LASER ABLATION MOLECULAR ISOTOPIC SPECTROMETRY (LAMIS): AN OVERVIEW

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1. INTRODUCTION

Since the LAMIS introduction in 2011 [Russo 2011], our research team [Russo 2011, Russo 2013, Bol'shakov 2014, Bol'shakov 2015a, Bol'shakov 2015b, Bol'shakov 2017, Dong 2013, Hou 2015, Mao 2011, Mao 2016, Sarkar 2013] and others [Brown 2014, Brown 2016, Choi 2019, Gaft 2020, Hartig 2016, Santos 2020, Yee 2013, Zhu 2019] have focused a great deal of effort on developing this novel laser ablation-based approach to detect isotopic information from the laser-induced plasma. This presentation is meant to give an overview of LAMIS origins and its foundation; we discuss some experimental considerations, review some case studies and advances, quantification approaches, and LAMIS's future.

Laser ablation is commonly used as a direct and rapid sampling technique to measure optical emission or mass spectra for the elemental and isotopic analysis of a sample. Laser Ablation Molecular Isotopic Spectrometry (LAMIS)[Russo 2011] is a similar technique that explores optical spectra of transient molecules produced in ablation plumes in air or buffer gases for rapid isotopic analysis directly on the samples. LAMIS measures molecular emission as the plasma cools when free molecules are formed in the plasma afterglow via several mechanisms, including radiative and three-body association of atoms and recombining ions. The isotopic constituents produce excited isotopologues of dimers, oxides, nitrides, or halides in plasma reactions between atomized matter from the sample and ambient atmosphere.

Isotopologues have isotopic spectral shifts that are considerably larger than those in atomic spectra, and therefore the former can be measured with a general-purpose spectrometer, **Figure 1**. Molecular quantum energy levels, particularly the vibrational and rotational components, strongly depend on the mass difference between isotopes. In contrast, the electronic energy is primarily determined by the Coulomb field but significantly less dependent on nuclei's mass [Russo 2011]. Consequently, molecular transitions involving a change of vibrational and rotational states can exhibit up to several orders of magnitude larger isotopic shifts than atomic transitions, which are purely electronic [Russo 2011]. Larger isotopic shifts significantly relax requirements on the spectral resolution.
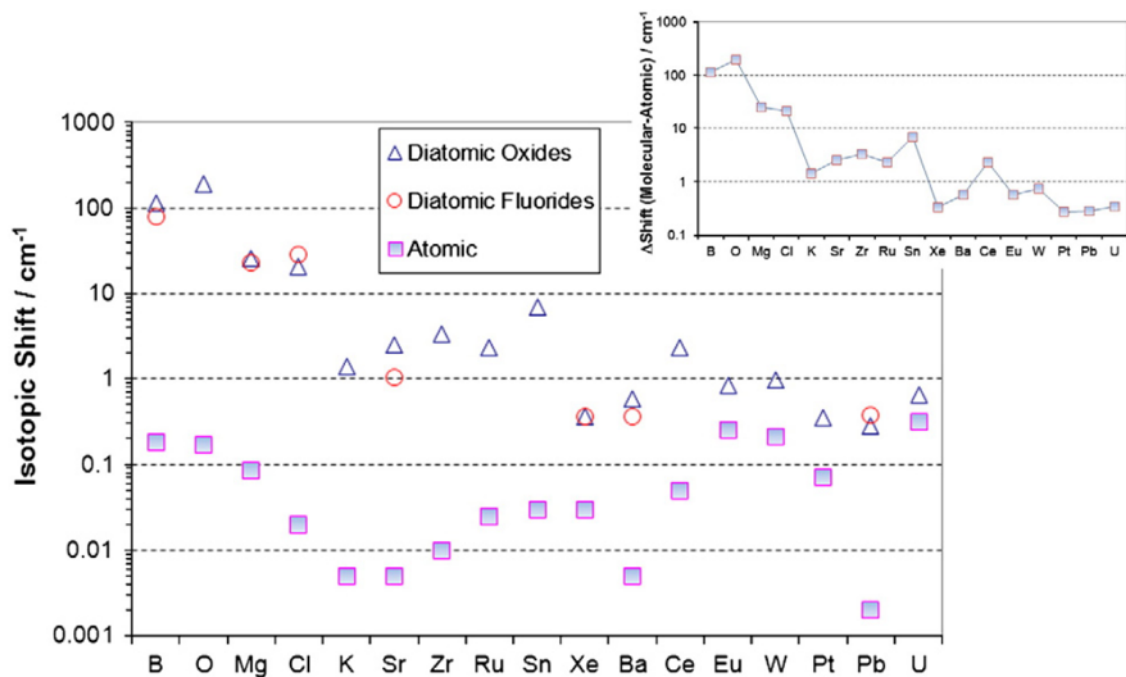
Figure 1. Molecular vs. atomic isotopic shifts for various elements. Molecular shifts were calculated for either the diatomic oxide or fluoride for each element considered in this plot. Isotopic shifts are much larger, up to several orders of magnitude, for molecular species as opposed to atomic species. The inset is a different plot of isotopic shifts. Atomic isotopic shift values were taken from Stern and Snavely.

