IR ($\lambda_{\text{ex}} = 400$ nm) of *p*-CH₃O-C₆H₄CN₂CH₃ in chloroform produces a transient band at 2030 cm^{-1} (Figure 4).

The 2030 cm^{-1} band formed upon excitation is readily assigned to the isomeric diazo compound. The growth of the diazo compound (274 ± 8 ps, inset in Figure 4) is nicely correlated with the decay of the S₁ state recorded at 1580 cm^{-1} ($\tau = 245 \pm 10$ ps, Figure 2). This is direct evidence that the diazo compound is formed from the S₁ state.

2.3. Ultrafast IR Spectroscopy With 270 nm Excitation. Previously, we have reported that 270 nm excitation of phenyldiazirine produces phenyldiazomethane and singlet phenylcarbene instantaneously (<1 ps).³¹ Herein, we performed ultrafast IR spectroscopy (using 270 nm excitation) of *p*-CH₃OC₆H₄CN₂CH₃ diazirine, and the transient IR spectra produced in the 2080–1940 cm^{-1} region are shown in Figure 5.

The diazo isomer *p*-CH₃OC₆H₄CN₂CH₃ is formed with excess vibrational energy and undergoes vibrational cooling within ~50 ps time after the laser pulse. A narrowing and blue-shift of the diazo band was evident and is assigned to vibrational cooling.³¹ The time evolution of the integrated diazo band reveals that it is formed with two time constants of 4.4 and 240 ps with an intensity ratio of 75:25 (Figure S7, Supporting Information). The slow component (240 ps) is in good agreement with the S₁ state lifetime (245 ps, Figure 2) within experimental error and

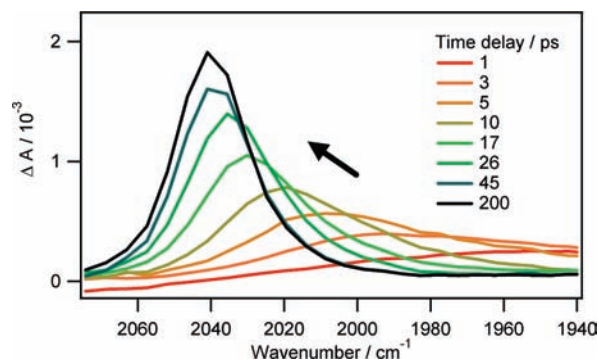


Figure 5. Transient IR spectra produced by ultrafast photolysis of *p*-methoxy-3-phenyl-3-methyl diazirine in chloroform. The spectra were generated by ultrafast LFP ($\lambda_{\text{ex}} = 270$ nm) with a time window of 1–200 ps.

is therefore assigned to the rate of diazo formation from the S₁ state of the diazirine. The fact that 75% of the diazo compound is formed faster than the S₁ state of diazirine decay indicates that there is a second pathway for diazo formation. Since TD-B3LYP calculations (Table S1, Supporting Information) predict that 270 nm excitation can pump *p*-CH₃OC₆H₄CN₂CH₃ diazirine to the S₂ state,³⁸ we propose that the fast component of diazo formation originates from the S₂ state, and that the S₂ state decays to the S₁ state as well as to the diazo compound. We note that the S₂ lifetime could be shorter than 4.4 ps, because the diazo band detected before 10 ps is quite broad and a large part of the spectrum is outside of our detection window (Figure 5). As a result, the band integration is not very accurate at early delay times (<10 ps). Therefore we conclude that diazo formation is competitive with S₂→S₁ internal conversion.

Ultrafast IR spectroscopy with 270 nm excitation of *p*-CH₃OC₆H₄CN₂CH₃ in chloroform produces transient absorption in the 1640–1550 cm^{-1} region, shown in Figure 6. Again, this transient band undergoes vibrational cooling and shifts to 1582 cm^{-1} within 50 ps of the laser pulse. This band then decays approximately to baseline within 3 ns of the laser pulse.

