Investigation of Emission Enhancement in Dual-Pulse and Resonance-Enhanced Laser-Induced Breakdown Spectroscopy

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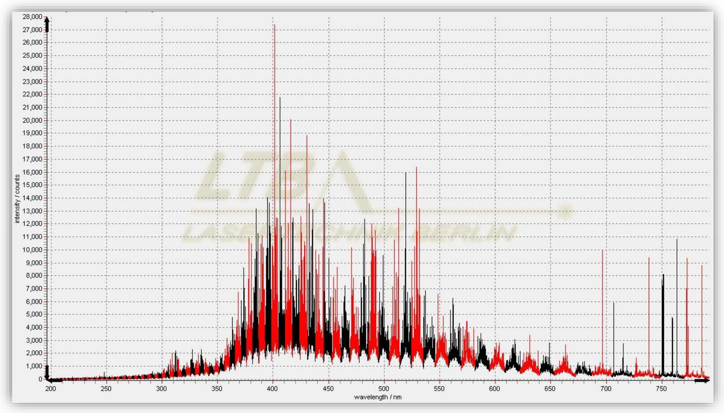
Introduction

Laser-induced breakdown spectroscopy (LIBS) is an elemental analysis technique in which a high pulse energy laser is used to create a plasma on the surface of a sample. The light emitted from this plasma is collected and dispersed to identify and quantify the elemental composition of the sample.



Typical LIBS spectrum obtained from a neodymium sample. Plasma emission intensity plotted as a function of wavelength. (Software: LTB Sophi)

There are a number of techniques that involve coupling a second laser pulse into the LIBS plasma. These include:

Dual-pulse LIBS (DP-LIBS): A second laser pulse thermally re-excites the plasma, increasing the overall light emission from the plasma.

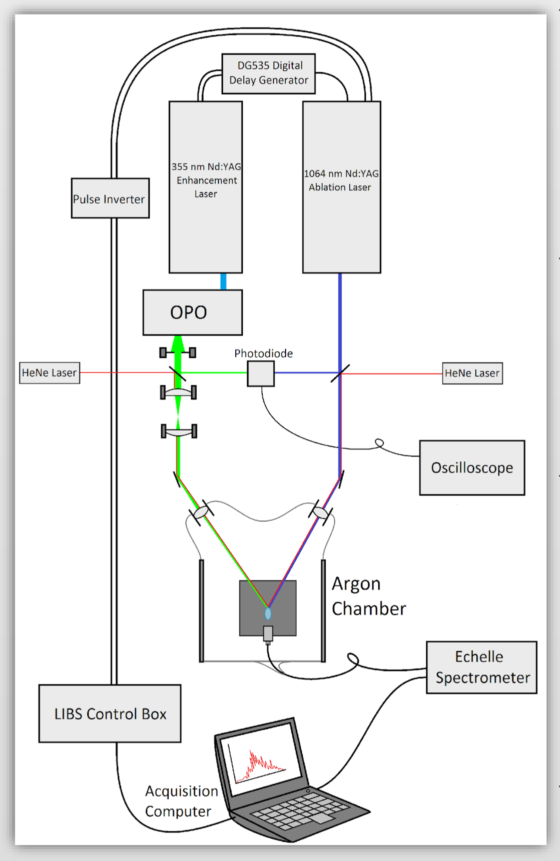
Resonance-enhanced LIBS (RELIBS): Identical to DP-LIBS except that **the wavelength of the second laser is tuned to match an atomic transition of the target sample** (which may improve the coupling of the second laser to the plasma).

LIBS Laser-induced fluorescence (LIBS-LIF): Also uses a second laser that is tuned to an atomic transition of the sample. However, the second laser is set to a much lower pulse energy (or is unfocused) so that **the dominant effect is fluorescence rather than a thermal re-excitation of the plasma.**

Why use two lasers?

