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Femtosecond and nanosecond LIBS studies of nitroimidazoles: correlation between molecular structure and LIBS data⁺

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In the present study, seven novel explosive molecules (nitroimidazoles) have been investigated for laser induced breakdown (LIB) spectral signatures of molecular and atomic species in air and argon atmospheres utilizing both femtosecond (fs) and nanosecond (ns) laser pulse excitation. The molecular emissions were observed to be stronger in the fs spectra whereas atomic emissions were prominent in the ns spectra recorded in both air and argon atmospheres. The C_2 Swan band was strongest in an argon atmosphere while the CN violet band was strongest in ambient environment. The LIB spectra were analysed for understanding (a) the influence of molecular structure i.e. type of bonds (C-C, C=C, C-N and C=N) on atomic (C, H, N and O) and molecular (CN, C2 and NH) emissions, (b) effect of surrounding atmosphere on the fs and ns LIB spectra, (c) correlation between stoichiometric and intensity ratios of molecular as well as atomic species, (d) effect of the number of substituents and their position in the ring on the fragmentation pathways and (e) correlation between oxygen balance and LIB spectra. Furthermore, time resolved spectroscopic studies of the plasma induced by fs and ns laser pulses have been carried out to understand the temporal evolution and possible reaction mechanisms of various molecular species. An attempt has been made to correlate the spectral emission with the chemical structure for this series of energetic materials. Our detailed studies and analyses clearly suggest that the atomization/fragmentation ratio could serve as a performance metric for high energy materials.

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1. Introduction

Over the last decade, there has been remarkable interest in exploring laser based techniques,^{1–5} such as laser induced breakdown spectroscopy (LIBS), Raman, terahertz, and photo-acoustic techniques *etc.* for the detection of hazardous materials including explosives. The major aim here is to achieve unambiguous detection of trace explosive molecules with the ultimate goal of standoff detection capability for trace molecules. The LIBS technique, which has been successfully employed for elemental analysis of a wide range of materials,^{6,7} is one of the potential techniques for the detection of explosives due to its standoff detection capability along with its ability to detect ppm (parts per million) concentrations in real time. In recent studies, LIBS in combination with several chemometric

approaches has been employed for detection/discrimination/ identification of explosive molecules, land mines, chemical and biological warfare agent stimulants on various surfaces including polymers, metals etc.8-15 Moreover, the standoff detection capability of man-portable LIBS systems has also been demonstrated by several research groups.16-18 A single-shot standoff LIBS for the detection of energetic materials at distances up to 45 m has also been efficaciously demonstrated.13 In other fields such as lithography, micromachining, and medical applications the pre-eminence of fs pulse usage over ns pulses has been indisputably established.¹⁹ However, there are certain issues that need to be addressed for application of LIBS for the detection and discrimination of explosive materials with high success rate for on-field applications. Traditionally LIBS experiments have been performed with nanosecond (ns) pulses. Several modifications such as double pulse LIBS and LIBS studies employing femtosecond (fs) pulses have been shown to provide certain advantages for exploring various classes of materials including explosives.20-28 The characteristics of the laser induced plasma (LIP) are found to depend strongly on the laser parameters such as pulse width, pulse energy, pulse repetition rate, and laser irradiance as well as the surrounding atmosphere. Femtosecond pulses offer several advantages in LIBS applications such as (a) low fluence

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threshold, (b) precise interrogation with the material, (c) efficient ablation, (d) lower continuum emission and (e) competency of traveling few kilometres of distance through the filamentation process.²⁹ In fact there are a few studies reported on filament induced LIBS wherein they demonstrate that the pulses need not be focused to obtain the LIB spectra. Furthermore, a small amount of ablated mass (as in the case of fs-LIBS) is an advantage when analyzing unique samples. The relatively lower plasma temperature in the fs-LIBS also favours the formation of molecular species such as CN and C₂ in explosives and related materials. Our earlier LIBS studies on a series of energetic molecules clearly suggested the difference in molecular signatures in LIBS data obtained with fs pulses.³⁰⁻³² Moreover, matrix effects are found to be detrimental in determining traces of explosive molecules on different substrates (e.g. paper, metal, polymer, leather, etc.).^{33,34} A deeper understanding of the interaction of fs pulses with material surfaces, atmospheric contribution, focusing conditions, etc. is, therefore, essential to further the application of the fs-LIBS technique.35

The most prevalent peaks in the LIB spectra of organic explosive related compounds (ERCs) are from the elemental constituents, such as C, H, O, and N and molecular emissions from CN and C2 species. Weaker emissions corresponding to CH, NH, and OH species have also been reported.³⁶ Many of the intermediates generated during the ablation process are not detected by optical emission either due to their short lifetimes or due to emissions beyond the detection range of the spectrometer. It is extremely difficult to ascertain the origin of molecular emissions i.e. whether the species are released directly from native bonds by way of fragmentation or are generated as a result of recombination with ambient constituents. The plasma produced by ns-LIB is assumed to be in a state of local thermodynamic equilibrium and is characterized by an excitation temperature (typically ~ 9000 K)³⁷ and electron number density ($\sim 1.5 \times 10^{16} \text{ cm}^{-3}$) sufficiently high for sustaining the collisional processes. This gives rise to a significant population of molecules in dissociative states which in turn opens up many fragmentation/dissociative pathways. As the plasma expands these species, created in the breakdown zone, recombine with the surrounding atmospheric constituents to yield new species. Despite plethora of reactions taking place in the organic plasma, the emission spectra of the ERCs recorded in a narrow detection window (\sim 800 ns) are seemingly alike.

Extensive time-resolved studies on expansion dynamics of graphite plume³⁸ demonstrated the temporal evolution of fast and slow components of C₂ emission. The slow component was assigned to dissociative processes (with long duration C₂ Swan emission) whereas the fast component arose from recombination processes (within a narrow temporal window). Recently, laser ablation molecular isotopic spectroscopic (LAMIS) studies³⁹ have also indicated that generation of CN either involves atomic carbon or a species with a single carbon atom. The data obtained from a homologous series of nitro toluenes, mono-, di- and tri-nitro toluene, suggested that C₂ originated from unsubstituted carbon atoms in the ring.⁴⁰ A recent study with 4-nitro aniline and 4-nitro toluene has also established a correlation between the stoichiometry of the compound and

the corresponding emission intensities.⁴¹ Several groups have presented various kinetic models to describe the formation of molecular emission and have monitored the relative intensities of the atomic C/H/N/O emissions lines towards discrimination of different molecules.^{42–44} Hermann *et al.*⁴⁵ have modelled the local thermal equilibrium plasma for the analysis of gas-phase reactions. Vivien *et al.*⁴⁶ employed a time- and space-resolved optical emission spectroscopic technique to investigate the kinetics of excited plasma species C₂, CN and N₂⁺ generated by an excimer laser ablation of a graphite sample in a low-pressure N₂ atmosphere. These studies have led to a better understanding of the gas-phase reactions during the thin film deposition.

