

Femtosecond transient absorption studies of two novel energetic tetrazole derivatives [☆]

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ARTICLE INFO

Keywords:

Transient absorption
Energetic materials
Nitro compounds
Tetrazoles
Excited-state dynamics

ABSTRACT

Excited-state dynamics of two novel energetic nitrogen-rich aryl-tetrazole molecules were investigated using femtosecond transient absorption spectroscopy. The internal conversion from S_0 to S_1 occurred in the 0.3–0.5 ps; vibrational relaxation within S_1 states transpired in a 1.8–5 ps time scale and, subsequently, the intersystem crossing was observed with lifetimes of 7.8 ps and 129 ps. The nitro-substituted tetrazole demonstrated a faster decay with a weaker fluorescence compared to the amino-substituted derivative. We believe that the high nitrogen content in the former resulted in a possible more rapid nonradiative decay.

Introduction

Energetic Materials (EMs) store a large amount of chemical energy that can be converted to mechanical energy by molecular decomposition for industrial and military applications [1]. Excited electronic states of EMs are proven to play a crucial role in molecular decomposition, which can be generated by different ignition processes such as shocks, sparks, and heat [2–8]. Theoretical calculations show that compression at a pressure of greater than 30 GPa can induce electronic transition equal to 2–2.5 eV, which is comparable to the low lying excited states of the EMs [6]. The velocity of the detonation wave in an explosive is about 10 km/s. This means at the molecular dimension, the time it takes to go over is about 100 femtoseconds. Some molecular processes must be efficient to release energy within the molecular transit time to equip the molecule with the energy needed for a sustained detonation wave. Therefore, the excitation of EMs by UV laser pulses provides an effective means of studying the excited state decomposition of these materials. Furthermore, to understand the complete process of excited state decomposition of EMs, the topography of excited-state potential surfaces is also an important parameter [9]. The conical intersections due to the crossing of excited potential surfaces play an essential role in the excited electronic state process of EMs [10]. The potential energy surfaces of electronic excited and ground states play a crucial role in deactivation pathways in EMs, which can be and have been probed, to a certain extent, by the quantum chemical theories and time-resolved spectroscopies. Also, they can give insight into the conical intersection

and transition states [11–14]. It is pertinent to note that the nonradiative relaxation process of excited states can lead to the formation of hotspots, which can initiate the chain reaction in EMs [9,15]. The decomposition of EMs occurs in a sub-picosecond time scale, which can be probed by using an ultrafast pump-probe technique [15–20]. The dynamical and spectral properties of high energy materials are rarely studied due to their absorption, which lies in the UV region. Direct optical excitation can initiate the excited state decomposition in high energy materials and, therefore, understanding those processes will have implications on the development of novel EMs for optical initiation [21].

The energetic materials/explosives are generally nitrogen containing aromatic compounds (TNT, DNT, RDX) which can undergo self-oxidation [22,23]. The initial decomposition product after UV excitation of nitrated explosives is found to be NO molecule [20]. This was understood from the ultrafast internal conversion from the excited electronic state to the ground state in the presence of a conical intersection is reported [9,19]. Transient absorption (TA) spectroscopy is a pump-probe technique in which a pump pulse triggers the photo-induced reaction, and the delayed probe pulse probes subsequent evolution. TA spectroscopy records the change in optical density (ΔOD) by the pump-probe technique. The TA spectra contain the overlapping of several processes, i.e., ground state bleach (GSB), stimulated emission (SE), and excited-state absorption (ESA) arising from the different-species in the excited-state [15,24]. To elucidate the various components contributing to the TA spectra, the obtained TA spectra is globally analyzed by using sequential and target models [25]. The different com-

