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Direct Observation of a Sulfonyl Azide Excited State and Its Decay Processes by Ultrafast Time-Resolved IR Spectroscopy

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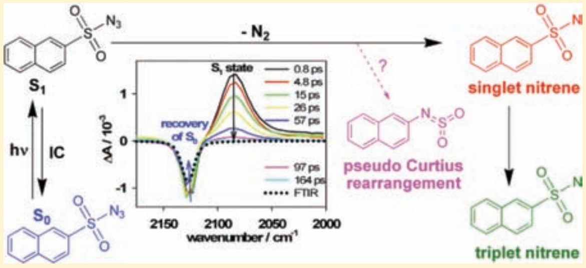
Supporting Information

ABSTRACT: The photochemistry of 2-naphthylsulfonyl azide (2-$NpSO_2N_3$) was studied by femtosecond time-resolved infrared (TR-IR) spectroscopy and with quantum chemical calculations. Photolysis of 2-$NpSO_2N_3$ with 330 nm light promotes 2-$NpSO_2N_3$ to its S_1 state. The S_1 excited state has a prominent azide vibrational band. This is the first direct observation of the S_1 state of a sulfonyl azide, and this vibrational feature allows a mechanistic study of its decay processes. The S_1 state decays to produce the singlet nitrene. Evidence for the formation of the pseudo-Curtius rearrangement product (2-$NpNSO_2$) was inconclusive. The singlet sulfonylnitrene ^{1}(2-$NpSO_2N$) is a short-lived species ($\tau \approx 700 \pm 300$ ps in CCl_4) that decays to the lower-energy and longer-lived triplet nitrene ^{3}(2-$NpSO_2N$). Internal conversion of the S_1 excited state to the ground state S_0 is an efficient deactivation process. Intersystem crossing of the S_1 excited state to the azide triplet state contributes only modestly to deactivation of the S_1 state of 2-$NpSO_2N_3$.



1. INTRODUCTION

We have recently reported the earliest events that transpire during the photochemistry of acyl azides, $RC(=O)N_3$, using ultrafast time-resolved spectroscopy and computational chemistry.[1−3] The lowest singlet (S_1) excited states of acyl azides have prominent azide vibrational bands which facilitated their direct detection and allowed ready monitoring of the excited-state dynamics. Singlet acylnitrenes were directly observed and their rates of formation correlated with the decay of the excited state of the azide precursors. Ultrafast time-resolved experiments demonstrated that the S_1 state of acyl azides also decay to form isocyanates, the products of Curtius rearrangement.[1−3] Earlier, we reported the first direct detection of a phosphorylnitrene $^1(PhO)_2PON$ by ultrafast time-resolved UV−vis spectroscopy after irradiation of diphenylphosphoryl azide, $(PhO)_2PON_3$, as the precursor.[4] These results motivated us to study a class of structurally related compounds, sulfonyl azides (RSO_2N_3), and to compare their mechanistic photochemistry with that of the acyl azides.

Sulfonyl azides exhibit rich photochemistry.[5−9] Sulfonylnitrenes were initially studied using both chemical and physical methods by irradiation of sulfonyl azides. Triplet sulfonylnitrenes were detected by electron paramagnetic resonance spectroscopy upon photolysis of sulfonyl azides at low temperature.[9,10] These studies demonstrated that the triplet states of sulfonylnitrenes are the ground states. Triplet sulfonylnitrenes have also been detected in matrixes at low temperature using infrared spectroscopy.[11]

Nanosecond time-resolved laser flash photolysis (LFP) of *p*-methylphenylsulfonyl azide (*p*-$CH_3PhSO_2N_3$) allowed the direct observation of the corresponding triplet nitrene and the measurement of its lifetime in ethanol and cyclohexane. The triplet nitrene lifetimes are on the order of microseconds.[12] Given the time resolution available at the time to Maloney et al.,[12] the formation of singlet and triplet nitrenes could not be monitored. That study was also unable to explain why the presence of oxygen shortened the lifetime of the assigned triplet sulfonylnitrene (from 9 to 0.3 μs, in the absence and presence of oxygen, respectively), relative to arylnitrenes.[13−16] As a result, the authors only *tentatively* assigned the bands observed by nanosecond LFP methods to triplet sulfonylnitrene, ^{3}(*p*-CH_3PhSO_2N).

Given the possibility of concerted pseudo-Curtius rearrangements in the excited states of sulfonyl azides, studies with other sulfonylnitrene precursors have also been reported.[17] Mesylnitrene and tosylnitrene were studied by photolysis of independent precursors, *N*-mesyl and *N*-tosyldibenzothiophene sulfimides, by Toscano, Jenks, and co-workers.[17] This study employed nanosecond time-resolved infrared (TR-IR) spectroscopy and the chemical analysis of stable products along with computational chemistry. Theory predicted strong triplet nitrene vibrations (1241 and 1058 cm^{-1} using C_s symmetry or 1134 and 1023 cm^{-1} using C_1 symmetry). In the case of phenyl substitution, in-plane C−H vibrations have some contribution

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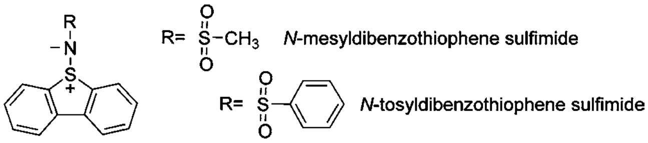
in this spectral range as well. Unfortunately, neither the singlet nor the triplet nitrene was detected by means of nanosecond TR-IR spectroscopy with 50 ns time resolution. The authors *tentatively* claimed the detection of sulfonoazepine arising from the attack of singlet nitrene onto the dibenzothiophene nucleus.



The stable products formed upon photolysis of *N*-mesyldibenzothiophene sulfimide suggest that the triplet nitrene was produced upon irradiation. No evidence of pseudo-Curtius rearrangement was found with the sulfimide precursor. This result suggests that neither singlet nor triplet nitrenes are the precursors of pseudo-Curtius rearrangement photoproduct in solution at room temperature.

