Optical Pumping Within a Laser-Induced Plasma to Enhance Trace Element Signal Intensity

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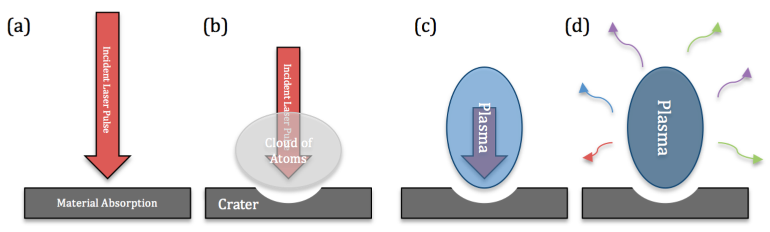
What is LIBS?

Laser-induced breakdown spectroscopy (LIBS) is a spectroscopic technique that uses a pulsed laser to create a high temperature plasma of atoms and ions from an ablated target. The spectrum of light emitted is characteristic of the atoms in the plasma and the intensity is proportional to the concentration of elements in the target.

What is LIBS-LIF?

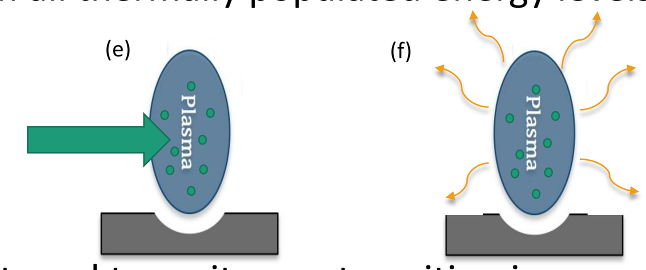
Despite many advantages, one limitation of LIBS is that it can only detect elements at a part per million level. One technique used to improve the limit of detection is laser-induced breakdown spectroscopy/laser-induced fluorescence (LIBS-LIF). In this technique a resonant laser pulse illuminates the plasma at some time after plasma formation. By pumping atoms to a specific energy level, spontaneous emission out of this level (fluorescence) is enhanced, making this element easier to detect and thus improving sensitivity. This has been shown in multiple elements [1,2].

LIBS



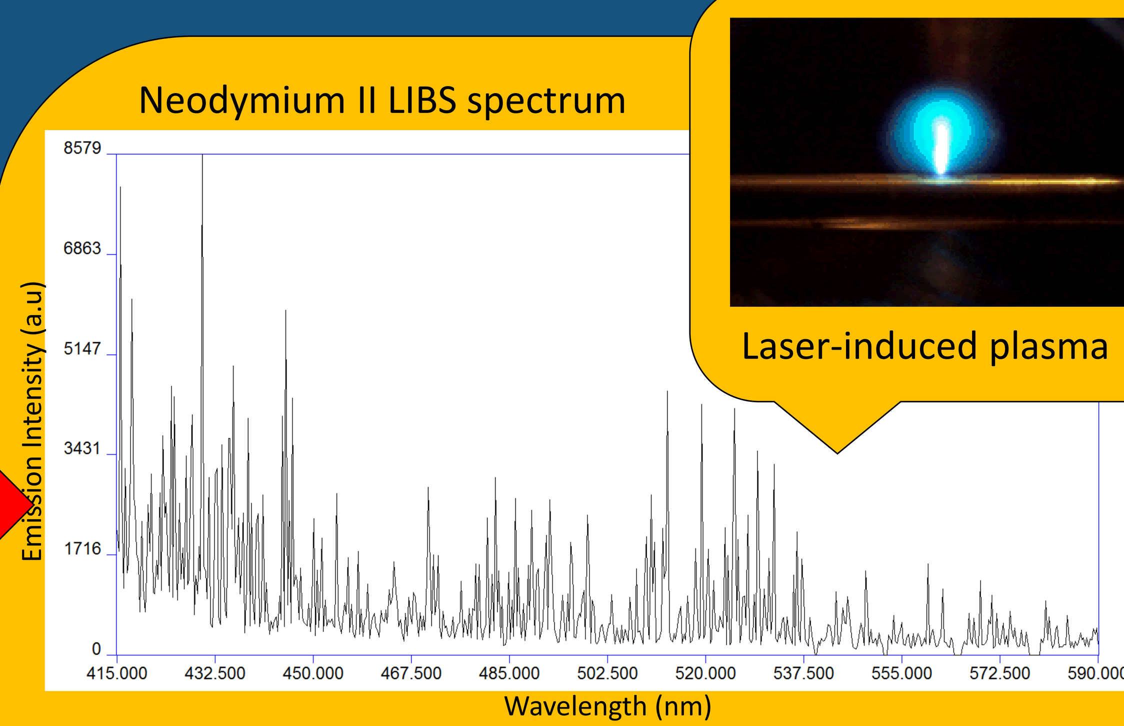
Non-resonant laser pulses (a) create a hot plasma (c). Atoms spontaneously emit from all thermally populated energy levels.