These concepts will be demonstrated using a few examples of the isotopic systems studied so far, and some of the experimental conditions considerations and data reduction and analysis approaches.

2. EXPERIMENTAL

Both nano- and femtosecond pulsed lasers have been used for LAMIS measurements. Femtosecond ablation yielded significantly stronger molecular emission at a lower background than nanosecond ablation at the same laser power delivered to the sample. The use of a femtosecond laser reduces the analysis's destructiveness due to lower pulse energies applied to the sample relative to nanosecond laser pulses. Double-pulse excitation was found to enhance the sensitivity of LAMIS substantially. Echelle or Czerny-Turner spectrographs fitted with ICCD or EMCCD cameras were generally recognized as suitable for LAMIS. Simultaneously, femtosecond ablation and numerical filtering of spectra enabled LAMIS measurements with a non-gated CCD detector.

Usually, optical emission spectra in LAMIS are measured at longer delays after an ablation pulse than the LIBS delays, **Figure 2**. Accordingly, LIBS and LAMIS's optimal conditions are different but can be achieved with the same instrument. A possibility of combining LIBS and LAMIS for simultaneous elemental and isotopic analysis can enable multiple applications anticipated in the nuclear power industry, medical diagnostics and therapies, forensics, carbon sequestration, geochemistry, agronomy, and many other

studies. Potentially LIBS and LAMIS can be built into a portable device for the elemental and isotopic analysis directly in the field.
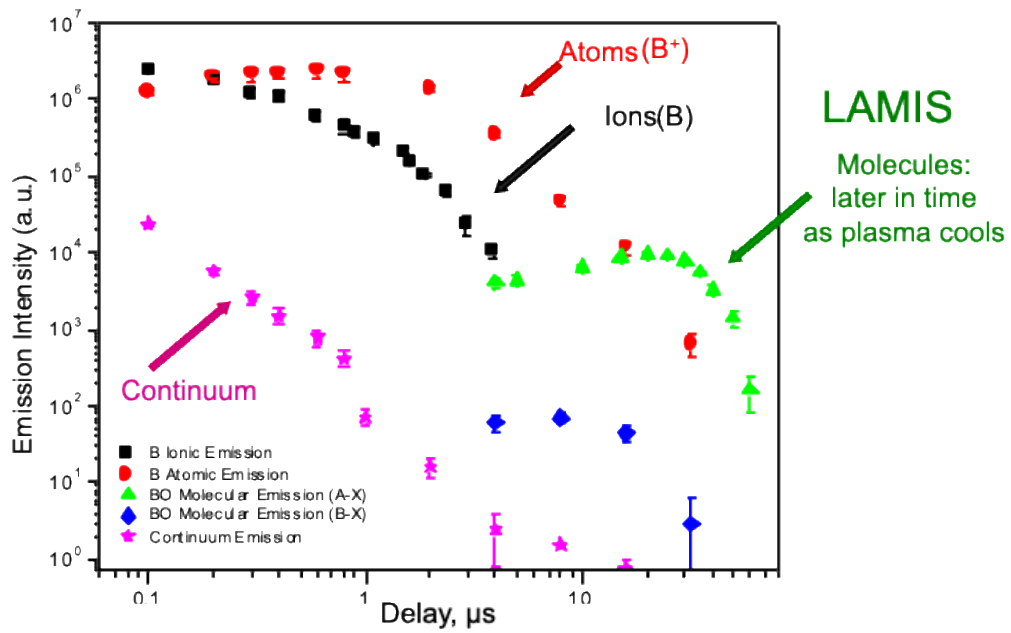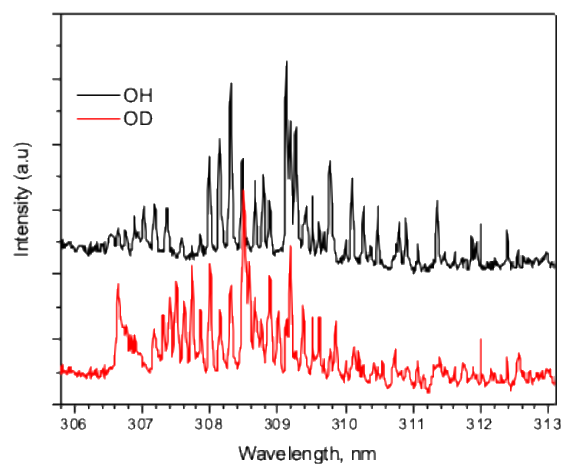