Despite numerous studies and the availability of huge data on discrimination and identification of ERCs, there is no clear understanding of the influence of molecular structure (for e.g., the nature, position and number of substituent groups) on the optical emission spectra. An exhaustive understanding of the fs (and ns) LIBS data correlating with the molecular structure and surrounding environment is indispensable keeping in view the impending applications of LIBS for the detection of explosives. The knowledge of atmospheric contribution to the LIBS data is indispensable for on-field/practical applications. In this work we present the results from LIBS studies of seven different molecules belonging to a family of ERCs (nitroimidazoles), carried out under different environmental conditions (air, argon) and pulse durations (fs and ns pulses). Nitroimidazoles have been used in medicines as antibiotic drugs, radio sensitizers and recently as explosives.47 Imidazole derivatives with more than two nitro groups, particularly 2,4-dinitro imidazole (2,4-DNIm), are potential candidates for civil and military applications due to its good thermal stability, impact and shock insensitivity, better performance, and economic and environmentally friendly synthesis. The nitroimidazoles presented in this study were synthesized and characterized in our laboratory. The LIB spectra were analysed for understanding (a) the influence of molecular structure *i.e.* type of bonds (C-C, C=C, C-N and C=N) on the atomic and molecular emissions, (b) effect of surrounding atmosphere on the fs and ns LIB spectra, (c) correlation between stoichiometric and intensity ratios of molecular and atomic species, (d) effect of the number of substituents and their position in the ring on the fragmentation pathways and (e) correlation between oxygen balance and LIB spectra. Furthermore, time resolved spectroscopic studies of the plasma induced by fs and ns laser pulses have been carried out to understand the temporal evolution and possible reaction mechanisms of various molecular species. We have attempted to correlate the spectral emission data with the chemical structure for this series of energetic materials.

2. Experimental set-up

The fs LIBS data were recorded with two different 1 kHz fs laser systems located in two different labs (ACRHEM, University of Hyderabad, Hyderabad^{31,48} and BARC, Mumbai). In general, the fs laser system comprises of a Ti–sapphire oscillator, a chirped pulse regenerative amplifier and a grating compressor. In both

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the LIBS experiments, the laser pulses with a duration of ${\sim}50$ fs, delivering ~ 1 mJ energy at a central wavelength of 800 nm were used. The pulse-to-pulse energy fluctuation of the input laser pulses was <5%. Plasma for LIBS analysis was generated by focussing the 1 mJ pulse energy onto the surface of the sample pellets using a plano-convex lens of focal length 100 mm. The estimated beam diameter at focus was 12 \pm 3 μ m. The samples were mounted on a motorized Y-Z translational stage which is interfaced to LabVIEW and provided automated sample translation during data acquisition. This ensures that a fresh area of the sample was always investigated. Collection of plasma emission in both the experimental setups was performed with a collimator fibre coupled to an Echelle grating spectrograph (Andor Mechelle ME5000) and detected by using a thermoelectric cooled ICCD (Andor DH734-18mm-CCI-01U). The ICCD provided a spectral coverage from 200-900 nm with 0.1 nm wavelength resolution. The ICCD was gated in synchronization with the fs laser pulses to achieve a good signal to noise ratio (S/N). The gate delay, gate width and the detection system were computer controlled through a digital delay generator embedded in the ICCD. The experiments aimed at understanding the influence of atmosphere (air versus argon) were carried out at ACRHEM. Argon gas flow was directed through a nozzle onto the sample surface at the point of laser impact.

The ns LIBS data were recorded at ACRHEM and the details of the experimental setup are discussed in our previous studies.49,50 A Q-switched pulsed Nd-YAG laser system (SpitLight 1200, InnoLas) delivering ns pulses of wavelength at 532 nm with a pulse duration of \sim 7 ns and a repetition rate at 10 Hz was used. The typical pulse energy used in our experiments was \sim 25 mJ. The ns laser pulses were focused on the target sample with a plano-convex quartz lens with a focal length of 100 mm. The fs-LIB spectra of all nitroimidazoles were recorded in air and argon atmospheres using a gate delay of 100 ns and a gate width of 800 ns. The ns-LIB spectra were recorded in air and argon atmospheres with a gate delay of 1100 ns and a gate width of 10 µs. For time resolved fs-LIBS studies, a gate width of 50 ns and a step size of 50 ns were employed following an initial gate delay of 90 ns up to 590 ns. In the ns case, a series of time resolved spectra were recorded with a gate delay of 500 ns, a gate width of 500 ns, and a step size of 500 ns up to 5000 ns in both air and argon atmospheres.

3. Sample preparation

Seven novel ERCs are being studied for comparison of fs and ns spectral signatures in air and argon atmospheres. These ERCs are (a) imidazole, Im $(C_3H_4N_2)$ (b) 4-nitroimidazole, 4-NIm $(C_3H_3N_3O_2)$ (c) 1,4-dinitroimidazole, 1,4-DNIm $(C_3H_2N_4O_4)$ (d) 2,4-dinitroimidazole, 2,4-DNIm $(C_3H_2N_4O_4)$ (e) 1-methyl-4-nitroimidazole, 1M-4NIm $(C_4H_5N_3O_2)$, (f) 2-methyl-4(5)-nitroimidazole, 2M-4(5)-NIm $(C_4H_5N_3O_2)$, and (g) 1-methyl-2,4-dinitroimidazole, 1M-2,4-DNIm $(C_4H_4N_4O_4)$. All the samples were prepared as pellets using a manual hydraulic press (4–6 metric tonnes of pressure and 3–4 minutes duration) with a diameter of ~12 mm and weight ranging from 600 to 800 mg with a thickness of 2–3 mm.

4. Results and discussion

4.1 fs and ns-LIB spectral signatures in air and argon atmospheres

The fs-LIB spectra of imidazole recorded in air is shown in Fig. 1a. The LIB emission spectra evidently are dominated by molecular emission bands corresponding to CN and C2. The CN molecular bands corresponding to $\Delta \nu$ values of -1, 0 and +1 were observed at 357-360 nm, 384-389 nm and 414-423 nm, respectively. Amongst these, the molecular emission at 388.32 nm corresponding to the CN violet band $(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ ($\Delta \nu = 0$ sequence) was the strongest. C₂ molecular bands corresponding to $\Delta \nu = -1$, 0 and +1 transitions were located in the spectral regions of 460-475 nm, 510-520 nm and 550-565 nm, respectively. The strongest C_2 emission was observed for the Swan band $(D^3\Pi^g \rightarrow a^3\Pi^u)$ at 516.52 nm ($\Delta \nu = 0$ sequence). The atomic emissions corresponding to the elemental constituents C(I) (247.86 nm), H_{α} (656.33 nm), O(1) (777.42 nm), N(1) triplet lines (742.46 nm, 744.28 nm, 746.85 nm), and N (868.23 nm) are relatively weaker. The ns-LIB spectra (Fig. 1a) demonstrated additional features such as unresolved O(1) triplet lines (777.23 nm, 777.42 nm and 777.51 nm), N(1) emission lines at 818.49 nm, 818.79 nm, 821.04 nm, 821.69 nm, 824.50 nm and 863.18 nm along with weaker atomic emissions of Ca(I), Na(I) and Fe(I), which possibly were from the sample impurities assimilated during the pellet preparation. The overall signal levels in fs spectra were superior to those in the ns spectra. Fig. 1b



Fig. 1 Comparison of LIB spectra of imidazole (Im) obtained with fs and ns excitations in (a) air and (b) argon atmospheres. A gate delay of 100 ns and gate width of 800 ns at 1 mJ energy were used in the fs case while in the ns case the delay was 1100 ns, gate width was 10 μ s and input pulse energy was ~25 mJ. Each spectrum is a resultant of average of five independent measurements.

shows the fs and ns-LIB spectra of imidazole recorded in an argon atmosphere. In addition to the spectral features discussed above, Ar(1) atomic emission lines were observed at 696.61 nm and in the spectral region of 750 nm to 850 nm. The details of the peaks observed in fs and ns LIB spectra of seven nitroimidazoles recorded in air and argon atmospheres are summarized in Table 1. Strong CN molecular emissions corresponding to different vibrational transitions ($\Delta \nu = -1$, 0 and +1) are observed for all these compounds whereas C₂ molecular bands have been observed only for Im, 4-NIm, 1M-4NIm and 2M-4(5)-NIm. The dinitroimidazole (1,4-DNIm, 2,4-DNIm and 1M-2,4-DNIm) spectra exhibited very weak C2 emissions [see ESI Fig. 1-3[†]]. The corresponding bar graph (data presented in Fig. 2) shows variation in intensity distribution thus indicating the feasibility of qualitatively distinguishing different compounds. Hence, it is of interest to study any correlation that exists between the emission intensities and the chemical structure of these molecules (ESI Fig. 4[†]).

