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# Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy for Improving the Detection of Molecular Bands.

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## Abstract

Enhancement of molecular band emission in laser-induced plasmas is important for improving sensitivity and limits of detection in molecular sensing and molecular isotope analysis. In this work we introduce the use of Nanoparticle Enhanced Laser Induced Breakdown (NELIBS) for the enhancement of molecular band emission in laser-induced plasmas, and study the underlying mechanisms responsible for the observed enhancement. The use of Ag nanoparticles leads to an order of magnitude enhancement for AlO ( $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ ) system emission from an Al-based alloy. We demonstrate that the mechanism responsible for the enhancement of molecular bands differs from that of atomic emission, and can be traced down to the increased number of atomic species in NELIBS which lead to AlO molecular formation. These findings showcase the potential of NELIBS as a simple and viable technology for enhancing molecular band emission in laser-induced plasmas.

## Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is an optical emission spectroscopy technique that is based on the interaction of an intense pulsed laser beam with a material surface leading to transient plasma formation [1]. While LIBS is largely considered as an elemental analytical technique, the molecular emission also present in the laser induced plasma has received increasing attention in the past few years [2]. Unlike atomic emission lines which are commonly associated with a distinct transition, molecular emission is the result of a group of emission lines from vibrational states originating from electronic transitions of the molecule [3]. The intensity of molecular emission in laser-induced plasmas varies based on the exact molecular transition, the laser parameters, and the background atmosphere.

LIBS molecular band emission has been used in a variety of applications including biological matter [4], complex organic materials such as polymers [5], and explosive residue [6]. Molecular spectra are also the basis for isotopic analysis at atmospheric pressure via Laser Ablation Molecular Isotopic Spectrometry (LAMIS) [7,8]. LAMIS exploits relatively large isotope shifts in spectra of transient molecular isotopologues formed in laser-induced plasmas, thereby enabling isotopic analysis in various material systems in air. Molecular band emission has been also used to elucidate processes in the expanding laser-induced plasma and provide information on complex chemical reactions [3].

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