LIBS-LIF



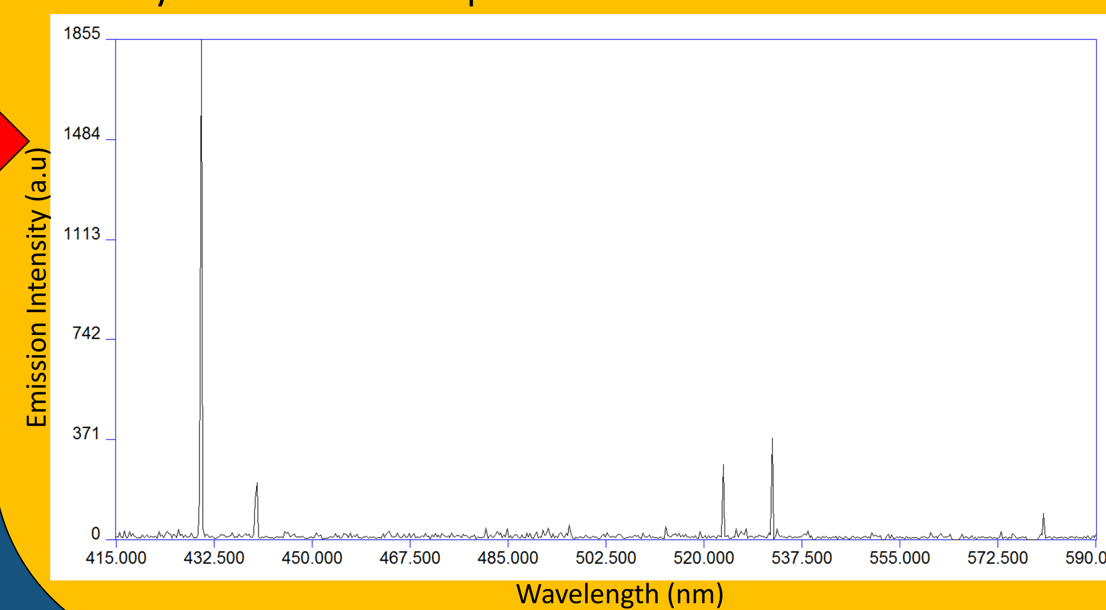
A resonant laser pulse tuned to excite one transition in a specific element (e) is incident on a LIBS plasma (c) and at a very short delay afterwards, enhanced emission from that single excited state is observed (f).