The lifetime of this transient, probed at 1584 cm^{-1} , is 1.3 ns (Figure S8, Supporting Information). The 1.3 ns lifetime is too long to assign the carrier of the band to the S₁ state, despite the fact that the S₁ state has been observed in this region (Figure 2) with 400 nm excitation but with a lifetime of 245 ± 10 ps. Previously, singlet phenylcarbene (¹PhCH, $\tau = 414$ ps), *p*-biphenylcarbene (¹BpCH, $\tau = 599$ ps), and *p*-biphenylmethylcarbene (¹BpCCH₃, $\tau = 667$ ps) have been observed by ultrafast IR techniques.³¹ The carrier of the 1584 cm^{-1} band is assigned to singlet carbene *p*-CH₃OC₆H₄CCH₃ as the lifetime of this species is within a factor of 3 of other reported singlet carbene lifetimes. Singlet carbene *p*-CH₃OC₆H₄CCH₃ is predicted to have a strong vibrational mode at 1585 cm^{-1} (Table S3, Supporting Information), in excellent agreement with this assignment. B3LYP calculations predict that the triplet state is the ground state with a small energy gap in the gas phase (Table S4), but the gap is expected to be smaller because this method has been reported to consistently favor triplet as ground state.³⁹ In addition, calculations predict that the singlet is significantly

(38) Calculations suggest that photolysis with 270 nm light will lead to the S₂ and/or S₃ excited state. For simplicity, we refer to this excitation as the S₂ excited state, but the reader should be aware that the S₃ excited state may also be populated.

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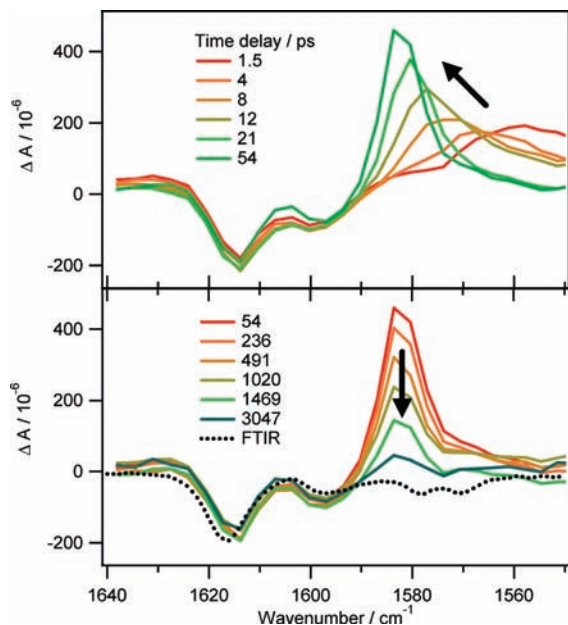


Figure 6. Transient IR spectra produced by ultrafast photolysis of *p*-methoxy-3-phenyl-3-methyl diazirine in chloroform. The spectra were generated by ultrafast LFP ($\lambda_{\text{ex}} = 270$ nm) with a time window of (a) 1.5–54 ps, and (b) 54–3047 ps.

stabilized in polar solvent (Table S4, Supporting Information). Therefore intersystem crossing to the triplet state is slow, or the singlet state may be the ground state in solution, accounting for the extended singlet carbene lifetime. Finally, and most convincingly, the assignment of the 1584 cm^{-1} transient (1.3 ns lifetime) to the singlet carbene is consistent with the fact that methanol, a potent singlet carbene scavenger, significantly shortens the decay lifetime (Figure S11, Supporting Information) of the carrier of the 1580 cm^{-1} band produced by 400 nm excitation assigned to the S_1 state of the diazirine.

Integration of the carbene band reveals that the singlet carbene has a growth time constant of 3.8 ps (Figure. S9, Supporting Information). The carbene growth time constant is very close to that of the fast component of diazo formation (4.4 ps); therefore, we conclude that the carbene is formed directly from the S_2 state, even though we acknowledge again that band integration is not very accurate at early delay times, so it is likely that the S_2 lifetime is somewhat shorter than 3 ps.

