JAAS

PAPER

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Cite this: DOI: 10.1039/c7ja00136c

Received 9th April 2017 Accepted 19th June 2017 DOI: 10.1039/c7ja00136c rsc.li/jaas

Introduction

Laser induced breakdown spectroscopy (LIBS) is a versatile optical emission spectroscopic technique with several advantages such as robustness and in situ elemental analysis of widespread range of samples in their unconventional states.¹⁻³ This analytical technique is now routinely used in various fields such as pharmaceuticals, soil and environment monitoring, cultural heritage, detection of metal traces/toxic elements in water, etc. 4-9 Over the last couple of decades, LIBS, accompanied by other laser based analytical techniques such as terahertz, photo-acoustic, and surface enhanced Raman spectroscopy, has been successfully employed for identification of explosives.10-12 LIBS has tremendous potential for underwater and space exploration missions, standoff and remote detection of explosives. Femtosecond (fs) pulses, due to their capability of delivering high energies over long distances (even up to several hundreds of meters) through the phenomenon of filamentation13-21 can be advantageously employed to this end. The

Correlation of molecular, atomic emissions with detonation parameters in femtosecond and nanosecond LIBS plasma of high energy materials[†]

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In the present work, six novel high energy materials (HEMs) were investigated by femtosecond and nanosecond LIBS techniques with an intention to comprehend the influence of different functional groups as well as their positions on the LIBS emission. The examined HEMS are functional and structural isomers of triazole-substituted nitroarene derivatives and have methyl (CH₃), methoxy (OCH₃), and amino (NH₂) groups in *ortho* and *para* positions. CN and C₂ molecular bands along with atomic lines of C, H, N and O were identified in the ns and fs LIBS spectra. As expected, the molecular signatures in the earlier times of plasma expansion were observed to be prominent in femtosecond LIBS spectra. The various formation pathways for CN and C₂ as well as the correlation of emission intensities with C–C, C=C, C–N, and C=N bonds and % O are investigated using the fs and ns LIBS data recorded in air and argon atmospheres. The influence of functional groups and their position on CN and C₂ emissions is elucidated through the CN/C₂ ratio. Furthermore, the detonation parameters of these materials namely oxygen balance, velocity of detonation, detonation pressure and chemical energy of detonation were found to correlate well with the (CN + C₂)/(C + H + N + O) ratio. Such correlation studies are expected to support the understanding and improve the discrimination procedures for such hazardous materials.

specificity and sensitivity of LIBS is moderate when compared to other analytical techniques such as the Raman technique. However, sustained efforts are directed towards improving this. The combination of LIBS with various multivariate analytical methods such as PCA, SIMCA and PLSDA, has led to enhanced specificity in discriminating soil, pharmaceuticals and explosives with few false alarms.²²⁻²⁶ Myakalwar et al.²⁷ have successfully demonstrated that the judicious selection of a few spectral signatures of the LIB spectrum combined with simple statistical techniques can yield superior classification of explosives. Giacomo et al.28 have recently proposed and demonstrated nanoparticle enhanced laser induced breakdown spectroscopy (NE-LIBS), where sensitivity of analyte (sub-ppm level) was enhanced by the coupling between nanoparticles and analyte in the presence of nanosecond pulses. In general, explosives and other organic samples have similar constituents of C, H, N and O; hence their emission spectra look similar with predominant CN and C2 molecular emission bands. Several researches have investigated the formation pathways of CN and C₂ species in various organic materials and explosives and tried to correlate the emissions with their structures. Grégoire et al.29 employed time resolved spectroscopic imaging to understand the correlation between CN and C2 emissions with native bonds present in polymeric materials. Mousavi et al.30 and Bravo et al.31 have also investigated the influence of molecular structure on CN and C2 emissions for different organic materials



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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ja00136c

with varying % C-C and % C=C linkages. Dong et al.32 have experimentally studied the molecular emissions of solid materials containing C and N. Serrano et al.33 have investigated the formation pathways of CH, NH, and OH diatomic radicals in femtosecond plasmas of deuterated isotopologues of urea, terephthalic acid and anthracene. Delgado et al.34,35 had investigated several possible fragmentation pathways in organic explosives under a controlled atmosphere with different background gases and at different laser fluences. R. Glaus et al.36 have reported the formation of isotopic labelled C_2 peaks ${}^{12}C_2$, ¹²C¹³C and ¹³C₂ in isotopic ally labelled fumaric acid. Rao et al.³⁷ have studied influence of varying nitro groups among nitropyrazoles on molecular emissions with fs excitation in air, argon and nitrogen. Sreedhar et al.38,39 have investigated molecular formation dynamics of CN and C2 in RDX, NTO and TNT subjected to different ambient gases namely ambient air, argon and nitrogen with both fs and ns excitations. Recently, our group has investigated the role of the position and number of substituents on ring fragmentation pathways in nitroimidazoles using both fs and ns ablation schemes and established the correlation between the molecular structures of explosive nitroimidazoles with intensity ratios of molecular and atomic species.⁴⁰ The type, position and number of substituents seem to have a strong bearing on the spectral emission signatures. To elucidate this, we have considered, in this work, a set of six novel high energy materials (HEMs) which are structural and functional isomers of triazole substituted nitroarene derivatives⁴¹ that possess methyl (CH₃, hereafter referred to as Me), methoxy (OCH₃, hereafter referred to as OMe) and amino (NH₂) groups at para and ortho positions. The emission signatures in laser induced plasma (LIP) from various organic materials depend on the molecular structure, constituents and the atmosphere surrounding the LIP. The LIBS emission spectra were recorded using fs (in air) and ns (in air and argon) pulses. An attempt has been made to correlate the molecular and atomic emission signatures with principal detonation parameters viz., oxygen balance (O.B.), velocity of detonation (V.O.D.), detonation pressure (D.P.) and chemical energy of detonation (Q). Furthermore, we try to understand and explain the mechanisms leading to these correlations.

