Femtosecond Laser-Induced Breakdown Spectroscopy Studies of Nitropyrazoles: The Effect of Varying Nitro Groups

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The technique of femtosecond laser-induced breakdown spectroscopy (FLIBS) was employed to investigate seven explosive molecules of nitropyrazole in three different atmospheres: ambient air, nitrogen, and argon. The FLIBS data illustrated the presence of molecular emissions of cyanide (CN) violet bands, diatomic carbon (C2) Swan bands, and atomic emission lines of C, H, O, and N. To understand the plasma dynamics, the decay times of molecular and atomic emissions were determined from time-resolved spectral data obtained in three atmospheres: air, argon, and nitrogen. The CN decay time was observed to be longest in air, compared to nitrogen and argon atmospheres, for the molecules pyrazole (PY) and 4-nitropyrazole (4-NPY). In the case of C₂ emission, the decay time was observed to be the longest in argon, compared to the air and nitrogen environments, for the molecules PY, 4-NPY, and 1methyl-3,4,5-trinitropyrazole. The intensities of the CN, C₂, C, H, O, and N emission lines and various molecular/atomic intensity ratios such as CN/C₂, CN^{sum}/C₂^{sum}, CN/C, CN^{sum}/C, C₂/C, C₂^{sum}/C, $(C_2 + C)/CN$, $(C_2^{sum} + C)/CN^{sum}$, O/H, O/N, and N/H were also deduced from the LIBS spectra obtained in argon atmosphere. A correlation between the observed decay times and molecular emission intensities with respect to the number of nitro groups, the atmospheric nitrogen content, and the oxygen balance of the molecules was investigated. The relationship among the LIBS signal intensity, the molecular/atomic intensity ratios, and the oxygen balance of these organic explosives was also explored.

Index Headings: Femtosecond laser-induced breakdown spectroscopy; FLIBS; Nitropyrazoles; Temporal dynamics; Nitro groups; Intensity ratios.

INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS), an emerging tool for multi-elemental analysis, has specific advantages compared to other techniques such as inductively coupled plasma mass spectrometry, atomic absorption spectroscopy, and atomic emission spectroscopy, mainly due to its capability for standoff detection.^{1–6} It is a versatile and popular technique for detecting traces in any form of solids, liquids and gases.^{4–7} Laser-induced breakdown spectroscopy is an advantageous technique compared to other types of elemental analysis because of its fast response, high sensitivity, and real-time detection.⁴ This technique has been successfully employed for the discrimination and identification of biological materials,^{8,9} plastics,¹⁰ phar-

environmental decontamination, demining, and other applications relevant to homeland security is an active area of research, and in this regard, the LIBS technique has been proven to be effective. It has been regularly tested for deployment in the field of explosives detection. The standoff detection capability of the technique for explosives has been accomplished up to 200 m.¹⁴ However, there are a number of challenges to be addressed and remedied before this technique can be implemented for the practical detection of explosives.^{4,20-22} The plasma is formed as a result of focused laser pulses on the sample target and emits radiation (light). The light emanating from the plasma consists of molecular and atomic elemental signatures present in the sample and is usually resolved through a spectrometer with a gating capability. Several atomic and molecular emissions transpire in different time scales of the plasma evolution. A thorough understanding of the progression dynamics of atomic and molecular species in the plasma will provide better opportunities to further explore and enhance the capabilities of this technique. There have been a large number of LIBS studies using nanosecond laser pulses as an excitation source. However, there are few reports on LIBS studies using femtosecond pulses in general, and for highenergy materials (HEMs) in particular.²³⁻²⁹ Femtosecond LIBS (FLIBS) offers the advantages of, among others, a low breakdown threshold, minimal atmospheric interference, and the possibility of delivering pulses very long distances through filamentation.^{10,30} Zhang et al.³¹ studied ablation and ionization for elemental determination and successfully demonstrated that the matrix effects are significantly reduced (by 50%) when using femtosecond pulses compared to nanosecond pulses. De Lucia and Gottfried²⁵ studied a series of organic polymers and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) using the FLIBS technique under the influence of argon. A correlation between the molecular structure and plasma emission was established by means of the percentages of atomic species, such as C, H, N, and O, and the bond types (C-C, C=C, C-N, and C \equiv N) in combination with the atomicmolecular emission intensities and decay times. Timeresolved emission spectra were collected to estimate the life times of both the atomic and molecular species, and the differences in decay times observed were accredited to the alterations in the molecular structure of the organic polymers-RDX and chemical reactions occurring in the plasma. These differences, they strongly argued, could

maceuticals,^{11,12} bacteria,^{13,14} and explosives.^{15–21} The

detection of explosive residues for security screening,

Received 12 November 2014; accepted 14 May 2015.

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potentially be exploited in the improvement of the discrimination of explosive residues using FLIBS data.²⁵ Therefore, we strongly feel that a complete understanding of time-resolved molecular emissions in LIBS data is crucial, although challenging, for several applications and for explosives detection in particular.²⁵

The LIBS spectra typically comprise several atomic peaks of C, H, N, and O and some molecular peaks, such as cyanide (CN), diatomic carbon (C_2) , methine (CH), and hydroxyl (OH). Several researchers have pointed out that CN and C₂ emissions are an effective signature that can help to predict the compound. In addition, most organic explosives contain C, H, O, and N in their composition. Therefore, it is of great interest to researchers to detect and understand the formation of the molecular species CN and C₂ and the atomic fragments C, H, O, and N, and these studies have become been prevalent over the last decade.³²⁻³⁷ St-Onge et al.³⁸ demonstrated that C₂ and C are released directly from the target of the graphite and that CN is formed later on by the interaction of C₂ with atmospheric nitrogen (N₂). Nishimura et al.³⁹ established that large C molecular formation is initiated with the ion collision, followed by the formation of C₂. The formation of CN molecular species also results from reactions between native C atoms and nitrogen present in ambient air.40 The surrounding atmosphere, therefore, plays a major role during plasma evolution. In the absence of an atmosphere (e.g., in a vacuum or in the presence of an inert gas such as argon), the molecular formation is purely from native radicals and recombination with sample constituents present in the plasma.