3. Discussion

In this study, we report the direct detection of the S_1 state of an aryldiazirine compound *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CH}_3$ by ultrafast time-resolved UV–vis and IR spectroscopies. This assignment is consistent with excited state calculations which predict the aromatic $\text{C}=\text{C}$ vibrational mode of this S_1 state can be used as a diagnostic band. This is the first direct observation of an aryldiazirine S_1 state by UV–vis and IR spectroscopic methods. The excited states of aryl diazo compounds are reported to undergo denitrogenation within 300 fs;^{1–5} however, the specific excited states involved in fragmentation were not characterized and it is not clear if the S_1 state of aryl diazo compound was detected. The S_1 states of aryl diazirines have longer lifetimes (10–1000 ps) than the excited states of the isomeric diazo

compounds. The greater kinetic stability of diazirine group than its diazo counterpart is reminiscent of the ground state behavior.⁴⁰

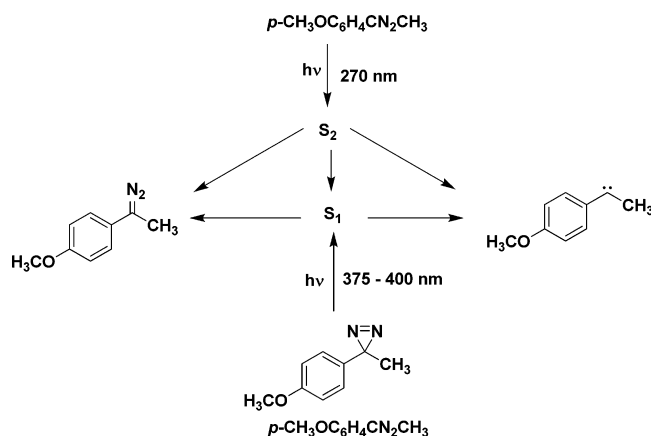
Some simple dialkyldiazirines are known to exhibit weak fluorescence,^{13,41} indicating that the excited states of dialkyldiazirines are intermediates with finite lifetimes in solution, consistent with the finding of this study. The fluorescence lifetime of adamantyldiazirine is on the order of 240 ps at ambient temperature.⁴¹ This fluorescence decay time constant is of the same order as the S_1 state lifetime detected in these ultrafast studies. However, to the best of our knowledge, no fluorescence has been reported for aryldiazirines and we found that the *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CH}_3$ compound does not fluoresce detectably under our experimental conditions. The extent to which arylalkyl diazirine's photochemistry resembles that of dialkyldiazirines is unclear.

It is well-known that diazirines fragment into carbenes as well as isomerize into diazo compounds under thermolysis and photolysis conditions. Previously a $\text{C}=\text{C}$ stretching band of singlet phenylcarbene at 1580 cm^{-1} and a diazo stretching band of phenyl diazomethane at 2030 cm^{-1} have been detected directly by ultrafast IR spectroscopy ($\lambda_{\text{ex}} = 270$ nm) of phenyldiazirine.³¹ However, the excited state involved was not characterized in that study. In this study, we demonstrate that the decay of the S_1 state of *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CH}_3$ is correlated with the growth of the diazo compound. Unfortunately a distinct band attributable to the singlet carbene could not be detected from the S_1 state decay. Calculations predict that singlet carbene *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CCH}_3$ has a $\text{C}=\text{C}$ vibrational mode at 1585 cm^{-1} (Table S2, Supporting Information). On the basis of this result, one could posit that the S_1 state does not form carbene. However, it is likely that the singlet carbene $\text{C}=\text{C}$ vibrational band is obscured by the S_1 state due to severe spectral overlap. Indeed, examination of the kinetics at 1580 cm^{-1} indicates that an offset is present at long delay times in chloroform (Figure 2, inset) and cyclohexane (Figure S3b, Supporting Information), which is not present in methanol (Figure S3a, Supporting Information), an excellent carbene scavenger. Therefore we posit that the singlet carbene contributes to the 1580 cm^{-1} band in chloroform and cyclohexane. In final support of this assignment, we note that the lifetime of 1.3 ns (Figure S8, Supporting Information) for singlet carbene *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CCH}_3$ in chloroform observed by 270 nm excitation is consistent with the lifetime of the background absorption observed after the S_1 state, produced by 400 nm excitation, has decayed.