4.2 Correlation between atom percent (C, H, N and O), stoichiometric ratios and corresponding atomic emission intensities (ratios)

We have attempted to study the degree of correlation between the atomic spectral lines of carbon (247.86 nm), H_{α} (656.32 nm), oxygen (777.42 nm) and nitrogen (868.68 nm) and also the molecular emissions of CN (388.32 nm) and C₂ (516.52 nm) using fs LIBS data recorded in air and argon atmospheres.



Fig. 2 Bar graph of molecular and atomic emission intensities of CN, CN^{Sum} , C_2 , C_2^{Sum} , C, H_{α} , O and N observed in the fs-LIB spectra of seven nitroimidazoles in an argon atmosphere. Each bar chart corresponds to an average intensity of 15 spectral events and the error bar represents standard deviation.

Table 2 shows the percentages of elemental constituents (C, H, N and O), bonds (C–C, C=C, C–N and C=N) and oxygen balance (OB) values for all the imidazoles studied (ESI Table 1^+). The

Table 1 Wavelengths of molecular (CN, C₂ and NH) and atomic (C, H, N, O, Ca, Na, Fe and Ar) emissions observed in LIB spectra of seven nitroimidazoles in air and argon atmospheres with fs and ns excitations

	Emission lines (nm) in femtosecond LIB spectra		Emission lines (nm) in nanosecond LIB spectra				
Species	Air	Argon	Air	Argon			
CN	388.32, 387.12, 386.17, 385.5, 385.11 ($\Delta \nu = 0$); 359.05, 358.54, 358.36, 356.04 ($\Delta \nu = -1$); 421.6, 419.66, 418.52,		388.32, 387.12, 386.15, 385.44, 385.01 ($\Delta \nu = 0$);			
			359.01, 358.57, 358.38 ($\Delta \nu = -1$);	,,			
			422.67, 421.58, 419.69, 418.06, 416.72, 415.78	$(\Delta u = +1)$			
	418.01, 416.78, 415.83	$(\Delta u = +1)$					
C_2	516.52, 512.87 ($\Delta \nu = 0$),		516.52, 512.9 ($\Delta \nu = 0$);				
	473.66, 471.5, 469.67, 468.45, 467.82 ($\Delta \nu = -1$);		$473.59, 471.49, 469.69, 468.45, 467.84 (\Delta \nu = -1);$				
	563.48, 558.51, 554.04, 545.22, 544.61 ($\Delta \nu = +1$)		563.48, 558.51, 554.1 ($\Delta \nu = +1$)				
			516.52 observed only in 4-NIm, 1,4-DNIm and 2,4-DNIm in argon atmosphere				
NH	336.00	Not observed	336.02	Not observed			
C & H	247.86 & 656.24	247.88 & 656.24	247.86 & 656.32	247.86 & 656.28			
0	777.42	777.41	777.23, 777.47 (doublet), 777.51	777.23, 777.47 (doublet)			
Ν	868.23,	868.23	742.41, 744.38, 746.89 (triplet), 818.54,	742.41, 744.38, 746.89 (triplet)			
	742.41, 744.38, 746.89		818.84, 821.64, 824.50, 844.7, 863.29,				
	(triplet)		868.48, 868.69, 870.59, 871.44, 872.13				
Ca I, II	393.36 (Ca I)	_	393.36 (Ca I), 396.86 (Ca II)	—			
Fe I, II	Fe I (306.32, 589.05,	_	Fe II (335.98, 354.88, 353.84), Fe I (353.25,	—			
	589.64)		355.56, 394.69, 394.48)				
Na I, II	Na II (309.98, 309.64,	_	Na II (309.98, 309.64, 308.99),	—			
	308.99)		(Na I) (588.99, 589.59)				
Argon lines	-	Ar II (696.61), Ar I	_	Ar II (696.65), Ar I (738.55,			
(Ar I, II)		(738.52, 750.39, 751.59,		750.52, 751.62, 763.74, 772.54,			
		763.72, 772.47, 794.81,		801.65, 810.50, 811.69, 826.67,			
		801.68, 811.63, 826.46,		840.98, 842.56)			
		840 93 842 67)					

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Compound	Structure	OB	%C	%H	%N	%O	%С-С	%C=C	%C-N	%C=N
Imidazole (C ₃ H ₄ N ₂)		-188.01	33	44	22	0	0	11	33	11
4-NIm (C ₃ H ₃ N ₃ O ₂)	O ₂ N N H	-77.83	27	27	27	18	0	9	36	9
1,4-DNIm $(C_3H_2N_4O_4)$	O ₂ N N NO ₂	-30.37	23	15	31	31	0	8	31	8
2,4-DNIm (C ₃ H ₂ N ₄ O ₄)	O ₂ N NO ₂ H	-30.37	23	15	31	31	0	8	38	8
1M-4NIm ($C_4H_5N_3O_2$)	O ₂ N N CH ₃	-107	29	36	21	14	0	7	36	7
2M-4(5)-NIm (C ₄ H ₅ N ₃ O ₂)	O ₂ N N CH ₃	-107	29	36	21	14	7	7	29	7
1M-2,4-DNIm $(C_4H_4N_4O_4)$	O ₂ N N NO ₂ CH ₃	-55.78	25	25	25	25	0	6	38	6

(1a)

(1b)

Table 2 OB, % of atoms (C, H, O and N), % of C-C, C=C, C-N and C=N bonds of all nitroimidazoles with their structure and molecular formula

percentage of atomic elements (C, H, N and O) and bond type (C–C, C=C, C–N and C=N) were calculated from the molecular formula ($C_aH_bN_cO_d$) of the compound using the equations:

% element =
$$\frac{\text{number of element atoms present in the molecule}}{\text{total number of atoms present in the molecule}} \times 100$$

% bond =
$$\frac{\text{number of particular bonds present in the molecule}}{\text{total number of bonds present in the molecule}} \times 100$$

When the % for every element in the compound is added together, the result will be 100. Percentages of all atomic

elements and bond types were measured by this simple method for all the nitroimidazoles studied. The correlation was performed by estimating the linear regression coefficient (r^2) values. Fig. 3a-g depict the correlation data between stoichiometric values (i.e. % O, H, N and C) and the atomic emission intensities for each sample with fs excitation in argon and air atmospheres. The correlation of O emission intensity in air with %O atom [Fig. 3a] was poor ($r^2 = 0.62$) and it did not show any improvement in an argon atmosphere $[(r^2 = 0.60), \text{ Fig. 3b}].$ However, by using normalized intensity as suggested by Lucia et al.,14 we observed a significant improvement in the correlation ($r^2 = 0.86$, Fig. 3c). The atomic emission lines of interest are normalised with another atomic emission line of an internal standard (in this case argon) in order to minimize the differences in laser-material interactions. Ideally, the atomic lines so chosen should have similar upper energy levels and closely located emission wavelengths for best normalization. It may be