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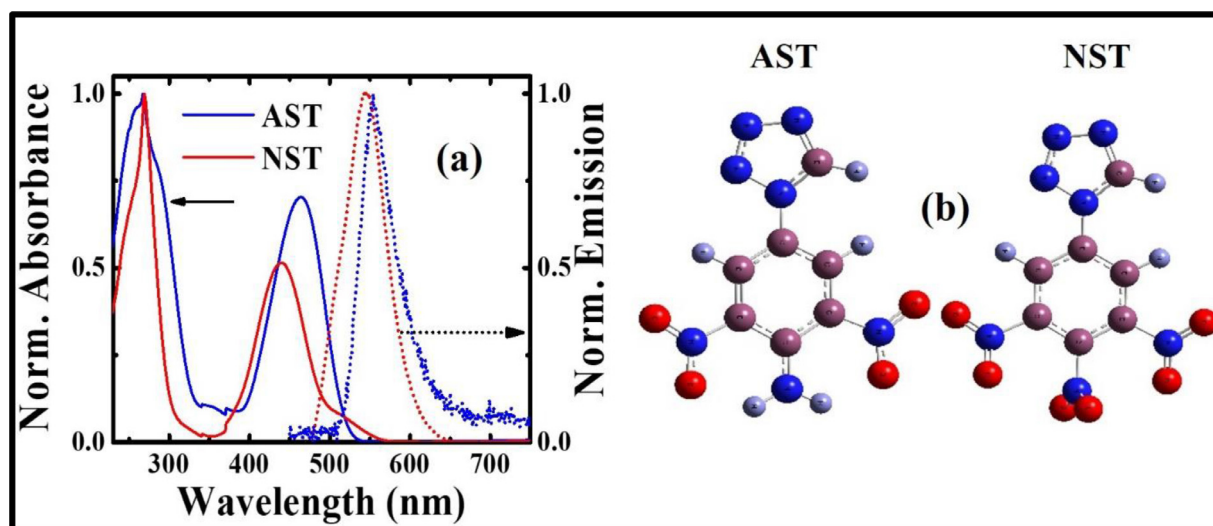


Fig. 1. (a) Steady-state absorption and emission spectra and (b) Molecular structure.

ponents are estimated by using the singular value decomposition (SVD) method. This provides a complete description of the transient absorption spectra.

In continuation of efforts in understanding the excited state dynamics of EMs, we have performed femtosecond transient absorption studies on an amino-substituted tetrazole derivative and a nitro-substituted tetrazole derivative [26]. In continuation of our previous work, Katturi et al. [27] in this present work we have explored the electronic dynamics of these molecules. To avoid the ambiguity in the description of TAS data, we have labeled the two tetrazole molecules 2,6-dinitro-4-(1H-tetrazole-1-yl)aniline ($C_7H_5N_7O_4$) and 1-(3,4,5-trinitrophenyl)-1H-tetrazole ($C_7H_3N_7O_6$) as AST and NST, respectively. The structure of tetrazole derivatives conserves more energy than other azole derivatives and exhibits a high positive heat of formation and excellent detonation performance. Furthermore, these compounds have demonstrated superior energetic performance than the standard explosive TNT. From the target analysis of transient absorption spectra, we have obtained four different time constants and their physical significance is discussed.

Experimental details

The experimental details of the femtosecond transient absorption spectroscopy (TAS) are documented in our previous work [28]. Briefly, a 50-fs laser delivering pulses at a 1 kHz repetition rate at 800 nm wavelength was used to pump the commercial HELIOS transient absorption spectrometer. A part of the laser beam was split into two parts; one part of the laser beam was used to generate a white light continuum by focusing on a 2 mm thick sapphire plate, which was used as the probe beam. The other part of the laser beam was used to generate a second harmonic 400 nm. This was achieved by passing the fundamental beam 800 nm through BBO crystal, which was used to pump the sample. The data acquisition was carried by using Helios software at 0.2 mM concentration in pure DMF solvent with a 1-mm cuvette and the pump fluence approximately was $4.4 \mu J/cm^2$. The global analysis procedure was carried on TA data with a kinetic model [25,29]. It gives an accurate description of the obtained data at all measured wavelengths and time points simultaneously. The number of independent components was estimated by using the singular value decomposition (SVD) method. The global fitting procedure was performed in Glotaran (R-package TIMP) software [30].

Table 1

Summary of the steady-state absorption and emission peaks of AST and NST measured in DMF (ϵ is the extinction coefficient).