- The second laser pulse provides emission enhancement in cases where a single-pulse LIBS plasma would be too weak to use for accurate measurements, such as in handheld LIBS or on materials where plasma formation is poor (e.g. in liquids).
- It can increase the spectrum's signal-to-noise ratio.
- In LIBS-LIF, the limit of detection of trace elements in a sample can be improved to sub-ppm, especially in samples with spectra that are dense with many emission lines.

Experimental Setup

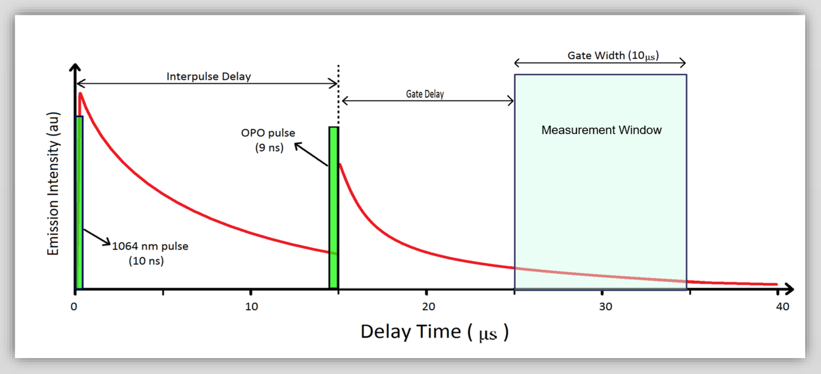


Continuum Surelite SL-10 Nd:YAG
- 1064 nm wavelength
- Pulse duration: ~10 ns
- Attenuation optics allow for variable pulse energy
- Max pulse energy: 150 mJ/pulse
- Pulse repetition rate: 10 Hz

Spectra Physics Nd:YAG
- 355 nm wavelength
- Pulse duration: ~9 ns
- Max pulse energy: 220 mJ/pulse
- Used to pump the OPO
- Pulse repetition rate: 10 Hz

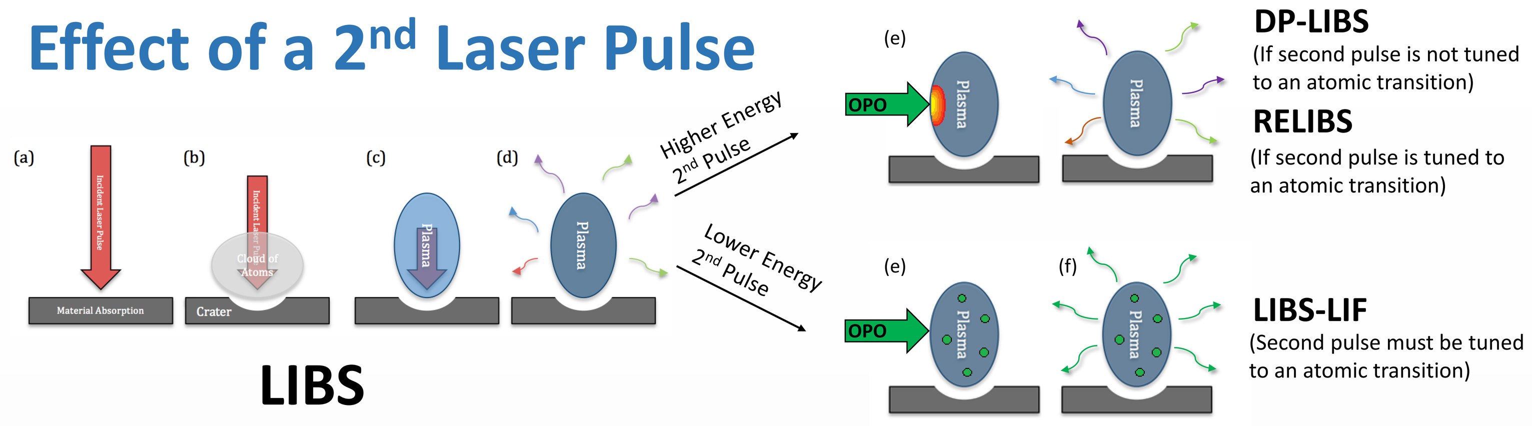
GWU versaScan OPO
- Optical Parametric Oscillator
- Can be tuned continuously from 400 nm - 700 nm
- Attenuation optics allow for variable pulse energy
- Output pulse energy: 10 to 100 mJ/pulse, depending on wavelength