Fig. 3 Correlation between O atomic emission intensity in fs-LIB spectra and O atom% in (a) air (b) argon atmosphere (c) O/Ar intensity ratio *versus* O atom% (ii) H atomic emission intensity *versus* %H atom in (d) air (e) argon; (iii) correlation between C atom% *versus* C atomic intensity in (f) air and (g) argon atmospheres. 15 spectra in argon and five spectra in air were used for these calculations.

pointed out here that the upper energy levels for the O(I)(777.42 nm) and Ar(I) (772.42 nm) emission lines are not similar $[86\ 627\ cm^{-1}\ for\ O(I)$ as compared to 107 496 $cm^{-1}\ for\ Ar(I)]$. The H(I) emission intensity in ambient atmosphere correlated well with %H atom ($r^2 = 0.85$) for ablation in air but deteriorated in an argon atmosphere ($r^2 = 0.72$) (Fig. 3d and e). The C(1) emission intensity exhibited poor correlation with %C atom in air ($r^2 = 0.51$) with marginal improvement in argon ($r^2 = 0.68$) (Fig. 3f and g). It needs to be mentioned here that since there was no Ar(I) emission satisfying the selection criteria discussed above, normalization procedures could not be carried out for C(1) and H lines. Furthermore, we have studied the correlation between stoichiometric elemental ratios and emission intensity ratios for each sample. Fig. 4a-f illustrate the extent of correlation between O/C, O/H and N/H emission intensity ratios and the corresponding stoichiometric ratios in air and argon atmospheres. The relatively superior correlation coefficients observed for all ratios in an argon atmosphere indicate that the LIBS spectral lines faithfully reflected the changing elemental ratios. Generally an r^2 value >0.9 for a particular ratio represents a strong correlation.

4.3 Correlation between molecular emission intensities and the molecular structure

All the compounds in the imidazole series (Im, 4-NIm, 2,4-DNIm, 1M-4NIm and 1M-2,4-DNIm) exhibited a weak NH $(A^{3}\pi_{i}-X^{3}\Sigma^{-})$ system of (0, 0) vibrational transition emission band near 336 nm. Serrano et al.⁵¹ proposed, for the first time, the formation pathways of CH, NH, and OH radicals in fs laserproduced plasma of molecular solids. Their data clearly suggest the direct release of native molecular bonds as a substantial source that populates fs laser-produced plasma with NH radicals. In the present case the first three compounds have native N-H bonds whereas the methyl substituted 4-NIm and 2,4-DNIm are devoid of any native NH bonds. Further, the absence of any correlation between NH intensity and %N or %H suggests that NH may also be formed by recombination processes taking place in the plasma (ESI Fig. 5[†]). In the following discussion, we try to probe whether the molecular structure of these compounds has any bearing on emission intensities of C2 (Swan) and CN (violet) molecular bands in the LIB spectrum.



Fig. 4 Correlation between (i) O/C stoichiometric ratio *versus* O/C atomic emission ratio correlation for (a) fs case air and (b) fs case in argon (ii) O/H stoichiometric ratio *versus* O/H atomic emission ratio correlation for (c) fs case in air (d) fs case in argon and (iii) N/H stoichiometric ratio *versus* N/H atomic emission ratio correlation for (e) fs case in air (f) fs case in an argon atmosphere.

4.3.1 CN emission. The strongest CN emission line at 388.32 nm is considered in this section. All the compounds in the imidazole series have native C-N and C=N bonds, so CN emission may come from the direct emission of native CN bonds. But it is evident from Fig. 5a and b that the CN emission intensities do not seem to correlate well with the %C=N in air and the summation of %C-N and %C=N bonds in argon for these compounds. This suggests that in addition to CN emission from native CN bonds, there may be secondary sources for CN generation such as the reaction between C_2 (formed via native C=C bonds or C_2 formed by recombination in the plasma) and atmospheric N2, as well as the recombination of C with N or N₂. In our LIB emission spectrum we did not observe any signature of NO owing to its short lifetime and, probably, because of interference from the CN band (421.6 nm).⁵² It may be mentioned here that Delgado et al.53 had detected NO and CH_n by laser ablation mass spectroscopic methods.

4.3.2 C_2 emission. Among the seven compounds studied in the imidazole series, only Im, 4-NIm, 1M-4NIm and 2M-4(5)-NIm exhibited strong signatures of C_2 . On the other hand, weak signatures of C_2 emission were observed in 1,4-DNIm, 2,4-DNIm and 1M-2,4-DNIm. Although, Fig. 5c and d clearly demonstrate a superior correlation between the percentage (%) of carbon atoms and the strongest C_2 peak intensities in air and argon atmospheres, we failed to observe any correlation between the



Fig. 5 The correlation between the (i) CN emission intensity in fs-LIB spectra versus C = N and sum of C - N and C = N in (a) air, (b) argon(II) C₂ versus C in (c) air, (d) argon(III) C₂ versus C = C in (e) air, (f) argon.



Fig. 6 Trend in C_2 Swan band emission intensities for the five imidazole series recorded at a gate delay of 283 ns and a gate width of 800 ns with fs excitation in air atmosphere.

 C_2 intensities and %C=C bonds in both the atmospheres (Fig. 5e and f). This behaviour is indicative of the occurrence of two routes for the formation of C_2 species as suggested by Harilal *et al.*⁵⁴ They observed that in the low intensity regime, C_2 species were formed by the direct fragmentation of the parent molecule and dissociation of large carbon clusters with the final release of C_2 dimers. In the high intensity regime, recombination processes played a predominant role in the formation of C_2 . In two separate studies, St-Onge *et al.*⁵⁵ and Portnov *et al.*⁵⁶

Table 3Decay times of CN, C2 and C species in Im, 1,4-DNIm, 2M-4(5)-NIm and 1M-4NIm using fs and ns excitations in air and argonatmospheres. CN represents the strongest peak at 388.32 nm, whereas C_2 represents the strongest peak at 516.52 nm and C at 247.86 nm

	Peak	Air (ns)		Argon (ns)		
Sample		fs-LIBS	ns-LIBS	fs-LIBS	ns-LIBS	
Im	CN	213 ± 28	165 ± 23	1135 ± 15	575 ± 91	
	C_2	219 ± 47	192 ± 2	431 ± 18	876 ± 2	
	С	44 ± 3	1186 ± 35	130 ± 36	815 ± 54	
1,4-DNIm	CN	79 ± 23	2420 ± 150	916 ± 56	926 ± 38	
	C_2	33 ± 4	342 ± 20	39 ± 2	626 ± 3	
	C	26 ± 4	854 ± 39	372 ± 29	1171 ± 80	
2M-4(5)-NIm/1M-4NIm (ns)	CN	369 ± 120	7128 ± 100	309 ± 91	561 ± 41	
	C_2	373 ± 90	496 ± 33	98 ± 6	485 ± 13	
	С	71 ± 8	1014 ± 66	148 ± 14	667 ± 27	

Table 4	C–NO ₂ bond	dissociation	energies	(BDEs);	bond	highlight	ed
in black	is the weakest	bond					

Compound	Bond	BDE (kcal mol^{-1})
4-NIm	C4-NO ₂	73.5
2,4-DNIm	C2-NO ₂	69.1
	C4-NO ₂	70.1
1M-4NIm	C4-NO ₂	73.9
1M-2,4-DNIm	C2-NO ₂	Data not available
	C4-NO ₂	

had suggested the presence of C=C and C=C bonds as a prerequisite for the observance of C₂ emission. The C₂ species could be formed either by fragmentation of the aromatic ring or from reactions between the resulting hydrocarbon species present in the plasma. This was further corroborated by Lucena et al.40 who had observed significant C2 emission in a series of aromatic compounds but extremely weak or zero C2 intensity in the case of RDX and PETN both of which are devoid of C=C bonds. These studies have indicated that the ring opening and fragmentation processes are significantly affected by changes in the stability of the ring. Further, they experimentally verified this conjecture by ablating a series of substituted nitrotoluenes. The C2 emission intensity decreased substantially with the increase in the number of nitro groups. They have reported that C₂ emission might be due to fragments from unsubstituted C atoms formed after ring opening. At this point we are tempted to understand the influence of type and number of substituents on C₂, CN intensities and fragmentation pathways in the imidazole series.

