The Use of Resonant Laser Pulses for Emission Enhancement in Laser-Induced Plasmas

presented at the 2017 Pittcon
Chicago, IL March 2017

New Developments and Challenges in
Laser Induced Breakdown Spectroscopy

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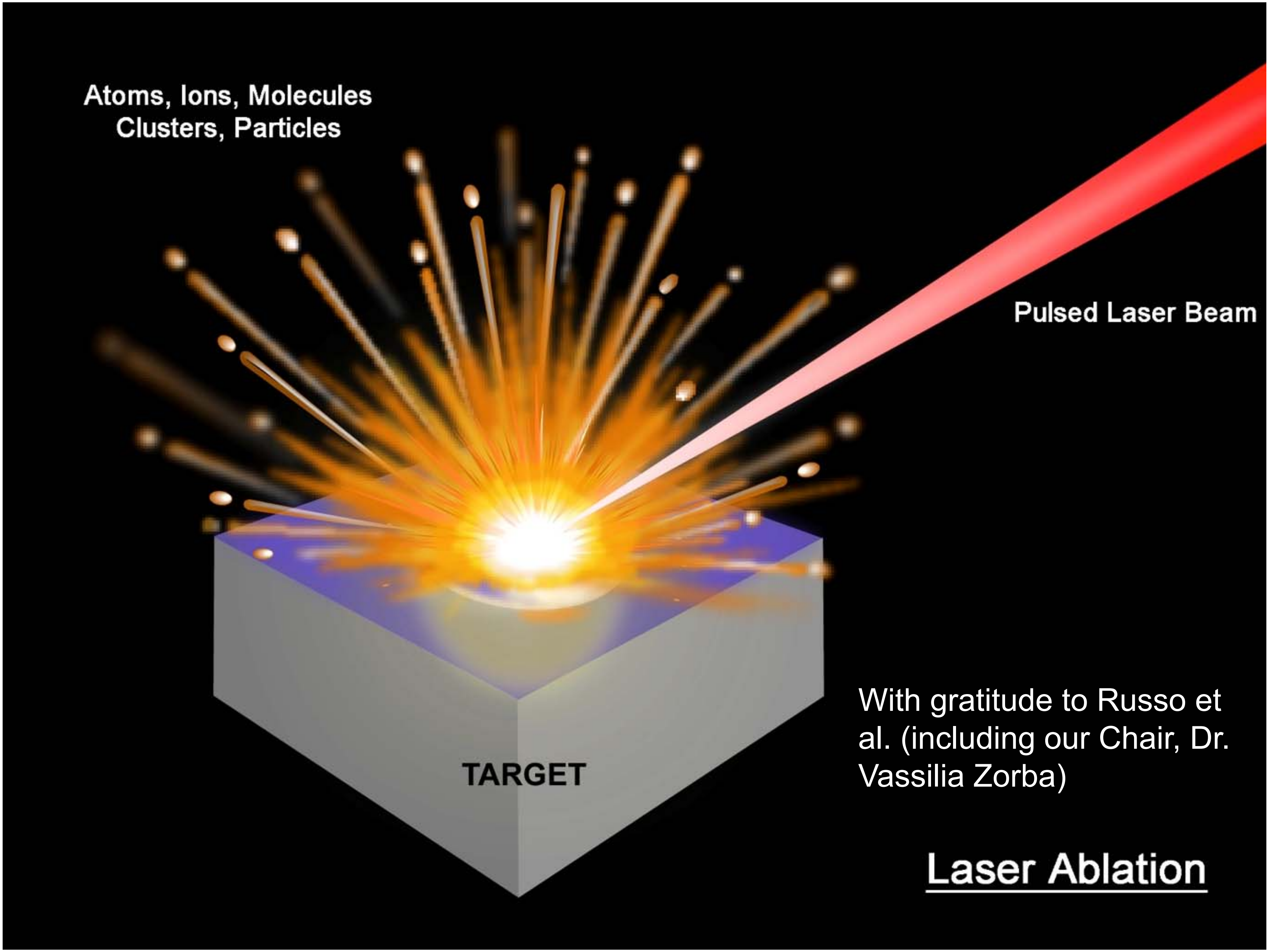
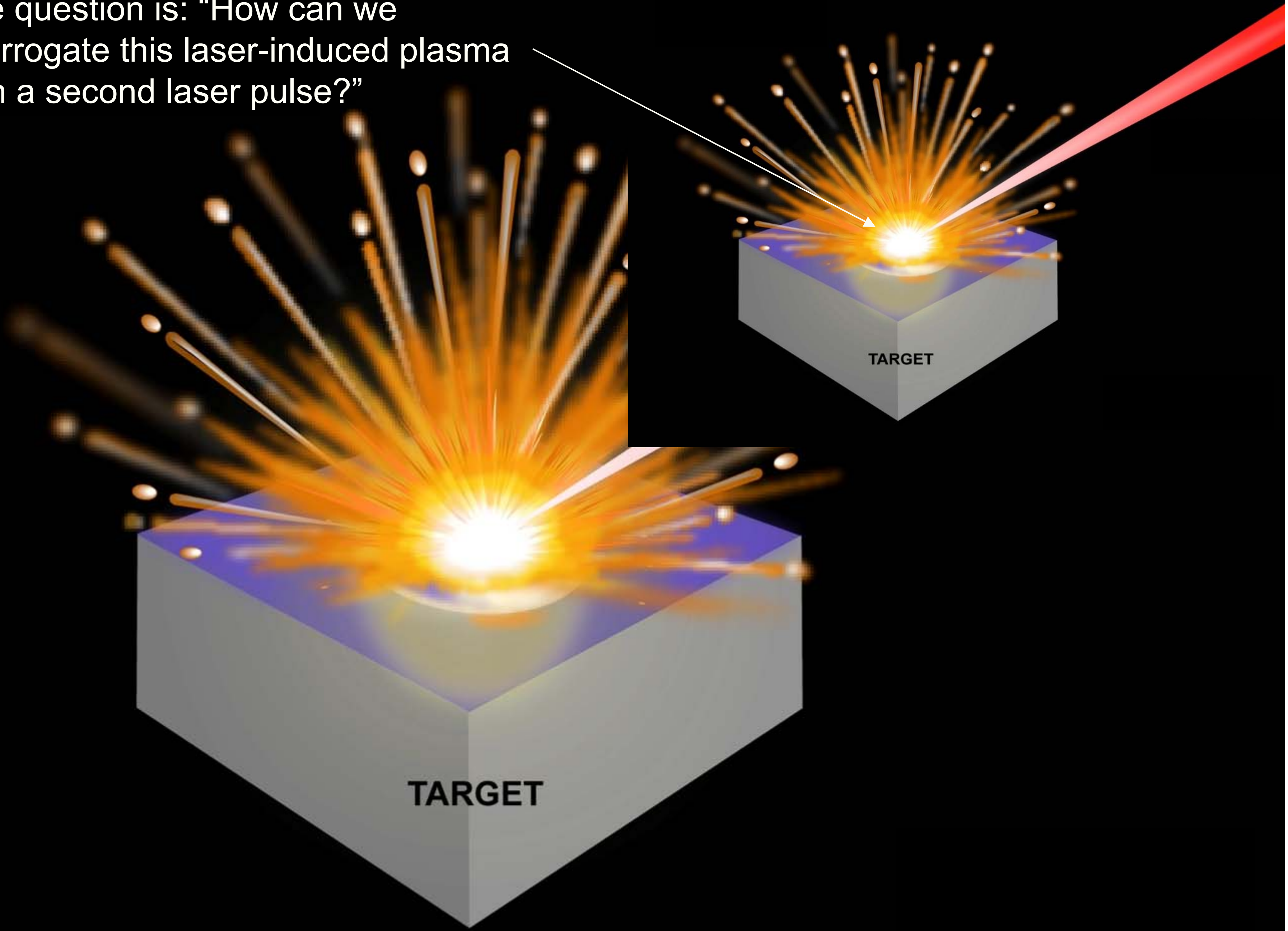