The origin and routes of molecule production are not yet completely understood in view of the complex nature of laser-induced plasma chemistry. From the detailed studies performed by Lucena et al.,²¹ three main routes can be envisaged: (i) the reaction of C in the plume with the surrounding air, (ii) the direct vaporization of CN radicals from the sample, and (iii) the recombination of C and N atoms from the compound in the plasma. Furthermore, Lucena et al.²¹ established that the fragmentation seemed to be the dominant pathway for the production of C_2 in aromatic compounds and in molecules containing C=C double bonds. Harilal et al.41 studied the time- and space-resolved spectroscopic analysis of C₂ species in the laser-induced plasma produced from a highly pure graphite target using 1.06 µm nanosecond radiation. At low laser fluences, C₂ intensity exhibited only single-peak structure, while beyond a threshold laser fluence, a twin-peak distribution over time was observed. They argued that the faster velocity component at higher laser fluences occurred due to species generated from recombination processes while the delayed peak occurred due to the dissociation of higher C clusters, resulting in C₂ molecular formation. Dong et al.⁴² studied several solid materials containing C and N; they determined whether the molecular species are directly vaporized from sample or generated through the dissociation or the interaction between the plasma and air molecules. Their studies asserted that the inert gas can enhance the emission intensities that are directly vaporized from the sample, such as C and emission of the molecular species C2.

The molecular emission of CN in graphite when ablated in low-pressure nitrogen gas or in ambient air was studied by Vivien et al.43 They proposed that C₂ is emitted from the target surface or formed in its vicinity, while CN forms in the periphery of the C₂ vapor plume, principally through the reaction $C_2 + N_2 \rightarrow 2CN$. Zelinger et al.⁴⁴ and Fuge et al.⁴⁵ monitored the CN and C_2 molecules using spatial and time-resolved spectroscopy of a graphite target in a nitrogen atmosphere. Babushok et al.46 studied RDX using the LIBS technique and analyzed the reaction processes in the RDX plasma through kinetic modeling. They observed that the main generation reactions of the excited states were electronimpact processes. It was also noticed that the evolution of C_2 in the RDX plasma plume demonstrated doublepeak behavior. They expressed the possibility of identifying explosives using the unique ratios of atomic intensities. Ma and Dagdigian⁴⁷ discussed a few possible reactions involved in the formation of the C2 and CN molecular bands and also proposed that other chemical reactions contribute to formation of CN. They also concluded that the reaction of C with atmospheric nitrogen accounted for the increasing CN concentration at longer gate delays while the reaction of C with carbon monoxide (CO) or CN was responsible for the increasing C₂ concentration. Portnov et al.^{48,49} used the C₂/CN and O/N intensity ratios and analyzed several organic compounds, aromatic nitro compounds, and polycyclic aromatic hydrocarbons in ambient air. Park et al.⁵⁰ reported on time-resolved optical emission studies and the temporal properties of laser ablation of graphite in He, nitrogen, and argon background gases. Baudelet et al.⁵¹ performed detailed time-resolved ultraviolet (UV) LIBS studies to understand the mechanisms for the detection and identification of native atomic or molecular species from organic samples. Dagdigian et al.52 proposed a kinetic model to describe the formation of molecular emissions and predicted the relative intensities of the atomic C, H, N, and O emission lines in the spectra.

Nitropyrazoles have been used as biologically active compounds, including antibiotics or their analogs, agrochemicals, dyestuffs, phosphors, nonlinear optical materials, and, recently, energetic materials.53 Pyrazoles have been studied as the models of the aromatic systems. In the present study, we performed FLIBS studies of seven different pyrazole samples that differ in the number of nitro groups in their structure. These nitropyrazole compounds were synthesized in house. Our aim was to investigate the differences in molecular and atomic spectral emissions of nitropyrazole compounds with increasing numbers of nitro groups in their structure. We observed that the LIBS spectrum was affected by two important factors-the characteristics of the sample structure and the surrounding environment. Using simple ratiometric methods (in which the atomic or molecular peak-intensity ratios were used), we analyzed the LIBS data for the possible discrimination of these molecules. For the ratiometric analysis, the data were recorded in air and argon atmospheres to evaluate the contribution of the atmosphere to the spectrum. The intensities of molecular CN (where the label CN refers to the most intense peak at 388.32 nm and CN^{sum} refers to

sum of all the 12 peaks) and C2 (where the label C2 refers to the most intense peak at 516.52 and C₂^{sum} refers to the sum of all nine peaks) and the atomic emission lines of C, H, O, and N were considered for ratios. The various molecular and atomic intensity ratios, such as CN/C₂, CN^{sum}/C_2^{sum} , CN/C, CN^{sum}/C , C_2/C , C_2^{sum}/C , $(C_2+C)/CN$, $(C_2^{sum}+C)/CN^{sum}$, O/H, O/N, and N/H, were calculated in argon atmosphere and ambient air. The formation of molecular species (especially CN and C₂) has been observed to be affected by the surrounding atmosphere. Therefore, we recorded the LIB spectra of all the samples in argon atmosphere to avoid the contribution from atmospheric interaction. In the present study, the time-resolved spectroscopic investigation of the plasma induced by femtosecond laser pulses has also been carried out to understand the nanosecond dynamics of various molecular species.

