

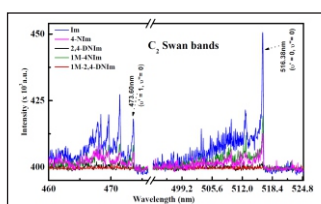
# जटिल पदार्थों का विश्लेषण

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## फेमटोसेकंड लेजर-प्रेरित ब्रेकडाउन स्पेक्ट्रमिक्की: जटिल पदार्थों का उन्नत विश्लेषण

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इमिडाजोल सीरीज के लिए वायु में अंकित  $C_2$  स्वान बैंड उत्सर्जन तीव्रता में प्रवृत्ति।

### सारांश

फेमटोसेकंड (fs) स्पंद प्रगत तत्व उष्मा प्रभावित क्षेत्र और मैट्रिक्स प्रभावों को कम करके विश्लेषण को आगे बढ़ाते हैं, जिससे सटीक संरचना निर्धारण संभव होता है। केस स्टडीज जटिल मैट्रिक्स के भीतर तत्व संरचना को मैप करने में फेमटोसेकंड लेजर-प्रेरित ब्रेकडाउन स्पेक्ट्रमिक्की ( $f_s-LIBS$ ) की प्रभावकारिता को रेखांकित करते हैं। ( $f_s-LIBS$ ) पारंपरिक तरीकों के बराबर पूर्वानुमान सटीकता के साथ, अक्रिय धातु उत्प्रेरकों की मात्रा निर्धारित करने के लिए एक अर्ध-गैर-विनाशकारी उपकरण के रूप में कार्य करता है। इसके अलावा, इसका अनुप्रयोग विस्फोटक की पहचान करना है, जो रासायनिक संरचनाओं के साथ वर्णक्रमीय उत्सर्जन के सहसंबंध के कारण होता है। यह तकनीक विश्लेषणात्मक

मुख्य शब्द : फेमटोसेकंड, ताप प्रभावित क्षेत्र, प्लाज्मा, उत्प्रेरक, उच्च ऊर्जा पदार्थ।

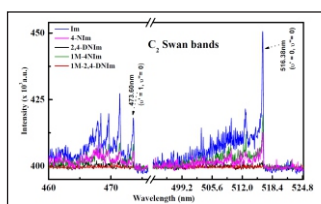
## Analysing Complex Materials

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## Femtosecond Laser-Induced Breakdown Spectroscopy: Advancing Analysis of Complex Materials

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Trend in  $C_2$  Swan band emission intensities for the imidazole series recorded in air.

### ABSTRACT

Femtosecond (fs) pulses advance elemental analysis by minimizing heat affected zone and matrix effects, enabling precise composition determination. Case studies underscore the efficacy of femtosecond laser induced breakdown spectroscopy (fs-LIBS) in mapping elemental compositions within intricate matrices. fs-LIBS serves as a quasi-nondestructive tool for quantifying noble metal catalysts, with predictive accuracy comparable to conventional methods. Furthermore, its application extends to explosive detection, leveraging spectral emissions' correlation with chemical structures. This technique holds significant implications for analytical chemistry and security applications.

KEYWORDS: Femtosecond, Heat affected zone, Plasma, Catalyst, High energy materials

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## Introduction

Over the past two decades, LIBS has become a widely used analytical technique with broad applications, spanning pharmaceuticals, environmental monitoring, cultural heritage preservation, and water quality assessment [1]. Its allure lies in its adaptability across solid, liquid, and gaseous samples, remarkable sensitivity, minimal sample preparation, and real-time analysis capability. LIBS also presents an enticing opportunity for remote analysis, opening new avenues for hazardous material detection and industrial monitoring.

Traditionally, LIBS employs nanosecond lasers, but these suffer from drawbacks such as plasma reheating and large heat-affected zones (HAZ) that extends beyond the irradiated volume due to thermal diffusion thereby limiting spatial and depth resolution. In contrast, ultrashort femtosecond pulses offer enhanced spatial and depth resolution by minimizing HAZ formation. Furthermore, fs-ablation reduces matrix effects, facilitating more precise elemental composition determination. The distinctive attributes of fs-laser ablation present valuable prospects for mapping elemental compositions in intricate matrices and characterising a variety of physical and chemical processes. The case studies discussed in this article will elucidate several of these capabilities.

