आण्विक उत्सर्जन को अनुकूलित करना

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शोर से ज्ञान तक : लेज़र-प्रेरित प्लाज़्मा में बोरॉन आण्विक उत्सर्जन स्पेक्ट्रा का उपयोग

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अव्यवस्थित शोर जैसे पैटर्न को क्रमबद्ध करना और कार्यात्मक आण्विक संकेतों में परिवर्तित करना।

सारांश

यह अध्ययन लेज़र प्रेरित प्लाज़्मा (एलआईपी) में बोरॉन आण्विक उत्सर्जन स्पेक्ट्रा की खोज करता है और अंशांकन-मुक्त लेज़र अब्लेटेड मॉलिक्यूलर आइसोटोपिक स्पेक्ट्रोमेट्री (सीएफ-एलएएमआईएस) का उपयोग करके आइसोटोपिक विश्लेषण के लिए इसकी क्षमता पर प्रकाश डालता है। BO और BO_2 जैसी क्षणिक प्रजातियों का विश्लेषण करके, शोध वर्णक्रमीय व्यतिकरण में चुनौतियों और आण्विक उत्सर्जन को अनुकूलित करने हेतु प्लाज़्मा तापमान की भूमिका को उजागर करता है। समस्थानिक संरचना में ~2% सटीकता प्राप्त करते हुए, निष्कर्ष गुणात्मक और मात्रात्मक दोनों अनुप्रयोगों के लिए आण्विक उत्सर्जन की व्यावहारिक और विश्लेषणात्मक प्रासंगिकता को रेखांकित करता है।

Optimizing Molecular Emissions

2

From Noise to Knowledge: Harnessing Boron Molecular Emission Spectra in Laser-Induced Plasma

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Conversion of chaotic noise-like patterns into ordered and functional molecular signals.

ABSTRACT

This study explores boron molecular emission spectra in Laser Induced Plasma (LIP) and highlights their potential for isotopic analysis using Calibration-Free Laser Ablated Molecular Isotopic Spectrometry (CF-LAMIS). By analyzing transient species such as BO and BO_2, the research identifies challenges in spectral interferences and the role of plasma temperature in optimizing molecular emissions. Achieving ~2% accuracy in isotopic composition, the findings underscore the practical and analytical relevance of molecular emissions for both qualitative and quantitative applications.

KEYWORDS: *Laser induced plasma, Molecular isotopic spectrometry, Plasma temperature, Isotopic composition*

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Introduction

Laser-induced plasma (LIP) is a powerful analytical tool that generates transient plasma through the interaction of high-intensity laser pulses with matter. This plasma contains a complex mixture of ions, atoms, and molecules, emitting signals that can be ionic, atomic, or molecular depending on acquisition delay times. These molecular emission signatures are uniquely characterized by molecular band structures, enabling experiments under ambient conditions. Such emissions have significant applications, including isotopic and actinide detection [1].

Early studies by Hornkohl et al. investigated CN molecular spectra in LIP, followed by work from Harilal et al., who explored vibrational temperature and population distribution of CN bands [2,3]. Russo et al. later introduced isotopic analysis using diatomic molecular emissions, while Sarkar et al. refined isotopic ratio predictions for boron using chemometrics techniques [4,5].

Building on this foundation, our research delves deeper into the potential of boron molecular emissions, focusing on diatomic (BO) and polyatomic (BO_2) species. Through high-resolution optical setups, we aim to advance the understanding of molecular emission signatures and optimize their analytical applications.

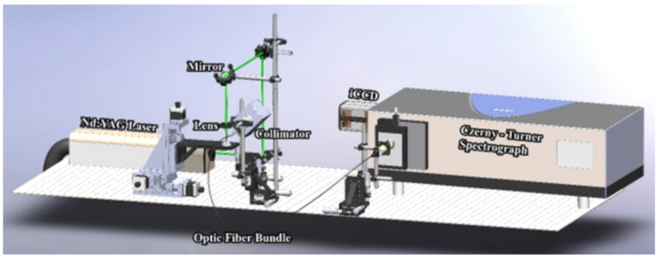


Fig.1: Instrumentation setup.