The nature and distribution of the persistent products formed upon photolysis of methylsulfonyl azide ($CH_3SO_2N_3$)[18] and *N*-mesyldibenzothiophene sulfimide[17] are also quite different. This may be due either to an additional, unique process (e.g., pseudo-Curtius rearrangement) in the sulfonyl azide excited state or to very different distributions of the initially formed singlet and triplet nitrenes. Once again, with *N*-tosyldibenzothiophene sulfimide,[17] the triplet nitrene was responsible for the formation of the major fraction of photoproducts. Unfortunately, photolysis of tosyl azide gave an "intractable" mixture.[17] Therefore, it was assumed that the efficiency of triplet nitrene formation is larger for *N*-tosyldibenzothiophene sulfimide than for tosyl azide.

Nitrenes are not the only species produced upon photolysis of sulfonyl azides, as demonstrated by product studies.[6] As mentioned previously, there are reports that pseudo-Curtius rearrangement photoproducts are also formed upon irradiation. Tentative evidence of the direct observation of *N*-sulfonylphenylamine ($PhNSO_2$) in a low-temperature matrix has been reported.[11] However, in this experiment, this species was produced by irradiation of the triplet nitrene rather than the azide. The identification of *N*-sulfonylphenylamine was uncertain because photolysis of triplet benzenesulfonylnitrene promotes SO_2 extrusion to form triplet phenylnitrene along with 1,2,4,6-azacycloheptatetraene and the complex of this ketenimine with sulfur dioxide. The complex photochemistry and spectral congestion prevented unambiguous detection of $PhNSO_2$. So it is not clear if *N*-sulfonylphenylamine is a primary photoproduct of the sulfonyl azide in a low-temperature matrix or a product of secondary reactions.

In this study, we will address these mechanistic questions in the photochemistry of sulfonyl azides using ultrafast time-resolved LFP methods. 2-Naphthylsulfonyl azide (2-$NpSO_2N_3$) was chosen to be the lead compound in this study because we have recently studied the photochemistry of 2-naphthoyl azide (2-$NpCON_3$),[2] thereby facilitating ready comparison of these two classes of compounds. Additionally, 2-$NpSO_2N_3$ has a convenient chromophore for UV−vis excitation, and it is possible to excite the azide to the S_1 state directly, thereby avoiding photochemistry from multiple excited states.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1. Synthesis. 2-Naphthylsulfonyl azide (2-$NpSO_2N_3$) was made from 2-naphthylsulfonyl chloride and sodium azide by following a procedure described in the literature.[19] Briefly, a solution of 2-naphthylsulfonyl chloride (0.227 g, 1 mmol) in 5 mL of acetone was added dropwise into a solution of sodium azide (0.65 g, 10 mmol) in 10 mL of acetone in an ice−water bath with stirring. The reaction was continued overnight at room temperature. The mixture was evaporated to dryness and was purified by flash chromatography with hexane/ethyl acetate (5:1) as the eluent. The resulting white solid was confirmed to be 2-$NpSO_2N_3$ by ^1H and ^{13}C NMR spectroscopy and was stored for further use at −20 °C.

2.2. Ultrafast Experiments. Ultrafast time-resolved experiments were performed on a home-built, pump−probe femtosecond laser spectrometer in the Center for Chemical and Biophysical Dynamics at The Ohio State University.[20] All experiments were repeated at least two times on different days. Usually, three experiments were performed to determine the data reproducibility from cycle to cycle. However, when the detected signals were very weak, at least six cycles were used to improve the data quality. To avoid rotational diffusion effects, the angle between polarization of the pump beam and the probe beam was set to the magic angle (54.7°). Kinetic traces were analyzed by fitting to a sum of exponential terms. All experiments were performed at room temperature. The solution was constantly circulating. The volume of solution was equal to about 50 mL. The pump power was less than 4 μJ, and the beam diameter was about 0.25 mm. The absorbance of the sample solutions was approximately 1.0 in a 1 mm cell at the excitation wavelength (the concentration of 2-$NpSO_2N_3$ was $\sim 10^{-3}$ M). Sample solutions were excited in a stainless steel flow cell equipped with 2 mm thick BaF_2 windows.

2.3. Computational Methods. Geometry optimizations and transition-state searches were performed with the 6-31G(2df,p)[21] basis set (and others) in conjunction with Becke's three-parameter hybrid exchange functional with the Lee−Yang−Parr correlation functional (B3LYP) density functional theory (DFT) method.[22,23] The nature of all stationary points, either minima or transition states, was confirmed by calculating the vibrational frequencies at the corresponding level of theory; i.e., minima were characterized by the absence of any imaginary vibrational frequencies, while a transition state possessed only one imaginary vibrational frequency. Vertical excitation energies were computed at the time-dependent (TD)-B3LYP[24,25] level of theory using the corresponding ground-state (S_0) geometries. To characterize the vertical excited states, we computed electron density difference plots (between S_0 and the S_1−S_4 states) as described in a previous report.[26] All calculations were performed with the Gaussian 09 software suite.[27]

3. RESULTS AND DISCUSSION

3.1. The 2170−2000 cm^{-1} Spectral Range (N_3 Stretching Region).

Ultrafast LFP of 2-$NpSO_2N_3$, using 330 nm excitation in carbon tetrachloride, produced transient IR bands in the spectral range of 2170−2000 cm^{-1} as shown in Figure 1. A prominent transient band was detected at 2083 cm^{-1} within 1 ps after irradiation, and this band then decayed exponentially over 100 ps. Analysis of the kinetic trace indicated that the 2083 cm^{-1} band decayed with a time constant of 32 ± 2 ps (Figure 1b). TD-B3LYP calculations predict that 330 nm light directly populates the S_1 excited state of 2-$NpSO_2N_3$ (*vide infra*). Similar positive bands were detected in our study of acyl azides and were assigned to the S_1 excited state of the acyl azide.[1−3] Therefore, the 2083 cm^{-1} band was similarly assigned as the S_1 state of 2-$NpSO_2N_3$. However, the decay lifetime of the S_1 state (32 ps) was significantly shorter than that of the S_1 state of 2-$NpCON_3$ (τ = 690 ± 60 ps) in the same solvent (CCl_4).[1−3] The substantial difference between these S_1 excited-state lifetimes, despite the structural similarity between 2-$NpSO_2N_3$ and 2-$NpCON_3$, will be discussed in more detail below.