## Experimental Setup

The LIBS system comprises of several components: femtosecond laser system (Amplitude Systems), a high resolution echelle spectrometer (Mechelle, ME5000, Andor), an Intensifier Charge Coupled Device (ICCD), (Andor DH734-18mm-CCI-01U) outfitted with gate/delay generator and optomechanical components. The fs-laser system comprises of Ti:Sapphire oscillator, chirped pulse regenerative amplifier, and a grating compressor. This system operates at a repetition rate of 1 kHz, delivering 3 mJ per pulse at a central wavelength of 800 nm with a pulse duration of 50 fs, and pulse-to-pulse energy fluctuation of <5%.

The fs-LIBS experiments were carried out by focusing 1 mJ of energy onto the sample surface using a BK7 plano-convex lens ( $f = 10$  cm). Samples were securely mounted on a motorized Y-Z translational stage, seamlessly integrated with LabVIEW for automated sample translation during data acquisition. Plasma emission was collected using a collimator, fiber-coupled to a cross-dispersion Echelle spectrograph,

which covers the spectral range of 230–830 nm in a single scan with 0.1 nm wavelength resolution. This, in conjunction with a thermoelectric cooled intensified charge-coupled device (ICCD), is used for the acquisition of spectra. The ICCD is gated in synchronization with the fs laser pulse to get the maximum S/N ratio. The gate delay, gate width, and the detection system are controlled through a digital delay generator.

## Case study I - Quantitative Analysis of Noble Metal Catalysts on Cordierite Substrates using Femtosecond Laser-Induced Breakdown Spectroscopy

The distinctive advantages of fs-LIBS such as a small HAZ and pronounced reduction in matrix effects are effectively leveraged for trace elemental analysis in complex matrices such as catalyst surfaces. An illustrative instance is the assessment of Pd and Pt concentrations in a cordierite ( $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}$ ) supported xPd-yPt bimetallic catalyst [2]. These noble metal-based catalysts play a pivotal role in the combustion of unburnt hydrocarbons. To better comprehend the catalyst's functionality, it is imperative to extract analytical insights concerning both the substrate surface and the concentration of platinum group metals. Analyzing cordierite-supported catalysts via LIBS poses specific challenges. Cordierite contributes to a complex LIBS spectrum, while the unpolished nature of the support further complicates the quantitative analysis of noble metals.

The time and space integrated fs-LIB spectra are recorded for characterizing both the cordierite matrix and the bimetallic catalysts supported on cordierite. The use of an Echelle spectrometer allows for simultaneous multi-element measurements, facilitating the selection of the most appropriate emission line for analysis within the range of 240 – 830 nm.

The spectral emission of the cordierite matrix and noble metals are systematically studied to identify 270.2 nm and 340.4 nm lines for quantitative estimation of Pt and Pd respectively (Fig.1a, b). Quantification of the LIBS signal is further aided by measurement of excitation temperature and electron density of the laser ablated plasma. Further assuming local thermodynamic equilibrium, the fs-LIP source is characterized for excitation temperature and electron number densities by using the Boltzmann plot method and Saha equation respectively. Time resolved LIBS under optimized conditions is employed for evaluating the analytical predictive ability of this technique. Calibration curves for Pt and Pd exhibit