Let us consider the series Im, 4-NIm, 2,4-DNIm, 1M-4NIm and 1M-2,4-DNIm. The C_2 emission intensity decreases along this series (Fig. 6). The significantly high C_2 yield in imidazole can be attributed to the presence of one unsubstituted C==C bond (this is zero for 4-NIm and 2,4-DNIm); the fragments formed from unsubstituted carbon atoms following ring opening give rise to a high C_2 yield. 4-NIm and 2,4-DNIm do not possess any unsubstituted C==C bonds, yet C_2 emission band intensity in 4-NIm is substantially higher than that of 2,4-DNIm. This trend can be attributed to the difference in the number of nitro-functional groups along this series. The nitro group by way of inductive effect pulls the electrons towards it and introduces significant charge separation on the carbon atom to which it is attached. Additionally the highly electronegative atom pulls the electron pair of the multiple bond which results in withdrawal of electron density from the aromatic ring, thus giving rise to different canonical forms. Thus, resonance causes decrease of electron density in the imidazole ring. Both the resonance and inductive effect act in a synergistic fashion. The drain of electrons from the ring makes it easily susceptible to atomization. This is reflected by the low C₂ intensity and large CN emission signal in 4NIm. An increase in the number of electron withdrawing nitro groups, as in 2-4-DNIm, further weakens the ring structure making it more prone to atomization *i.e.* a large CN signal and almost zero C₂ emission. This argument is in line with results from quantum chemical studies by Su et al.57 They found that the increase in the number of NO2 groups on the imidazole ring reduces the stability of the molecule, which is characterized by the decrease of the weakest C-NO₂ bond energy, Table 4. Bond dissociation energies (BDEs) provide valuable information in understanding the stability of nitroimidazoles. The stability of a compound depends on temperature, nature of materials, and substituent groups. The weak C_2 emission band in 2,4-DNIm also suggests that C_2 formation does not proceed via the recombination pathway.



Fig. 7 The correlation between the C_2 intensity *versus* O atom% with fs excitation in (a) air and (b) argon atmospheres.

Another interesting observation is the strong correlation between C_2 emission intensity and the oxygen atom% in both air and argon atmospheres [Fig. 7a and b]. The C_2 emission intensities decreased with increasing oxygen content. This suggests possible scavenging of C and C_2 species by oxygen which may proceed by the following mechanism:⁵⁸

$$C + O \rightarrow CO$$
 (2)

$$C_2 + O \to CO + C \tag{3}$$

$$C_2 + O_2 \to 2CO \tag{4}$$

Further, the effect of alkyl substitution with regard to atomization/fragmentation of the ring structure in nitro imidazoles can be understood by comparing the C₂ emission intensities in 1M-4NIm vs. 4-NIm and 1M-2,4-DNIm vs. 2,4-DNIm. The CH₃ group gives rise to a special resonance called hyper conjugation or no-bond resonance which involves the interaction of sigma electrons. This relatively weaker intra molecular charge transfer (in comparison to strong electron releasing groups like -NH₂ and -OH) does not extend π electron delocalization. Although the NO₂ group is electron withdrawing, the CH₃ group does not allow resonance, which leads to partial localization of single and double bonds. Consequently 1M-4NIm resists atomization thereby exhibiting nearly similar C_2 intensities as 4-NIm. A similar argument holds good for 1M-2,4-DNIm *versus* 2-4-DNIm (ESI Fig. 6†).

Further evidence of the competition between fragmentation and atomization can be seen in the LIP emission spectra of six membered aromatics like 4-nitro aniline and 4-nitro phenol. The OH group is more electron releasing than –NH₂; the charge transfer from the donating group through the π system to the accepting group gives rise to a large number of resonant structures. The relatively larger aromatic π -electron delocalization in 4NP as compared to 4NA is manifested as a higher CN/C₂ ratio (ESI Table 2†). The nature of the substituents thus plays a crucial role in favouring/restricting π electron delocalization which in turn dictates the fragmentation/atomization as well as the (C₂/CN) relative intensities.

5. Decoding the LIBS spectra in terms of performance of the energetic materials: correlating with the oxygen balance

The detonation properties of energetic materials depend on their oxygen balance which is a measure of the degree to which an explosive can be oxidized. It is calculated from the empirical



Fig. 8 fs-LIB signal emission intensity of molecular bands CN (388.32 nm), C_2 (516.52 nm) and atomic line C (247.86 nm) in (a) air, (b) argon atmosphere and (c) CN/ C_2 and (C_2 + CN)/(C + H + N + O) versus oxygen balance (OB) in (c) air and (d) argon atmosphere.

formula of the compound and is defined as the ratio of the oxygen content of a compound to the total oxygen required for the complete oxidation of all carbon, hydrogen and other oxidizable elements to CO_2 , H_2O , *etc.* Lothrop and Handrick⁵⁹ provided the procedure for calculating the oxygen balance of a nitro compound with molecular formula $C_aH_bN_cO_d$. The oxygen balance (Ω) of a nitro compound with molecular formula $C_aH_bN_cO_d$ as defined by Lothrop and Handrick⁵⁹ is expressed as:

$$\Omega = (d - 2a - b/2) \, 1600/M \tag{5}$$

where M is the relative molecular mass of the energetic material.

The molecule is said to have zero oxygen balance if it contains just enough oxygen to convert all the carbon to carbon dioxide, hydrogen to water, and all of its metal to metal oxide; in this case the heat of explosion will be maximum. The oxygen balance will be positive if it contains more oxygen than is needed and a negative if it contains less oxygen than is required. Energetic materials are classified as either oxygen deficient or oxygen rich. Most energetic materials are oxygen deficient. The oxygen balance calculated for the imidazole series of compounds studied here is listed in Table 2. In our recent work on nitropyrazoles, we reported a correlation between LIBS data of nitropyrazoles in an argon atmosphere with oxygen balance (OB).³² In the present study, the correlation between the LIB signal intensity of atomic and molecular species with oxygen balance has been explored for fs excitations in imidazole series of compounds in argon and air atmospheres.