Neodymium II LIBS spectrum



Laser-induced plasma

Neodymium II LIBS-LIF spectrum

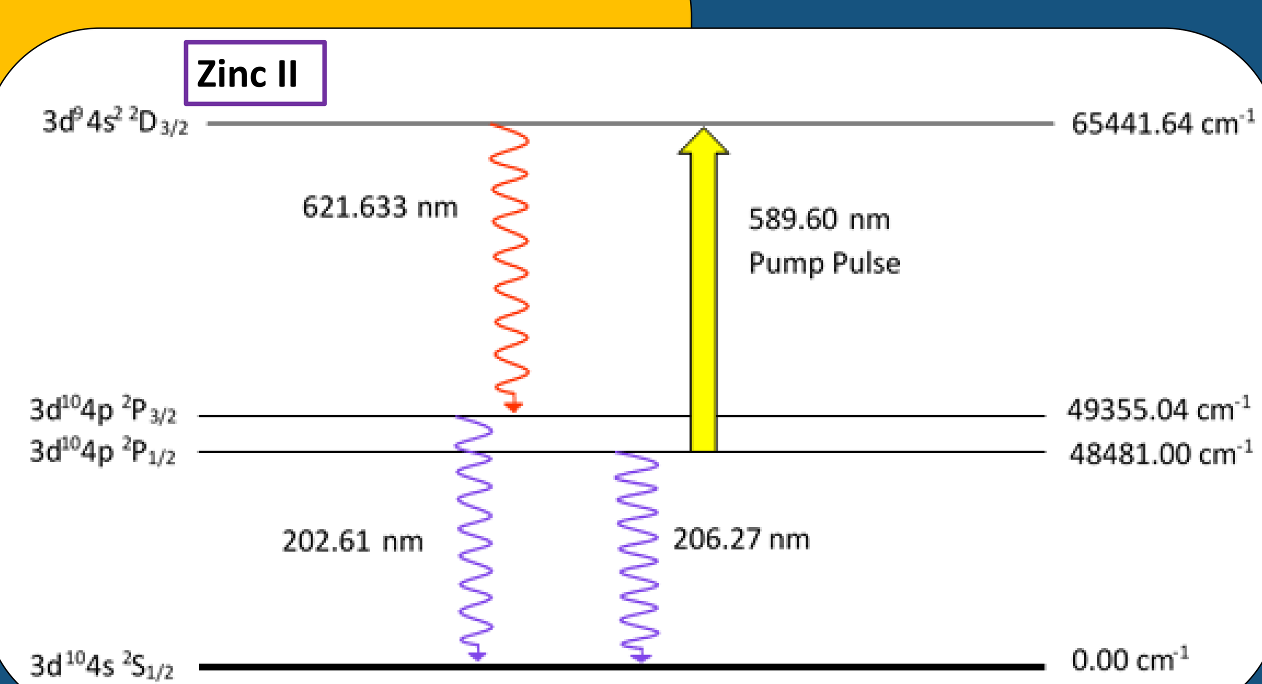


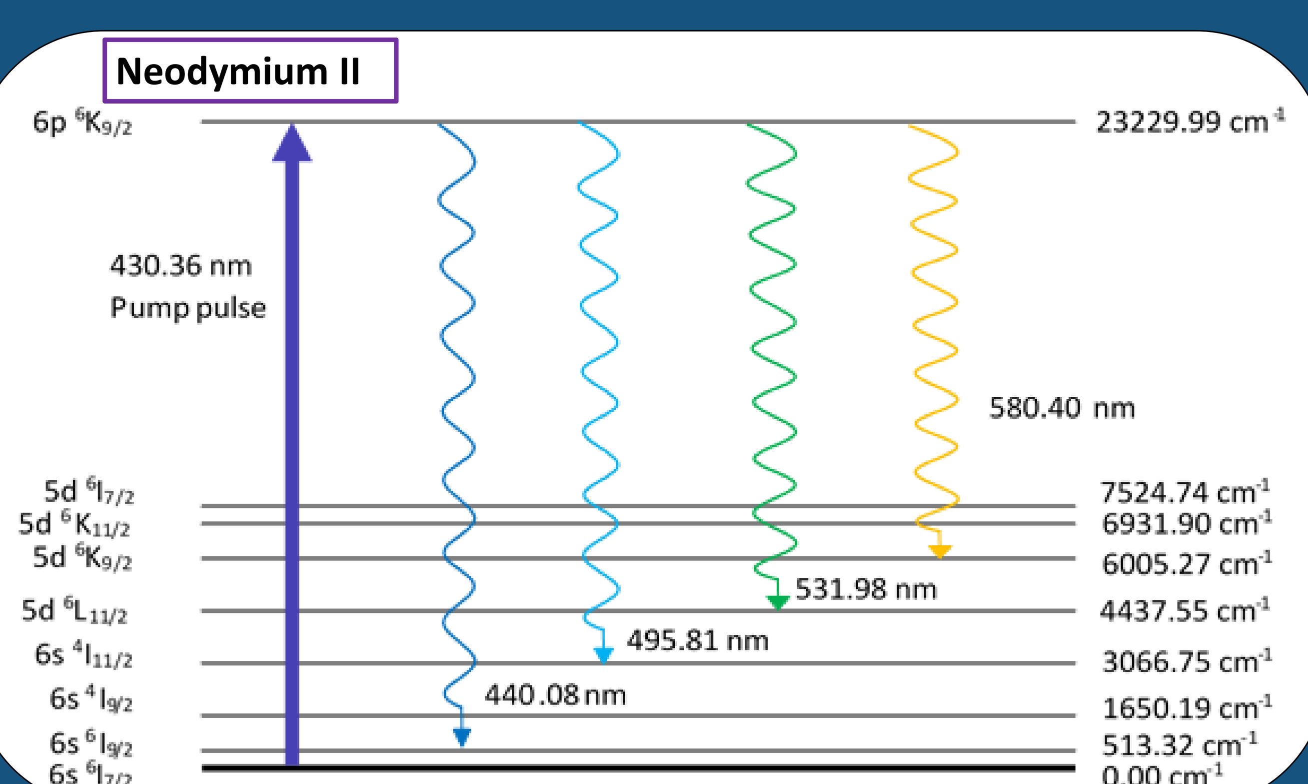
Motivation

There are three main reasons for using LIBS-LIF in our lab:

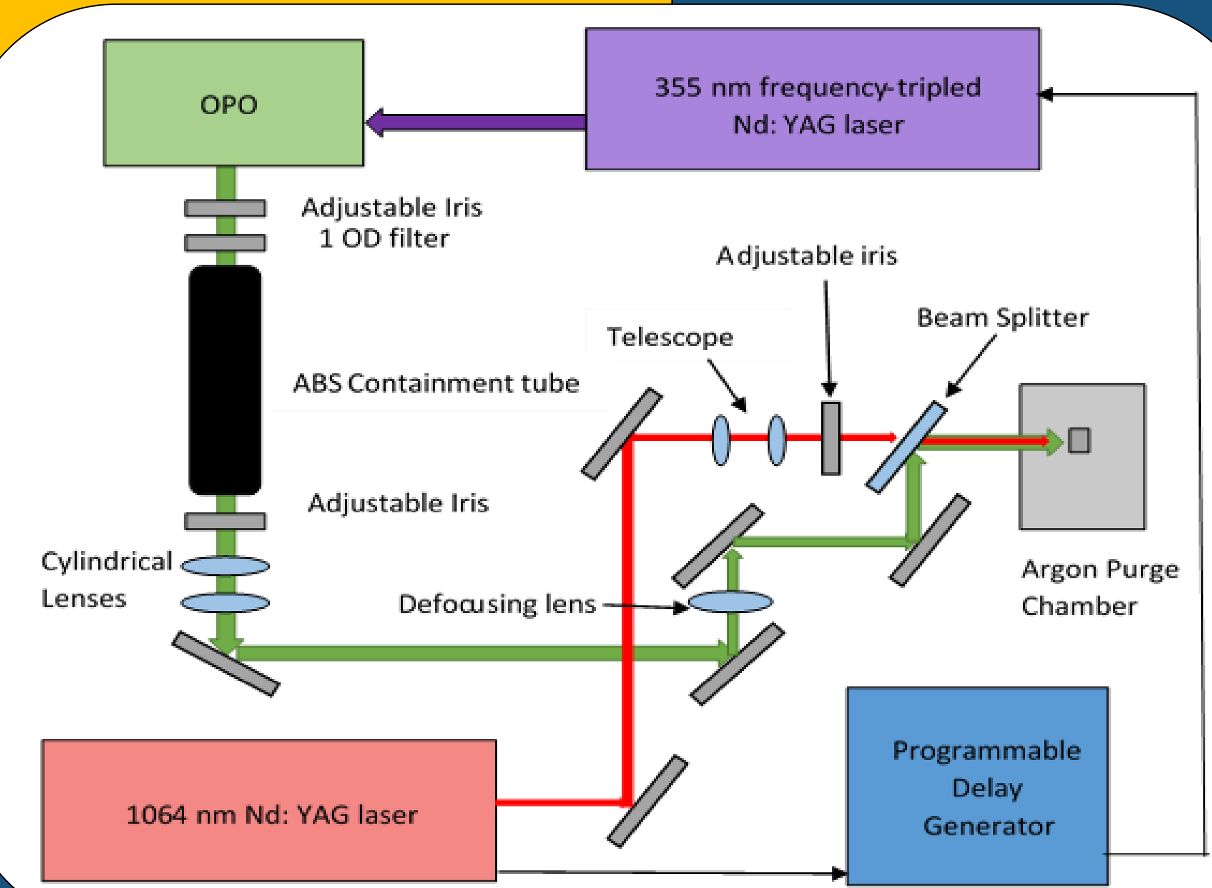
1) Signal enhancement to allow detection of trace elements at the sub-ppm level (in bacteria)
2) Measuring branching ratios by selectively elevating lines above the noise (in lanthanides)
3) LIF can also be used for atomic lifetime studies in laser-induced plasmas *(not currently done in our lab)*