Atoms, Ions, Molecules
Clusters, Particles
Pulsed Laser Beam
TARGET
With gratitude to Russo et al. (including our Chair, Dr. Vassilia Zorba)
Laser Ablation

The question is: “How can we interrogate this laser-induced plasma with a second laser pulse?”



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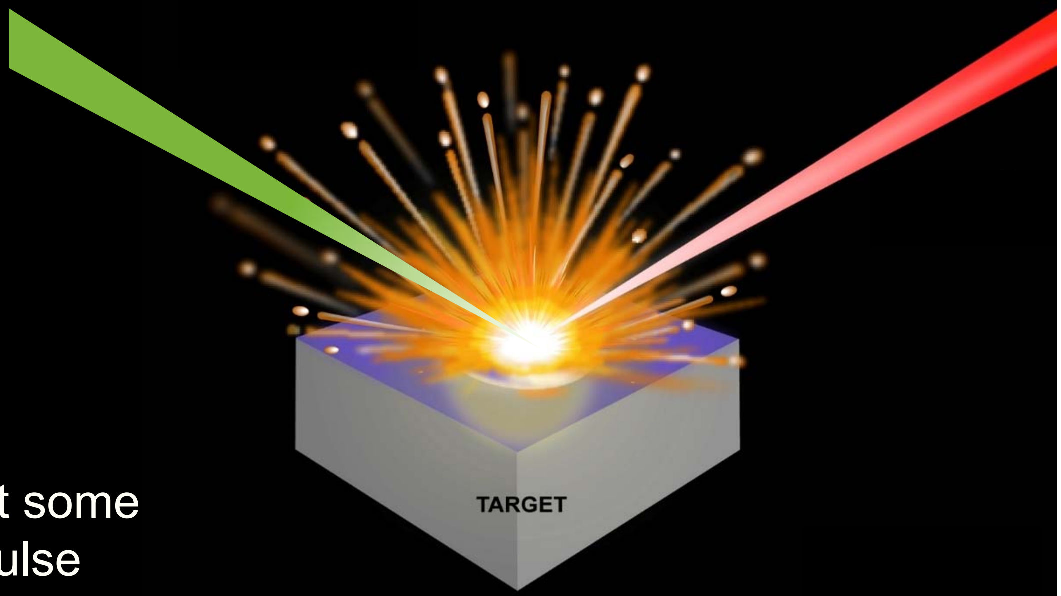

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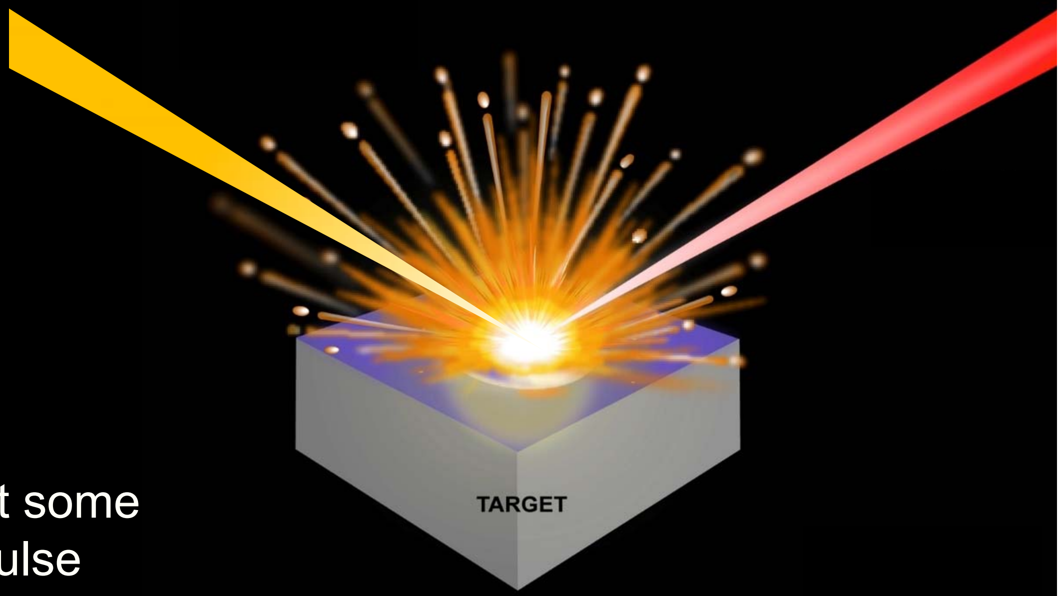

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If this second pulse is on resonance with an atomic transition of an atom/ion in the plasma and it can form a second spark, we call this “resonance-enhanced LIBS” (**RELIBS**)

[see *Yip and Cheung SAB 2009* or *Goueguel et al. JAAS 2010*]