Sample	Absorption (nm) [ϵ , $M^{-1} cm^{-1}$]		Emission (nm)	Radiative Lifetimes (μs)
	$n-\pi^*$	$\pi-\pi^*$		
AST	269 [17,000]	440 [10,340]	525 [1516]	1.17
NST	266 [18,400]	463 [14,040]	554	1.16

Results and discussion

Fig. 1 shows the steady-state absorption and emission spectra of amino (AST) and nitro (NST) substituted tetrazole derivatives in DMF at $\sim 50 \mu M$ concentration. The steady-state absorption spectra have two distinct bands located at 270 nm and 463 nm for NST and 440 nm for the compound AST. In contrast to NST, the AST depicted a different signature at 525 nm. The peak at 270 nm corresponds to the $\pi-\pi^*$ transition, and the second peak at 463 nm and 443 nm are due to possible $n-\pi^*$ transitions [31,32]. In Fig. 1, right arrow shows the steady-state emission spectra of two molecules obtained by exciting with 400 nm wavelength. The compound AST emission was at a maximum of 552 nm whereas in NST the maximum emission was observed at 545 nm. It is evident from Fig. 1 NST is less fluorescent compared to AST due to the presence of the nitro group. The photophysical parameters of the investigated molecules obtained from steady-state measurements are summarized in Table 1. As seen in Fig. 1, the presence of the nitro group increases the conjugation and reduces the bandgap.

The time-resolved photoluminescence (TRPL) was measured using FLS 1000 spectrometer (Edinburgh Instrument) using a multichannel scaling technique. The excitation wavelength was 370 nm, and the emissions were observed at 544 nm and 521 nm for NST and AST in the DMF solution, as shown in Fig. 2. The experimental data were fitted using a bi-exponential decay function convolved with instrument response function (IRF). The fitted data confirmed the long radiative decay lifetimes of $\sim 10 \mu s$ in both the molecules. We believe this long lifetime is associated with the triplets but with the present limited PL data it is not possible to assign the $\sim 10 \mu s$ lifetime to the triplet states. Additional experiments are required to clearly assign the origin of this lifetime to the triplet states.

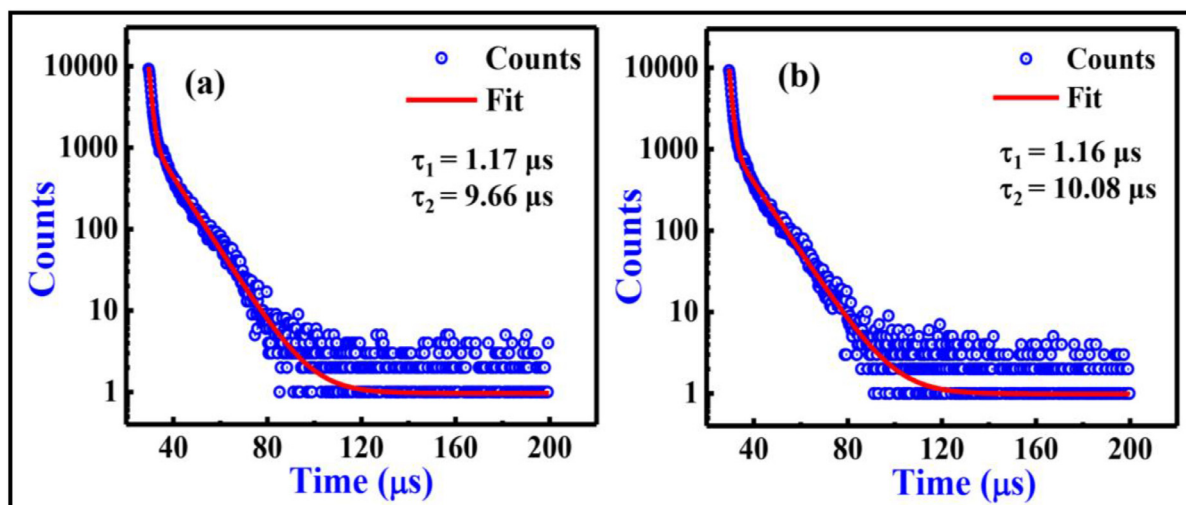


Fig. 2. TRPL measurements of compound (a) AST and (b) NST in DMF at 370 nm photoexcitation.