EXPERIMENTAL SETUP

The use of ultrafast lasers with pulse lengths in the tens of femtoseconds has, until recently, been limited to laboratory experiments.⁵⁴ The introduction of self-mode locking in Ti : sapphire-based lasers in 1991 brought simplicity of use and the commercialization of ultrashort laser-pulse technology so that 10 fs laser pulses can be routinely used in laser applications.55 Furthermore, the use of femtosecond pulses in combustion diagnostics has been successfully demonstrated very recently by two research groups.56,57 Complete details of the experiments using femtosecond pulses were reported in our previous studies.^{24,29,58} Studies using FLIBS have been performed using a Ti: sapphire laser-based system. The pulse duration was \sim 40 fs (measured at the sample), with a maximum energy of \sim 2.5 mJ (1 kHz, 800 nm). In all the FLIBS experiments, the input laser pulses had a bandwidth of ~ 26 nm (full width halfmaximum, or FWHM). The femtosecond laser pulses were focused on the target sample with an 80 mm planoconvex lens. The estimated beam diameter at focus was 12 \pm 3 μ m, corresponding to a peak irradiance of \sim 2.5 TW/cm². The typical pulse energy used in our experiments was ~ 1 mJ. The FLIBS spectra were recorded in air, argon, and nitrogen atmospheres. An optical fiber was coupled to the spectrometer (Andor Technologies, Mechelle 5000). The spectrally resolved lines were detected using an intensified charged coupled device (ICCD) camera (Andor I star, DH 734). The ICCD camera was operated in the gated mode. The spectral resolution measured at 577 nm (FWHM) was \sim 0.11 nm using a 10 μ m slit. The spectral resolving power of the spectrometer, *R*, was \sim 5000. The gate delay and gate width were adjusted so that the LIBS spectra were obtained using different gate widths and gate delays. The samples were translated manually in the XY directions. In the present case, we performed the movement of the sample manually since the sample quantity available was small and we could not make large pellets (only a maximum diameter of \sim 12 mm was possible); our translation stages had limitations (in speed); 1 kHz pulses were incident on the samples; and when we tried translating using a motorized stage, we observed that the pellets were not strong enough to withstand the laser pulses and particles were ejected from the surface, forming a smoky region around the sample. Two separate sets of data were collected for one particular sample, and we observed that the data and analysis were consistent, implying that the manual sample movement was reliable. A collection lens system unit was placed to collect the light originating from the plasma; the light passed through a fiber optic cable and then was transferred to the gated ICCD spectrometer. The samples were prepared as 2–3 mm thick pellets. To prepare the pellets, we ground the sample powder in an agate motor and pelletized the resulting powder using a hydraulic press under a base weight of 4–6 metric tonnes.

Seven nitro group compounds, which differed in the number of nitro groups and possessed different numbers of C-C and C-N bonds, were used in the present study: pyrazole (PY, $C_3H_4N_2$), 1-nitropyrazole (1-NPY, C₃H₃N₃O₂), 3-nitropyrazole (3-NPY,C₃H₃N₃O₂), 4-nitropyrazole (4-NPY, C₃H₃N₃O₂), 1,3-dinitropyrazole (1,3-DNPY, $C_3H_3N_3O_2$), 3,4-dinitropyrazole (3,4-DNPY, $C_3H_2N_4O_4$), and 1-methyl-3,4,5-trinitropyrazole (1-M-3,4,5-TNPY, C₄H₃N₅O₆). Pyrazole has no nitro groups and has two C–C bonds and two C–N bonds. The next three (1-NPY, 3-NPY, and 4-NPY) have one nitro group, two C-C bonds, and three C-N bonds. In the case of the dinitropyrazoles (1,3-DNPY and 3,4-DNPY), there are two nitro groups and two C-C bonds; for 1,3-DNPY, there are three C-N bonds and for 3,4-DNPY, there are four. Finally, 1-M-3,4,5-TNPY has largest number of nitro groups (three) of all the pyrazoles, with six C-N bonds and two C-C bonds. The pyrazoles were nitrated with nitric acid-sulfuric acid, nitric acid-acetic anhydride, and nitric acid-trifluoroacetic anhydride. The presence of a nitro group in the pyrazole ring considerably enlarges the possibility of the functionalization of the various types of pyrazole derivatives. The methods for synthesizing nitropyrazoles are diverse and depend on, among other things, the nature of substituent groups in the pyrazole ring, the electron density distribution in it, the nitration mixtures, and the nitration conditions. We synthesized these compounds so we would be able to predict the heat of explosion, density, detonation performance, stability, and sensitivity. The molecular formulae and the chemical structure of these samples are summarized in Table I.

RESULTS AND DISCUSSION

Spectral Features Obtained Using Pyrazole Samples. Figure 1 shows a typical spectrum of the sample PY recorded in argon and ambient air. We observed several atomic (C, H, N, and O) and molecular (CN and C_2) spectral signatures in the spectral range 200-900 nm. For the molecular signatures, CN violet bands were observed corresponding to $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transitions at 357–360, 384–389, and 414–423 nm with $\Delta\upsilon$ values of –1, 0, and +1, respectively; C_2 Swan bands corresponding to $D^3\Pi_a \rightarrow a^3\Pi_u$ transitions at 460–475, 510–520, and 550– 565 nm with $\Delta v = -1$, 0, and +1, respectively, were also observed. The spectral range covering both the CN and C₂ peaks is illustrated clearly in Fig. 2. The complete assignment of each molecular peak and the corresponding vibrational transitions are listed in Table II. For a detailed ratiometric analysis, 25 individual spectra were

Sample name	Chemical formula	Structure	Number of nitro groups	Number of C-C bonds	Number of C-N bonds
Pyrazole	$C_3H_4N_2$	N	0	2	2
1-Nitropyrazole	$C_3H_3N_3O_2$		1	2	2
3-Nitropyrazole	$C_3H_3N_3O_2$	NO ₂	1	2	3
4-Nitropyrazole	$C_3H_3N_3O_2$		1	2	3
1,3-Dinitropyrazole	$C_3H_2N_4O_4$		2	2	3
3,4-Dinitropyrazole	$C_3H_2N_4O_4$	NO2 NO2 NO2	2	2	4
1-Methyl-3,4,5- trinitropyrazole	c₄H₃N₅O ₆	O_2N NO2	3	2	6
		O ₂ N N CH ₃			

recorded for each sample in argon atmosphere and four spectra were recorded in air. All the spectra were obtained using a gate width of 800 ns and a gate delay of 100 ns. It is evident from the data presented in Fig. 1 that the peak intensity corresponding to the CN band at 388.32 nm is stronger than the C_2 peak intensity at 516.52 nm recorded in air, whereas the C_2 molecular peak intensity was more prominent than the CN peak in the spectra recorded in argon. Furthermore, the C peak (247.88 nm) intensity was stronger in the argon atmosphere than in the air atmosphere. The H peak (656.28 nm) intensity was stronger in argon atmosphere. The data clearly emphasize the role of the surrounding environment in the formation of atomic and molecular species such as C, CN, and C_2 .