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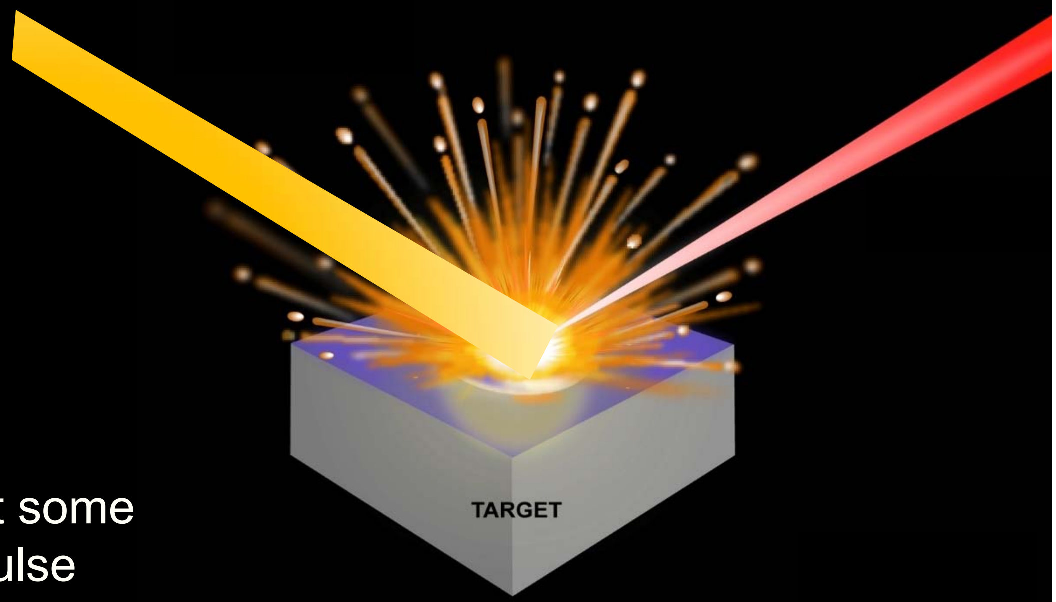

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If this second pulse is on resonance with an atomic transition of an atom/ion in the plasma and the pulse is very weak or unfocused, we call this (**LIBS-LIF**)

[see *Hilbk-Kortenbruck et al.* or *Telle et al. SAB 2001*]

Advantages of the Two-Beam Technique

- Substantial improvement in plasma emission from difficult targets (i.e. liquids)
- Significant reduction of LOD of trace analytes
  - ppb concentrations;
  - attomole, sub-fg mass limits
- Elimination of overlapping emission peaks in dense spectra

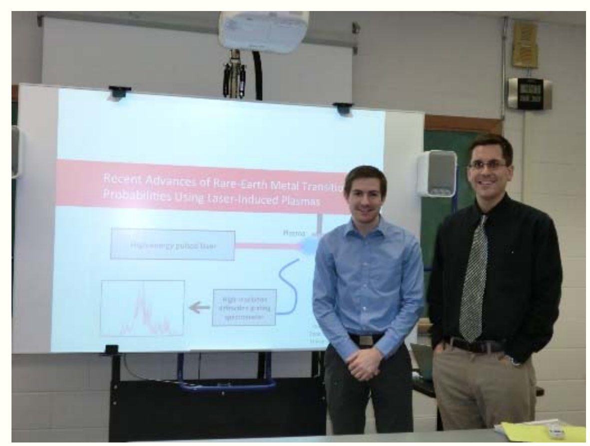
Outline

- Investigation of LIBS-LIF in low-pressure lanthanide plasmas
- Investigation of RELIBS in atmospheric pressure lanthanide plasmas
- Future plans for LIBS-LIF in biomedical/biological specimens

This work was motivated by a desire to measure absolute transition probabilities in lanthanide ions using a laser-induced plasma (laboratory astrophysics).

Initiated by Caleb Ryder (PhD, 2012)

Concluded by Russell Putnam (MSc, 2014)