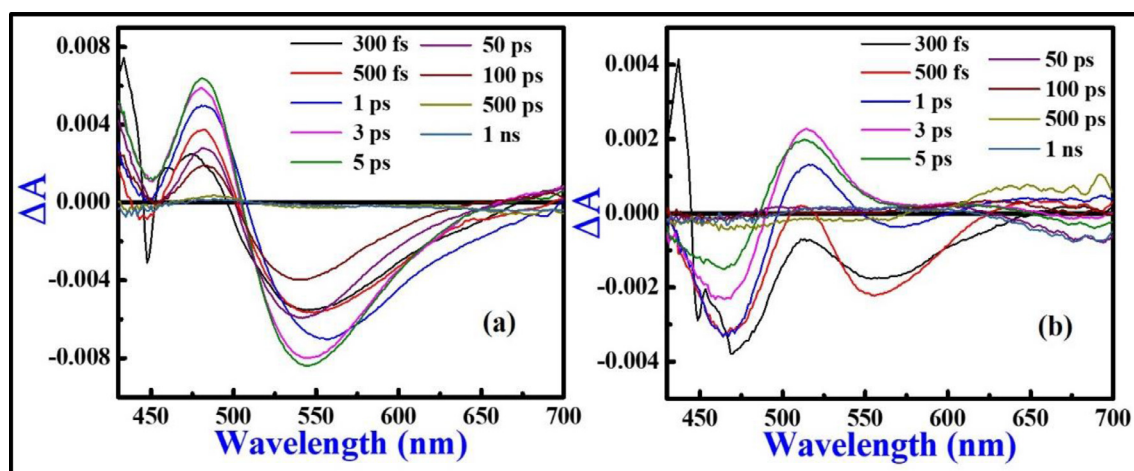


Fig. 3. TA spectra of samples (a) AST and (b) NST at 400 nm photoexcitation.

Transient absorption spectroscopy

Transient absorption (TA) experiments were performed at 400 nm photoexcitation with 0.2 μJ pump energy and probed with a white light continuum from 430 to 700 nm range in DMF, as shown in Fig. 3. From Fig. 3(a) it is evident that the TA spectra of AST depicts negative signal at 450 nm and 545 nm corresponding to the GSB or SE. The negative band at 545 nm was increased up to 5 ps, and later, it starts decaying due to the depopulation of the excited states. The stimulated emission peak at 552 nm is overlaid within the ground state bleach signal at 545 nm. A positive absorption signal at 480 nm is observed due to the excited state absorption, which increased up to 1 ps time scale and later depicted a decay, implying appearance of new excited state at this time scale. After a 1 ps time scale, the bleach signal at 550 nm has shown a blue shift, which confirms the formation of new excited species at this time scale. Later the positive band at 480 nm gradually drops due to the depopulation of electronically excited states. A negative TA signal at 450 nm decayed within one (1) ps probe delay, which corresponds to the decay of higher electronic excited states (S_n) since the 400 nm photoexcitation allows the population to occupy higher electronic states.

The TA spectra of NST [Fig. 3(b)] had a strong bleach signal at 466 nm and a stimulated emission at 551 nm, which decayed within 1 ps. It is evident from the TA spectra at 400 nm photoexcitation NST is recovered faster compared to AST. The presence of large nitrogen con-

tent in NST allows the possible nonradiative decay pathways. The formation of the GSB signal at 468 nm is evident at 0.3 ps time scale later it starts recovering gradually with a small blue shift. A positive band at 518 nm was observed to be increasing up to 3 ps time scale. Subsequently, it starts decaying due to the depopulation of higher excited states and the possible formation of a new excited state at this time scale. One should not ignore the solvent effects in excited state population relaxation. The solvent mainly influences the vibrational energy redistribution processes. We have ensured the solvent effects are accounted for by recording the TAS spectra of pure DMF solvent separately. To obtain relevant decay constants, a global analysis was performed based on a kinetic model [25], as illustrated in Fig. 4, and four-time constants were chosen to fit the full TA spectra.