LTB Aryelle échelle spectrometer
- Spectral range: 200 nm - 800 nm
- Spectral resolution on the order of picometers and time resolution on the order of nanoseconds



Timing Parameters
- **Interpulse delay:** The time between the first laser pulse (which creates the plasma) and the second pulse (which interacts with the plasma). Typically set between 1 μs and 25 μs.
- **Gate delay:** The time between the second laser pulse and when the spectrometer begins collecting light from the plasma.
- **Gate width:** The amount of time that the spectrometer collects light from the plasma.

Effect of a 2nd Laser Pulse

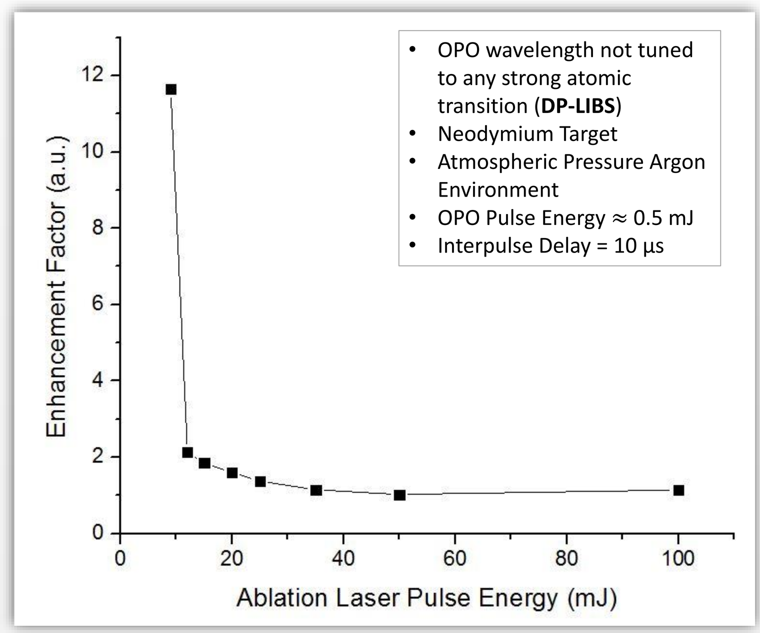


KEY IDEA

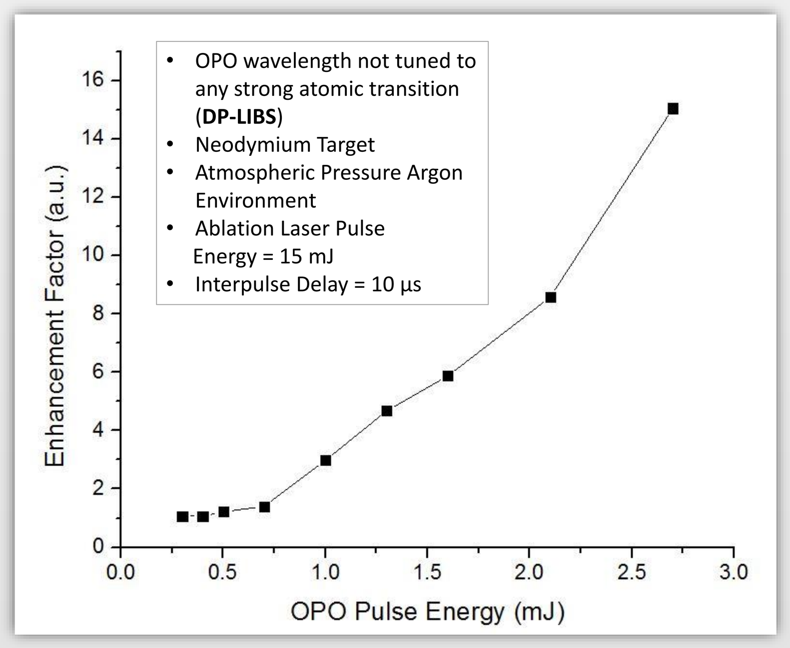
Although extensive studies have been conducted using dual-pulse techniques, **the effects of using a second laser with a tunable wavelength have not been exhaustively studied**. Thus the goal of this work is to establish the groundwork for a more in-depth investigation of how and why the wavelength of the second pulse affects RELIBS and LIBS-LIF measurements.