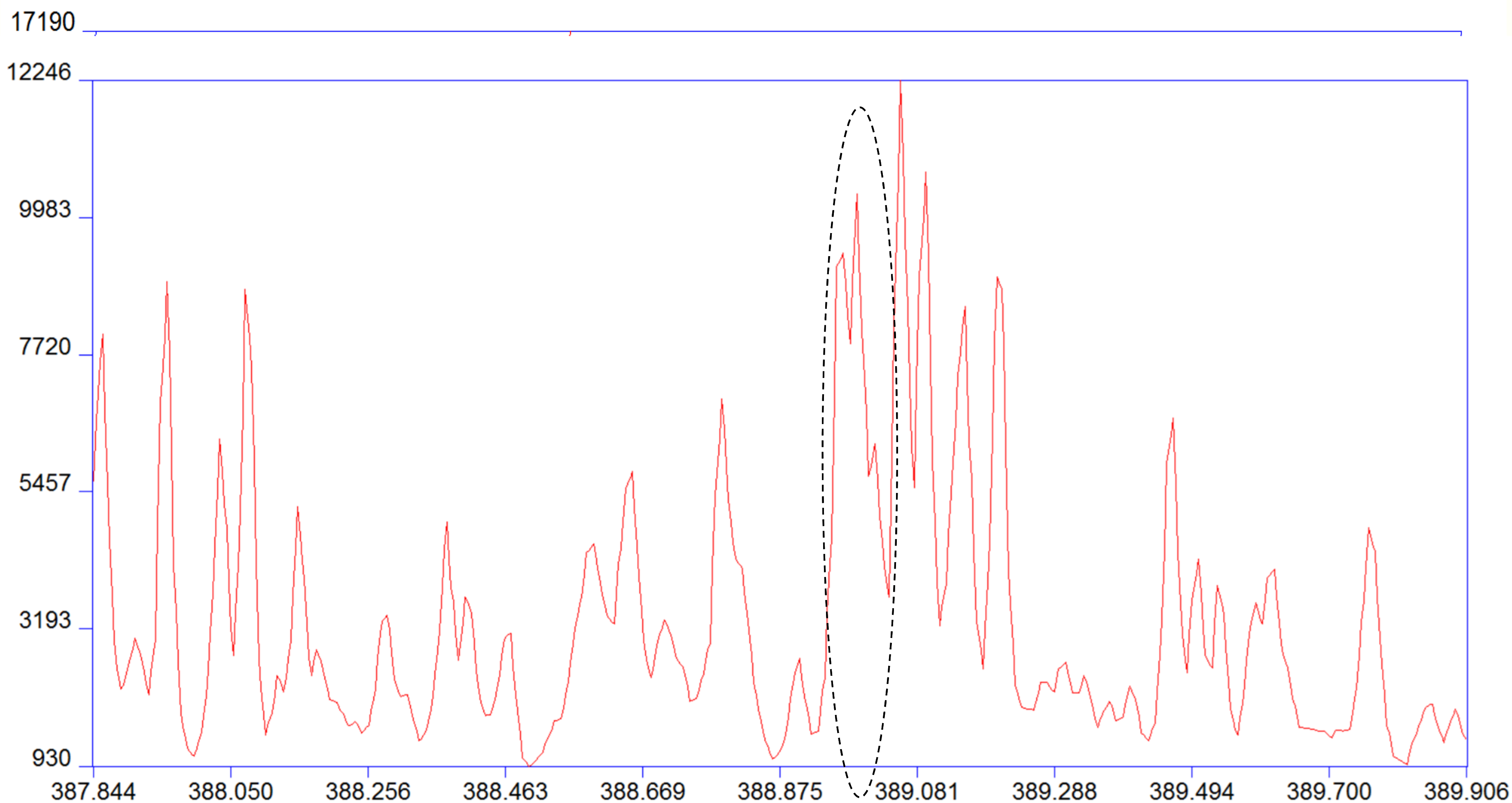
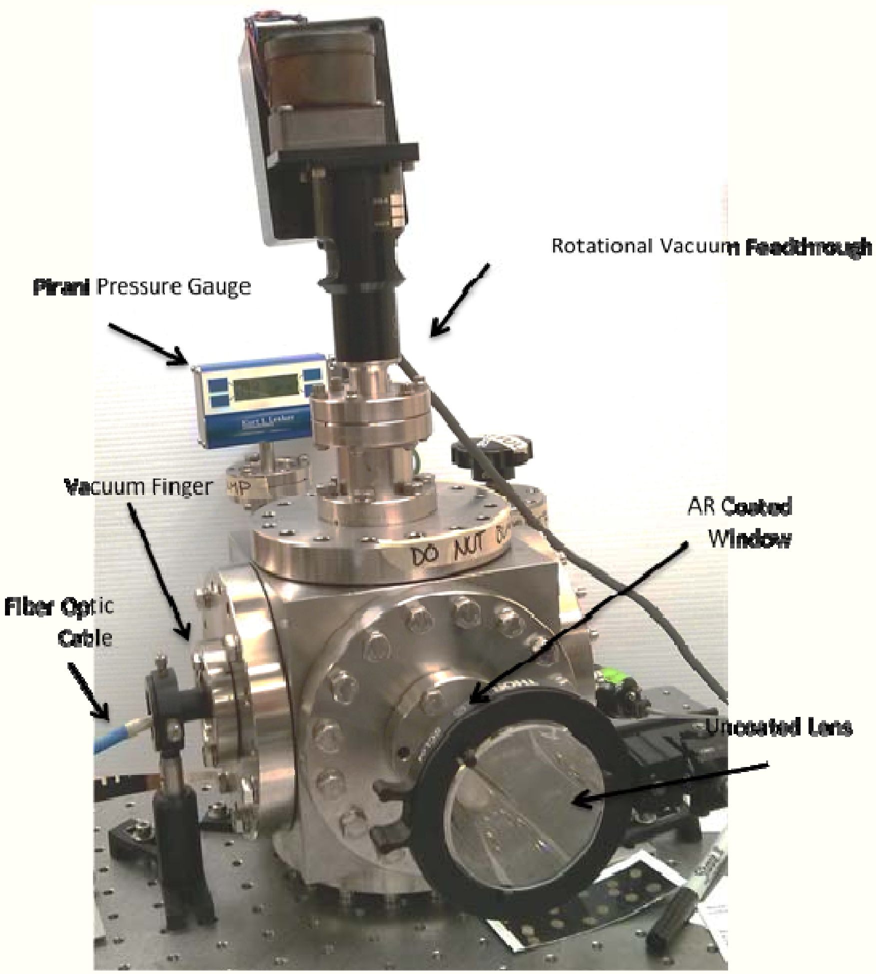