Fig. 5 shows the results from the global analysis of AST TA spectra. Fig. 5(a) shows the species associated difference spectra (SADS), considering the 400 nm photoexcitation the SADS1 is assigned to the internal conversion from S_n to S_1 state with strong negative bands at a maximum of 450 nm and 575 nm. The population from S_n is transferred to hot S_1 state through internal conversion with a lifetime of 350 fs. The SADS2 has a positive signal at 480 nm and a negative signal at 550 nm, which corresponding to the vibrational relaxation within S_1 state with a lifetime of ~ 5 ps. SADS3 corresponds to the excited singlet state S_1 with distinct peaks at 468 nm and 518 nm with a lifetime of 116 ps ($\tau_{s1} = 1/(k_r + k_{nr})$) which involves the intersystem crossing from S_1

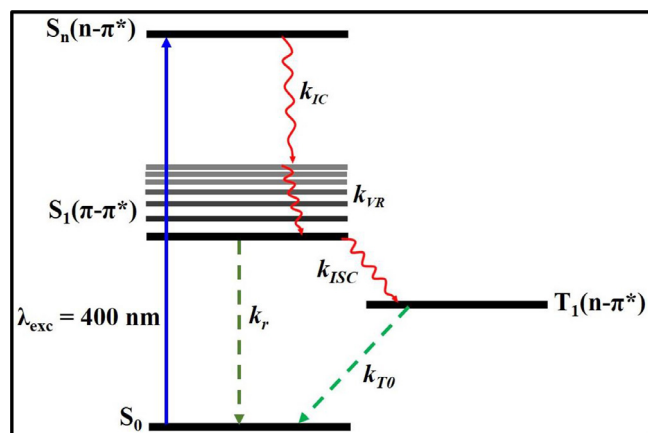


Fig. 4. Schematic of the photophysical model used to fit the TA spectra.

to triplet state T_1 with a lifetime of ~ 129 ps (90%) and radiative recombination S_1 - S_0 with ~ 1.1 ns (10%) lifetime. However, experimental evidence of the S_1 state lifetime is required to measure the relaxation of the S_1 state accurately. SADS4 corresponds to the T_1 state with a lifetime of $5 \mu\text{s}$. This value was fixed with the average value obtained from TRPL measurements. Fig. 5(b) shows the population decay profiles of corresponding species associated spectra, and Fig. 5(c)–5(d) illustrates the goodness of fit initial and final probe delays and at different wavelengths.

Fig. 6 shows the target analysis of the NST TA spectra. As seen from Fig. 6(a), the first SADS1 corresponds to the internal conversion to the

Table 2

Estimated photophysical parameters of the tetrazole derivatives obtained from the target analysis.

Sample	τ_{IC}	τ_{VR}	$\tau_{r(S1-S0)}$	$\tau_{nr(S1-T1)}$	τ_{T1-S0}
AST	350 fs	5 ps	1.1 ns	129 ps	$5 \mu\text{s}$
NST	500 fs	1.8 ps	148 ps	7.8 ps	$5 \mu\text{s}$

higher excited electronic states S_n to the S_1 state with strong negative signals at 454 nm and 546 having a lifetime of 0.5 ps. The SADS2 spectrum with a time constant of 1.8 ps is attributed to vibrational relaxation within S_1 , and SADS3 spectrum corresponds to the S_1 state with a lifetime of 7.4 ps, which contains possible intersystem crossing from S_1 to T_0 with lifetime 7.8 ps (95%) and S_1 - S_0 relaxation with lifetime 148 ps (5%). The SADS4 spectra correspond to the triplet state T_1 with a lifetime of $5 \mu\text{s}$. Fig. 6(b) shows the population decay profiles and corresponding species associated spectra, while Fig. 6(c) shows the goodness of fit at 0.3 ps and 1 ns delay times. Fig. 6(d) shows the kinetic profiles at different wavelengths. The estimated photophysical parameters are given in Table 2.

In contrast to most nitroarenes, the tetrazole molecules have weak fluorescence occurring from their lowest singlet excited state with an estimated lifetime of 0.148–1.1 ns [33,34]. The time scale of vibrational relaxation and the intersystem crossing is faster in nitro substituted tetrazole, which could be due to the steric effects or lesser conjugation between the nitro group and aromatic ring [31,35–39]. It is observed that the nitro substituted tetrazole (NST) depicted a faster intersystem crossing, which depopulated the S_1 state within 7.8 ps. On the other hand, AST has demonstrated a slower intersystem crossing with