Pumping schemes

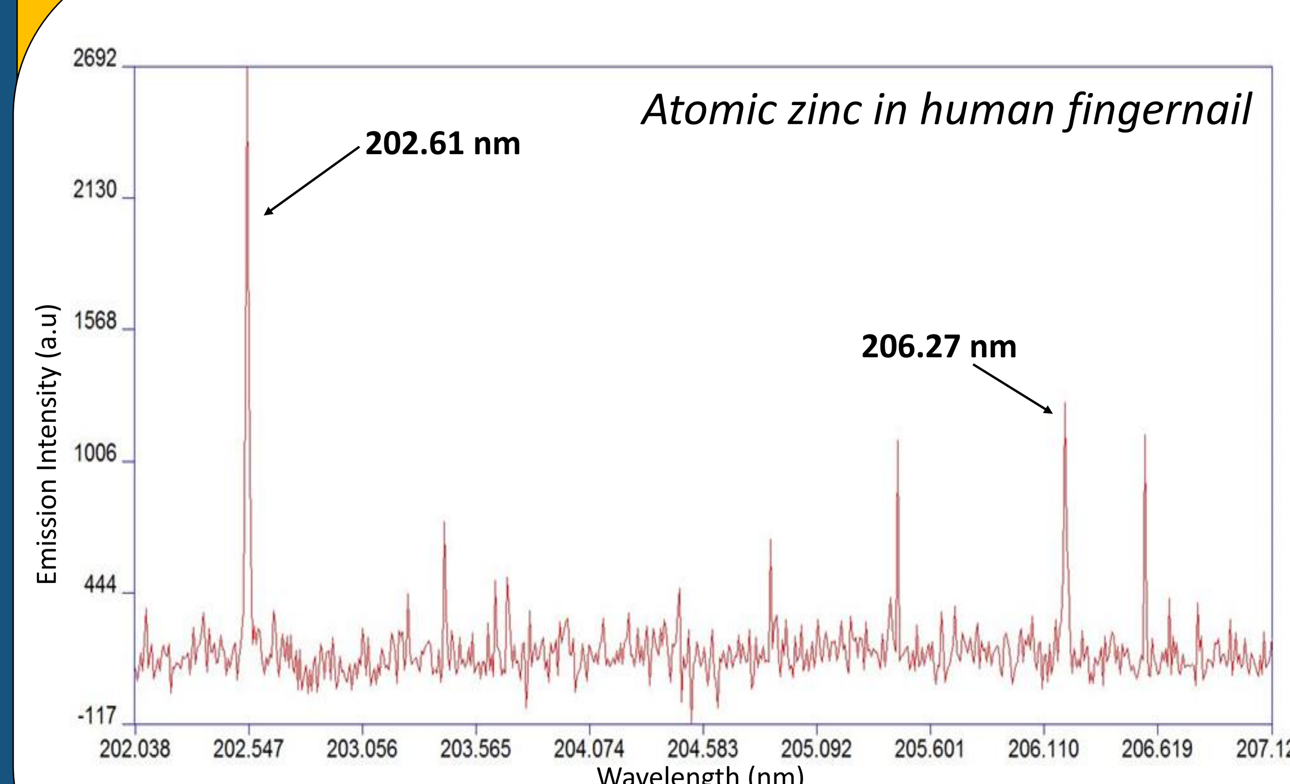




How is LIBS-LIF performed?