Experimental details

An ultrafast Ti:Sapphire laser system (amplitude, \sim 3 mJ, 1 kHz) delivering \sim 50 fs laser pulses and operating at 800 nm was employed to perform the fs LIBS experiments at the Radiation & Photochemistry Division, BARC, India. fs LIBS experiments were carried out in ambient air using 900 µJ pulse energy. Fig. 1 illustrates the schematic of the fs LIBS experimental setup at BARC.

The ns ablation experiments were carried out at ACRHEM, University of Hyderabad. Q-Switched Nd:YAG laser (INNOLAS, \sim 1.2 J@1064 nm, 10 Hz) delivering \sim 7 ns pulses were employed to carry out ns experiments in air and argon with 15 mJ at 532 nm wavelength. A 100 mm focal length lens fixed on a translational stage was used in both the cases for focusing and precise interrogation of laser pulses with the sample. The



Fig. 1 Schematic of the LIBS setup depicting the plasma source and collection system.

plasma emissions were collected by using an Andor CC52 collector/collimator at 15 cm from plasma and fed to an Andor Mechelle (ME 5000) + Andor iStar ICCD (DH 334T-18U-E3) system *via* an optical fiber of 600 μ m diameter. The Mechelle spectrometer was calibrated by using two standard calibration lamps namely the mercury argon calibration source (253–922 nm) for wavelength and the deuterium halogen calibration source for intensity. Its resolution is 0.05 nm and the effective



Fig. 2 Molecular formulae, structures and IUPAC names of the HEMs along with the labels used in the present study.

Table 1 Atom percentages of C, H, N, O and C–C, C=C, C–N, C=N linkages and detonation parameters of HEMs. "a" and "b" are taken from ref. 42 and ref. 41. V.O.D., D.P., O.B. and Q stands for velocity of detonation, detonation pressure, oxygen balance, and chemical energy of detonation

Label	C%	H%	N%	O%	C-C% + C=C%	C-N% + C=N%	V.O.D. ^a (m s ⁻¹)	D.P. ^a (GPa)	O.B. ^b	Q ^b (Cal per g)
A1	36	28	20	16	26.5	26.7	6980	17.25	-112.37	1122.86
A2	34.6	26.9	19.2	19.2	22.1	25.4	7108	18.47	-99.56	1063.78
A3	33.3	25	25	16.6	24	32	7222	18.88	-95.93	1024.65
A4	36	28	20	16	26.5	26.7	6980	17.13	-112.37	1115.48
A5	34.6	26.9	19.2	19.2	22.1	25.4	7008	17.77	-99.56	1053.96
A6	33.3	25	25	16.6	24	32	7167	18.51	-95.94	1017.81

wavelength range is 200–850 nm. For experiments in the argon atmosphere, the sample was purged with argon gas with the help of a nozzle at the rate of \sim 3 L min⁻¹. Pellets were placed on the translation stage controlled with a Newport ESP 300 motion controller to expose fresh surfaces to each pulse.

In the ns excitation case, 20 spectra were recorded for samples A1-A6 (Fig. 2), in accumulation mode (10 accumulations) with a gate delay of 1 µs, gate width of 4 µs and ICCD gain at 120, in air and argon environments. Exposure time of ICCD was 0.002 s. In the fs case, the spectra were recorded in accumulation mode (6 accumulations) to obtain a good signal to noise ratio, using a gate delay of 100 ns, gate width of 800 ns, exposure time of CCD is 1.5 s, and ICCD gain at 180. Thus, a single spectrum is the result of optical emissions collected from 9000 pulses. Three such spectra were recorded for the samples of A1-A6 in air. The fs LIBS spectra could not be recorded in the argon environment due to the insufficient sample size. The spectra were recorded in the range of 220-850 nm. The gate delays of 100 ns (fs case) and 1 µs (ns case) were adjusted such that the recorded spectrum is practically devoid of continuum.

Materials

A set of six novel functional and structural isomers of triazolesubstituted nitroarene derivatives (labelled as A1–A6) were investigated in this work. Details of the synthesis procedure of these high energy materials were reported earlier by Kommu *et al.*^{41,42} About 150 mg of fine ground powder of six explosive molecules was pressed at 3 tonnes of pressure to make a pellet of 2–3 mm thick and 12 mm in diameter. The detonation parameters namely the velocity of detonation (V.O.D.) and detonation pressure (D.P.) were calculated by Explo5 version 6.02 and are listed in Table 1. These compounds have different functional groups namely, methyl (CH₃), methoxy (OCH₃), and amino (NH₂) attached at *para* (A1–A3) and *ortho* (A4–A6) positions. Their structures, IUPAC names and molecular formulas are summarized in Fig. 2.