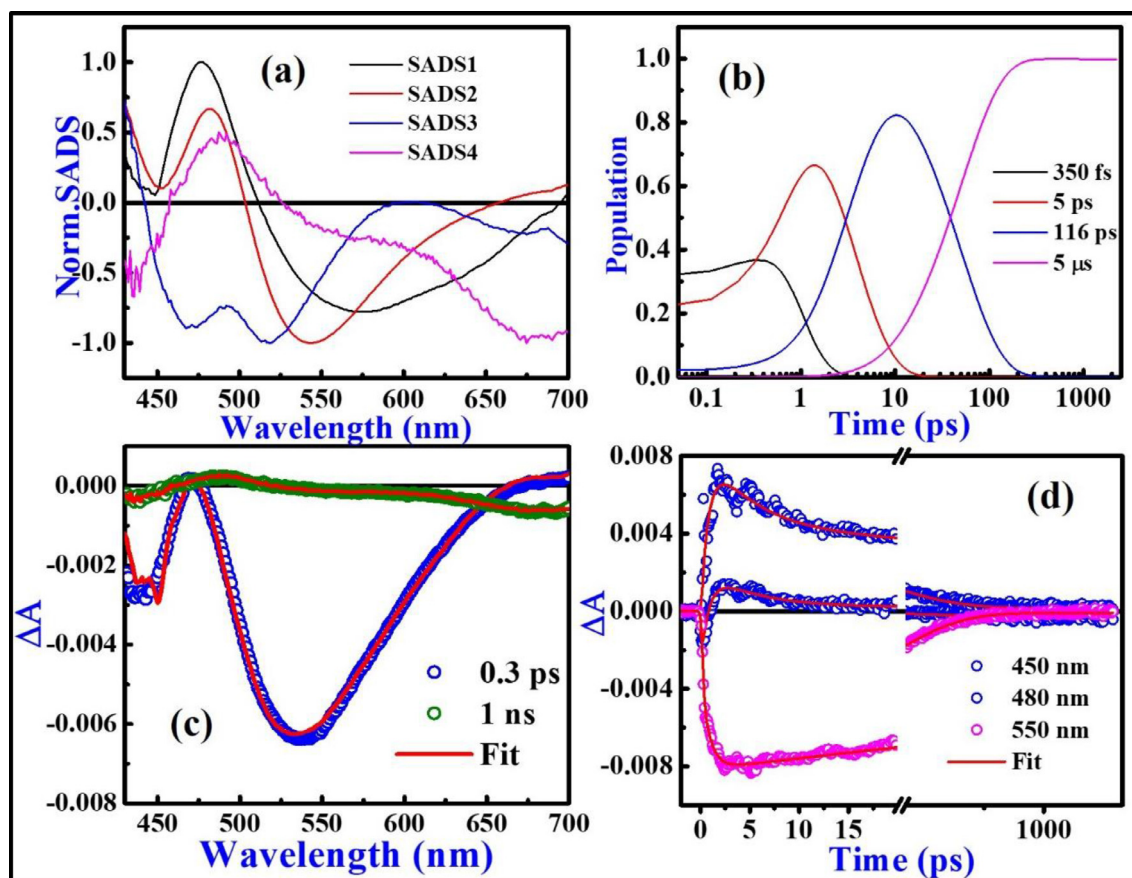


Fig. 5. Global analysis of the TA spectra correspondent to AST (a) species associated difference spectra (SADS) (b) Population decay profiles (c) global fit at 0.5 ps and 2 ns (d) kinetic profiles at different wavelengths after global fitting.