A negative band observed at 2129 cm^{-1} was assigned to the bleaching of the sulfonyl azide's vibrational band in the ground state, upon excitation. We found that the kinetic trace of this

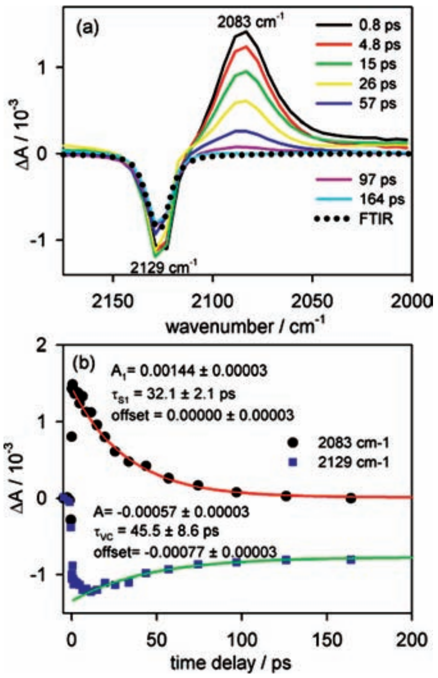


Figure 1. (a) Transient IR spectra produced by photolysis of 2-$NpSO_2N_3$ in carbon tetrachloride (λ_{ex} = 330 nm) at selected time delays. The dotted line presents the scaled steady-state IR absorption spectrum (FTIR) of 2-$NpSO_2N_3$ in CCl_4. (b) Transient kinetics observed at 2083 cm^{-1} (the S_1 state decay) and 2129 cm^{-1} (the ground-state recovery).

negative band at 2129 cm^{-1} clearly indicated the recovery of the ground state (Figure 1b). On the basis of our kinetic trace analysis at 2129 cm^{-1} ($\Delta A = -0.00057 \times \exp(-t/46\text{ ps}) - 0.00077$, cf. Figure 1b), we estimate that about 42% of the ground-state molecules were repopulated in CCl_4. Therefore, we conclude that internal conversion (IC) $S_1 \rightarrow S_0$ (i.e., recovery of the ground state) is an efficient process for deactivation of the S_1 state ($\Phi_{IC} \approx 0.42 \pm 0.04$) in 2-$NpSO_2N_3$. The rate constant of IC (k_{IC}) is estimated to be $(13 \pm 1) \times 10^9$ s^{-1} in CCl_4 ($k_{IC} = \Phi_{IC}\tau_{S1}^{-1}$). We have shown previously that no recovery of the ground state was observed up to 3 ns after photolysis of 2-$NpCON_3$, and we concluded that both IC and fluorescence are inefficient deactivation processes for the S_1 state of 2-$NpCON_3$.[1−3] Hence, we speculate that the relatively short lifetime of the S_1 excited state of 2-$NpSO_2N_3$ relative to its acyl azide (690 ± 60 ps) counterpart, in the same solvent, is at least partly due to fast IC to repopulate the S_0 ground state.

Given that IC controls 42% of the decay of the S_1 state of 2-$NpSO_2N_3$, one can deduce a 66 ps time constant for this process—if it is the sole mechanism of decay of the excited state. It is also possible to estimate that the sum of the rate constants of the other two decay processes (58% decay: singlet nitrene formation, $k_{nitrene}$, and pseudo-Curtius rearrangement, $k_{Curtius}$, *vide infra*) is equal to $k_{nitrene} + k_{Curtius} = (18 \pm 1) \times 10^9$ s^{-1}. In CCl_4, for 2-$NpCON_3$, the sum of rate constants of these two processes in equal to $(1.03 \pm 0.27) \times 10^9$ s^{-1} (see Table 2 in ref 2). There is no experimental evidence that excited sulfonyl azide deactivates to form triplet sulfonyl azide (*vide infra*). Thus, it is evident that the rate of singlet nitrene formation and pseudo-Curtius rearrangement for sulfonyl azide is much faster than that of the analogous acyl azide.

Additional experiments were performed in dichloromethane where the S_1 state lifetime is only 4.3 ± 0.1 ps. For comparison, the lifetime of the S_1 state for 2-$NpCON_3$ is 70 ± 6 ps in CH_2Cl_2.[2] Once more, the same spectral features were observed for photolysis of 2-$NpSO_2N_3$ in CH_2Cl_2 as in CCl_4 (Supporting Information, Figure S1). However, in CH_2Cl_2, the hot ground state is populated much faster than in CCl_4, and this is why the instantaneous concentration of hot ground state is much higher than in CCl_4. Moreover, in CH_2Cl_2, about 12 ps after the laser pulse, the concentration of S_1 is about 6% of its initial concentration. Therefore, the spectrum observed in CH_2Cl_2 after 12 ps is almost completely due to vibrational cooling (VC) of the hot ground state. Indeed, the typical spectral evolution caused by VC of the hot ground state[28] was detected in CH_2Cl_2 (see evolution of transient spectra recorded at 12, 26, 45, and 197 ps, Figure S1).

As was the case in CCl_4, the S_1 lifetime in CCl_4 is almost the same as the rate of VC. Thus, we could not distinguish spectral changes caused by the decay of the S_1 state from VC of the hot ground state of the azide. However, the kinetics observed at 2112 cm^{-1} in CCl_4 confirms that VC takes place in this solvent as well. The signal recorded at 2112 cm^{-1} grows initially up to about 25 ps and then it decays (Figure S2). This dynamical behavior is typical of VC.[28]

We have mentioned previously that in CH_2Cl_2, the $S_1 \rightarrow S_0$ IC is a more efficient process ($\Phi_{IC} = 0.60 \pm 0.05$) of deactivation of S_1 state 2-$NpSO_2N_3$ than in CCl_4. The rate constant of IC (k_{IC}) is estimated to be $(139 \pm 24) \times 10^9$ s^{-1} in CH_2Cl_2. If IC alone controlled the S_1 state lifetime of 2-$NpSO_2N_3$, one would deduce that its decay time constant would be 7 ps in CH_2Cl_2. The sum of the rate constants $k_{nitrene} + k_{Curtius} = (93 \pm 18) \times 10^9$ s^{-1}. In CH_2Cl_2, for 2-$NpCON_3$, the sum of the rate constants of these two processes is equal to $(14.0 \pm 3.6) \times 10^9$ s^{-1} (see Table 2 in ref 2). Once again, the rate of singlet nitrene formation and pseudo-Curtius rearrangement is much faster for the excited state of the sulfonyl azide relative to the analogous acyl azide.