Another piece of evidence for *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CCH}_3$ formation from the S_1 state of the diazirine is provided by ns spectroscopy. Solutions of *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CH}_3$ containing various concentrations of pyridine were pumped with a 355 nm, 4 ns, laser pulse, and the expected carbene-pyridine ylides were readily detected at 420 nm (Figure S10, Supporting Information). Since TD-B3LYP theory predicts that 355 nm light pumps the *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CH}_3$ diazirine directly to the S_1 state (Table S1, Supporting Information), we take this as evidence that some singlet carbene *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CCH}_3$ is formed from the S_1 state. However, we acknowledge that the experiments presented in this study can not rule out the possibility that singlet carbene could also be formed via the intermediacy of diazo compound, which is produced from the initially populated diazirine S_1 state.

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Scheme 1. Proposed Decay Pathways from the Excited States of *para*-Methoxy-3-phenyl-3-methyl Diazirine

The detailed mechanism of carbene formation from the diazirine and diazo compounds warrants further theoretical studies and will be reported later.

Ultrafast IR spectroscopic studies with 270 nm excitation demonstrate that the diazo compound is formed by two pathways, a fast component (75%) from the S₂ state, and a slow component (25%) from the S₁ state. However, the diazirine S₁ state is not clearly observed by IR spectroscopy with 270 nm excitation. We posit that a low yield of S₁ state is formed but that its vibrational band strength is weak due to the low efficiency of internal conversion and the severe overlap of the two bands (carbene and the S₁ state of diazirine). To test this possibility, methanol-*O-d* was used to trap the singlet carbene and in this solvent, the transient carbene band at 1584 cm⁻¹ decays biexponentially ($\tau_1 = 35$ ps, $\tau_2 = 390$ ps, Figure S11, Supporting Information). The fast component is assigned to carbene decay, consistent with the expectation that methanol solvent rapidly scavenges the carbene, and consistent with the 19 ps lifetime of ¹BpCH carbene in the same solvent.³¹ The slow component of 390 ps is in excellent agreement with the lifetime of the diazirine S₁ state in CD₃OD (Figure S2e, Supporting Information). We can propose the following mechanism on the excited states of diazirine (Scheme 1). Ultrafast LFP (375–400 nm) excites the *p*-CH₃OC₆H₄CN₂CH₃ diazirine to the S₁ excited state, which isomerizes into the diazo compound as the major decay pathway, as well as the formation of singlet carbene *p*-CH₃OC₆H₄CCH₃ as a minor decay pathway. Ultrafast LFP (270 nm) excites to the S₂ electronic state. The direct formation of diazo compound and singlet carbene is so rapid that it can even compete with the internal conversion leading to the S₁ state.

4. Experimental Section

4.1. Ultrafast Spectroscopy. Ultrafast UV–vis and IR spectroscopic studies were performed using the home-built pump–probe spectrometer described previously.^{4,6} Samples were prepared in 50 mL of solvent with absorption 1.0 at the excitation wavelength with 1.0 mm optical length. The entire set of pump–probe delay positions (cycle) is repeated at least three times, to achieve reproducibility from cycle to cycle. To avoid rotational diffusion effects, the angle between polarizations of the pump beam and the probe beam was set to the magic angle (54.7°). Kinetic traces are analyzed by fitting to exponential terms. All experiments were performed at room temperature.