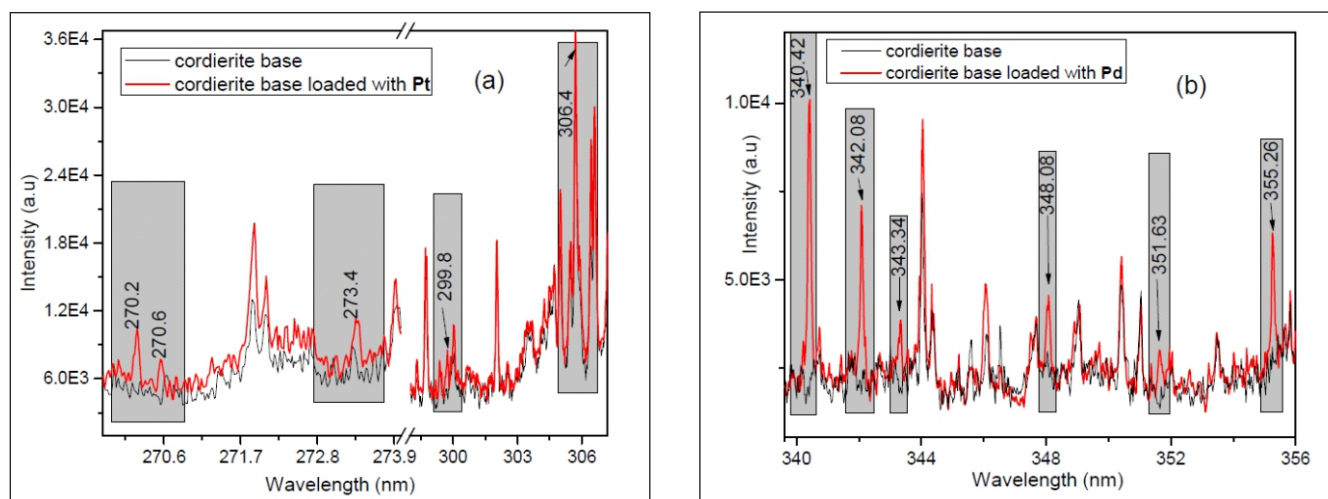


Fig.1: (a), (b) fs-LIB spectra (red curve) showing prominent emission lines of Pt(I) and Pd (I) loaded on the cordierite substrate. Spectrum of cordierite base (black curve) is also shown for the purpose of comparison.

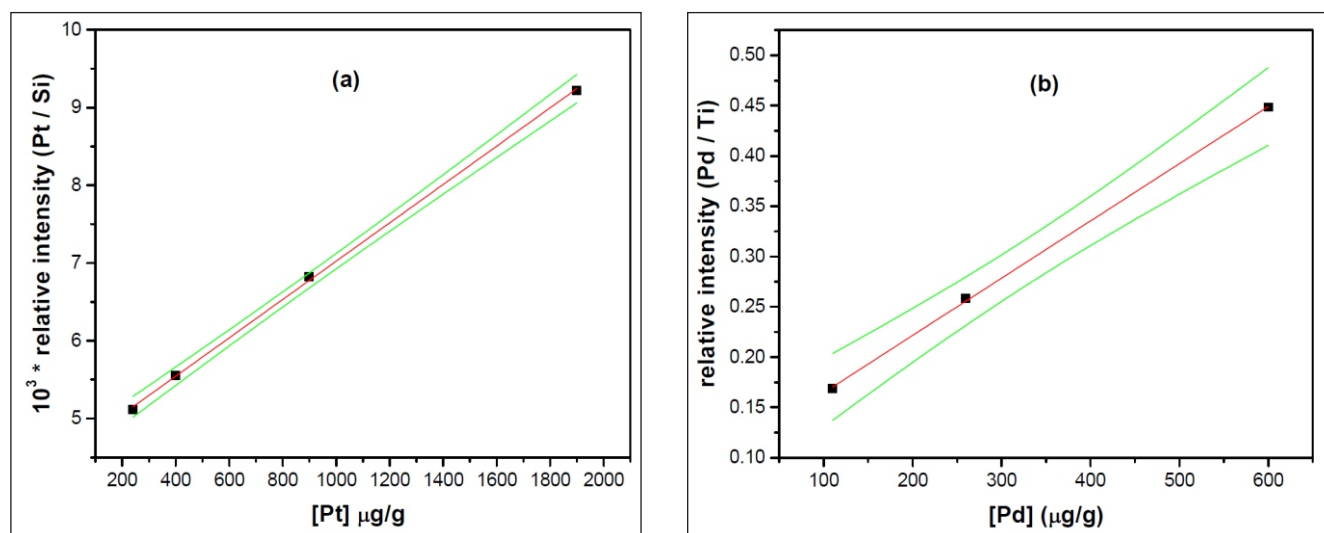


Fig.2: Calibration curve: (a) Pt on Cordierite support; (b) Pd on Cordierite support. Red curve: linear fit, green curve: prediction bands at 95%.

good linearity. The limit of detection for Pt and Pd is estimated to be 55  $\mu\text{g/g}$  and 17  $\mu\text{g/g}$  of cordierite respectively (Fig.2a, b). Further the predictive accuracy of this method in good agreement with results from conventional neutron activation analyses. fs-LIBS, a quasi non-destructive analytical tool can therefore be employed for quantification of noble metal catalysts.

### Case study II- Bridging Molecular Structures to Spectral Signatures of high energy materials (HEMs)

The precise identification and discrimination of explosive materials using LIBS faces a formidable obstacle from the matrix effect, especially when detecting explosive molecules across diverse substrates, including paper, metal, polymer, and leather. Fortunately, using fs-pulses for ablation effectively mitigates these matrix effects, rendering them negligible. Furthermore, femtosecond excitation is marked by lower continuum and plasma temperatures due to the absence of plasma re-heating, along with minimal plasma-atmosphere interaction, which favours molecular fragmentation. These unique attributes make fs-LIBS an attractive method for explosive detection.