The ultrafast time-resolved experiments indicate that IC is much more efficient in CH_2Cl_2 than in CCl_4 solvent. This predicts that 2-$NpSO_2N_3$ should be photo-decomposed more rapidly in the latter solvent. Indeed, upon steady-state photolysis (330 nm) of azide solutions of equal absorption, 2-$NpSO_2N_3$ is consumed more rapidly in CCl_4 relative to CH_2Cl_2.

The literature on IC is not large, due to an absence of good experimental tools, and deals almost exclusively with polycyclic hydrocarbons.[29] Theory teaches that the rate of IC depends critically on the S_1−S_0 energy gap and the density of states.[30] For sulfonyl azides the situation is even more complex because the S_1 states of sulfonyl azides, unlike aromatic hydrocarbons, decompose by fragmentation to nitrenes and by pseudo-Curtius rearrangements, in addition to IC and intersystem crossing (ISC). Thus, in this class of molecules, one expects a solvent effect on the conical intersection of S_1 with the ground-state surfaces of the singlet nitrene and pseudo-Curtius rearrangement product.

We found no experimental evidence for formation of the triplet state of 2-$NpSO_2N_3$. Calculations predict a rather intense N_3 vibration at 2166 cm^{-1} (Table 2) for triplet 2-$NpSO_2N_3$. Given the expected accuracy of the calculation (Table 2) and the fact that the calculated frequency of the N_3 vibration in the triplet state of sulfonyl azide is shifted by about 10 cm^{-1} relative to the calculated N_3 vibration in the S_0 ground state, one would expect formation of the triplet band on the low-energy side of the bleaching of the azide vibrational band in the ground state.

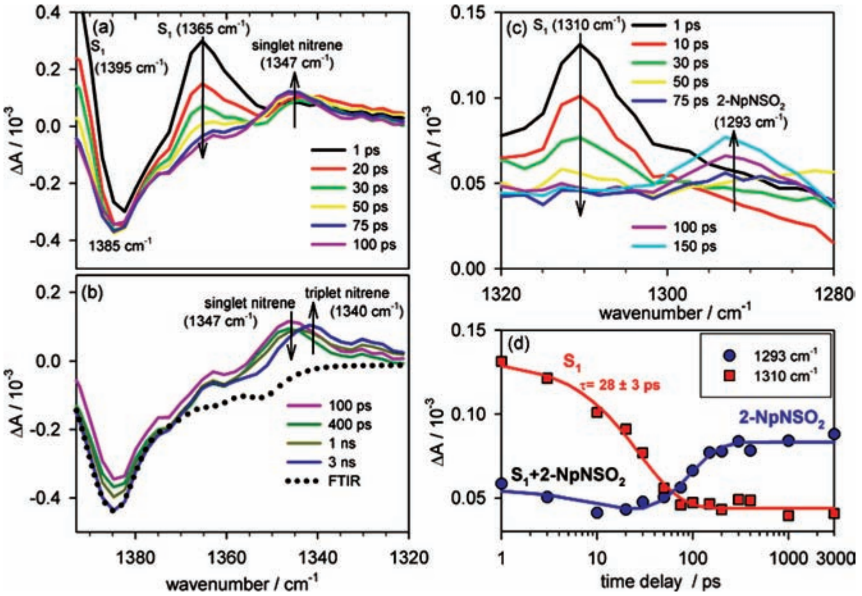


Figure 2. (a,b) Transient IR spectra in the 1395−1320 cm^{-1} spectral range, as produced by photolysis of 2-$NpSO_2N_3$ in carbon tetrachloride (λ_{ex} = 330 nm). The dotted line represents the scaled steady-state IR absorption spectrum (FTIR) of 2-$NpSO_2N_3$ in CCl_4. (c) Transient IR spectra in the 1320−1280 cm^{-1} spectral range. (d) Transient kinetics observed at 1293 cm^{-1} (the 2-$NpNSO_2$ formation) and 1310 cm^{-1} (the S_1 state decay). A logarithmic scale was applied for the time delay.

However, that triplet N_3 vibration was not observed experimentally. In CCl_4, all spectral changes are complete within 164 ps of the laser pulse. The transient spectrum recorded at this time delay has a very similar shape to the scaled steady-state IR absorption spectrum (FTIR) prior to photolysis (Figure 1a). The presence of the triplet band should be visible as a difference between the scaled FTIR and transient spectra at long time delays, as shown earlier for the acyl azides.[2] Since 58% of the excited molecules do not return to the ground state within 3 ns, and the calculated IR intensities of the ground and triplet states of 2-$NpSO_2N_3$ are similar, one can estimate that the yield of triplet formation must be very low ($\Phi_{ISC} < 5\%$). The method of estimation of the efficiency of triplet formation is described in detail in the Supporting Information.

Thus, we conclude that triplet sulfonyl azide is not formed by photolysis of 2-$NpSO_2N_3$ upon promotion to its S_1 state. This is in contrast to the behavior of the S_1 state of 2-$NpCON_3$, which *does* form a small amount of the corresponding triplet azide.[2] One reason for this difference is that the calculated S_1−T_1 energy gap is larger for 2-$NpSO_2N_3$ (32 kcal/mol) than for 2-$NpCON_3$ (26 kcal/mol). Taking the rate constants k_{ISC} obtained for 2-$NpCON_3$ in CH_2Cl_2, $(0.29 \pm 0.10) \times 10^9$ s^{-1}, and in CCl_4, $(0.51 \pm 0.15) \times 10^9$ s^{-1} (see Table 2 in ref 2), and the sum $k_{nitrene} + k_{Curtius}$ calculated for 2-$NpSO_2N_3$ as shown above, it is possible to estimate the value of $\Phi_{ISC} = k_{ISC}/(k_{nitrene} + k_{Curtius})$ for 2-$NpSO_2N_3$. Assuming that k_{ISC} is the same for both compounds, the estimated Φ_{ISC} for 2-$NpSO_2N_3$ is equal to ∼0.03 in CCl_4 and <0.01 in CH_2Cl_2. This is consistent with the fact that the triplet azide was not observed for 2-$NpSO_2N_3$ upon direct S_1 excitation.