Figure 3 presents the FLIBS spectra of the seven pyrazole samples recorded in an argon atmosphere under similar experimental conditions. Several argon peaks were observed at 738.57, 763.67, 772.52, 794.95, 811.67, 826.61, 842.56, and 852.19 nm. The variations in molecular and atomic peak intensities for the different pyrazole samples are evident from the data presented.



 $F_{IG.}$ 1. The FLIB spectra of PY recorded in argon and air atmospheres. A gate width of 800 ns and a gate delay 100 ns were used to record the spectra.

The C₂ peak intensity at $\Delta \upsilon = 0$ decreased from PY to 1-M-3,4,5-TNPY, and a similar behavior was observed for the $\Delta \upsilon = -1$ and $\Delta \upsilon = +1$ transitions. The H and O intensities were observed to be weak in all spectra. The data presented in Fig. 4 shows the intensities of the different atomic and molecular species, in the form of bar charts, deduced from averaging 25 independent spectra for each sample collected in an argon atmosphere. Here, CN^{sum} represents the sum of 12 peak intensities at 388.33, 387.12, 386.12, 385.46, 385.01, 421.58, 419.66, 418.63, 416.75, 359.03, 358.61, and 358.28 nm, and C₂^{sum} represents the sum of 9 peak intensities at 516.52, 512.88,



Fig. 2. (a) Detailed spectrum of the resolved CN violet-band emission for $\Delta \upsilon = -1$, 0, +1 and C at 247.88 nm recorded for the PY molecule in air. (b) Spectra of the C₂ Swan band emission for $\Delta \upsilon = -1$, 0, +1 and C at 247.88 nm in air.

TABLE II. Summary of molecular CN and C₂ bands of different wavelengths with transitions at $\Delta v = 0$, $\Delta v = -1$, and $\Delta v = +1$.

Molecular species	System	Electronic transition	Vibrational transition	Wavelength (nm)
CN	Violet	$B^2\Sigma^+ \to X^2\Sigma^+$	(0-0)	388.33
		$\Delta \upsilon = 0$	(1-1)	387.12
			(2-2)	386.12
			(3-3)	385.46
			(4-4)	385.01
		$\Delta \upsilon = -1$	(1-0)	359.03
			(2-1)	358.61
			(3-2)	358.28
		$\Delta \upsilon = +1$	(0-1)	421.58
			(1-2)	419.66
			(2-3)	418.63
			(3-4)	416.75
C ₂	Swan	${\sf d}^3\Pi_{\sf g} ightarrow {\sf a}^3\Pi_{\sf u}$	(0-0)	516.52
		$\Delta \upsilon = 0$	(1-1)	512.88
		$\Delta \upsilon = -1$	(0-1)	563.48
			(1-2)	558.51
			(2-3)	554.01
		$\Delta \upsilon = +1$	(1-0)	473.66
			(2-1)	471.47
			(3-2)	469.70
			(4-3)	468.48

563.48, 558.51, 554.01, 473.66, 471.47, 469.70, and 468.48 nm. The variation in spectral intensities was clearly observed in the experimental data. Some of the important features in these data can be summarized as:

- (i) The C₂^{sum} intensity decreased as the number of nitro groups increased from PY to 1-M-3,4,5-TNPY. The C and N peak intensities increased from PY to 1-M-3,4,5-TNPY. The CN^{sum} intensity decreased steadily from 1-NPY to 1-M-3,4,5-TNPY.
- (ii) The CN intensity (at 388.32 nm) was observed to increase from PY to 1-NPY, it was constant for the isomers (1-NPY, 3-NPY, and 4-NPY), and it had a decreasing trend for DNPY and TNPY. The C₂ band



FIG. 3. The FLIB spectra of (*a*) PY, (*b*) 1-NPY, (*c*) 3-NPY, (*d*) 4-NPY, (*e*) 1,3-DNPY, (*f*) 3,4-DNPY, and (*g*) 1-M-3,4,5-TNPY recorded using a gate width of 800 ns and a gate delay of 100 ns. For each sample, 25 spectra were recorded in an argon atmosphere for ratiometric analysis.



Fig. 4. Intensities of molecular and atomic emissions of pyrazoles with different numbers of nitro groups, recorded in an argon atmosphere. In each case, 25 spectra were considered and an average value of intensity was calculated. The label C₂ refers to the peak at 516.52 nm only, whereas C_2^{sum} refers to the sum of all nine C_2 peaks. The label CN refers to the peak at 388.32 nm only, whereas CN^{sum} refers to the sum of all 12 CN peaks.

intensity at 516.52 nm decreased as the number of nitro groups increased.