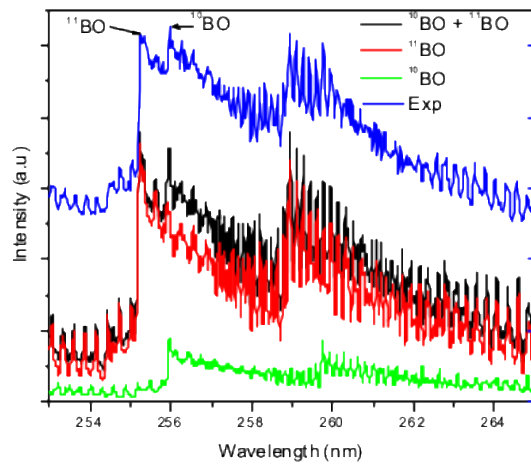*Figure 5.* Optical emission signal evolution.

3. RESULTS AND DISCUSSION

These are some of the case studies we will be discussing during the presentation
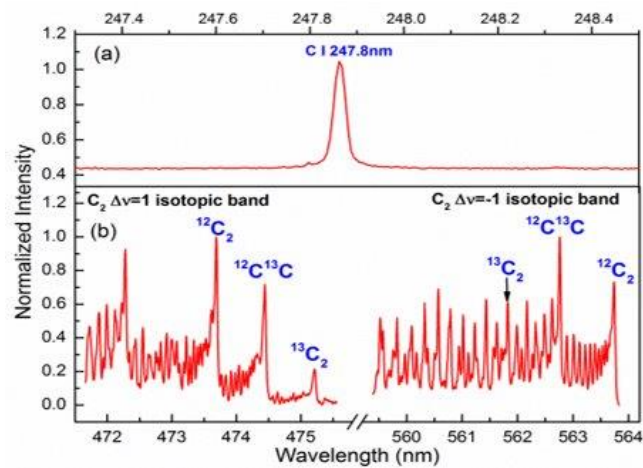
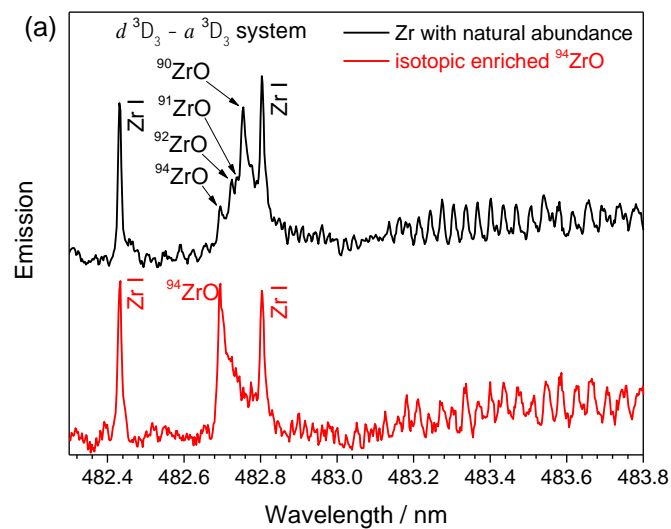   a.   Hydrogen and Deuterium – [Sarkar 2013]
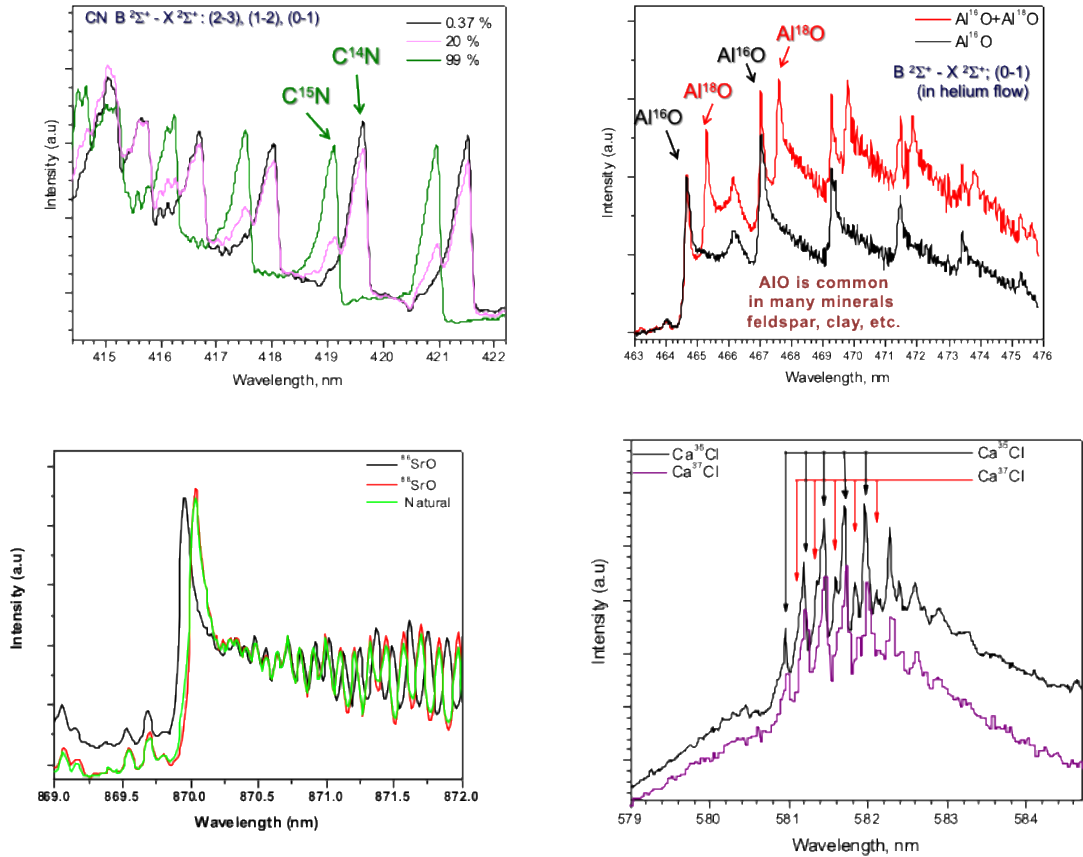
b.   Boron - [Yee 2013]

c.   Carbon - [Dong 2013]

d.   Zirconium [Hou 2015]

e. Nitrogen, Oxygen, Chlorine, Strontium [Bol'shakov 2014, Mao 2011]

Quantitative calibration of spectral data in LAMIS can be achieved by different means. A common empirical approach involves measuring spectra from a set of known reference samples and building a partial least square regression (PLSR) model to relate them to the nominal abundances of isotopes in the samples. This model is applied to compare the spectra of the analyzed unknown samples to the reference spectra. Quantification is based on proportionality between emission from the plasma-generated isotopologues and the isotopic abundances in the sample. Such calibration alleviates errors caused by possible isotope fractionation in the ablation plumes.

Another quantification approach in LAMIS uses simulated spectra of relevant isotopologues, and a proportional sum of them is fitted to the experimental emission spectra. The isotope ratio is entered as a fitting parameter and is determined from the best fit. This approach does not require isotopic standards but depends on the quality of tabulated molecular parameters and equilibrated and homogeneous plasma assumptions.

4. ACKNOWLEDGMENTS

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