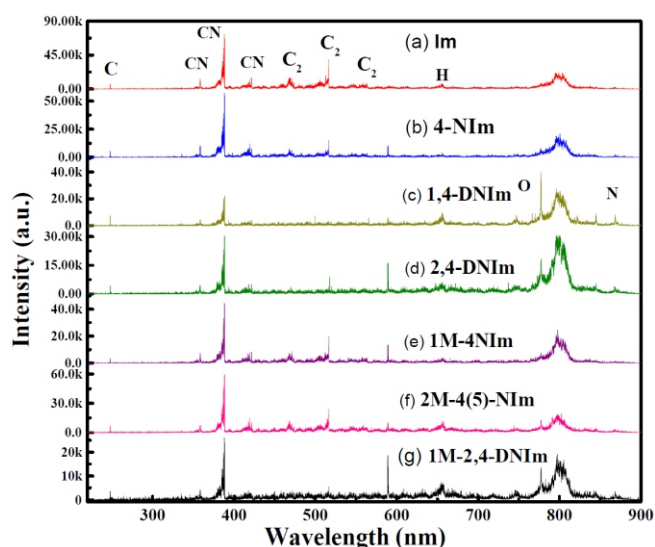


Fig.3: fs-LIBS spectra recorded in air at gate delay 100 ns and gate width 800 ns at 1 mJ pulse energy (a) Im (b) 4-NIm (c) 1,4-DNIm (d) 2,4-DNIm (e) 1M-4NIm (f) 2M-4(5)-NIm and (g) 1M-2,4-DNIm.

Organic HEMs, characterized by common elements of C, H, N, and O, yield similar emission spectra, featuring prominent CN and  $\text{C}_2$  molecular emission bands alongside atomic emissions reflecting their elemental constituents. This similarity poses a challenge for utilizing fs-LIBS for explosive discrimination. Our primary research thrust revolves around elucidating the correlation between the molecular structures of these compounds, focusing on the type, position, and number of substituents, and their impact on the intensity ratios of molecular and atomic species. To achieve this, we have selected imidazole and its nitro derivatives for study, as they show promise for both civil and military applications due to their exceptional thermal stability, impact and shock insensitivity, superior performance, as well as their cost-effective and environmentally friendly synthesis. The selected HEMs are (a) Imidazole (Im), (b) 4-Nitroimidazole (4-NIm), (c) 1,4-Dinitroimidazole (1,4-DNIm), (d) 2,4-Dinitroimidazole (2,4-DNIm), (e) 1-Methyl-4-Nitroimidazole (1M-4NIm), (f) 2-Methyl-4(5)-Nitroimidazole (2M-4(5)-NIm), and (g) 1-Methyl-2,4-Dinitroimidazole (1M-2,4-DNIm).

The emission spectra prominently feature CN and  $\text{C}_2$  molecular bands (Fig.3). CN bands, characterized by  $\Delta v$  values of -1, 0, and +1, were observed within ranges of 357–360 nm, 384–389 nm, and 414–423 nm, respectively, with the highest intensity at 388.3 nm corresponding to CN violet band.  $\text{C}_2$  molecular bands, corresponding to  $\Delta v = -1, 0,$  and  $+1$  transitions, were observed in the spectral regions spanning 460–475 nm, 510–520 nm, and 550–565 nm, respectively; the most intense being the Swan band at 516.4 nm. Conversely, atomic emissions linked to elemental constituents C(I), H $\alpha$ , O(I), and N(I) triplet lines appeared comparatively subdued. While robust CN molecular emissions were observed for all compounds,  $\text{C}_2$  molecular bands were only observed in Im, 4-NIm, 1M-4NIm, and 2M-4(5)-NIm, with decreasing emission intensity across the series. Notably, the dinitroimidazoles (1,4-DNIm, 2,4-DNIm, and 1M-2,4-DNIm) exhibited notably feeble  $\text{C}_2$  emissions (Fig.4).