3.2. The 1450−1280 cm^{-1} Spectral Range (SO_2 Stretching Region). Ultrafast LFP studies of 2-$NpSO_2N_3$ were also performed to scan other interesting spectral regions based on the predictions of quantum calculations (*vide infra*), and a few bands were detected in the 1450−1280 cm^{-1} range in CCl_4 (Figure 2, Figure S4). As the efficiency of the ground-state recovery was large in CH_2Cl_2, we expected that photolysis in CCl_4 would produce transient signals sufficiently intense to be recorded by femtosecond TR-IR spectroscopy. Indeed, three positive bands (1395, 1365, and 1310 cm^{-1}) were observed immediately (1 ps) after the laser pulse. Kinetic analysis (for example, see the kinetics recorded at 1310 and 1365 cm^{-1} in Figure 2d and Figure S5, respectively) indicated that all positive bands decayed with a common time constant of ∼30 ps, which is in excellent agreement with the decay of the vibrational band at 2083 cm^{-1}. Hence these bands were assigned to the S_1 excited state of 2-$NpSO_2N_3$. Calculations of the ground state of this sulfonyl azide predict that there will be three relatively intense peaks in the vibrational range discussed for the SO_2 vibration coupled with some C−C or C−H in-plane vibrations (Table 2, Table S1). Therefore, in this spectral region, one would expect three positive bands to be present for the S_1 state. Additionally, C−H in-plane vibrations may also give some contribution to the detected signal.

A negative bleaching band at 1385 cm^{-1} was observed due to the depletion of the ground state of 2-$NpSO_2N_3$ (SO_2 vibration) upon excitation. Surprisingly, this bleaching band showed little change over 3 ns. If the ground state is recovered, as at 2129 cm^{-1}, then the same recovery is expected for the band at 1385 cm^{-1} as well. We speculate that this apparent disparity is probably due to contributions from the two positive bands (1395, 1365 cm^{-1}, Figure 2, Figure S4) overlapping with the bleaching negative band at 1385 cm^{-1}. Additionally, as shown above, the rate of the S_1 state decay is almost the same as the rate of the VC in CCl_4. Thus, we could not separate the spectral changes caused by S_1 decay and VC of hot ground state of azide. Therefore, if the peak position and amplitudes of the bleaching band and the S_1 state absorption are similar, the absorption at the 1385 cm^{-1} will exhibit little change. Indeed, from the transient spectra, it is possible to discern that the 1385 cm^{-1} band is on the edge of the 1395 cm^{-1} positive band (only ∼10 cm^{-1} difference). In contrast, the negative band at 2120 cm^{-1} is relatively well separated from the positive band at 2083 cm^{-1} (∼40 cm^{-1} difference), and as a result, observation of

Table 1. Experimental and Calculated IR Frequencies (cm^{-1}) for the 2-$NpSO_2N_3$ Ground State Using B3LYP with Different Basis Sets[a]

basis set	N_3 stretch	scaled N_3 stretch	N_3 deviation (calc − exp)	SO_2 stretch	scaled SO_2 stretch	SO_2 deviation (calc − exp)
TZVP	2234	2155	19	1319	1272	−113
6-31G(d)	2242	2152	16	1337	1284	−101
6-31+G(d)	2243	2164	28	1337	1290	−95
6-31G(2d)	2235	2156	19	1353	1306	−79
6-31+G(2d)	2234	2156	19	1352	1305	−80
6-31+G(2df)	2243	2164	28	1378	1330	−55
6-31G(2df,p)	**2256**	**2177**	**41**	**1407**	**1358**	**−27**
6-311+G(3df,2p)	2251	2177	41	1400	1354	−31
experiment in CCl_4	2136			1385		

[a] Scaling factor = 0.960 for 6-31G(d), 0.967 for 6-311+G(3df,2p), and 0.965 for 6-31G(2df,p), TZVP, and other basis sets.[33]

ground-state recovery is possible. The assignment of some other bands (assigned as the singlet and triplet nitrene and pseudo-Curtius rearrangement photoproduct) will be discussed after presenting the computational results.

3.3. Computational Results. The ground-state geometry of 2-$NpSO_2N_3$ was first optimized at the B3LYP/TZVP level of theory, as reported for 2-$NpCON_3$.[2] The N_3 vibrational frequency of the 2-$NpSO_2N_3$ ground state was well reproduced by calculation, after application of a scaling factor. However, the SO_2 vibrational frequencies are significantly underestimated (Table 1). Previous studies showed that a better approximation of SO_2 frequencies may be obtained when large basis sets, including d and f functions, are used.[11,31,32] Hence, different basis sets were used, and the corresponding vibrational frequencies are shown in Table 1. These calculations showed that the addition of a polarization function to the basis set improved the estimation of SO_2 frequencies, but with little effect on the predicted N_3 vibrational frequencies.

Due to the large computational cost of a big basis set, we compromised and used the 6-31G(2df,p) basis set for further calculations of the various species that might present transient IR bands, as this basis set gave the best predicted SO_2 frequency without negatively impacting the calculated N_3 frequency (<50 cm^{-1}). Moreover, this basis set accurately predicts the broad nature of the SO_2 band found experimentally (Figure S6), as three peaks (1363, 1358, and 1344 cm^{-1}) with similar intensities were computed at this level. Table 2 shows some selected computed diagnostic frequencies for the possible species formed during photolysis of 2-$NpSO_2N_3$. The list of selected calculated vibrations for the singlet (S_0) ground state, the triplet state of 2-$NpSO_2N_3$, singlet nitrene, triplet nitrene, and pseudo-Curtius rearrangement photoproduct is given in Table 2. The full list of predicted vibrational frequencies for the azide's singlet ground state, the triplet state of 2-$NpSO_2N_3$, singlet nitrene ^{1}(2-$NpSO_2N$), triplet nitrene ^{3}(2-$NpSO_2N$), and pseudo-Curtius rearrangement photoproduct 2-$NpNSO_2$ are collected in Tables S1 and S3. In order to make a fair comparison of the computed IR intensities across different species, the calculated IR intensities are normalized against the sum of intensities of all seven modes of the C−H stretches (~3000 cm^{-1}) computed for the ground state of 2-$NpSO_2N_3$. These seven C−H stretching modes are chosen because they exist in all species and are independent of the regions that we are observing experimentally.