Results and discussion

1. Effect of laser pulse duration on fragmentation patterns in triazole-substituted nitroarenes

Fig. 3(a) and (b) illustrate the fs and ns LIBS spectra, respectively, of six novel HEMs recorded in air. The fs LIBS spectra were dominated by molecular emission signatures from CN and C₂ (as compared to atomic species). Three CN bands were observed in the spectral regions of 358-360 nm, 386-390 nm, and 410–422 nm corresponding to the $\Delta \nu$ values of -1, 0, and +1respectively. The CN violet band ($\Delta \nu = 0, B^2 \Sigma^+ \rightarrow X^2 \Sigma^+$) had maximum intensity. Three C₂ bands ($\Delta \nu = -1, 0, +1$) were observed in the spectral range of 465-475 nm, 510-518 nm, and 555-565 nm with maximum intensity at the C2 Swan band $(\Delta \nu = 0, d^3 \Pi_g \rightarrow a^3 \Pi_u)$. Besides the molecular bands including NH (336.3 nm), atomic emission lines of C, H, N, O and Ca, Na, Fe (impurities) are identified and tabulated in Table 2 along with standard spectroscopic data43,44 for comparison. Iron emissions (predominantly seen in A1, in both fs and ns case) are possibly from an impurity which might have entered during the sample preparation or in the pellet preparation phase. In contrast to the fs-LIB spectra, the ns-LIB spectra were dominated by atomic emission lines.

Fig. 4 illustrates the strikingly different ablation behavior observed when analyzing the LIBS spectra obtained with fs and ns pulses. The fs-plasma is relatively cooler (~7000 K) compared to ns plasma (\sim 10 000 K). The continuum background in fs-LIB emission spectra is significantly lower than the ns-plasma due to the absence of plasma re-heating and negligible plasmaatmosphere interaction due to narrower angular distribution in fs plasma expansion and, therefore, favored molecular formation15,45-47 via associative mechanisms of atoms or ions in a laser ablation plume. The various radiative transitions of these molecular species give rise to the molecular emissions. The persistence of emission (lifetime) of spectral lines is hugely dependent on the laser pulse energy, extent of laser-plasma coupling and in turn the plasma temperature. Owing to the higher laser pulse energy and improved laser-plasma coupling combined with a higher plasma temperature, the emission lines from ns-plasma possess higher persistence when compared to those from fs-plasma. Hence, the molecular formation is delayed in ns-plasma. The persistence of emission of spectral lines in ns-plasma is at least an order of magnitude longer than that from femtosecond plasmas.38,39 This will certainly impact the ratio of the sum of molecular emission intensities to the sum of atomic emission intensities (MSAS), $(CN + C_2)/(C + H + N)$ + O), when recorded at later delay times. The MSAS ratio (obtained from time integrated spectra) using fs pulses is distinctly higher (i.e. predominantly stronger molecular emissions) than that from the corresponding ns pulses. This MSAS ratio was



Fig. 3 LIBS spectra of six novel HEMs in air with (a) fs and (b) ns excitation. Molecular (CN and C_2) and atomic emissions (C, H, N, and O) with impurities are labelled.

later analyzed to evaluate its correlation with detonation parameters. In the following discussion, we present our arguments towards understanding the origin of CN and C_2 species.

(i) Origin of CN species and correlation studies. Despite several extensive studies, the origin and evolution of laser induced plasma (LIP) is not clear due to the simultaneous involvement of numerous mechanisms such as heating, vaporization, shock wave generation & it's collapse, *etc.*^{48,49} Species present in the surrounding environment near the focal zone may react with the species present in the plasma and result in different bond formation pathways. Serrano *et al.*⁵⁰ had investigated several organic compounds and proposed various pathways in which a diatomic radical can be formed by considering all dissociation and recombination processes involving single and double displacement reactions and surviving native fragments. They have also demonstrated that excitation with fs pulses better reflects the structure of the molecular solid as compared to ns excitation. Besides native CN bonds, other possible secondary sources for the generation of CN species could be the reaction of C₂ and C with N or N₂, where N and N₂ could be of native origin (*i.e.* from the sample) or from the ambience (from air).

$$C + N \rightarrow CN$$
 (1)

$$C + N_2 \rightarrow CN + N \tag{2}$$

$$C_2 + N \to CN + C \tag{3}$$

$$C_2 + N_2 \to 2CN \tag{4}$$

To establish the existence of possible channels, the correlation between CN intensities and C–N% + C==N% as well as C–C% + C==C% was evaluated using fs (in air) and ns (air and argon atmosphere) pulses. In all correlation graphs, Pearson's correlation coefficient has been used to deduce the correlation in paired data sets. The value of Pearson's "*r*" coefficient closer to 1 or -1 indicates a stronger positive or negative linear correlation between the predictor variable (*x*) and the response (*y*). In all correlation graphs for ablation in air, data points corresponding to *para* (*ortho*) isomers are represented by square (circle) symbols and black color (red). For ablation in argon, the corresponding symbols are hollow. The solid (dash) line represents the linear fit for *para* (*ortho*) isomers. In this article, integrated line intensities of C, CN and C₂ emissions with baseline correction were used for the analysis (ESI Fig. 1†).