Fig. 8a and b depict the variation in the signal intensity of CN (388.32 nm), C₂ (516.52 nm) and C (247.86 nm) emissions with OB using fs excitations in air and argon atmospheres, respectively. The CN violet band, C2 Swan band and C atomic emission intensities decreased with increasing OB. As the number of nitro groups increases along the series of Im, 4-NIm, and 2,4-DNIm, the oxygen balance tends to -30. The concomitant rise in atomisation/fragmentation and the CN/C₂ ratio in both air and argon atmospheres is clearly seen in the plot of CN/C2 versus OB (Fig. 8c and d). As the OB tends to zero, atomization becomes the dominant pathway in the laser produced plasma. Therefore, the atomisation/fragmentation ratios could serve as a performance metric for high energy materials (ESI Fig. 7⁺). The CN/C₂ ratio was lower in an argon atmosphere than that in air with ns excitation due to the C₂ formed by the partial fragmentation of the parent molecule and there is no nitrogen influence on the molecule from the atmospheres (ESI Fig. 8[†]). Serrano et al.8 presented a diagnostic tool for inferring the predominance of atomization or fragmentation reactions in the plasma, which was the ratio of CN/C2.

6. Temporal studies of molecular emissions (CN, C_2) and the C atomic line in air and argon atmospheres with fs and ns pulses

To gain a deeper insight into possible reaction mechanisms for CN and C_2 formation, time-resolved LIBS (TRELIBS) studies were carried out using both fs and ns laser pulses. TRELIBS



Fig. 9 Time resolved emission decays of the molecular bands of the CN (388.32 nm), C_2 (516.52 nm) and C (247.86 nm). A gate delay of 90 ns and a gate width of 50 ns were used in fs excitation (argon) while in the ns excitation case a gate delay of 500 ns and a gate width of 500 ns were used in argon atmospheres for imidazole, 4-NIm, 1,4-DNIm and 2M-4(5)-NIm and 1M-4NIm. Each data point represents the average of three individual measurements and error bars represent the standard deviation of each data point.

spectra have been recorded for Im, 1,4-DNIm and 2M-4(5)-NIm with fs excitation and Im, 4-NIm, 1,4-DNIm and 1M-4NIm with ns excitation. The molecular bands CN ($\Delta \nu = 0$) at 388.32 nm, C₂ $(\Delta \nu = 0)$ at 516.52 nm and atomic emission carbon remain clearly observed up to 590 ns from the starting gate delay with fs excitation. The atomic emission line H of hydrogen remained significant up to 390 ns. In the case of ns excitation the molecular bands of CN ($\Delta \nu = 0$) at 388.32 nm and C₂ ($\Delta \nu = 0$) bands at 516.52 nm, and atomic emissions of C and H were observed for longer delays. In the ns excitation case (argon) the intensity of the continuum reduced significantly at about 1500 ns (see data presented in ESI Fig. 9[†]). Fig. 9 presents the temporal evolution data of molecular bands CN (388.32 nm), C₂ (516.52 nm) and C (247.86 nm) with fs and ns excitation in an argon atmosphere. The time resolved decays of molecular bands CN, C₂ and atomic emission C were fitted using a single exponential function. The decay constants were calculated for CN, C_2 bands and C line using exponential decay fits to the experimental using the equation

$$y = A_1 \times \exp(-x/t_1) + y_0$$
 (6)

The fitted decay rates of CN, C_2 and C are summarized in Table 3 (and also in ESI Table 3 and Fig. 10–12[†]).

Aguilera et al.⁶⁰ had shown that argon is efficiently heated by inverse Bremsstrahlung, and, therefore, the plasma created in argon has higher electron temperatures and electron densities thus justifying the higher emission intensities observed. It needs to be pointed out here that the decay times obtained for these species in air and argon atmospheres using ns excitation do not exhibit a clear trend. The multiple generation pathways arising out of atmospheric interference hinders the interpretation of time resolved data recorded in air. The data recorded in an argon atmosphere is devoid of such interference and can be used to gain insight into the reaction mechanisms. The persistence (decay times) for CN emission from fs excitation is relatively larger in an argon atmosphere. The higher plasma temperature and electron density may aid the generation of CN by recombination processes. The longest decay times for C₂ species in an argon atmosphere were observed for imidazole (431 ns) which is devoid of oxygen. The decay times for other compounds considered here decreased with increasing oxygen content. This observation seems to be consistent with the mechanism cited in eqn (2)-(4). Further investigations are warranted to confirm this. A very recent review article by Labutin et al.61 vindicates the usage and unique possibilities of fs pulses for LIBS studies. This article clearly outlines the various advantages of fs pulses for LIBS studies and we hope that these can be extended to studies of explosive molecules thereby enabling technologies for stand-off detection.

7. Conclusions

We have used fs and ns pulses to record the LIB spectra of seven energetic molecules (nitroimidazoles) in air and argon atmospheres. We have investigated the behaviour of molecular (CN,

C2 and NH) and atomic (C, H, N and O) emissions in air and argon atmospheres. The comparison of fs and ns LIB spectra in air and argon established the signature of the sample constituents in the plasma region. We observed a strong signature corresponding to molecular species in fs excitation and atomic species in ns excitation. CN emission was dominant for ablations carried out in air, whereas in C₂ emission features were prominent in the LIB spectra recorded in an argon atmosphere. The usage of normalised intensities led to a significant improvement in the correlation between atomic emission intensities and the corresponding stoichiometric values. A good correlation coefficient seen for all ratios in an argon atmosphere indicates that the LIBS spectral lines faithfully reflect the changing elemental ratios. Time resolved data have given valuable insight into possible reaction mechanisms of various molecular species. The molecular emission intensities in the LIP spectra of these compounds exhibited a strong dependence on the number and position of substituents, particularly the nitro group. Both the resonance and inductive effect due the nitro group drain out the electrons from the ring thereby making it easily susceptible to atomization. This led to a reduction in C₂ intensity and an increment in CN intensity with increase in the number of electron withdrawing nitro groups. Further, we observed a strong correlation between C2 emission intensity and the % of oxygen atoms in the molecule; the C₂ emission intensity decreased with increase in the oxygen content. Our detailed studies and analyses clearly suggest that the atomization/fragmentation ratio could serve as a performance metric for discriminating high energy materials.

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References

- 1 D. A. Cremers and L. J. Radziemski, *Handbook of Laser-induced Breakdown Spectroscopy*, Wiley, 2006.
- 2 A. W. Fountain III, S. D. Christesen, R. P. Moon, J. A. Guicheteau and E. D. Emmons, Recent advances and remaining challenges for the spectroscopic detection of explosive threats, *Appl. Spectrosc.*, 2014, **68**(8), 795–811.
- 3 Laser-based Optical Detection of Explosives, ed. P. M. Pellegrino, E. L. Holthoff and M. E. Farrell, CRC Press, 2015.
- 4 J. B. Johnson, S. D. Allen, J. Merten, L. Johnson, D. Pinkham and S. W. Reeve, Standoff methods for the detection of threat agents: A review of several promising laser-based techniques, *J. Spectrosc.*, 2014, **2014**, 613435.
- 5 M. R. Leahy-Hoppa, J. Miragliotta, R. Osiander, J. Burnett, Y. Dikmelik, C. McEnnis and J. B. Spicer, Ultrafast laser-

based spectroscopy and sensing: Applications in LIBS, CARS, and THz spectroscopy, *Sensors*, 2010, **10**, 4342–4372.