Table 2. Selected (Scaled) IR Vibrational Frequencies (cm^{-1}) at the B3LYP/6-31G(2df,p) and TD-B3LYP/6-31G(2df,p) Levels of Theory for Possible Species Formed from the Photolysis of 2-$NpSO_2N_3$[a]

	IR range (cm^{-1})	
	2000−2170	1280−1450
ground-state 2-$NpSO_2N_3$	N_3: 2177 (520)	SO_2: 1363 (22), 1358 (74), 1344 (47)
triplet 2-$NpSO_2N_3$	N_3: 2166 (727)	SO_2: 1398 (139) C−H: 1354 (37)
singlet nitrene ^{1}(2-$NpSO_2N$)		SO_2: 1320 (127)
triplet nitrene ^{3}(2-$NpSO_2N$)		SO_2: 1292 (117)
2-$NpNSO_2$		SO_2: 1315 (112) C−N: 1274 (166)

[a] The calculated (and normalized) intensities are listed in parentheses (in km/mol); see text for details.

Table 3. TD-B3LYP/6-31G(2df,p) Vertical Excitation Energies, Oscillator Strengths (*f*), and the Dominant Occupied and Virtual Orbitals Contributing to the Three Lowest Energy Singlet excitations of 2-$NpSO_2N_3$[a]

state	character (% contribution)	energy (eV)	energy (nm)	oscillator strength (*f*)
S_1	60 → 61 (91%)	4.02	308	3.3×10^{-2}
S_2	59 → 61 (64%)	4.38	283	3.0×10^{-2}
S_3	60 → 62 (80%)	4.46	278	2.4×10^{-2}

[a] Orbital 60 is the highest occupied molecular orbital.

Using the optimized B3LYP/6-31G(2d,p) ground-state geometry of 2-$NpSO_2N_3$, we computed vertical excitations with TD-DFT (Table 3, Table S2). At the TD-B3LYP/6-31G(2df,p) level of theory, the lowest electronic transition (S_1) is calculated at 308 nm (*f* = 0.033), and the second electronic transition is calculated at 283 nm (*f* = 0.030). These predicted transitions are in good agreement with the ground-state electronic absorption spectrum (Figure S7). These results support our interpretation that 330 nm excitation of 2-$NpSO_2N_3$ populates the S_1 excited state directly (*vide supra*).

At the TD-B3LYP/6-31G(2df,p) level and using the B3LYP/6-31G(2df,p) optimized geometry for the S_0 ground state, we also calculated the electron density difference plots[26] of the singlet excited states in order to identify the character of the excited states (Figure 3). In these plots, a green contour demonstrates an accumulation of electron density in the excited state, while a red contour shows the depletion in the ground state. This approach clearly shows that the S_1 excited state corresponds to promotion of an electron from the π-orbital of the aryl moiety to the in-plane π^*-orbital of the azide group. However, some electron density accumulates in the π^* orbital of the terminal N(β)=N(γ). This aspect would be a significant requirement for a *dissociative* state to form the corresponding nitrene from the initially excited sulfonyl azide. The prediction that singlet nitrene can be formed from the S_1 state is consistent with our experimental observation (*vide infra*).

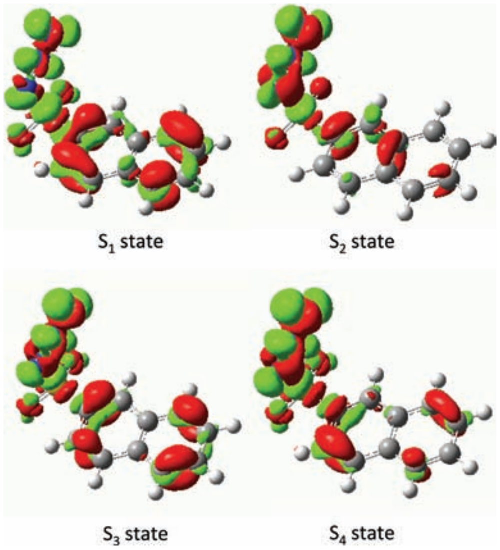


Figure 3. Relative to the S_0 ground state, electron density difference plots for the S_1–S_4 states for 2-$NpSO_2N_3$ as calculated at the TD-B3LYP/6-31G(2df,p) level of theory. The green contours depict the accumulation of electron density in the excited state, and the red contours illustrate the depletion of electron density from the S_0 ground state. The isocontour value is ±0.002 au.

3.4. Singlet Nitrene Formation. Dissociation of the excited states of aryl[34] and acyl azides[1−3] allowed the direct detection of the corresponding singlet nitrenes by ultrafast LFP. As discussed above and depicted in Figure 3, calculations indicate that the S_1 excited state is a *dissociative* state, producing singlet 2-naphthylsulfonylnitrene, ^{1}(2-$NpSO_2N$), and molecular nitrogen, N_2. Calculations also predict that the singlet nitrene has a relatively strong (scaled) vibrational frequency at 1320 cm^{-1} (Table 2, Table S3). Indeed, a positive band at 1347 cm^{-1} is detected about 100 ps after the laser pulse (Figure 2a). This band is clearly distinguishable from the absorption of the S_1 state of the sulfonyl azide, because of the very low concentration (<5%) of the S_1 state of the sulfonyl azide 100 ps after the laser pulse. The hot ground state of 2-$NpSO_2N_3$ is excluded as the carrier of this band because VC is almost complete[28,35−37] at this delay time. Therefore, the 1347 cm^{-1} band can be reasonably assigned to relaxed singlet 2-naphthylsulfonylnitrene, ^{1}(2-$NpSO_2N$). The transient spectra reveal that the rate of formation of the 1347 cm^{-1} band is roughly correlated with the decay of S_1 state of the sulfonyl azide. Hence, we conclude that the S_1 state of 2-$NpSO_2N_3$ is the precursor of the singlet nitrene. *To the best of our knowledge, this is the first direct observation of the singlet state of a sulfonylnitrene.* This assignment is supported by the nature and distribution of the persistent photoproducts.[17,18,38] On the basis of the singlet nitrene lifetime that we obtained, it is clear why this species was not detected in the earlier nanosecond TR-IR efforts as the temporal resolution of that experiment was only 50 ns.[17]