Fig. 5a shows the correlation of CNVsum (where CNVsum is the integrated line intensity of the $\Delta v = 0$ band for CN, in the region of 384-389 nm, achieved with the MATLAB program after base line correction) with respect to percentages of C-N and C=N bonds obtained from the fs LIBS data recorded in air. In comparison, the corresponding plots (Fig. 5b) obtained for the ns case demonstrate poor correlation in air [r(P) = -0.3][r(O) =-0.68] and argon [r(P) = -0.17] and [r(O) = -0.18]. This observation clearly suggests that CN does not originate solely from native CN bonds, but can also be formed from other secondary sources such as recombination reaction channels. This can be verified by carrying out the ablation in the argon atmosphere. In the argon atmosphere, there is no ambient N₂ (as opposed to 80% N₂ in the air medium). Therefore, in the argon atmosphere, the formation of CN from reaction channels (1) and (2) (using N from ambience) is not expected to take place. Hence, the CN intensity was lower compared to the corresponding signal intensities obtained for ablation in air.

Molecular system and atomic species	Transitions observed in fs LIBS (air) (nm)	Transitions observed in ns LIBS (air) (nm)	Standard wavelengths (nm)
CN violet $(B^2\Sigma^+ - X^2\Sigma^+)$	$\Delta v = +1:359.03,358.61,358.4$	$\Delta \nu = +1:359.04,358.58,358.42$	359.04, 358.59, 358.39
	$\Delta \nu = 0$: 388.31, 387.11, 386.16,	$\Delta \nu = 0$: 388.32, 387.15, 386.17,	388.34, 387.14, 386.19, 385.47
	385.45, 385.05	385.46, 385.01	
	$\Delta u = -1: 421.59, 419.7, 417.99,$	$\Delta u = -1: 421.52, 419.71, 418.09,$	421.60, 419.72, 418.10, 416.78,
	416.7, 415.71, 415.04	416.78, 415.72, 415.16	415.81, 415.24
$C_2 (d^3 \Pi_g \rightarrow a^3 \Pi_u)$	$\Delta \nu = 1:473.68,471.49,469.71,$	$\Delta \nu = 1:473.71,471.55,469.75,$	473.71, 471.52, 469.76, 468.78,
	468.43	468.48, 467.84	467.86
	$\Delta \nu = 0:516.46,509.51^{**},512.8$	$\Delta \nu = 0:516.48,512.88$	516.52, 512.93, 509.77
	$\Delta \nu = -1:563.45,558.46,551.49$	$\Delta \nu = -1$: band was not observed	563.55, 558.55, 550.19
NH $({}^{3}\Pi \rightarrow {}^{3}\Sigma)$	336.12	336.04	336.0
OI	777.4	777.6, 844.76	777.4, 844.63
NI	746.8*	742.41, 744.28, 746.89, 818.44,	742.36, 742.23, 746.83, 818.48,
		821.59	821.63
ΗI	656.4*	656.3	656.28
CI	247.8	247.8	247.85
Na I	589.0, 589.7	588.98, 589.96, 818.26, 819.45	588.99, 589.59, 818.32, 819.48
Ca (I & II)	422.69	Ca I 422.72, Ca II 393.38, Ca II	Ca I 422.67, Ca II 393.36, Ca II
		396.88	396.84
Fe (I & II)	Fe I 251.64, Fe I 252.87, Fe II 288.18 (A1)	Fe I 251.64*, Fe II 288.19*	Fe I 251.76, Fe I 252.91, Fe II 288.07

Table 2	List of atomic em	hission lines and	d molecular bands	observed in the LIB	spectra obtained with	fs and ns nulse excitation
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^a *Weak emissions and ** was observed only in the fs spectra, standard wavelength for molecular emissions⁴³ and atomic transitions.⁴⁴



Fig. 4 Ratio of the molecular sum to atomic sum (MSAS), $(CN + C_2)/(C + H + N + O)$ in air with femtosecond (black) and nanosecond (red) excitation.

Furthermore, the poor correlation with % C-N + % C=N (Fig. 5c) suggests the prevalence of recombination reaction channels leading to CN formation.

CN can also be formed *via* reaction channels (3) and (4) involving C_2 species. The latter are predominantly seen in the case of ablation with fs pulses (Fig. 3a). If C_2 was formed from fragmentation (*i.e.* C–C or C=C), a good correlation of CNVsum with respect to C–C and C=C linkages (Fig. 6a) implies that there was not much depletion of C_2 by way of scavenging by O from air (reaction channel (5) and (6)) since the air in fs plasma is barely ionized and thus CN was formed *via* reaction channels of (3) and (4).

$$C_2 + O \rightarrow CO + C \tag{5}$$

$$C_2 + O_2 \to 2CO \tag{6}$$

This may not be the case for ablation with ns pulses where the surrounding air is also ionized. Under such conditions, the contribution to reaction channel (5) from "O" in the air needs to



Fig. 5 Correlation of CNVsum with respect to C–N linkages in air with (a) fs LIBS data (b) ns LIBS data and (c) in argon with ns LIBS data. P & O denote *para* & *ortho* isomers in all the correlation graphs.