Laser Energy

In the following experiments, the pulse energies of the ablation laser and OPO laser were varied and enhancement (as described in the 'Data Analysis' section) was measured. **The goal was to determine an energy regime for which DP-LIBS and RELIBS enhancement is most useful.**

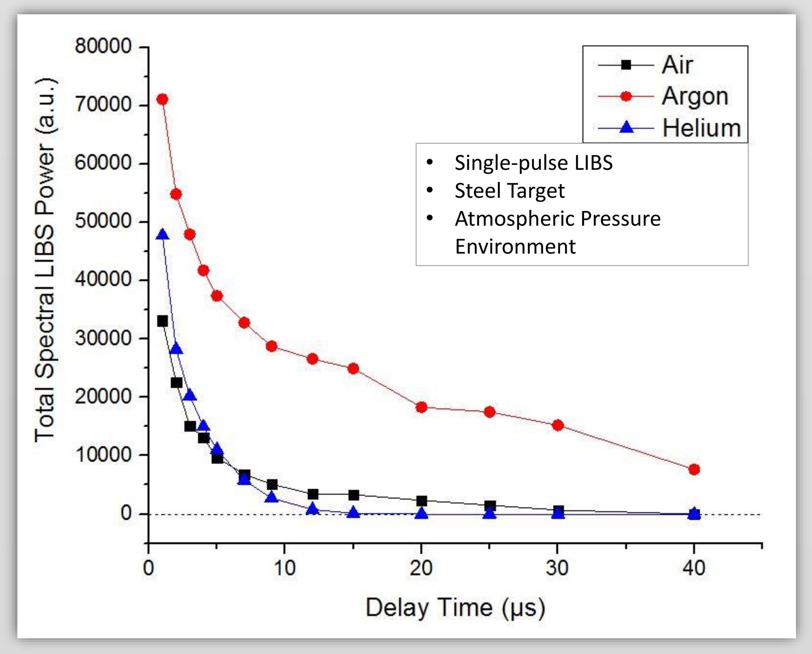


Conclusion: In the limit of lower ablation pulse energy and when the OPO pulse energy was held constant (at a pulse energy where ablation does not occur due to the OPO pulse), the signal enhancement increased substantially. This data indicates that DP-LIBS starts becoming most effective in regimes where the ablation pulse is near the ablation threshold (< 15 mJ in our experiment).