Experimental setup

The experimental setup mirrors the LIBS configuration, utilizing a Q-switched Nd:YAG laser (1064 nm) to ablate the sample surface and create micro-plasma. Second and fourth harmonic attachments enable additional laser wavelengths of 532 nm and 266 nm. Emissions are collected at a 45° angle using a collimator and delivered to a Czerny-Turner spectrograph via an optical fiber bundle. The spectrograph employs three gratings, offering resolutions of $\Delta\lambda$ = 55 pm, 35 pm, and 25 pm, depending on the grating used.

The plasma's emission spectrum is recorded by accumulating an optimized number of single laser shots on fresh sample surfaces. Ambient air conditions are maintained, and LabView software is employed for algorithm development and data analysis. This setup ensures precise spectral recording for subsequent analysis.

Results and Discussion

Molecular emission spectra of transient boron species

In an oxygen rich LIP, boron can form mainly two transient species BO and BO_2 by various reactions. Some of these reactions are $B + O \rightarrow BO$, $B + O_2 \rightarrow BO_2$, $BO + O \rightarrow BO_2$, $BO + O_2 \rightarrow$

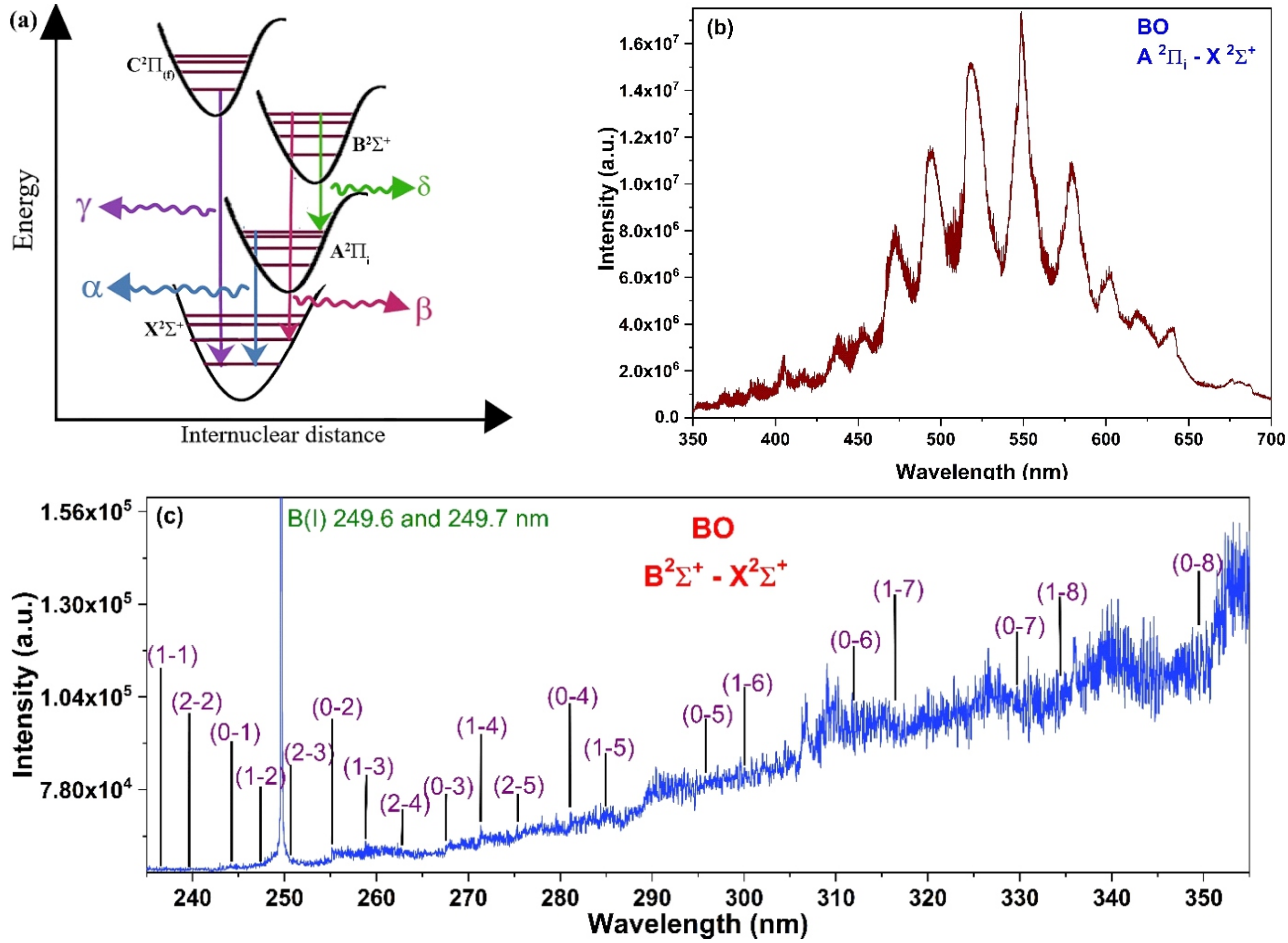


Fig.2: (a) Plausible electronic transitions of boron monoxide. Experimentally recorded spectra of (b) BO:A-X and (C) BO:B-X transitions.

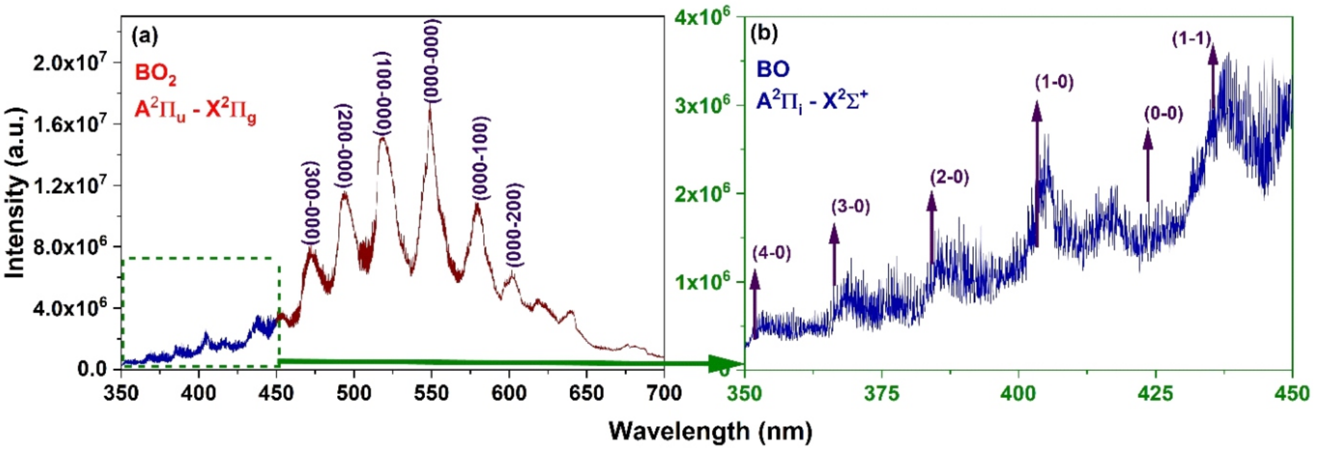


Fig.3: Revised emission spectra of (a) BO_2:A-X and (b) BO:A-X transition.

BO_2+ O [6]. These transient molecules show various emission signals according to the electronic transition taking place.