Fig. 6 Correlation of CN violet band emissions w.r.t. C-C linkages (a-c) and O% (d-f) from the LIBS data in air obtained with fs and ns pulses and in argon with ns pulses.

be considered. As the C2 concentration gets depleted (by reacting with O) the formation of CN is also reduced. This is reflected as a bad correlation (Fig. 6b). This aspect can be confirmed by carrying out the ablation in argon. When the ablation is carried out in argon, the reaction of C₂ with O (of air) is ruled out. In the absence of this scavenging reaction, most of the C2 will react with N to give CN thus yielding a better correlation between CN and % C-C + % C=C linkages (Fig. 6c). Furthermore, the CNVsum decreased with increasing % O in the molecules (data presented in Fig. 6d). This is possibly due to scavenging of C₂ by O (see above discussion), consequently there will not be many C2 species left to react via reaction channels (3) and (4). The correlation is superior due to the absence of any contribution from O of the atmosphere as the air in fs plasma is barely ionized. However, for the case of ns ablation where the surrounding air gets ionized, the probability for scavenging of C (more C than C₂ in ns ablation) by O (from the surrounding ionized air) is high thereby resulting in a poor correlation (Fig. 6e). In the argon atmosphere, the interference from atmospheric O is ruled out and the correlation improves (Fig. 6f).

(ii) Origin of C_2 species and correlation studies. The C_2 emissions from carbon (graphite) have been extensively studied in various ambient gases⁵¹⁻⁵³ and microwave discharge through CO.⁵⁴ These studies suggest that C_2 Swan band emission most probably originates from the electron collisional process through (i) direct excitation of C_2 molecules or (ii) formation of

 C_2 molecules in the excited state $(d^3\prod_g)$ *via* dissociative or recombinative processes, where the former pathway is favoured only when large carbon clusters are present in the plasma.⁵⁵ Anselment *et al.*⁵⁶ proposed that low-energy electron collisions with C_n cations $(n \ge 2)$ or neutrals (n > 2) followed by dissociation could result in an excited C_2 molecule. Little *et al.* proposed another mechanism⁵⁷ for populating the $d^3\prod_g$ state from the ${}^5\prod_g$ meta stable state *via* potential curve crossing. The LIBS studies on urea, thiourea,³⁰ and RDX^{38,58} molecules had linked the absence of C_2 emission bands to the lack of C==C linkage in these molecules; thereby suggesting fragmentation as the dominant mechanism for the formation of C_2 . However, the recombination process involving two carbon radicals can also yield C_2 species⁵⁹ according to the following reaction (7).

$$C + C + M \rightarrow C_2 + M \tag{7}$$

In our fs LIBS studies on azoles, a superior correlation (Fig. 7a) was observed between the C₂ emission intensity and % C–C + % C=C bonds. This is partly due to the absence of any contribution from O of the atmosphere (reaction channel (5): scavenging reactions for C₂) since the air in fs plasma is hardly ionized. Furthermore, the superior negative correlation (r = -0.83, *para* and r = -1, *ortho*) between C₂ intensities and O atom% in the molecules (Fig. 7d) suggests that the decay of C₂ proceeds mainly by reaction channel (5), where "O" is from the molecules. With ns pulses, the correlation between C₂ emission



Fig. 7 Correlation of C₂ emissions w.r.t. C–C linkages (a–c) and O% (d-f) from the LIBS data with fs and ns pulses in air and with ns pulses in argon.

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intensity and % C–C + % C=C deteriorated (r = 0.73, *para* and r = 0.9, *ortho*). This could be due to the formation of C₂ by recombination channels (in addition to fragmentation) along with a concomitant loss of C₂ (scavenging reactions involving "O" from the ionized air). The latter is also responsible for the poor negative correlation between C₂ and % O (Fig. 7e). In the argon atmosphere, there is a significant improvement in the correlation (Fig. 7c and f) largely due to the absence of scavenging reactions involving "O" from the atmosphere.

2. Plasma chemistry of CN and C₂ emissions

The feasibility of above discussed reactions were examined at different temperatures *viz.*, 3000 K, 4000 K, 5000 K, and 6000 K by evaluating the standard enthalpy change (ΔH_r), Gibbs free energy change (ΔG_r) and equilibrium constant (K_{eq}). Table 3 lists the ΔH_r , ΔG_r and K_{eq} at 3000 K and 6000 K (for calculations at different temperatures, refer ESI Table 2†). The standard enthalpy of formation and the Gibbs free energy of formation of reactants and products are taken from NIST-JANAF thermochemical tables.⁶⁰

Reactions (1), (3), (5), (6) and (7) are exothermic in nature $(\Delta H_r < 0)$ while the reactions (2) and (4) are endothermic in nature $(\Delta H_r > 0)$. If $K_{eq} \ge 1000$, then usually product species will be present at equilibrium (forward reaction). If it is <0.001, then we expect that mostly reactant species will be left at equilibrium (backward reaction). If the condition $0.001 < K_{eq} < 1000$ is satisfied then both reactants and products co-exist at equilibrium.

As mentioned earlier, CN is formed during the laser ablation (LA) process by collisions of C neutrals with N neutrals and N₂ molecules (from the ambience). As can be seen from Table 3, reaction (1) strongly favours the formation of CN by the recombination of C and N (1.1@6000 K < K_{eq} < 5.7 × 10⁶@3000 K). Reaction (3) also supports the formation of CN with C₂ and N recombining (23@6000 K < K_{eq} < 593@3000 K). The reaction of C and C₂ with atmospheric nitrogen N₂ to form CN seems to be in equilibrium as their K_{eq} ranges between 0.06 to 0.001 and 1.4 to 0.65, respectively. Thus, the formation of CN is more favourable *via* the reaction of C and C₂ with N.