3.5. Triplet Nitrene Formation. As the singlet nitrene band at 1347 cm^{-1} decays, a very weak, persistent (>2 ns) band is observed with its maximum near 1340 cm^{-1} (Figure 2b). This band is tentatively assigned to the triplet sulfonylnitrene, ^{3}(2-$NpSO_2N$), for the following reasons. First, the assignment of this band to ^{3}(2-$NpSO_2N$) is in excellent agreement with the reported triplet phenylsulfonylnitrene, ^{3}($PhSO_2N$), band detected at 1342 cm^{-1} in matrix isolation studies.[11] Second, a C−Cl insertion product of singlet nitrene with CCl_4 is unlikely because the predicted, scaled IR band at 1358 cm^{-1} (Table S4) is similar to the predicted, scaled IR band of the 2-$NpSO_2N_3$ ground state, which is at higher wavenumber than the 1340 cm^{-1} band detected experimentally. Taking into account the accuracy of the calculated SO_2 frequencies (Tables 1 and 2), the calculated SO_2 vibration (1292 cm^{-1}) for the triplet nitrene is in fair agreement with the experimental band assigned herein to the triplet nitrene. Third, as the calculated singlet−triplet energy splitting (ΔE_{ST}) of 2-$NpSO_2N$ is 14 kcal/mol at the B3LYP/6-31G(2df,p) level of theory (Figure S8), the ISC rate should be faster than that of phenylnitrene,[39] which has a singlet−triplet energy splitting of 18 kcal/mol. More accurate CBS-QB3[40] calculations predict that the 2-$NpSO_2N$ singlet−triplet energy gap is actually only 8 kcal/mol, further supporting more rapid ISC relative to singlet phenylnitrene. Finally, the oxygen−nitrogen interaction in singlet sulfonylnitrene results in the ground state having a closed-shell configuration. This interaction is also present in acylnitrenes[41,42] and phosphorylnitrenes.[43] The closed-shell nature of ^{1}(2-$NpSO_2N$) is in contrast to the open-shell configuration of the ground state of phenylnitrene, thus rendering spin−orbit coupling a particularly effective mechanism for the ISC of singlet sulfonylnitrene, in a manner similar to phenylcarbene.[44] Since the absorption signals are very weak and it is difficult to precisely determine the singlet nitrene lifetime, we estimate the lifetime of ^{1}(2-$NpSO_2N$) to be 700 ± 300 ps.

Our results are consistent with earlier chemical and physical studies,[9,11−13,17] which show that triplet sulfonylnitrene is present after photoexcitation and that triplet sulfonylnitrene has a lower energy than the singlet sulfonylnitrene spin isomer. However, to the best of our knowledge, triplet sulfonylnitrene was not detected previously in solution at ambient temperature using IR spectroscopy. Toscano, Jenks, and co-workers studied CH_3SO_2N utilizing nanosecond TR-IR with a temporal resolution of ~50 ns.[17] They did not observe a characteristic vibrational band of triplet methylsulfonylnitrene ^{3}(CH_3SO_2N), but its presence was confirmed by product studies. Maloney et al. reported the presence of triplet sulfonylnitrene ^{3}(*p*-CH_3PhSO_2N) in solution at room temperature using nanosecond LFP with UV−vis detection.[12] This group could not explain why molecular oxygen so efficiently quenched the resulting triplet sulfonylnitrene (about 9 μs lifetime without O_2 and about 0.3 μs in the presence of O_2); even after assuming a bimolecular rate constant about 10^9 M^{-1} s^{-1}, this quenching rate is much larger than expected.[14−16] Unfortunately, the time range of our experiment (3 ns) does not allow us to resolve this dilemma.

3.6. Pseudo-Curtius Rearrangement in the Azide Excited State. As shown in Table 2, the pseudo-Curtius rearrangement photoproduct, *N*-sulfonyl-2-naphthylamine, 2-$NpNSO_2$, is predicted to have two intense (scaled) IR markers: one at 1315 cm^{-1} (112 km/mol) and a second at 1274 cm^{-1} (166 km/mol) (Figure 4c). The former IR marker is an SO_2 vibration, and the latter vibration is localized on the CNS moiety. The first calculated IR marker (1315 cm^{-1}) of 2-$NpNSO_2$ overlaps with the calculated singlet nitrene (1320 cm^{-1}) IR marker (Figure 4c). Unfortunately, the triplet nitrene was detected experimentally in the same spectral range at 1340 cm^{-1} (Figure 4a). Thus, it is not possible to monitor 2-$NpNSO_2$ formation through the SO_2 vibration of this species, as its IR signature is obscured by the SO_2 vibrations of the singlet and triplet sulfonylnitrenes.

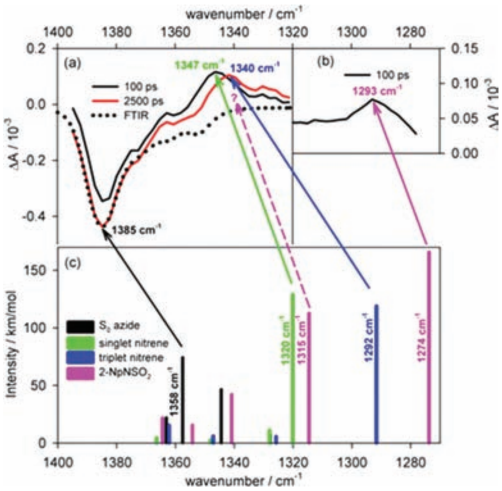


Figure 4. Comparison of calculated (and scaled) IR vibrational frequencies with transient spectra recorded after 330 nm photolysis of 2-$NpSO_2N_3$ in CCl_4. Only transient spectra at selected delays are shown. (a) Transient spectra taken from Figure 2b. Dotted line shows scaled FTIR spectrum of ground-state 2-$NpSO_2N_3$ in CCl_4. (b) Transient spectrum at 100 ps delay is taken from Figure 2c. (c) Calculated frequencies are taken from Tables 1 and 2 and Tables S1 and S3. Arrows present our assignment of specific species to the detected bands.

The second, relatively intense CNS IR marker (predicted to be observed at 1274 cm^{-1}, Figure 4c) of 2-$NpNSO_2$ is not obscured by vibrational SO_2 bands of singlet and triplet sulfonylnitrene. Indeed, we observe a positive band at 1293 cm^{-1} (Figure 4b) within 150 ps of the laser pulse, and its amplitude does not change up to 3 ns (Figure 2c,d, Figure S9). Based on its position and formation kinetics (see the blue line in Figure 2d), this band is *tentatively* assigned to the pseudo-Curtius rearrangement photoproduct, 2-$NpNSO_2$.