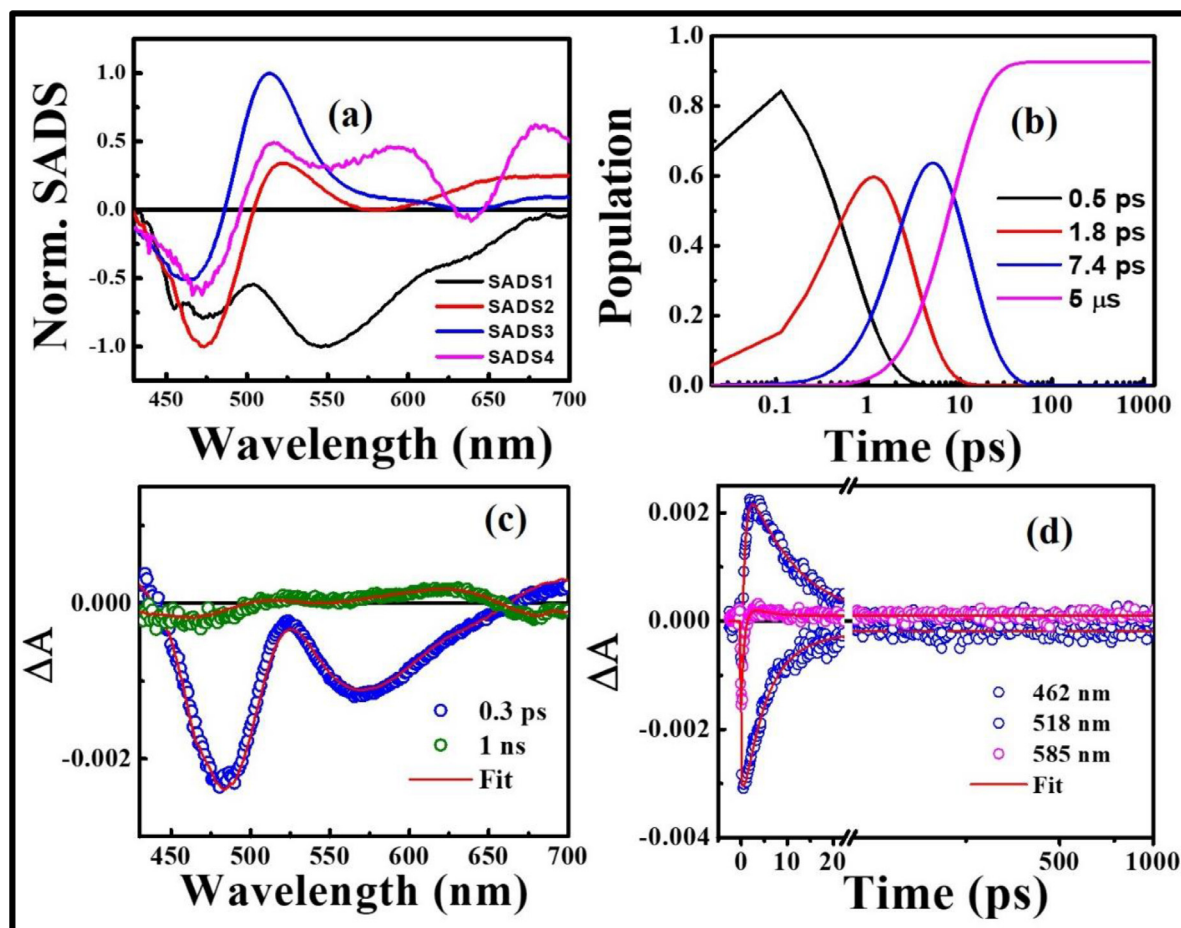


Fig. 6. Global analysis of the TA spectra correspondent to NST (a) global fit at 0.3 ps and 100 ps (b) kinetic profiles at different wavelengths after global fit (c) Evolution associated spectra (d) Population decay profiles (inset shows the short time scale).

a lifetime of 129 ps, which could possibly be due to smaller coupling between the triplet state and the first excited singlet state due to the stabilization of S_1 state [32,36–38].

Lopez-Arteaga et al. [40] studied photophysical properties of 2-nitrofluorene and 2-diethylamino-7-nitrofluorene wherein they observed the amino 2-diethylamino-7-nitrofluorene exhibited slower ISC due to the stabilization of the first singlet excited state concerning the triplet state due to the puss-pull effect induced by the diethylamino group. Vogt et al. [41] have shown the intersystem crossing time of 200 fs in 2-methyl-1-nitronaphthalene, 2-nitronaphthalene, and 1-nitronaphthalene, and the population transfer S_1 - T_1 was controlled by the energy gap between them. The lifetime of the triplet state was recognized as a prominent feature in the energy conversion of energetic materials. Smit and co-workers [36] have recently proposed an intramolecular steric hindrance effect on the triplet lifetime of HNS and 4, 4' and 2, 2'-DNS compounds in acetonitrile solution. The triplet lifetime of HNS and 2, 2'-DNS was observed to be shorter than 4, 4'-DNS and was proposed as due to the steric effects which reduce the influence of the nitro groups on the triplet excited state conjugation, which may decrease the conjugation between the aromatic ring and ethylenic bridge or twisting can result in overlapping of potential energy surfaces of S_0 and T_1 in HNS. Chu et al. [31] have studied the excited state dynamics of 2,2',4,4',6,6'-hexanitrostilbene by using femtosecond TAS they have observed a faster intersystem crossing from S_1 to T_1 with a lifetime of 6 ps and a long-lived triplet state with 4 ns lifetime. Recently, Yi et al. [32] have investigated the ultrafast response of ortho-Nitroaniline with the help of TAS and a combination of chemometrics quantum mechanics