BO exhibits transitions across four electronic states: $C^2\Pi_{(f)}$, $B^2\Sigma^+$, $A^2\Pi_i$ and $X^2\Sigma^+$. The transition between these states result in various electronic transitions such as A-X or α-band (350–650 nm), B-X or β-band (230–330 nm), C-X or γ-band (181–230 nm), and B-A or δ-band (458–595 nm) (Fig.2(a)). The occurrence of the γ-band in the deep UV region makes it difficult to record with the available detector setup. The δ-band is difficult to record spectroscopically due to its low intensity and overlap with the α-band. This leaves the α-band and β-band as the most straightforward for studying the ro-vibrational band (RVB) structure [7]. Fig.2(b) shows the experimentally recorded spectra of the BO:A-X transition and Fig.2(c) shows the recorded spectra of various RVBs in the BO:B-X transition.

For transient BO_2 species, the highly intense transition was identified to be the BO_2: A-X transition, which coexists with the BO:A-X molecular bands. Since the possibility of polyatomic transient molecule formation in LIP was not recognized until recent times [8], researchers initially assumed that the recorded spectral region belonged to the BO:A-X transition, and various analyses were performed. The BO_2:A-X transition is observed to be an electronic transition with higher emission intensity compared to the electronic transitions of BO molecules [7]. The revised RVB emission bands of polyatomic BO_2 species and BO:A-X molecular bands are shown in Fig.3.