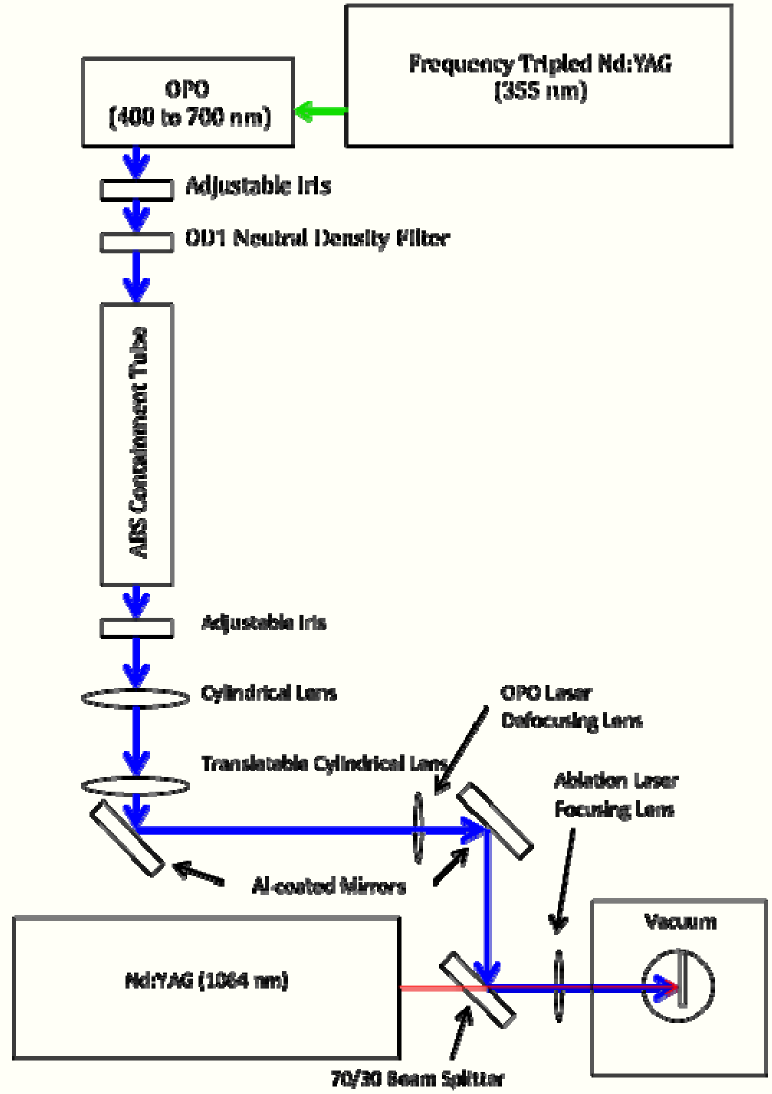