methods, and they have observed an intermediate state S^* in the intersystem crossing process. Further, the triplet state lifetime was found to be 2 ns, with intersystem crossing at 19 ps time scale from S^* to T_1 . Nelson et al. [20] have recently investigated the photo-dissociation dynamics of nitromethane by using TAS and nonadiabatic excited-state molecular dynamics (NA-ESMD) simulations. They have found the formation of relatively fast NO_2 product with a lifetime of 80 fs and slow product methyl nitrite with lifetime 480 fs at 266 nm photoexcitation. The UV excitation of HMX, RDX, and imidazole energetic materials confirmed the formation of the initial photoproduct of NO molecule [14].

The intersystem crossing from the fluorescent state to the triplet state plays a crucial role in the energy conversion process [10,31,40,42]. The time scale of ISC is found to be faster in nitro-substituted tetrazole 7.8 ps than amino-substituted tetrazole 129 ps, which might be due to the reducing coupling between triplet state due to stabilization of fluorescent state by the addition of electron-donating amino group than electron-withdrawing nitro group [33]. Recently, Cole-Filipiak et al. [8] have studied vibrational energy transfer (VET) dynamics from pentaerythritol tetranitrate (PETN) using an infrared pump-probe technique and they have shown that a long-lived (>150 ps) vibrational excitation governs the VET and further detonation process. These ultrafast dynamics studies help to understand the correlation between decomposition of these energetic molecules and their electronically excited states. However, in solid-state, these electronic excitations localize these excitations at different sites of the crystal (impurity defect or structure), leading to the formation of radicals by faster migration of electronic excitations in contrast to diffusion process where the slow movement of heavy metal

takes place [6,43,44]. Also, one needs substantial theoretical support to completely understand these experimental results qualitatively, such as quantum chemical methods or DFT studies [25].

Conclusions

Transient absorption spectroscopic studies on two nitro and amino-substituted tetrazoles were performed with 400 nm photoexcitation. The target analysis of the TAS spectra revealed the possible relaxation mechanism. The nitro substituted tetrazole has shown a faster vibrational relaxation at 1.8 ps and an intersystem crossing time of 7.8 ps. The obtained time constants are similar to some of the energetic compounds reported in literature. Also, their ultrafast internal conversion and intersystem crossing suggest their application in energy deactivation or formation of radicals is relatively faster. The TRPL measurements confirmed the long decay of the triplet state with an average lifetime of few μ s, which could possibly be attributed to the phosphorescence from its lowest triplet state to ground state. We believe, these studies help to understand the excited state molecular decomposition of this new energetic molecules.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Naga Krishnakanth Katturi: Data curtion, Formal analysis, Investigation, Validation, Methodology, Writing – original draft, Writing – review & editing. **Chinmoy Biswas:** Data curtion, Formal analysis, Investigation, Validation, Methodology, Writing – original draft, Writing – review & editing. **Nagarjuna Kommu:** Data curtion, Formal analysis, Investigation, Validation. **Sai Santosh Kumar Raavi:** Data curtion, Formal analysis, Investigation, Validation, Methodology, Writing – original draft, Writing – review & editing. **Venugopal Rao Soma:** Conceptualization, Resources, Supervision, Formal analysis, Investigation, Validation, Methodology, Writing – original draft, Writing – review & editing.

Acknowledgments

We thank the DRDO, India, for financial support through the project #ERIP/ER/1501138/M/01/319/D(R&D).

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