Reaction (6) is strongly exothermic ($\Delta H < 0$) and as temperature decreases from 6000 K to 3000 K, the K_{eq} increases exponentially. Similarly, reaction (5) also leads to the consumption of C₂. The formation of C₂ by recombination of C atoms with the assistance of an intermediate is favored [K_{eq} (reaction (7)) increases by 3 orders, whereas K_{eq} (reaction (6)) increases by 8 orders] but the reaction (5) and (6) are competing with reaction (7). The increase in the negative ΔG_r value with a decrease in the temperature also shows that the reaction (7) is spontaneous and favors the formation of C₂. Thus, the thermodynamical quantities play a key role in the CN and C₂ formation pathways in laser induced plasma (LIP) and emphasize the importance of plume dynamics and plasma chemistry.

3. Trends in CN and C₂ peaks in fs-LIBS spectra for (i) *para* series and (ii) *ortho* series

The molecular emission intensities can also depend on the number of substituent groups, as revealed from our earlier studies³⁸ on nitroimidazoles. The nitro group, by way of resonance and inductive effects (which act synergistically), drains out the electrons from the ring, making it easily susceptible to atomization. As a consequence, the CN emission intensity was higher than the C₂ intensities and the CN/C₂ ratio was observed to increase with the number of electron withdrawing nitro groups.⁴⁰

In the present work, we attempted to understand how the nature of the substituents and their position influence the C_2 and CN emission intensities in the triazole-substituted nitroarene series. The trend in the CN/C₂ ratio as we move across the series A1–A3 and A4–A6, which have different functional groups (Me, OMe, and NH₂) at *para* and *ortho* positions, respectively, is illustrated in Table 4.

(i) Trend in CN/C₂ in the *para* series. The CN/C₂ emission intensity ratio within the *para* series followed the trend of A1 < A2 < A3 *i.e.* A3 had maximum tendency to atomize *vis-a-vis* fragmentation. This implies that there was extensive delocalization of electron density within the aromatic ring resulting in more canonical forms for A3 as compared to A2 and A1. The delocalization of π -electrons arises primarily from the presence of electron withdrawing –NO₂ groups (see the above discussion). All the triazole-substituted nitroarene compounds used in this study have the same number of nitro groups and differ in the type of substituent at *ortho* and *para* positions. Therefore, it is these substituents Me, OMe, and –NH₂ which play a crucial role in destabilizing the aromatic ring. The electron releasing

Table 3 The standard enthalpy change (ΔH_r), Gibbs free energy change (ΔG_r), and equilibrium constant (K_{eq}) for the proposed reaction channels are shown. Rxn stands for reaction

Rxn	$\Delta H_{\rm r} ({\rm kJ} {\rm mol}^{-1})$		$\Delta G_{ m r} (m kJ mol^{-1})$		K _{eq}	
	3000 K	6000 K	3000 K	6000 K	3000 K	6000 K
(1)	-769.854	-770.387	-387.964	930.927	$5.7 imes10^{6}$	1.136
(2)	195.232	218.311	169.928	210.979	0.001	0.064
(3)	-164.126	-160.607	-159.277	-1090.64	593.41	23.198
(4)	31.106	57.704	10.651	-879.658	0.652	1.485
(5)	-490.36	-505.07	-440.189	-722.128	4.6×10^7	$2.2 imes10^3$
(6)	-1072.97	-1103.26	-1000.41	528.219	$2 imes 10^{17}$	$9.8 imes10^7$
(7)	-605.728	-609.78	-228.687	2021.56	$9.6 imes10^3$	0.048

Table 4 Trend of CN and C2 line integrated intensities and their ratios obtained with fs excitation

Functional group	para	CN/C_2	ortho	CN/C_2
-Me	A1	5.48 ± 0.12	A4	4.94 ± 0.28
-OMe	A2	8.26 ± 1.05	A5	10.34 ± 0.03
$-NH_2$	A3	10.36 ± 0.35	A6	6.48 ± 0.62

-Me group pushes some electron density into the ring. Therefore, the pi electron cloud in the aromatic ring gets localized thus increasing the probability for fragmentation (*i.e.* more C_2 formation). It is the C-C and C=C bonds in the phenyl ring which will be instrumental in C_2 formation since the triazole ring is devoid of C-C or C=C linkages.

When -Me is replaced by the -OMe group, it is expected that the comparatively stronger electron releasing -OMe group will limit the extent of delocalization of the ring π -electron cloud. However, the 'O' atom due to its electronegative character pulls away the electrons leading to reduction in electron density in the phenyl ring. This facilitates delocalization of π electrons within the ring and increases the chances of atomization leading to a higher CN/C₂ ratio. In the case of the -NH₂ group (maximum electron releasing tendency amongst the three functional groups) as the substituent, it is expected that the extent of delocalization will be drastically reduced. Additionally, (as discussed above), due to the electron withdrawing effect of the N atom (less electronegative than O of OMe), a small fraction of electron density may be withdrawn towards the amino group, thereby allowing for more delocalization of the ring π electron cloud. However, another important factor that needs to be considered here is the H-bonding (intra and inter molecular) involving the -NH2 group and the -NO2 groups on either side of it⁴¹ (ESI Table 1[†]). Since the lone pair electrons on N are involved in H-bonding, they will not be available for coupling with the π -electron cloud of the phenyl ring. This further promotes π -electron delocalization thereby increasing the probability of atomization. Thus the -NH2 substituted compound (A3) exhibits the highest CN/C₂ ratio among the para isomers.