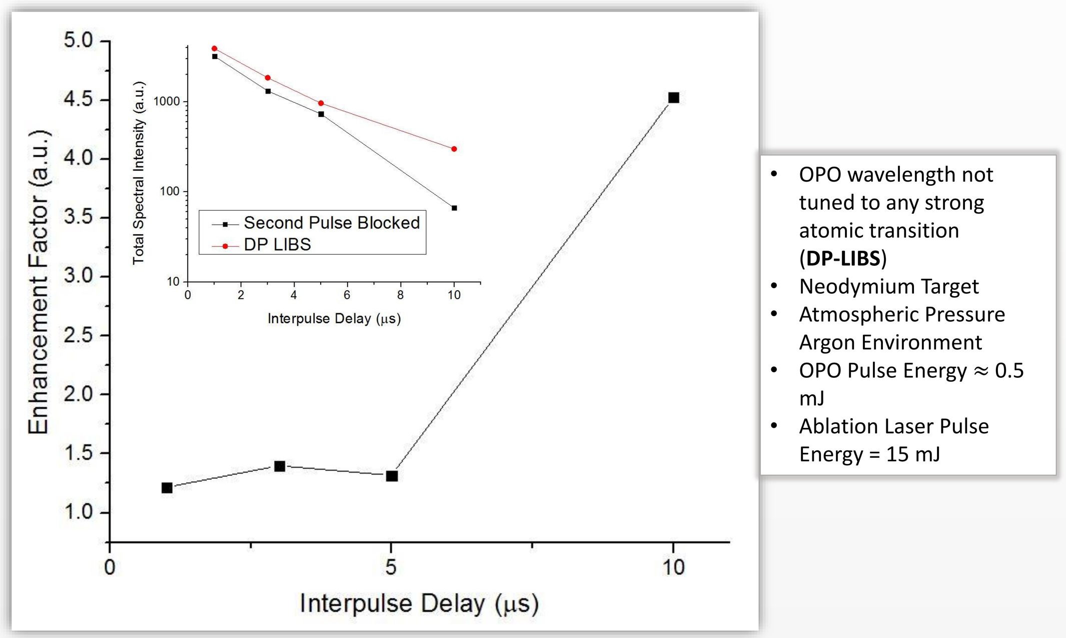
Conclusion: When ablation pulse energy was held constant and OPO pulse energy was increased, enhancement increased. However some of this enhancement was a result of the OPO pulse becoming more ablative itself as the pulse energy increased.

Gaseous Environment



Conclusion: This plot shows the behaviour of plasma intensity as a function of gate delay time in three different gaseous environments. The plasma emission in air and helium decayed more quickly than it did in argon. This information helps determine which gate delay times to use when utilizing dual-laser techniques. This is important for LIBS-LIF, since the LIF pulse should hit the plasma at a time when no LIBS emission is observed, which allows for the measurement of fluorescence.

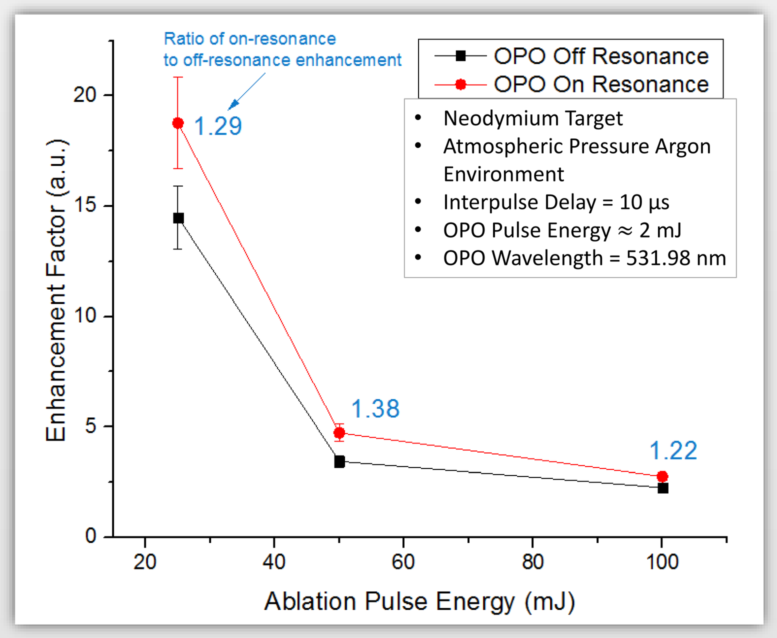
Interpulse Delay



Conclusion: In this experiment, dual-pulse enhancement was measured as a function of interpulse delay time. As the time between the two laser pulses was increased, the signal enhancement (which is a ratio) increased; although the intensities of both signals (inset) decreased.