Zinc II spectrum to be enhanced

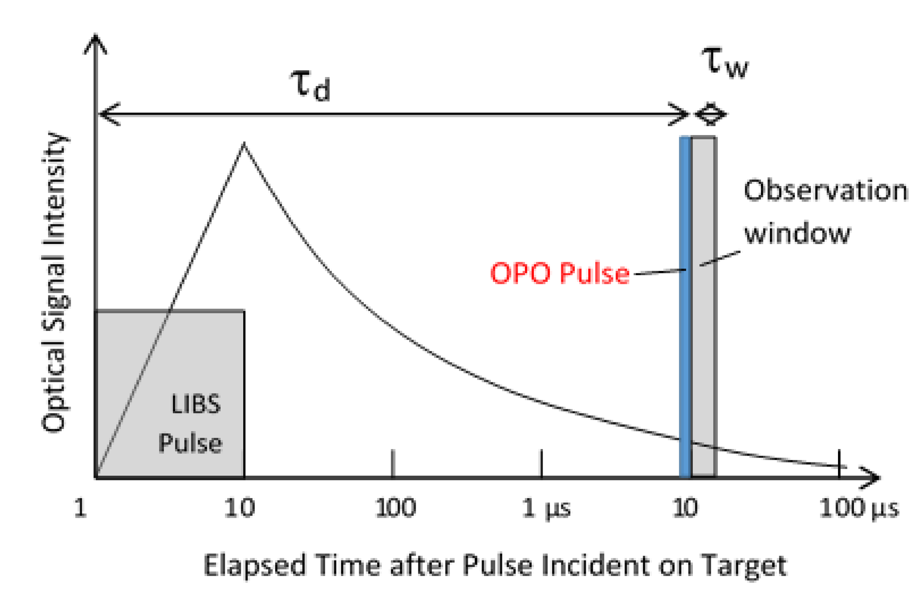


The 202.61 nm line is the most intense and the target for enhancement via pumping (lowering LOD).

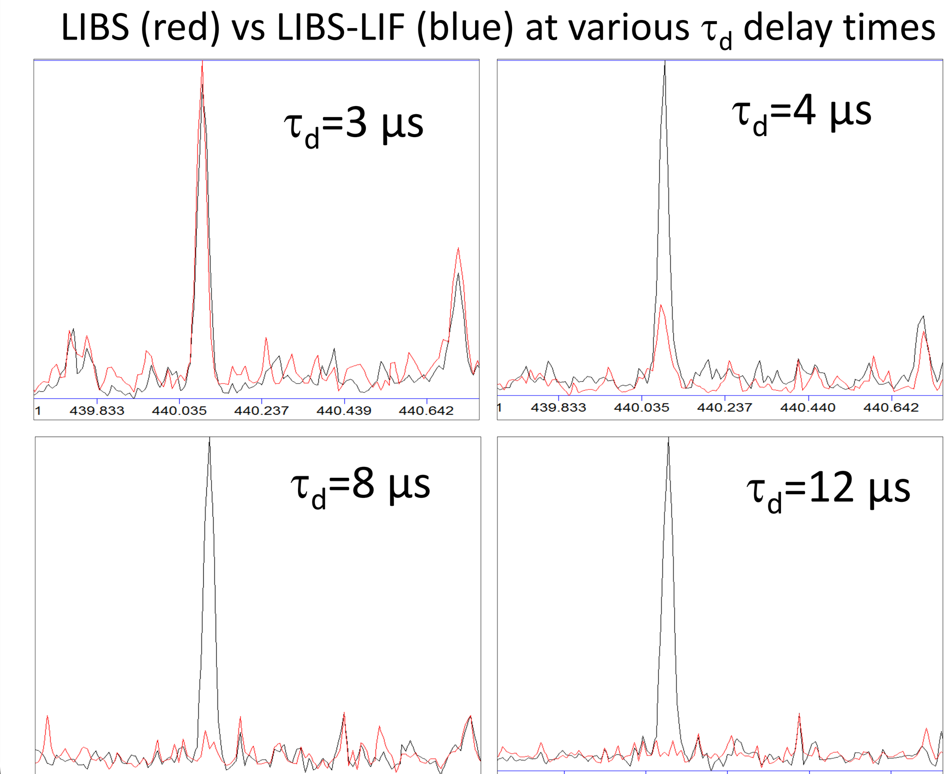
How are the laser pulses timed?