Molecular emission signatures and spectral interferences

To understand the amount of useful information in molecular emission spectra, an analytical figure of merit, the signal-to-envelope ratio (SER), was introduced [7,9]. Intensity decay studies of BO:B-X, BO:A-X, and BO_2:A-X RVBs showed that all RVBs of similar electronic transitions exhibit the same intensity decay pattern unless the RVB is spectrally interfered with. This study also helps identify atomic and molecular spectral interferences in various molecular emission bands of transient boron molecular species. Since the BO:A-X transition occurs between the BO:B-X and BO_2:A-X transitions, the BO:A-X bands consistently experience interferences from other molecular transitions. The RVBs of the BO_2:A-X transition are always observed to be spectrally pure due to their high intensity compared to BO transitions [7].

Importance of plasma temperature

The study observed a linear relationship between plasma temperature decay and emission intensity decay for BO:B-X and BO_2:A-X transitions, with optimal temperatures of 10,000–11,000 K for BO and 8,000–9,000 K for BO_2 (Fig.4). Deviation from linearity in BO:A-X transitions was attributed to spectral interferences, underscoring the necessity of maintaining optimal plasma conditions for reliable data acquisition [10].

Analytical applications of molecular emissions

Despite the potential of LAMIS method, the scarcity of enriched isotopic standards necessitates a calibration-free approach where no standard is required for isotopic composition determination. Our group developed a CF-LAMIS methodology for the isotopic composition determination of

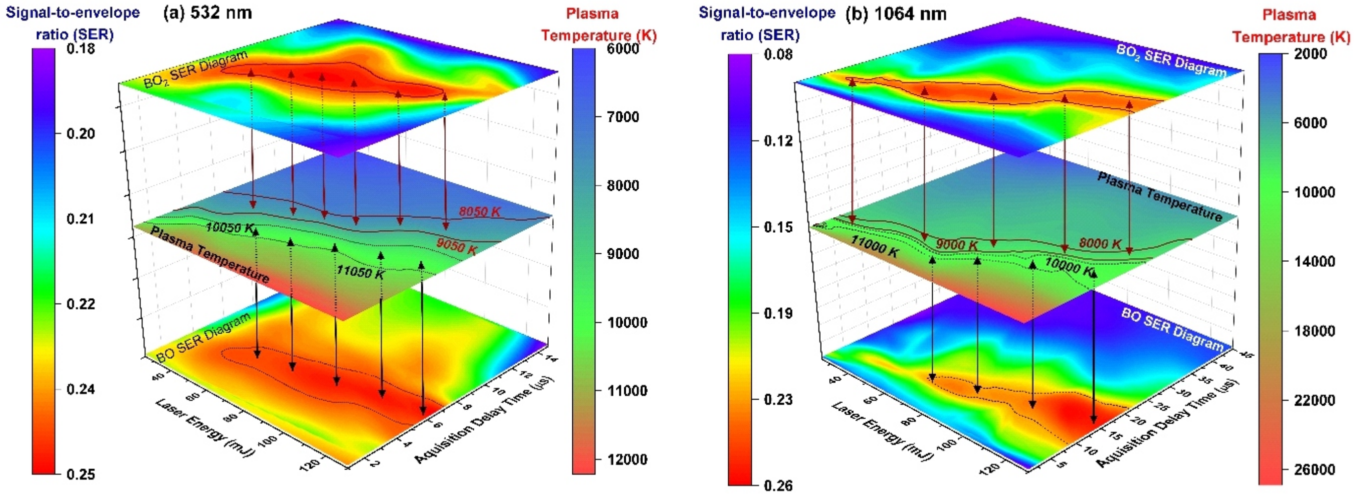
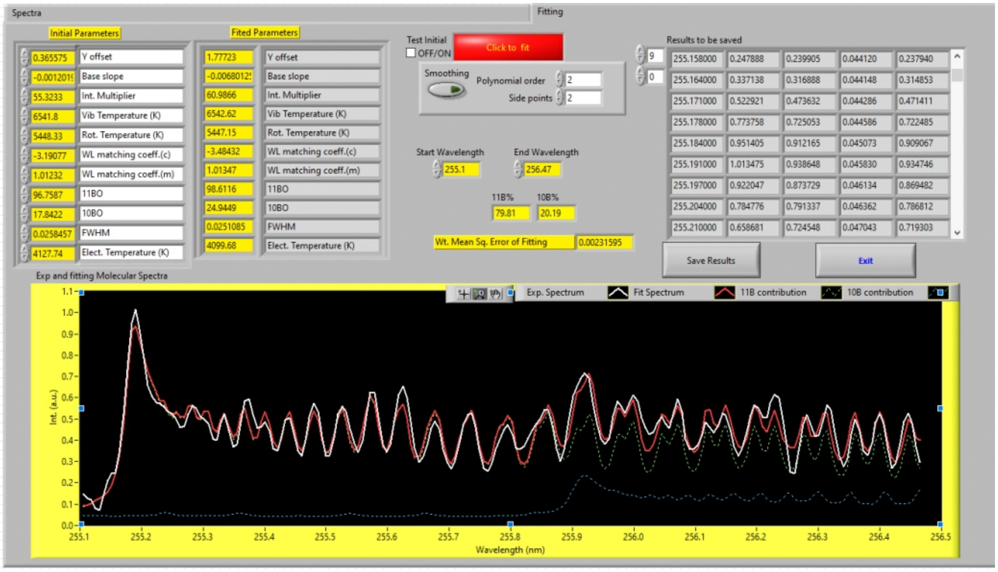