- (iii) The H peak (at 656.28 nm) intensity was nearly equal for PY, 1-NPY, 3-NPY, and 4-NPY, and it increased from the two dinitropyrazoles to 1-M-3,4,5-TNPY. The O-peak intensity (at 777.42 nm) increased from PY to 4-NPY, but no trend was observed beyond that.
- (iv) The intensity ratios (of the atomic and molecular species) were analyzed with respect to the C–C and C–N bonds. All the samples contain same number of C–C bonds but differ in number of C–N bonds. With an increasing number of C–N bonds and constant number of C–C bonds, the C2^{sum} intensity was observed to decrease. Surprisingly, with increasing number of C–N bonds, the CN^{sum} intensity also decreased. This clearly suggests that formation of C2 and CN have dominant contributions other than from the native bonds (C–C and C–N). In each of these molecules, there is one C=N and the rest are C–N bonds.
- (v) The samples 1-NPY, 3-NPY, and 4-NPY contain same number of nitro groups, but 1-NPY contains fewer C-N bonds (two) than the other isomers (which have three bonds). The C2^{sum} intensity decreased from 1-NPY to 3-NPY. These three are structural isomers possessing the same molecular formula but having different physical and chemical properties. Similarly, 1,3-DNPY and 3,4-DNPY possess same number of nitro groups but differ in the number of C-N bonds. However, we noticed a decreasing trend in the C2^{sum} and CN^{sum} intensities from 1,3-DNPY to 3,4-DNPY.
- (vi) The C_2^{sum} intensity was stronger in the PY spectra compared to CN^{sum} , whereas in other samples the CN^{sum} intensity than the C_2^{sum} intensity. The reason for this could be that in PY sample there is no nitro

group and a lower number of C–N bonds than in the other samples.

(vii) The C, N, and O peaks also demonstrated an increment behavior with varying the number of nitro groups and C-N bonds. The increment in O and N intensity from PY to 1-M-3,4,5-TNPY could be due to the higher number of N and O atoms present in their composition. Our data clearly suggest that the molecular structure affected the formation of atomic and molecular radicals in the LIBS plasma. Relative efficiency correction (REC) was not performed for the data we used for ratiometric analysis. Probably, this could have resulted in a larger scattering in the data presented. The REC correction was erratic in our case for wavelengths < 260 nm. In that spectral region, the noise was higher than the signal, and we could not achieve an accurate correction factor. In the present study, our interest was not in investigating any parameter guantitatively but only in investigating the qualitative behavior of the ratios. A greater accuracy and superior signal-to-noise ratio could possibly be achieved from the analysis of REC-performed LIBS data.

Lazic et al.¹⁹ investigated the effect of matrix effect on the LIBS data obtained from heterogeneously dispersed organic residues (pure explosives and interferents) on clean AI substrates. They recorded the variations in the magnitudes of atomic (C, H, N, and O) and molecular (C₂ and CN) species. Delgado et al.³⁴ examined the primary and recombined emitting species in the LIBS plasmas of organic explosives in controlled atmospheres. They performed in-depth studies on the effects of the surrounding gas type and pressure on the spectra of 2,4,6-trinitrotoluene (TNT) and pentaerythritol tetranitrate (PETN). They proposed probable fragmentation pathways for the compounds to account for the prevailing reactions. They have identified many non-emitting reactive species present in the plasma. Lucena et al.²¹ studied three nitro toluene compounds (mono-, di-, and tri-) using nanosecond LIBS and observed that the C2 emission decreased with an increased number of nitro groups. In their case, the CN emission also decreased with an increasing number of nitro groups. Further, their studies clearly suggested that the C signature has a poor diagnostic value for discrimination purposes and that, rather interestingly, H emissions followed the molecular structure of the compounds investigated. Figure 5 depicts the molecular to atomic intensity ratios of $\text{CN}^{\text{sum}}/\text{C}_2{}^{\text{sum}},\ \text{CN}^{\text{sum}}/\text{C},\ \text{C}_2{}^{\text{sum}}/\text{C},\ (\text{C}_2{}^{\text{sum}}+\text{C})/\text{CN}^{\text{sum}},\ \text{O}/$ H, and O/N in argon for the seven samples. These intensity ratios (bar charts) represent an average of 25 spectra. The formation of CN is dependent on both C2 and C species and the ratios with respect to C₂ and C are presented in Fig. 5. Some of the prominent features that can be deduced from the observed data include:

- (i) The CN^{sum}/C₂^{sum} ratio increased from PY to 1,3-DNPY. The ratio was almost constant for one nitropyrazole and two nitropyrazole group (isomers), while it increased for 3,4-DNPY and 1-M-3,4,5-TNPY.
- (ii) The C₂^{sum}/C ratio decreased from PY to 1-M-3,4,5-TNPY, with a small exception at 3-NPY. CN^{sum}/C ratio increased from PY to 1-NPY but it demonstrated a



Fig. 5. Molecular-to-atomic intensity ratios of CN^{sum}/C_2^{sum} , CN^{sum}/C , C_2^{sum}/C , $(C_2^{sum}+C)/CN^{sum}$, O/H, and O/N in an argon atmosphere. The value CN^{sum} is the sum of the intensities at 12 wavelengths (388.33, 387.12, 386.12, 385.46, 385.01, 421.58, 419.66, 418.63, 416.75, 359.03, 358.61, and 358.28 nm), and the value C_2^{sum} is the sum of the intensities of nine wavelengths (516.52, 512.88, 563.48, 558.51, 554.01, 473.66, 471.47, 469.70, and 468.48 nm). In calculating the ratios, 25 independent measurements were considered.

decreasing trend from 1-NPY to 1-M-3,4,5-TNPY. The $(C_2^{sum} + C)/CN^{sum}$ ratio also decreased from PY to 1-M-3,4,5-TNPY. The atomic intensity ratios of O/H and O/N depicted an overall increasing trend from PY to 1-M-3,4,5-TNPY; the ratios were constant for onenitro-group pyrazoles. The O/H ratio of 3,4-DNPY was highest of all. The O/H and O/N ratios increased moderately from PY to 1-M-3,4,5-TNPY. The O/N intensity ratio was nearly equal for one-nitro-group pyrazoles, and this intensity ratio was larger for the two- and three-nitro-group pyrazoles containing the additional oxygen atoms. The C/H ratio was in good agreement (data not presented) with the compound molecular formula. The O/H ratio was nearly equal for 1-NPY and 3-NPY, but it was lower for PY and higher for 3.4-DNPY and 1-M-3.4.5-TNPY: this behavior is related to the molecular formula.