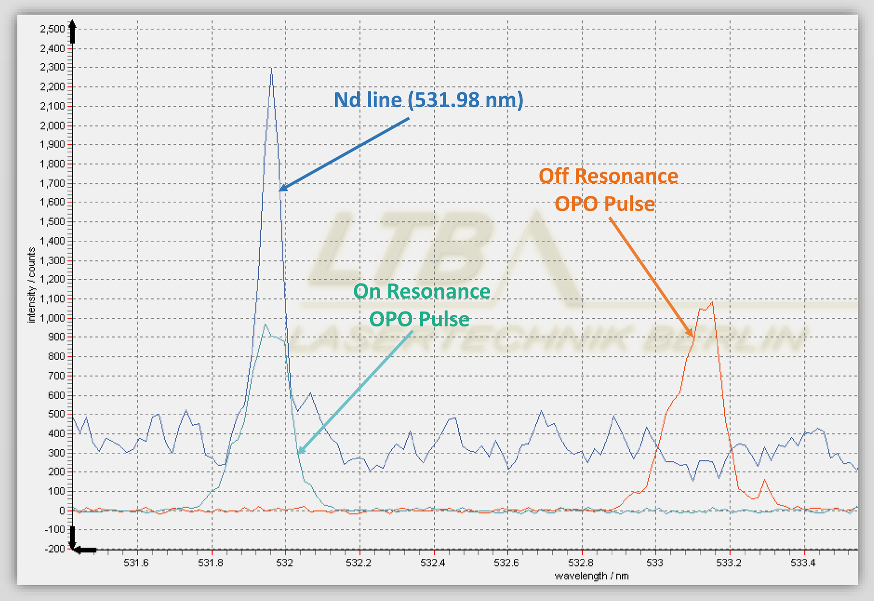
DP-LIBS is not advantageous if the only goal is greater intensity as one can normally achieve this by using a short delay time with single-pulse LIBS. However, **in circumstances where the plasma is initially weak, DP-LIBS can be useful** since the enhancement factor is greater for weak plasmas (which can be seen in the case of longer interpulse delay times).

OPO Wavelength



Conclusion: The above figure demonstrates the effect of tuning the OPO pulse's wavelength to that of a strong observable emission line (**on resonance** with a transition in neodymium) as opposed to it being tuned to a wavelength corresponding to a featureless part of the neodymium spectrum (**off resonance**).

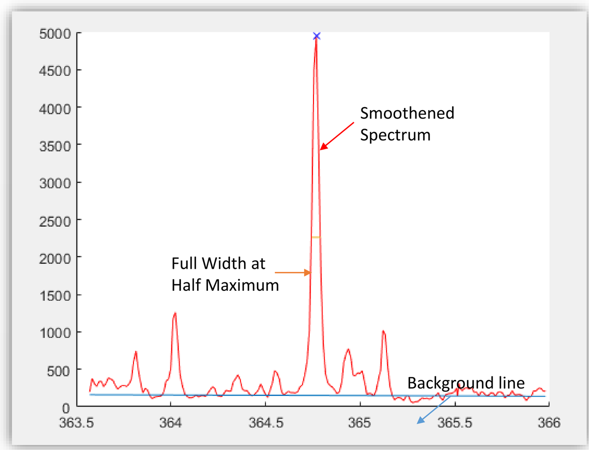
It is evident that being **on resonance** tends to increase the enhancement factor (with the numbers in the figure indicating the ratio of **on resonance** to **off resonance** enhancement as a function of pulse energy). Additional tests will be done to determine any trends in the ratio of **on resonance** to **off resonance** enhancement with respect to various parameters.