Fig.4: Relationship between the plasma temperature and molecular information (a) 532 nm and (b) 1064 nm.



Initial Parameters

0.365575	Y offset
-0.001201	Base slope
55.3233	Int. Multiplier
6541.8	Vib Temperature (K)
5448.33	Rot. Temperature (K)
-3.19077	WL matching coeff.(c)
1.01232	WL matching coeff.(m)
96.7587	11BO
17.8422	10BO
0.0258457	FWHM
4127.74	Elect. Temperature (K)

Fited Parameters

1.77723	Y offset
-0.0068012	Base slope
60.9866	Int. Multiplier
6542.62	Vib Temperature (K)
5447.15	Rot. Temperature (K)
-3.48432	WL matching coeff.(c)
1.01347	WL matching coeff.(m)
98.6116	11BO
24.9449	10BO
0.0251085	FWHM
4099.68	Elect. Temperature (K)

Test Initial ☐ OFF/ON

Smoothing
Polynomial order 2
Side points 2

Start Wavelength 255.1
End Wavelength 256.47

11B% 79.81
10B% 20.19

Wt. Mean Sq. Error of Fitting 0.00231595

Results to be saved

9
0

255.158000	0.247888	0.239905	0.044120	0.237940
255.164000	0.337138	0.316888	0.044148	0.314853
255.171000	0.522921	0.473632	0.044286	0.471411
255.178000	0.773758	0.725053	0.044586	0.722485
255.184000	0.951405	0.912165	0.045073	0.909067
255.191000	1.013475	0.938648	0.045830	0.934746
255.197000	0.922047	0.873729	0.046134	0.869482
255.204000	0.784776	0.791337	0.046362	0.786812
255.210000	0.658681	0.724548	0.047043	0.719303

Fig.5: Graphical user interphase of the MAHADEV algorithm.

boron samples using the MAHADEV algorithm. The algorithm is based on the Born-Oppenheimer approximation, Boltzmann equilibrium, and Lorentzian intensity, named **M**olecular spectr**A** simulator under Born-Oppen**H**eimer **A**pproximation an**D** Boltzmann **E**quilibrium en**V**ironment (MAHADEV) and isotopic compositions of boron samples were determined with ~2% accuracy. The algorithm's GUI, shown in Fig.5, enables efficient simulation and experimental data correlation, providing a robust framework for non-linear curve fitting [9].

Conclusion

This study underscores the transition of molecular emission signatures from perceived noise to valuable analytical signals. By addressing challenges like spectral interferences and optimizing plasma conditions, significant advancements were achieved in isotopic composition analysis using boron molecular emissions. The CF-LAMIS methodology offers a novel, accurate, and efficient approach, cementing the role of laser-induced plasma in cutting-edge spectroscopic applications. Future work aims to expand this methodology to other molecular systems, broadening its applicability across diverse fields.

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