Our recent work⁵⁸ indubitably demonstrated the case study of surrounding atmosphere influencing the formation of molecular bands in LIBS plasma for three organic explosives (RDX, TNT, and octogen (HMX, $C_4H_8N_8O_8$)). Lucena et al.²¹ demonstrated the use of the CN/C₂ ratio for molecular identification, and the CN/C₂ ratio increased with the number of nitro groups for aromatic nitro compounds. Portnov et al.^{48,49} studied the intensity ratios of C/CN and O/N and correlated them to the molecular structure, suggested the possibility of distinguishing one chemical class from another, and in optimum cases even identifying specific compounds by the use of LIBS data. As mentioned earlier, there are three main routes for the formation of CN and C₂ molecules. Since the experiments were carried out in argon atmosphere, the interaction of the surrounding nitrogen with the plasma can be completely eliminated. The remaining possibilities are native radical breakdown and chemical reactions in the plasma. The femtosecond pulses contain high peak intensity, the probability of molecular dissociation into atomic-molecular radicals is high during breakdown. Our observations of the CN/C2 ratio increasing with number of nitro groups (with exception of 1-M-3,4,5-TNP) are consistent with the observation of Lucena et al.²¹ in which they observed a similar trend in their LIBS data obtained in air and helium atmospheres. Our FLIBS data supports their argument that CN/C2 ratios could potentially be used for molecular identification. To determine the intensity ratios of the atomic emission lines, C at 247.88 nm, H at 656.40 nm, O at 777.42 nm, and N at 868.23 nm were considered. In all the data presented in Figs. 4 and 5, the bars represent the mean and the error bars represent the standard deviation of the 25 independent measurements. Table III summarizes the calculated intensity ratios. Here, CN refers to the strongest intensity at 388.33 nm, whereas CN^{sum} refers to sum of the 12 peak intensities; C₂ refers to the strongest peak at 516.52 nm, whereas C_2^{sum} refers to the sum of the nine peak intensities, as explained earlier.

Oxygen Balance. The molecular formula of an explosive is often related to the heat of explosion (Q or $\Delta_{\rm f}H$), detonation velocity (D), detonation pressure (P), thermal stability and impact or shock sensitivity ($h_{50\%}$). The oxygen balance (OB) is the percentage of oxygen liberated as a result of the complete conversion of the explosive molecule (general formula, $C_aH_bN_cO_d$) to CO, carbon dioxide, water, and other products. In other

TABLE III. Summary of molecular to atomic intensity ratios and atomic emission intensity ratios of the seven nitropyrazoles investigated.^a

Ratio	ΡY	1-NPY	3-NPY	4-NPY	1,3-DNPY	3,4-DNPY	1-M-3,4, 5-TNPY
CN/C ₂	0.63	1.41	1.42	1.36	1.58	4.85	3.88
CN/C	2.94	5.33	3.22	3.73	3.43	2.27	2.05
$(C_2 + C)/CN$	1.96	0.91	1.04	1.03	0.96	0.68	0.81
Ô/H	0.66	1.29	1.19	1.20	1.09	2.84	1.84
O/N	4.39	5.54	5.68	5.80	5.21	7.36	7.38
N/H	0.15	0.24	0.21	0.21	0.22	0.40	0.26

 $^{\rm a}$ For these ratios, the molecular bands of CN at 388.32 nm, C₂ at 516.52 nm, C at 247.88 nm, H at 656.28 nm, O at 777.42 nm, and N at 868.3 nm were considered. We used 25 spectra to compute the ratios and calculated an average value in each case.

words, the OB represents the deficiency in or excess oxygen required to produce water, CO, and carbon dioxide.⁵⁹

$$\mathsf{OB\%} = \frac{\left[d - 2a - \frac{b}{2}\right] \times 1600}{\mathsf{Mw}} \tag{1}$$

where Mw is the relative molecular weight of the explosive.

The heat of an explosion provides information about the work capacity of an explosive molecule. The OB values of PY, mononitropyrazoles, dinitropyrazoles, and trinitropyrazole are -188, -77, -30, and -26%, respectively. The molecule is said to have a +ve OB if it contains more oxygen than is required and a -ve OB if it contains less oxygen than is required. An explosive with an oxygen deficiency (-ve OB) will have incomplete combustion and will release a large amount of toxic gases such as CO. A zero oxygen balance indicates maximum energy release. An explosive with excess oxygen (+ve OB) will produce toxic nitric oxide (NO) and nitrogen dioxide (NO₂). 59

A correlation between the LIBS signal intensity of the atomic and molecular species and the OB has been explored using the FLIBS data. Figure 6a shows the CN^{sum} , CN, C_2^{sum} , C_2 , C, H, and O intensities plotted against the OB for all the nitropyrazoles studied. The intensity lines were normalized using the strongest argon atomic emission line at 811.67 nm in each spectrum for all the compounds.

- (i) The O atomic line intensity depicts an overall increasing trend with increasing OB. The O percentage increases from PY to 1-M-3,4,5-TNPY.
- (ii) The H intensity demonstrates a decreasing trend with increasing OB, probably due to the decrease in the H percentage from PY to 3,4-DNPY.
- (iii) The C intensity demonstrates an overall increasing trend with OB from 1-NPY to 1-M-3,4,5-TNPY. The C percentage changes only for 1-M-3,4,5-TNPY.
- (iv) The C_2 and C_2^{sum} intensities display a clearly decreasing trend with increasing OB from PY to 1-M-3,4,5-TNPY.
- (v) The CN^{sum} intensity, in the presence of atmospheric nitrogen, depicts a decreasing trend with increasing OB.

Figure 6b shows the molecular-to-atomic intensity ratios of CN^{sum}/C_2^{sum} and C_2^{sum}/C in argon atmosphere plotted against the OB of the molecules. The CN^{sum}/C_2^{sum} ratio increases with increasing OB, and the C_2^{sum}/C ratio decreases with increasing OB. Figure 6c shows the intensity ratios of CN^{sum}/C and $(CN^{sum} + C_2^{sum})/(C + H + O)$ plotted against OB, which demonstrate that the former ratio decreases with increasing OB. The three data points at one position in all the ratios are due to the OB values of all the one-nitro-group pyrazoles and two-



Fig. 6. (a) Intensity of CN^{sum}, CN, C_2^{sum} , C₂, C, H, and O with varying OBs. The intensities have been normalized with strongest argon peak at 811.67 nm. (b) The ratios CN^{sum}/C₂^{sum} and C₂^{sum}/C plotted against the OB. (c) The ratios CN^{sum}/C and (CN^{sum} + C₂^{sum})/(C + H + O) plotted against the OB for all the pyrazoles in this study.