As the 1293 cm^{-1} absorbing species is formed within 150 ps of the laser pulse, it cannot be formed from the relaxed singlet nitrene, which has a lifetime on the order of 700 ps. However, the rise observed at 1293 cm^{-1} (assigned tentatively to photoproduct 2-$NpNSO_2$) is a bit slower than the decay of the S_1 band of 2-$NpSO_2N_3$. Thus, we believe that the putative 2-$NpNSO_2$ species must be formed as a vibrationally hot species, and some additional time is needed to allow VC to proceed to completion. Unfortunately, the 1293 cm^{-1} band overlaps with the edge of the S_1 band of sulfonyl azide, the observed signals are very weak, and we did not clearly observe the spectral evolution of this band in order to provide direct evidence that this species is formed vibrationally excited. However, the shape of the transient spectra recorded at 30, 50, and 75 ps after photolysis suggests that 2-$NpNSO_2$ is formed vibrationally hot and then relaxes. This is expected because with 330 nm excitation, about 86.6 kcal/mol of energy is absorbed by the precursor. Additionally, the energy of 2-$NpNSO_2$ and N_2 is lower, by 32.9 kcal/mol, than the energy of 2-$NpSO_2N_3$ in its ground state (Figure S8). Thus, even though some energy is needed to break the N−N_2 bond, and some excess energy is distributed into the other photoproduct (N_2), one expects that 2-$NpNSO_2$ will be formed vibrationally excited and then will subsequently relax.

The kinetics recorded at 1293 cm^{-1} (blue solid line in Figure 2d) can be analyzed by taking into account a two-step process: formation of hot 2-$NpNSO_2$ and, subsequently, relaxed 2-$NpNSO_2$ after VC. Therefore, $\Delta A_1 \times \exp(-t/\tau_{S1}) + \Delta A_2 \times \exp(-t/\tau_{VC})$ + offset function may be applied to estimate the rise of the concentration of relaxed 2-$NpNSO_2$ (for details, see Supporting Information). The following parameters were obtained from the fit at 1293 cm^{-1}: τ_{S1} = 30 ps, τ_{VC} = 50 ± 10 ps, $A_1 = (0.13 \pm 0.05) \times 10^{-3}$, $A_2 = (-0.16 \pm 0.06) \times 10^{-3}$, and offset = $(0.083 \pm 0.002) \times 10^{-3}$ (Figure 2d). The τ_{VC} obtained here is typical of VC[35−37] and close to the value (46 ± 9 ps, Figure 1b) determined at 2129 cm^{-1}. The lifetime of the S_1 state was fixed during this fit. Therefore, based on the kinetics of the 1293 cm^{-1} band, it is reasonable to assume that the precursor of putative 2-$NpNSO_2$ is the S_1 state of the sulfonyl azide.

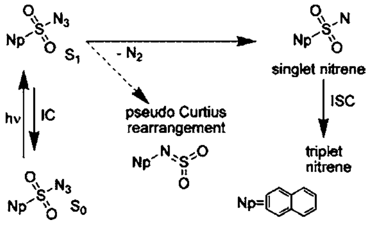
The presence of the pseudo-Curtius rearrangement photoproduct is consistent with reported chemical analyses of the stable products formed after irradiation of sulfonyl azides in solution.[6] The *N*-sulfonylphenylamine, $PhNSO_2$, was tentatively detected in a low-temperature matrix.[11] However, this species was produced by irradiation of the triplet sulfonylnitrene, along with triplet phenylnitrene, 1,2,4,6-azacycloheptatetraene, and the complex of this ketenimine with SO_2. Given the complex photochemistry of matrix-isolated triplet benzenesulfonyl azide and the resulting spectral congestion, the assignments of bands at 1371 and 1323 cm^{-1} to $PhNSO_2$ by Sheridan and Rempala was considered tentative. Our assignment of a 1293 cm^{-1} band, which is in poor agreement with Sheridan and Rempela,[11] must also be considered tentative as well.

In a key experiment by Toscano and Jenks,[17] utilizing a nonazide precursor of sulfonylnitrenes, there was no evidence of pseudo-Curtius rearrangement product, $RNSO_2$. Thus, the results of Toscano and Jenks demonstrate that neither singlet nor triplet sulfonylnitrenes are precursors of the pseudo-Curtius rearrangement photoproduct in solution at room temperature. This conclusion is consistent with our finding that the S_1 state of the sulfonyl azide might be the precursor of the pseudo-Curtius rearrangement photoproduct, 2-$NpNSO_2$ (Scheme 1).

4. CONCLUSIONS

In summary, the first direct observation of the S_1 state of a sulfonyl azide is presented along with a study of its decay processes. For 2-$NpSO_2N_3$ in CCl_4, internal conversion to S_0 is an efficient deactivation process for the S_1 state; however, intersystem crossing to the triplet azide is not. As the efficiency of azide decomposition in CCl_4 is relatively high, the yield of photoproducts (singlet nitrene and pseudo-Curtius rearrangement) was sufficiently large so as to allow their detection. The short lifetime of the singlet sulfonylnitrene ^{1}(2-$NpSO_2N$), about 700 ± 300 ps in CCl_4 at room temperature, is due to fast

Scheme 1. Reaction Scheme upon Excitation to the S_1 State of 2-$NpSO_2N_3$



ISC. The singlet sulfonylnitrene decays to the triplet sulfonylnitrene ^{3}(2-$NpSO_2N$), and the triplet is persistent over the 3 ns time range available in this ultrafast experiment. The photochemical pseudo-Curtius rearrangement reaction to form 2-$NpNSO_2$ is tentatively considered to proceed in concert with nitrogen extrusion in the excited state. We view this as another example of a "Rearrangement in the Excited State" (RIES) mechanism.[45] Our experimental results, in collaboration with computationally derived vibrational signatures, suggest that the putative 2-$NpNSO_2$ pseudo-Curtius rearrangement photoproduct is formed as a hot species that subsequently relaxes to its ground state. Scheme 1 summarizes our experimental findings and presents the early stages of reaction that follow 330 nm excitation of 2-$NpSO_2N_3$ to the S_1 state. The assignments of species to vibrational bands that were experimentally detected are supported by quantum chemical calculations (Figure 4).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Calculations, ultrafast transient spectra, and kinetic traces; absolute energies the coordinates of the atoms in all of the molecules whose geometries were optimized. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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