- 6 D. W. Hahn and N. Omenetto, Laser-induced breakdown spectroscopy (LIBS), part I: review of basic diagnostics and plasma-particle interactions: still-challenging issues within the analytical plasma community, *Appl. Spectrosc.*, 2010, **64**, 335–366.
- 7 D. W. Hahn and N. Omenetto, Laser-induced breakdown spectroscopy (LIBS), part II: review of instrumental and methodological approaches to material analysis and applications to different fields, *Appl. Spectrosc.*, 2010, **66**, 347–419.
- 8 J. Serrano, J. Moros and J. J. Laserna, Sensing signatures mediated by chemical structure of molecular solids in laser-induced plasmas, *Anal. Chem.*, 2015, **87**, 2794–2801.
- 9 R. S. Harmon, F. C. de Lucia Jr, A. La Pointe, R. J. Winkel Jr and A. W. Miziolek, LIBS for landmine detection and discrimination, *Anal. Bioanal. Chem.*, 2006, 385, 1140–1148.
- 10 L. Mercadier, J. Hermann, C. Grisolia and A. Semerok, Diagnostics of nonuniform plasmas for elemental analysis *via* laser-induced breakdown spectroscopy: demonstration on carbon-based materials, *J. Anal. At. Spectrom.*, 2013, 28(9), 1446–1455.
- 11 M. Abdelhamid, F. J. Fortes, M. A. Harith and J. J. Laserna, Analysis of explosive residues in human fingerprints using optical catapulting–laser-induced breakdown spectroscopy, *J. Anal. At. Spectrom.*, 2011, **26**, 1445–1450.
- 12 J. L. Gottfried, F. C. De Lucia Jr, C. A. Munson and A. W. Miziolek, Strategies for residue explosives detection using laser-induced breakdown spectroscopy, *J. Anal. At. Spectrom.*, 2008, 23, 205–216.
- 13 C. Lopez-Moreno, S. Palanco, J. Javier Laserna, F. DeLucia Jr, A. W. Miziolek, J. Rose, R. A. Walters and A. I. Whitehouse, Test of a stand-off laser-induced breakdown spectroscopy sensor for the detection of explosive residues on solid surfaces, J. Anal. At. Spectrom., 2006, 21, 55–60.
- 14 F. C. De Lucia and J. L. Gottfried, Influence of Molecular Structure on the Laser-Induced Plasma Emission of the Explosive RDX and Organic Polymers, *J. Phys. Chem. A*, 2013, **117**, 9555–9563.
- 15 J. L. Gottfried, F. C. De Lucia Jr, C. A. Munson and A. W. Miziolek, Strategies for residue explosives detection using laser-induced breakdown spectroscopy, *J. Anal. At. Spectrom.*, 2008, 23, 205–216.
- 16 F. C. de Lucia Jr, J. L. Gottfried, C. A. Munson and A. W. Miziolek, Multivariate analysis of standoff laserinduced breakdown spectroscopy spectra for classification of explosive-containing residues, *Appl. Opt.*, 2008, 47(31), G112–G122.
- 17 R. Gonzalez, P. Lucena, L. M. Tobaria and J. J. Laserna, Standoff LIBS detection of explosive residues behind a barrier, *J. Anal. At. Spectrom.*, 2009, **24**, 1123–1126.
- 18 I. Gaona, J. Moros and J. J. Laserna, New insights into the potential factors affecting the emission spectra variability in standoff LIBS, *J. Anal. At. Spectrom.*, 2013, **28**(11), 1750–1759.

- 19 B. N. Chichkov, C. Momma and S. Nolte, Femtosecond, picosecond and nanosecond laser ablation of solids, *Appl. Phys. A: Mater. Sci. Process.*, 1996, **63**, 134–142.
- 20 S. S. Harilal, J. Freeman, P. Diwakar and A. Hassanein, Femtosecond laser ablation: Fundamentals and applications, in *Laser-induced Breakdown Spectroscopy*, ed. S. S. Musazzi and U. Perini, Springer, Berlin, Heidelberg, 2014, vol. 182, ch. 6, pp. 143–166.
- 21 J. R. Freeman, S. S. Harilal, P. K. Diwakar, B. Verhoff and A. Hassanein, Comparison of optical emission from nanosecond and femtosecond laser produced plasma in atmosphere and vacuum conditions, *Spectrochim. Acta, Part B*, 2013, **87**, 43–50.
- 22 M. Oujja, M. Sanz, F. Agua, J. F. Conde, M. García-Heras, A. Dávila, P. Oñate, J. Sanguino, J. R. Vázquez de Aldana, P. Moreno, M. A. Villegas and M. Castillejo, Multianalytical characterization of Late Roman glasses including nanosecond and femtosecond laser induced breakdown spectroscopy, J. Anal. At. Spectrom., 2015, 30, 1590–1599.
- 23 M. Baudelet, L. Guyon, J. Yu, J.-P. Wolf, T. Amodeo, E. Fréjafon and P. Laloi, Femtosecond time-resolved laserinduced breakdown spectroscopy for detection and identification of bacteria: A comparison to the nanosecond regime, *J. Appl. Phys.*, 2006, **99**, 084701–084709.
- 24 R. K. Gill, F. Knorr, Z. J. Smith, M. Kahraman, D. Madsen, D. S. Larsen and S. Wachsmann-Hogiu, Characterization of femtosecond laser-induced breakdown spectroscopy (fsLIBS) and applications for biological samples, *Appl. Spectrosc.*, 2014, **68**, 949–954.
- 25 G. Gustinelli, A. de Carvalho, J. Moros, D. Santos Jr, F. J. Kruga and J. J. Laserna, Direct determination of the nutrient profile in plant materials by femtosecond laserinduced breakdown spectroscopy, *Anal. Chim. Acta*, 2015, 876, 26–38.
- 26 M. Kotzagianni and S. Couris, Femtosecond laser induced breakdown for combustion diagnostics, *Appl. Phys. Lett.*, 2012, **100**, 264104.
- 27 T. Ahmido, A. Ting and P. Misra, Femtosecond laser-induced breakdown spectroscopy of surface nitrate chemicals, *Appl. Opt.*, 2013, **52**, 3048–3057.
- 28 F. C. De Lucia, J. L. Gottfried and A. W. Miziolek, Evaluation of femtosecond laser-induced breakdown spectroscopy for explosive residue detection, *Opt. Express*, 2009, 17, 419–425.
- 29 E. L. Gurevich and R. Hergenroeder, Femtosecond laserinduced breakdown spectroscopy: physics, applications, and perspectives, *Appl. Spectrosc.*, 2007, **61**, 233A–242A.
- 30 S. Sreedhar, E. Nageswara Rao, G. Manoj Kumar, S. P. Tewari and S. Venugopal Rao, Molecular formation dynamics of 5nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one,1,3,5 trinitroperhydro-1,3,5-triazine, and 2,4,6-trinitrotoluene in air, nitrogen, and argon atmospheres studied using femtosecond laser induced breakdown spectroscopy, *Spectrochim. Acta, Part B*, 2013, **87**, 121–129.
- 31 S. Sunku, M. K. Gundawar, A. K. Myakalwar, P. P. Kiran,S. P. Tewari and S. Venugopal Rao, Femtosecond and nanosecond laser induced breakdown spectroscopic

studies of NTO, HMX, and RDX, *Spectrochim. Acta, Part B*, 2013, **79–80**, 31–38.