FIG. 7. (a) The FLIB spectra of PY obtained using femtosecond laser excitation in air, argon, and nitrogen atmospheres. (b) The FLIB spectra of 4-NPY obtained using femtosecond laser excitation in nitrogen, argon, and air atmospheres. (c) The FLIB spectra of 1-M-3,4,5-TNPY obtained using femtosecond laser excitation in the three atmospheres. A gate width of 50 ns and a gate delay of 800 ns were used to record the spectra.

nitro-group pyrazoles being the same. Each data point represents the average of 25 spectra obtained in an argon atmosphere with a gate delay of 100 ns and a gate width of 800 ns. Our conclusions deduced from these results are consistent with those reported by Lucena et al.,²¹ who investigated five organic explosive molecules. The relationship between the intensities and OBs suggests that the energy released in the plasma can be related to the heat of the explosion and, therefore, with the work capacity of an explosive molecule.

Time-Resolved Studies of Cyanide, Diatomic Carbon, and Carbon Emissions. In the present study, timeresolved spectra were also recorded for three pyrazoles: PY, 4-NPY, and 1-M-3,4,5-TNPY in air, argon, and nitrogen atmospheres. A series of spectra with a gate delay of 90 ns, gate width of 50 ns, and step size of 50-640 ns were recorded. Figure 7a depicts the LIBS spectra of PY obtained using femtosecond excitation in the three atmospheres (argon, air, and nitrogen). Figures 7b and 7c depict the corresponding spectra of 4-NPY and 1-M-3,4,5-TNPY. From these data, we have estimated the decay times of molecular emissions of the CN and C₂ bands and of the atomic fragments of C, H, O, and N in these atmospheres. We observed that the CN molecular band intensity was strongest in the nitrogen environment compared to the air and argon atmospheres for PY, 4-NPY, and 1-M-3,4,5-TNPY. In our previous study,⁵⁸ we studied three different explosives in argon, air, and nitrogen atmospheres and also observed that the CN molecular band was more prominent in nitrogen than in the air and argon environments. In the present context, nitrogen plays a major role in the formation of the CN band. The molecular C2 Swan band intensity was more prominent in the argon atmosphere than in the nitrogen and air atmospheres. The C emission line was more intense in the argon atmosphere than in the air and nitrogen environments. The H peak intensity was stronger in air than in the argon and nitrogen atmospheres. We studied the intensities of the molecular CN, C₂, and C emissions in detail as a function of time delay in these three atmospheres.

Figure 8 presents the decay rates of CN, C_2 , and C for three samples of PY, 4-NPY, and 1-M-3,4,5-TNPY in the three atmospheres. The decay times were calculated for the strongest band of CN at 388.32 nm, of C_2 at 516.52 nm, and of C in the air, argon, and nitrogen atmospheres using exponential decay were fitted to the experimental data. The decay times were also calculated in the three atmospheres for the atomic elements H, O, and N (the data are presented in the Supplemental Material). From our data, we draw the following conclusions (the fitted decay times for CN, C_2 , and C are summarized in Table IV):

(i) In case of PY, the CN decay time is longer in air and nitrogen than in argon. In the case of 4-NPY, the decay time of CN is clearly longest in air compared to the argon and nitrogen atmospheres. In the case of 1-M-3,4,5-TNPY, the decay time of CN is longest in nitrogen compared to air and argon. This clearly indicates that the complex plasma chemistry is involved in the formation of CN molecules in such



Fig. 8. Temporal decay of the molecular bands at CN at 388.33 nm in (a) PY, (b) 4-NPY, and (c) 1-M-3,4,5-TNPY (**left column**). Temporal decay of C₂ at 516.52 nm in (d) PY, (e) 4-NPY, and (f) 1-M-3,4,5-TNPY (**center column**). Temporal decay of C at 247.88 nm in (g) PY, (h) 4-NPY, and (i) 1-M-3,4,5-TNPY (**right column**). Spectra were recorded using a gate width of 50 ns and step size of 50 ns after an initial gate delay of 100 ns.

compounds even though the atmospheric nitrogen contribution is absent.

- (ii) For PY, 4-NPY, and 1-M-3,4,5-TNPY, the C₂ decay time is longer in argon than in the nitrogen and air atmospheres.
- (iii) For PY, 4-NPY, and 1-M-3,4,5-TNPY, the C decay time is longest in the argon atmosphere compared to air and nitrogen.
- (iv) The decay times of H, O, and N are shorter than the molecular emission decay times. For PY and 4-NPY, the decay times of H, O, and N are higher in argon than in the air and nitrogen environments. In the case of 1-M-3,4,5-TNPY, the values are quite

TABLE IV. Decay times of CN, C₂, and C for PY, 4-NPY, and 1-M-3,4,5-TNPY.^a

PY CN 373 ± 13 342 ± 12 368	± 8
C_2 207 ± 15 252 ± 9 217	± 16
C 54 \pm 5 189 \pm 6 64	± 2
4-NPY CN 377 ± 6 272 ± 12 86	± 6
C_2 199 ± 15 235 ± 8 189	± 8
C 67 ± 4 174 ± 20 55	± 5
1-M-3,4,5-TNPY CN 183 \pm 9 154 \pm 15 225	± 27
C_2 34 ± 2 44 ± 9 28	± 5
C 77 \pm 10 113 \pm 14 30	± 5

 $^{\rm a}$ Note that CN represents the strongest peak at 388.32 nm whereas C_2 represents the strongest peak at 516.52 nm and C at 247.88 nm.

different from PY and 4-NPY; the decay times of N are longest in air followed by nitrogen and argon.