It should be noted that since neodymium's spectrum is very dense with emission lines, it is possible that there were weak emission lines that overlapped with the **off resonance** pulse. However due to the weakness of these lines, it is assumed that any effects due to these lines was small compared to that of strong lines. Quantifying this will be the subject of future work.

How was Data Analysis Performed?

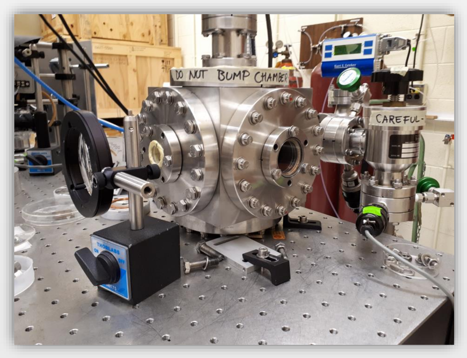
A MATLAB script was written to find the integrated area under specified emission lines in the measured spectra. This method provides a more accurate measurement of the emission intensity compared to using just the height of the peak.



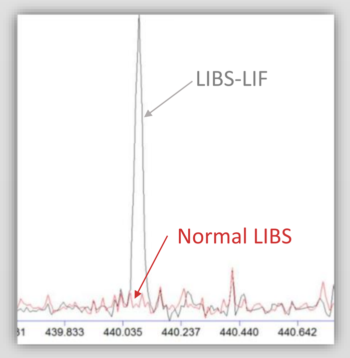
What the script does (MATLAB):
- Uses a Savitzky-Golay filter to smooth the data which in turn reduces noise.
- Finds peaks by referencing a file containing the wavelengths of interest.
- Calculates the area under the background-subtracted peaks using the built-in MATLAB trapezoidal integration method.

To measure overall spectrum intensity, several emission lines of the target sample that could be consistently measured in most conditions were chosen (10 lines for neodymium and 65 for steel). The sum of these values was used to represent the overall spectrum intensity. The **enhancement factor** was defined as the ratio of the overall spectrum intensity of the dual-laser enhanced plasma to the intensity of a single-pulse LIBS plasma under the same conditions.

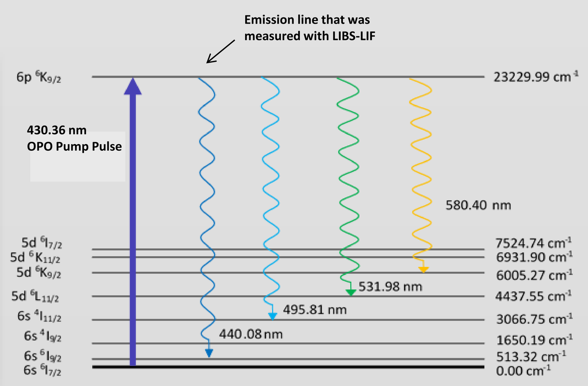
Future Work



- Investigating parameters for DP-LIBS and RELIBS in an evacuated environment using a vacuum chamber setup. Performing experiments at lower pressures can be favorable due to the reduced blending of lines and increase in spectral resolution.
- Working in low energy **(non-destructive)** regimes that showed evidence of significant enhancement.
- Testing the physical mechanisms that may be responsible for the observed RELIBS behaviour.
- Testing RELIBS on materials for which the initial plasma is too weak to measure the desired lines using only single-pulse LIBS (which is where RELIBS becomes most useful).
- **Performing a study of the parameters for LIBS-LIF on various samples (including neodymium).** LIBS-LIF can measure spectral lines that cannot normally be measured with LIBS due to the spectrum being too dense with lines or the emission of the line being too weak. This can be done by tuning the second laser pulse to an atomic transition that has the same upper energy level as the line of interest.



Nd II LIBS Spectrum



Nd II Grotrian Diagram

Acknowledgements

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[2] Russell A. Putnam, *Recent Advances in the Measurement of Rare-Earth Metal Transition Probabilities Using Laser-Induced Plasmas*, University of Windsor, 2014