- 32 E. Nageswara Rao, S. Sreedhar and S. Venugopal Rao, Femtosecond Laser-Induced Breakdown Spectroscopy Studies of Nitropyrazoles: Effect of Varying Nitro Groups, *Appl. Spectrosc.*, 2015, **69**(11), 1342–1354.
- 33 B. Zhang, M. He, W. Hang and B. Huang, Minimizing matrix effect by femtosecond laser ablation and ionization in elemental determination, *Anal. Chem.*, 2013, **85**, 4507–4511.
- 34 H. L. Xu, G. Méjean, W. Liu, Y. Kamali, J.-F. Daigle, A. Azarm, P. T. Simard, P. Mathieu, G. Roy, J.-R. Simard and S. L. Chin, Remote detection of similar biological materials using femtosecond filament-induced breakdown spectroscopy, *Appl. Phys. B: Lasers Opt.*, 2007, 87, 151–156.
- 35 C. A. Zuhlke, J. Bruce, T. P. Anderson, D. R. Alexander and C. G. Parigger, A fundamental understanding of the dependence of the laser-induced breakdown spectroscopy (LIBS) signal strength on the complex focusing dynamics of femtosecond laser pulses on either side of the focus, *Appl. Spectrosc.*, 2014, **68**, 1021–1029.
- 36 T. Delgado, J. M. Vadillo and J. J. Laserna, Primary and recombined emitting species in laser induced plasmas of organic explosives in controlled atmospheres, *J. Anal. At. Spectrom.*, 2014, **29**, 1675–1685.
- 37 N. M. Shaikh, B. Rashid, S. Hafeez, Y. Jamil and M. A. Baig, Measurement of electron density and temperature of a laserinduced zinc plasma, *J. Phys. D: Appl. Phys.*, 2006, **39**(7), 1384–1391.
- 38 C. G. Parigger, J. O. Hornkohl, A. M. Keszler and L. Nemes, Measurement and analysis of atomic and diatomic carbon spectra from laser ablation of graphite, *Appl. Opt.*, 2003, 42, 6192–6198.
- 39 M. Dong, G. C. Y. Chan, X. Mao, J. J. Gonzalez, J. Lu and R. E. Russo, Elucidation of C and CN formation mechanisms in laser-induced plasmas through correlation analysis of carbon isotopic ratio, *Spectrochim. Acta, Part B*, 2014, **100**, 62–69.
- 40 P. Lucena, A. Doña, L. M. Tobaria and J. J. Laserna, New challenges and insights in the detection and spectral identification of organic explosives by laser induced breakdown spectroscopy, *Spectrochim. Acta, Part B*, 2011, **66**, 12–20.
- 41 S. Rai and A. K. Rai, Characterization of organic materials by LIBS for exploration of correlation between molecular and elemental LIBS signals, *AIP Adv.*, 2011, **1**, 042103–042111.
- 42 M. Dong, X. Mao, J. J. Gonzalez, J. Lu and R. E. Russo, Timeresolved LIBS of atomic and molecular carbon from coal in air, argon and helium, *J. Anal. At. Spectrom.*, 2012, 27, 2066–2075.
- 43 V. I. Babushok, F. C. DeLucia Jr, P. J. Dagdigian, J. L. Gottfried, C. A. Munson, M. J. Nusca and A. W. Miziolek, Kinetic modeling study of the laserinduced plasma plume of cyclotrimethylenetrinitramine (RDX), *Spectrochim. Acta, Part B*, 2007, **62**, 1321–1328.
- 44 P. J. Dagdigian, A. Khachatrian and V. I. Babushok, Kinetic model of C/H/N/O emissions in laser-induced breakdown

spectroscopy of organic compounds, *Appl. Opt.*, 2010, 49, C58–C66.

- 45 J. Hermann and C. Dutouquet, Local thermal equilibrium plasma modeling for analyses of gas-phase reactions during reactive-laser ablation, *J. Appl. Phys.*, 2002, **91**, 10188–10193.
- 46 C. Vivien, J. Hermann, A. Perrone, C. Boulmer-Leborgne and A. Luches, A study of molecule formation during laser ablation of graphite in low-pressure nitrogen, *J. Phys. D: Appl. Phys.*, 1998, **31**(10), 1263–1272.
- 47 L. Larina, and L. Lopyrev, *Nitroazoles: Synthesis, Structure and Applications*, Springer, New York, 2009.
- 48 N. R. Epuru, S. Sunku, M. K. Gundawar and V. R. Soma, Femtosecond Time Resolved Laser Induced Breakdown Spectroscopy Studies of Nitroimidazoles, 12th International Conference on Fiber Optics and Photonics, OSA Technical Digest (Online), Optical Society of America, 2014, paper S5A.30.
- 49 S. Sreedhar, M. K. Gundawar and S. Venugopal Rao, Laser Induced Breakdown Spectroscopy for Classification of High Energy Materials using Elemental Intensity Ratios, *Def. Sci. J.*, 2014, **64**, 332–338.
- 50 A. K. Myakalwar, S. Sreedhar, I. Barman, N. C. Dingari, S. Venugopal Rao and P. Prem Kiran, Surya. P. Tewari, G. Manoj Kumar, Laser-induced breakdown spectroscopybased investigation and classification of pharmaceutical tablets using multivariate chemometric analysis, *Talanta*, 2011, 87, 53–59.
- 51 J. Serrano, J. Moros and J. J. Laserna, Exploring the formation routes of diatomic hydrogenated radicals using femtosecond laser-inducedbreakdown spectroscopy of deuterated molecular solids, *J. Anal. At. Spectrom.*, 2015, 30, 2343–2352.
- 52 T. Ahmido, A. Ting and P. Misra, Femtosecond laser-induced breakdown spectroscopy of surface nitrate chemicals, *Appl. Opt.*, 2013, **52**, 3048–3057.
- 53 T. Delgado, J. M. Vadillo and J. J. Laserna, Laser-induced plasma spectroscopy of organic compounds. Understanding fragmentation processes using ion-photon coincidence measurements, *J. Anal. At. Spectrom.*, 2013, **28**, 1377–1384.
- 54 S. S. Harilal, C. I. Riju, C. V. Bindhu, V. P. N. Nampoori and C. P. G. Vallabhan, Optical emission studies of C species in laser-produced plasma from carbon, *J. Phys. D: Appl. Phys.*, 1997, **30**, 1703–1709.
- 55 L. St-Onge, R. Sing, S. Béchard and M. Sabsabi, Carbon emissions following 1:064 μm laser ablation of graphite and organic samples in ambient air, *Appl. Phys. A: Mater. Sci. Process.*, 1999, **69**, S913–S916.
- 56 A. Portnov, S. Rosenwaks and I. Bar, Identification of organic compounds in ambient air *via* characteristic emission following laser ablation, *J. Lumin.*, 2003, **102–103**, 408–413.
- 57 X. Su, X. Cheng, C. Meng and X. Yuan, Quantum chemical study on nitroimidazole, polynitroimidazole and their methyl derivatives, *J. Hazard. Mater.*, 2009, **161**, 551–558.
- 58 F. C. De Lucia and J. L. Gottfried, Characterization of a Series of Nitrogen-Rich Molecules using Laser Induced Breakdown

Spectroscopy, Propellants, Explos., Pyrotech., 2010, 35, 268–277.

- 59 W. C. Lothrop and G. R. Handrick, The relationship between performance and constitution of pure organic explosive compounds, *Chem. Rev.*, 1949, **44**, 419–445.
- 60 J. A. Aguilera and C. Aragón, A comparison of the temperatures and electron densities of laser-produced

plasmas obtained in air, argon, and helium at atmospheric pressure, *Appl. Phys. A: Mater. Sci. Process.*, 1999, **69**, S475–S478.

61 T. A. Labutin, V. N. Lednev, A. A. Ilyin and A. M. Popov, Femtosecond laser induced breakdown spectroscopy, *J. Anal. At. Spectrom.*, 2016, **31**, 90–118.