(v) A clear decreasing trend in the C₂ decay time can be observed with the increasing number of nitro groups for the data recorded in argon. Similarly, the data suggest a decreasing trend for the C₂ decay time in the nitrogen and air atmospheres. The C decay time depicts a decreasing trend with the increasing number of nitro groups in the argon and nitrogen atmospheres for all the molecules. A clear increasing trend in the CN decay time can be observed with the increasing number of nitro groups for the data recorded in air and argon for all the molecules.

In one of our earlier studies,⁵⁸ we characterized the molecular formation dynamics of CN and C₂ bands in the spectra of 3-nitro-1,2,4-triazol-5-one (NTO), RDX, and TNT samples in air, argon, and nitrogen atmospheres, and we concluded that the longer decay times may be a result of the lack of available nitrogen. Sovová et al.⁶⁰ reported the temporal features of HEMs investigated in air and argon using nanosecond pulses. Their study identified that the decomposition of explosive molecules leads not only to the main stoichiometric products, such as nitrogen gas, carbon dioxide, and water but also to distinctive combinations of concentrations of more complex products. Dong et al.⁶¹ measured the spatial and temporal features of C₂ and CN molecular emissions from the ablation of benzoic acid with ¹³C labeling. They

proposed that some of the C2 molecules formed directly from molecular fragments of the sample. In addition, they argued that the opposite behavior of C₂ and CN that they observed unequivocally disproves the mechanism in which CN is formed from a C₂ precursor. According to their data, the formation of CN from atomic C (or a species with a single C atom) was a more viable option. Our recent studies^{62,63} on some inorganic and organic explosives clearly suggests that by simply using the simple intensity ratios of the atomic and molecular species one-dimensional, two-dimensional, and threedimensional models can be developed that could be used effectively to classify or identify different explosive molecules. However, as recently pointed out by Fountain et al.,⁶⁴ many more challenges remain in the discrimination of energetic materials and many more methodologies need to be developed and discovered for us to arrive at a foolproof and robust technique for the identification of explosives. Serrano et al.65 performed comprehensive investigations of laser-induced plasmas in organic solids and demonstrated that the electron distribution influenced the degree of atomization (in contrast to the extent of fragmentation); the cleavage routes that were directly reflected in the signals were associated with the CN radicals and C2 fragments, respectively. They emphasized that more studies are required to evaluate in which way and to what extent the molecular emission pattern evolves with time as the system cools down and the chemistry in the LIBS plasma progresses. Serrano et al.,65 using LIBS data obtained at 532 nm, evaluated the CN/C2 ratio for 1,2-dinitrobenzene (1,2-DNB), 1,3-dinitrobenzene (1,3-DNB), and 1,4-dinitrobenzene (1,4-DNB) and found them to be 4.5, 7.6, and 6.2, respectively. Similarly, for 2,3-dinitrotoluene (2,3-DNT), 2,4-dinitrotoluene (2,4-DNT), and 2,6-dinitrotoluene (2,6-DNT), they found the ratio to be highest for 2,3-DNT; they attributed this to the lesser steric effects of the 4-NO2 group on its neighboring groups. Our future studies will encompass complete decay-time studies in air and nitrogen atmospheres; evaluations of the molecular-toatomic intensity ratios in ambient air and nitrogen atmospheres; and nanosecond LIBS studies of all the molecules, including ratiometric, decay dynamics, comparing them to the FLIBS data.

CONCLUSION

We have used femtosecond pulses to record the LIBS spectra of seven nitropyrazoles with increasing numbers of nitro groups. The CN and C2 molecular bands in the various spectral regions and the atomic emission lines of C, H, O, and N have been observed. The CN intensity is strongest in nitrogen compared to the air and argon atmospheres. The C2 and C intensities were strongest in argon compared to the nitrogen and air atmospheres. Several intensities of the CN^{sum}, C₂^{sum}, C, H, O, and N emission lines and various molecular/atomic intensity ratios, such as CN/C₂, CN^{sum}/C₂^{sum}, CN/C, CN^{sum}/C, C₂/C, C₂^{sum}/C, (C₂ + C)/CN, (C₂^{sum} + C)/CN^{sum}, O/H, O/N, and N/H, have been deduced from the LIBS spectra of the seven nitro group compounds. The relationship between the molecular bands-atomic lines intensity ratios and the OBs of these organic explosives have also been investigated, demonstrating a correlation between the intensity of the atomic and molecular species and the OB. The decay times have been measured for the molecular CN and C₂ emissions along with the atomic C emission lines. The CN decay time is longest in the air atmosphere compared to nitrogen and argon for PY and 4-NPY, and strongest in the nitrogen atmosphere for 1-M-3,4,5-TNPY. For C₂, the decay time is longest in the argon atmosphere compared to air and nitrogen for PY, 4-NPY, and 1-M-3,4,5-TNPY. A clear decreasing trend can be observed in the CN and C_2 decay times with the increasing number of nitro groups in the data recorded in all the atmospheres. Similarly, the data also indicate a decreasing trend for the C decay time with the increasing number of nitro groups in the argon atmosphere. Some of the results presented here could be used as pointers for the identification of these molecules.

ACKNOWLEDGMENTS

Financial support by Defense Research Development Organization (DRDO), India, through the Advanced Centre of Research in High Energy Materials (ACRHEM) is gratefully acknowledged. The authors acknowledge the samples provided by Dr. Pasupala Ravi, ACRHEM. Soma Venugopal Rao thanks the Board of Research in Nuclear Sciences (BRNS), India, for funding through a project (34/14/48/2014-BRNS/2084). All the authors appreciate the referees for their important suggestions.

SUPPLEMENTAL MATERIAL

All supplemental material mentioned in the text, including three figures (various decay times and molecular-to-atomic ratios) and two tables (summaries of various decay times), is available in the online version of the journal at http://www.s-a-s.org.

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