(ii) Trend in CN/C₂ in the ortho series. For the ortho series, the CN/C₂ emission intensity ratio followed the trend A4 < A6 < A5. But for the positions of A6 and A5, this trend is like that observed in the para series. The CN/C2 ratio for A6 which has the -NH₂ group in the ortho position is lower than that for A5. This can be attributed to the reduction in the extent of intramolecular H-bonding (as there is only one -NO₂ group adjacent to the $-NH_2$ group). Hence, unlike the *para* case, the lone pair electrons of N are now available for coupling with the π -electron cloud of the phenyl ring. The delocalization of the ring π -electrons is then restricted. Furthermore, unlike the O-atom (of -OMe) whose electronegativity is higher than the N-atom (of the -NH₂ group), the latter cannot effectively withdraw electron density from the ring, thus further restricting delocalization. Therefore, A6 possibly exhibited greater probability of fragmentation (i.e. less atomization) compared to A5.

(iii) Trend in CN/C₂ with respect to the position of the substituent (*para vs. ortho*). The observed variation in CN/C₂ between A1 *versus* A4 and A2 *versus* A5 could be within the experimental error margin, we therefore, refrain from commenting on this. On the other hand, A3 displayed a significantly higher CN/C₂ ratio compared to A6. In other words, the presence of the amino group in the *para* position makes the molecule more vulnerable to atomization. The intra-molecular H-bonding⁴¹ involving the lone pair electrons on the $-NH_2$ group and the adjacent $-NO_2$ group (one on either side of the $-NH_2$ group) minimizes the chances of coupling of lone pair electrons with the ring π -electron cloud. Since delocalization is facilitated, atomization is favored over fragmentation, thus giving rise to a higher CN/C₂ ratio for A3 as compared to A6.

4. Energetic parameters

Globally, there is a continuous research focused on the synthesis of advanced novel HEMs with increased density, diminished toxicity and increased explosive performance *i.e.* high positive heat of formation (H.O.F.), possessing high heat of explosion (Q) resulting in high velocity of detonation (V.O.D.) and detonation pressure (D.P.).⁶¹⁻⁶⁴ Velocity of detonation (m s⁻¹) refers to the rate of propagation of the detonation front and detonation pressure (GPa) refers to the pressure that exists at the shock wave-medium interface as the shock wave travels through the medium. V.O.D. and D.P. are linearly proportional to the density of HEM. A general approach for the estimation of CHNO explosives is to use Kamlet–Jacobs (K–J) equations shown in eqn (8) and (9).⁶⁵

$$D (\rm{km s}^{-1}) = 1.01 (NM^{0.5}Q^{0.5})^{0.5} (1 + 1.30\rho)$$
(8)

$$P (\text{GPa}) = 15.58\rho^2 N M^{0.5} Q^{0.5}$$
(9)

where *D* is the velocity of detonation, *P* is the detonation pressure, ρ is the loading density, *N* represents the number of moles of gaseous detonation products per gram of explosive, *M* is the average molecular weight of the gases and *Q* is the heat of explosion in Cal per gram.

However, it is not always possible to experimentally measure the V.O.D. and D.P. of a new energetic sample as it requires a detonation chamber, testing apparatus and various dynamic methods based on different physical principles.⁶⁶ Therefore, a few advanced computer codes such as CHEETAH and EXPLO5 were designed and are now extensively employed to predict various performance parameters of metal-containing explosives, which accurately predict the detonation performance (better than the K–J equations).^{67,68} V.O.D. and D.P. used in this work were obtained using EXPLO5 version 6.02 under standard conditions, *i.e.* 298 K temperature and 1 bar pressure assuming that atmospheric gases do not react with the molecule during the detonation.

Chemical energy of detonation (C.E.D.) or heat of explosion is denoted by *Q*. It is and defined as the energy in kcal released by 1 kg of explosive at constant volume. The heat of explosion provides information about the work capacity of the explosive. Oxygen balance is an important property of explosives which indicates the degree to which an explosive can be oxidized. Deficiency of oxygen within the molecule may end up with CO or NO gases which are toxic. Thus, there must be enough oxygen available within the sample to convert all its carbon, hydrogen and nitrogen to stable products such as carbon dioxide, water and nitrogen dioxide. In this case the molecule is said to have a zero oxygen balance. In case the molecule is oxygen deficient, then it is termed negative oxygen balanced and if oxygen is surplus to that required then the molecule is termed positive oxygen balance. Oxygen balance of an explosive $(C_xH_yN_wO_z)$ where total C is converted into CO₂ was calculated as per eqn (10).

$$O.B.\% = \frac{1600\left(z - 2x - \frac{y}{2}\right)}{\text{molecular weight}}$$
(10)

For laboratory studies, the detonation products of the explosive molecules were computed using EXPLO5. C, CO, CO₂, N₂, H₂O, *etc.*, emerged as the major detonation products while NO, CH, HCN, and NH₂ were the minor products. Products (species) observed in LIBS spectra includes C, CO, CH, CN, C₂, N₂⁺, NO, NH, N, O, H, *etc.* It needs to be mentioned here that in real-time detonations numerous varieties of species can be expected. However, our aim in this study is to correlate the detonation parameters of a molecule with the LIBS signals observed.