The remarkable disparity in  $\text{C}_2$  yield between Imidazole and its derivatives, particularly 4-NIm and 2,4-DNIm, stems from structural nuances. In case of Imidazole, the unsubstituted C=C bond undergoes fragmentation following ring opening, thus contributing to high  $\text{C}_2$  yield. 4-NIm, despite the absence of this structural motif, exhibits markedly higher  $\text{C}_2$  intensity compared to 2,4-DNIm. The discrepancy is partly due to the nitro group's inductive effect, inducing significant charge

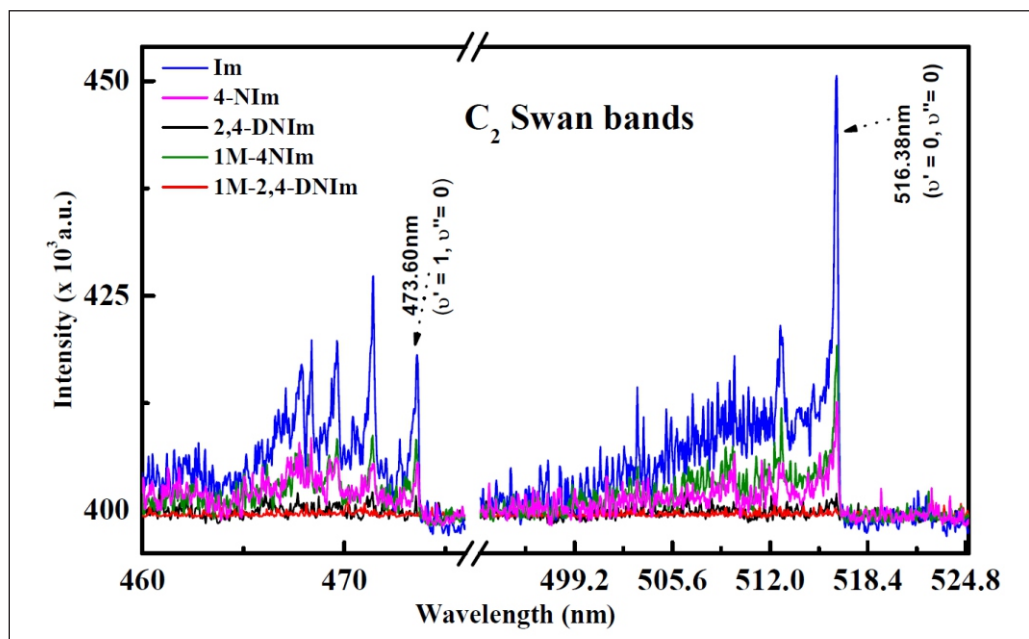


Fig. 4: Trend in  $C_2$  Swan band emission intensities for the imidazole series recorded in air. Reproduced from Ref. 3 with permission from the Royal Society of Chemistry.

separation on the carbon atom. Additionally, the electronegative oxygen atom reduces electron density in the aromatic ring, leading to varied canonical forms. Consequently, resonance effects diminish electron density within the Imidazole ring. Both the resonance and inductive effect act in a synergistic fashion rendering it more susceptible to atomization. This structural fragility in 4-NIm results in diminished  $C_2$  and pronounced CN intensity. Conversely, 2,4-DNIm, with additional electron-withdrawing nitro moieties, exhibits near-absent  $C_2$  emission. These findings suggest a clear correlation between spectral emissions and chemical structures, highlighting the potential use of the atomization-to-fragmentation ratio as a performance indicator for high-energy materials.

Expanding on these findings, we have examined a new set of high-energy materials, focusing on triazole-substituted nitroarenes with various functional and structural isomers. These compounds, feature methyl ( $CH_3$ ), methoxy ( $OCH_3$ ), and amino ( $NH_2$ ) groups in ortho and para positions. Despite their apparent similarity, correlation analysis of their spectra reveals significant differences based on molecular structure, including the types of bonds and the position of substituents within the aromatic ring. Moreover, detonation parameters including oxygen balance, detonation velocity, detonation pressure, and chemical energy of detonation were observed to correlate strongly with the  $(CN + C_2)/(C + H + N + O)$  ratio [4]. Consequently, the ratio of the sum of molecular emission intensities to the sum of atomic emission intensities emerges as a dependable performance metric for energetic compounds. Such correlation studies are anticipated to enhance comprehension and refine discrimination methodologies for hazardous materials of this nature.

## Conclusion

In summary, fs-LIBS emerges as a pivotal tool in the realms of analytical chemistry and security applications. It serves as a quasi-nondestructive means for assessing noble metal catalysts, with predictive precision akin to established methods. Furthermore, its scope encompasses explosive detection, leveraging spectral emissions' correlation with chemical structures. The proposed metric, measuring the ratio of molecular to atomic emission intensities, showcases promise in refining discrimination methodologies for identifying high-energy materials.

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