4.2. Calculations. The geometries of ground state *p*-methoxy-3-phenyl-3-methyl diazirine (*p*-CH₃OC₆H₄CN₂CH₃) and singlet

carbene *p*-methoxy phenylmethyl carbene (*p*-CH₃OC₆H₄CCH₃) were optimized at the B3LYP/6-31G(d) level of theory using hybrid B3LYP density functional theory^{32–35} as implemented in *Gaussian 03*.⁴² Vibrational frequency analyses at the same level of theory were utilized to verify that the obtained stationary points corresponded to energy minima. The calculated harmonic vibrational frequencies obtained were corrected with a scaling factor of 0.9614.⁴³ The electronic spectra were computed using Time-Dependent Density Functional Theory (TD-DFT) at the B3LYP/6-311+G(d,p) level using the B3LYP/6-31G(d) geometry; for these calculations, 10 electronic transitions were calculated. Geometry optimizations and vertical excitations for *p*-CH₃OC₆H₄CN₂CH₃ were also performed using the second-order coupled cluster method with the resolution-of-the-identity approximation (RI-CC2) method^{44–46} as implemented in *Turbomole 5.91*.⁴⁷ The ground state geometry, as optimized at the RI-CC2/TZVP level, was utilized as the starting point in optimization of the singlet excited states. The singlet excited state geometry optimizations were carried out using RI-CC2 methodology with the TZVP basis sets. The stationary points for the singlet excited states were confirmed to be minima by calculating the second derivatives numerically using the NumForce module as implemented in the Turbomole suite. All calculations were performed at The Ohio Supercomputer Center.

4.3. Materials. All materials and solvents were purchased from Aldrich. The solvents for ultrafast studies were spectrophotometric grade from Aldrich and used as received.

Synthesis of *p*-Methoxy-3-phenyl-3-methyl Diazirine. *p*-Methoxy-3-phenyl-3-methyl diazirine (*p*-CH₃OC₆H₄CN₂CH₃) was prepared following the method described for 3-phenyl-3-methyl diazirine.⁴⁸ Chromatography over silica gel with pentane as the eluent afforded yellow solids. λ_{max} /nm: 385 (pentane). δ_{H} (400 MHz, CDCl₃): 1.49 (s, 3H), 3.79 (s, 3H), 6.85 (d, 4H, $J = 2$ Hz). δ_{C} (100 MHz, CDCl₃): 159.12, 131.99, 126.66, 113.75, 55.32, 25.89, 17.86.

5. Conclusions

The photophysics and photochemistry of *p*-CH₃OC₆H₄CN₂CH₃ have been studied using ultrafast time-resolved UV–vis and IR spectroscopies and theoretical methods. Ultrafast time-resolved laser flash photolysis with 375 nm excitation produced transient absorption bands in the 400–700 nm visible region, which are assigned to the S₁ electronic excited state of *p*-CH₃OC₆H₄CN₂CH₃ based on modern theoretical studies. Consistent with this assignment, the strongest vibrational mode of the S₁ excited state of *p*-CH₃OC₆H₄CN₂CH₃, as predicted by calculations, was directly observed in the mid-infrared region. The ultrafast time-resolved spectroscopic experiments also indicate that the S₁ state of *p*-CH₃OC₆H₄CN₂CH₃ is a polar intermediate which undergoes solvation within 20 ps of formation in polar solvents. The ultrafast infrared studies allowed the direct observation of diazo compound and carbene formation from the S₂ and S₁ states of the diazirines. Carbene formation from the S₁ state was also indirectly demonstrated by the detection of carbene derived ylides using nanosecond time-resolved laser flash photolysis techniques (355 nm excitation). Ultrafast IR spectroscopy with 270 nm excitation promotes *p*-CH₃OC₆H₄CN₂CH₃ to the S₂ excited states, which decay quickly into diazo compounds via isomerization and into singlet aryl carbenes. In addition, about 25% of the isomeric diazo

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compound is produced from the S_1 state, which, in turn, is produced from the S_2 state via internal conversion.

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Supporting Information Available: Figures S1–S11 and Table S1–S4. Some ultrafast UV–vis and infrared spectroscopic data. The fittings of kinetic traces. Cartesian coordinates of all compounds under study. TD-DFT calculations. Complete citation for ref 42. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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