Johnson *et al.*,⁶⁹ have studied extremely short detonation interaction events in reactive materials such as aluminium, magnesium and boron with PBX-N9 pellets by simultaneous imaging and spectroscopy. Farhadian *et al.*⁷⁰ used CN and AlO molecular band emissions to investigate the aging of high energy materials. Rezaei *et al.*⁷¹ have correlated detonation parameters such as the heat of formation (H.O.F.), velocity of detonation (V.O.D.) of aluminium based RDX explosives with Al/O ratios and shown that molecular to atomic ratios can be used to understand the trend of energetic parameters. To evaluate the performance of the explosives (triazole-substituted nitroarenes), we have attempted to correlate the detonation parameters *viz.* O.B., V.O.D., D.P. and *Q* with CN/C₂ and (CN + C₂)/(C + H + N + O) ratios.

Fig. 8 and 9 depict the correlation of detonation parameters with respect to the CN/C_2 ratio and the MSAS ratio, $(CN + C_2)/$ (C + H + N + O), respectively. The integrated intensities of C at 247.8 nm, H at 656 nm, N at 746 nm and O 777.2 nm, CN at 388.3 nm, C2 at 516.4 nm were used to calculate CN/C2 and $(CN + C_2)/(C + H + N + O)$ ratios. A strong linear correlation was observed between the CN/C2 ratio and the explosive parameters (data in Fig. 8a-d) in the case of para isomers with fs excitation in air; the ortho isomers on the other hand exhibited inferior correlation [see discussion 3(ii)]. The (CN + C_2)/ (C + H + N + O) ratio obtained with fs excitation correlated very well with the energetic parameters, in both the ortho and para series with a maximum of 10-15% error. This error could probably be due to the weak intensities of atomic lines corresponding to H and N. We strongly feel that such correlation data will be accommodating in discrimination/identification/



Fig. 8 Correlation of the CN/C_2 emission ratio with respect to detonation parameters (a–d): (a) O.B., (b) V.O.D., (c) D.P. and (d) Q.

classification of hazardous materials using the LIBS technique. Furthermore, the possibilities with fs pulses of delivering over long distances makes it attractive even for standoff detection.

In future, we wish to utilize this correlation data along with other statistical techniques and time-resolved data concurrently to explore the possibility of unambiguous discrimination of these compounds. Our results also open a new avenue wherein the LIBS technique could possibly be used as a laboratory-scale technique to predict the detonation performance⁶⁵ with a minimal amount of the sample (~150 mg). For achieving this, comprehensive studies on standard energetic molecules and exhaustive correlation analyses are essential.



Fig. 9 Correlation of the CN/C_2 emissions ratio with respect to energetic parameters: (a) O.B., (b) V.O.D., (c) D.P., and (d) Q.

Conclusions

Novel high energy materials (triazole-substituted nitroarene derivatives with Me, OMe, and NH₂ functional groups) were investigated by fs and ns-LIBS techniques with an intention to elucidate the role played by substituents on the spectral emission signatures in LIBS. CN and C2 molecular bands were identified along with atomic lines corresponding to C, H, N and O. Molecular signatures were prominent in femtosecond LIB spectra whereas atomic emission lines dominated the ns-LIB spectra. The formation pathways for CN and C₂ species as well as the correlation of emission intensities with C-C, C=C, C-N, and C=N bonds and % O were investigated using the fs and ns LIBS data recorded in air and argon. These studies revealed that in case of ablation with fs pulses, CN species were formed mostly from native CN bonds while C2 species were formed mostly from fragmentation of C-C, C=C bonds. However, in the case of ablation with ns pulses, CN and C₂ are formed from other secondary sources as well. Furthermore, scavenging of C2 species by O from the ambience was also evident.

We had also investigated the trend in the CN/C2 ratio across the structural and functional isomers of triazole substituted nitroarenes, which revealed the significant impact of the type and position of substituents on the spectral emission signatures. The substituents, Me, OMe, and NH₂, in the order of increasing electron releasing tendency, served to increase the electron density in the ring thus limiting the extent of delocalization of the π -electron cloud in the aromatic ring. On the other hand, the electronegative 'O' atom (in OMe) and N atom (in NH₂) pulled away the electrons leading to reduction in electron density in the aromatic ring, thus facilitating the delocalization of pi electrons and increasing the chances of atomization (i.e. higher CN/C2 ratio). Furthermore, we concluded that the position of the -NH2 group played a crucial role in the stability of the aromatic ring. When the -NH₂ group was in the para position, the extensive H-bonding (intramolecular) with -NO2 groups on either side prevented the lone pair electrons on N from coupling with the π -electron cloud of the aromatic ring thus promoting π -electron delocalization and increasing the probability of atomization.

The ratio $(CN + C_2)/(C + H + N + O)$ obtained with fs excitation in air correlated very well with energetic parameters (O.B., V.O.D., D.P., and C.E.D.) for both the *ortho* and *para* series. The MSAS ratio can, therefore, be a reliable performance metric for energetic compounds.

Acknowledgements

All the authors acknowledge DRDO, India for constant funding. The authors acknowledge Dr Anuj Vargheese and Mr Ashutosh for their help in calculating BDE values using the Gaussian 09 package. S. Venugopal Rao and P. Mathi acknowledge the Board of Research in Nuclear Sciences (BRNS), India funding through a project (34/14/48/2014-BRNS/2084). Valuable comments from the two anonymous reviewers are gratefully acknowledged.

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