Timing parameters

- Observation of emission just after the OPO pulse for a short window of τ_w=60 ns yielded best results
- The most crucial timing parameter was the interpulse delay (τ_d)
- Longer delays (τ_d>8 μs) gave the best results by allowing more atoms to return to the ground state prior to pumping and decreasing LIBS emission

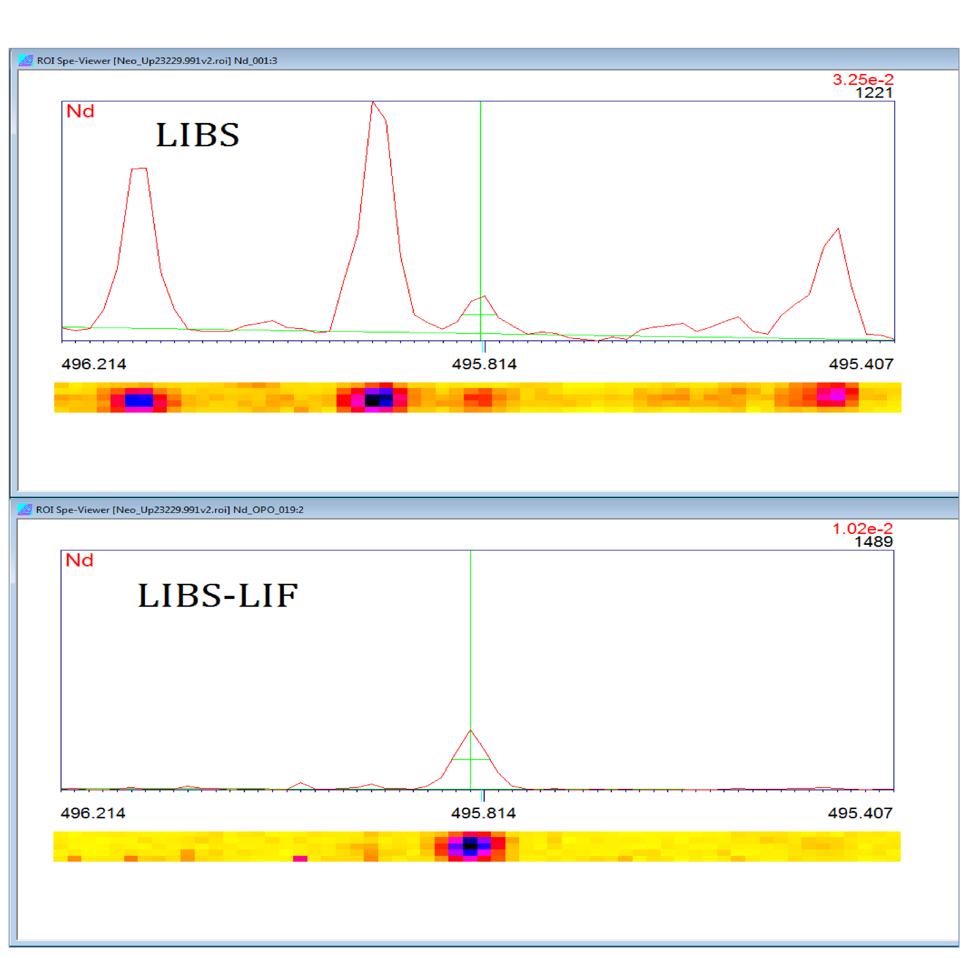


LIBS (red) vs LIBS-LIF (blue) at various τ_d delay times



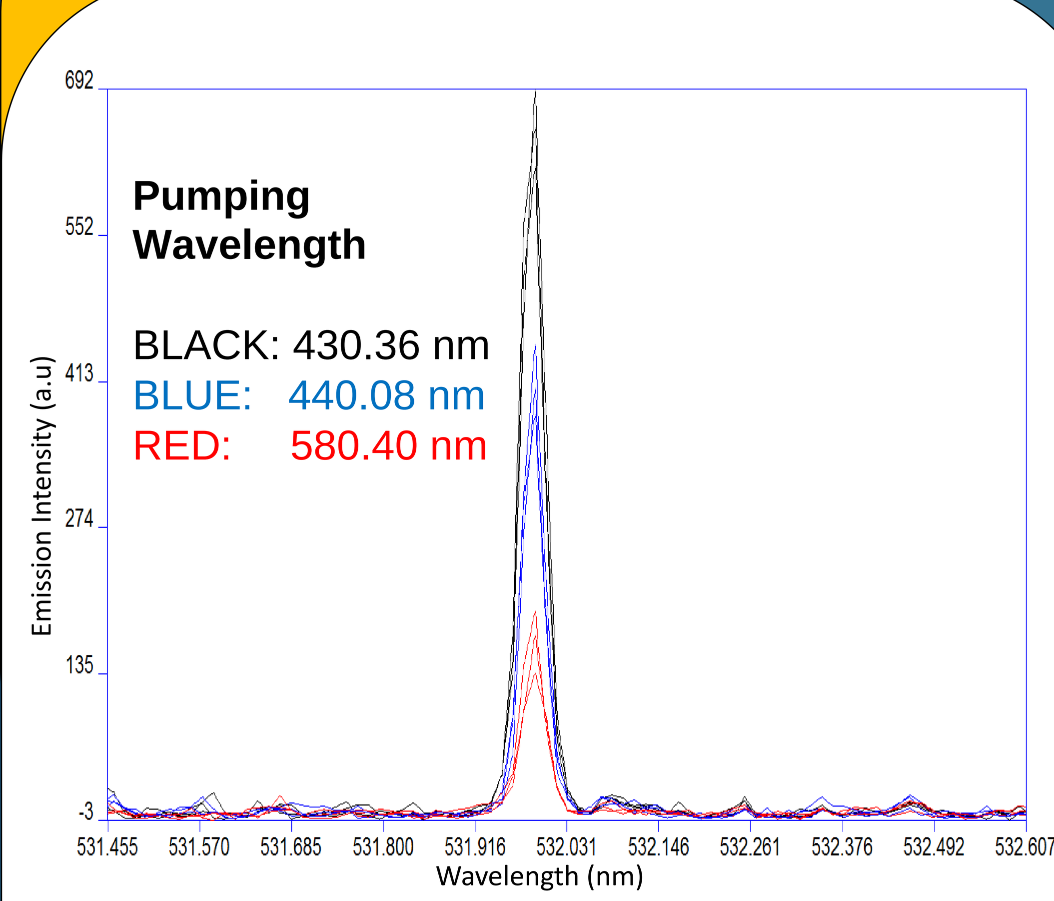
Pumping on 430.36 nm transition in neodymium II

Background reduction using LIBS-LIF



SNR and SBR enhancement of the 495.81 nm line in Nd II, pumping on 430.36 nm

Effect of pumping wavelength on LIF intensity



Nd II pumping with three different OPO wavelengths. The effect on the LIF intensity of the 531.98 nm line can be seen to depend on the lower state initial population.

Future work

In the future, this LIBS-LIF setup may be applied to several projects:

- Quantifying trace amounts of zinc in fingernails as an indicator of nutrition.
- Analysis of pesticide composition.
- Quantifying trace element concentrations in bacteria.
- Detection of heavy metals in blood specimens.
- Improvement of branching ratio measurements in elements with dense spectra.

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References

[1] H. Loudyi , K. Rifaï , S. Laville , F. Vidal , M. Chaker and M. Sabsabi, Improving laser-induced breakdown spectroscopy (LIBS) performance for iron and lead determination in aqueous solutions with laser-induced fluorescence (LIF), *J. Anal. At. Spectrom.* **24**, 1421-1428, (2009).

[2] R.A. Putnam, *Recent Advanced in the Measurement of Rare-Earth Metal transition Probabilities using Laser-Induced Plasma*, University of Windsor, 2014.