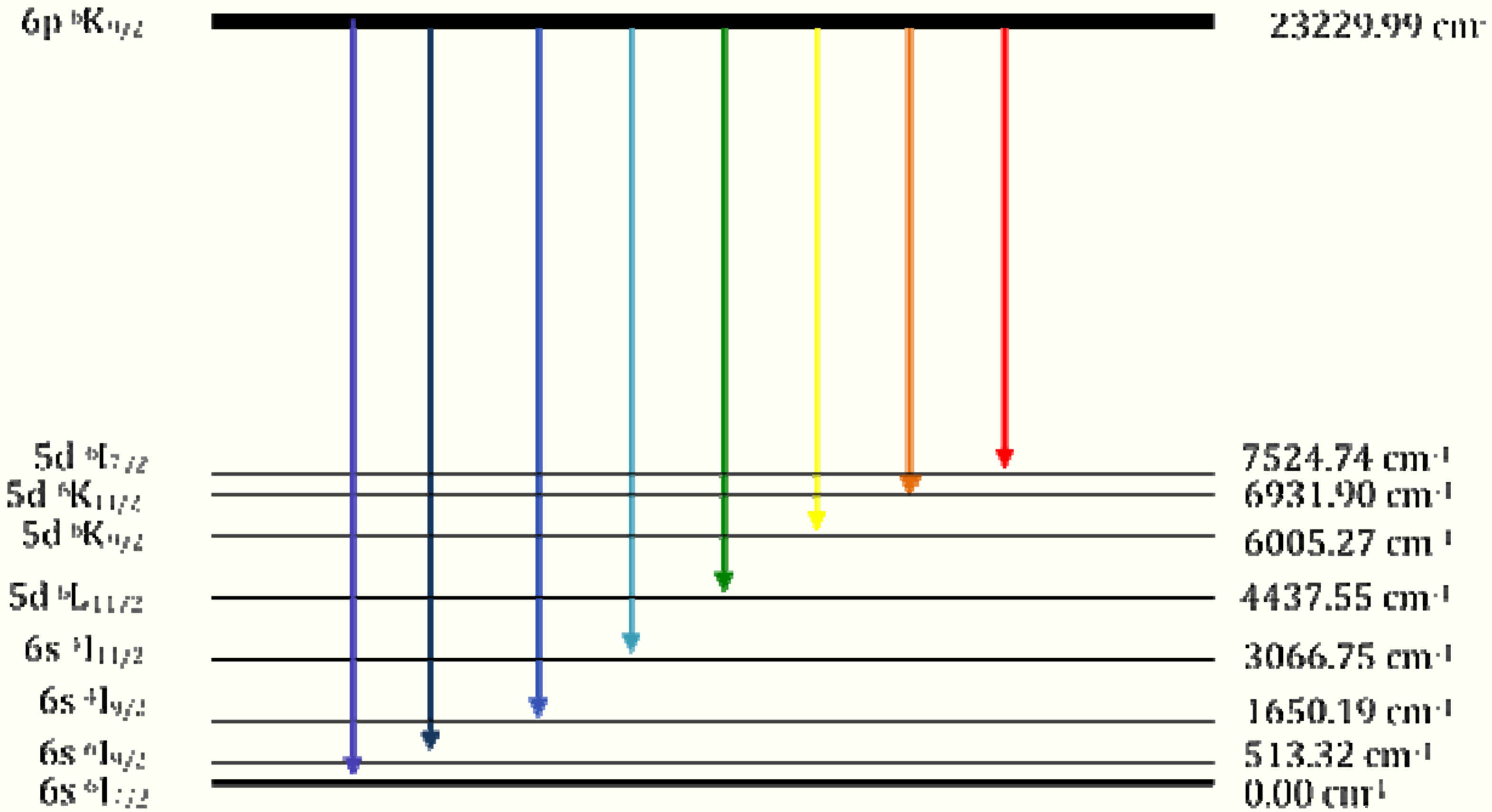
Figure 4.3 A neutral neodymium LIBS spectrum with a gate delay of 3000 ns and gate width of 10000 ns. The majority of the neutral emission lines are between 370 and 550 nm.

Investigation of LIBS-LIF in low-pressure lanthanide plasmas

- 1 torr Ar environment
- 99.99% Nd target

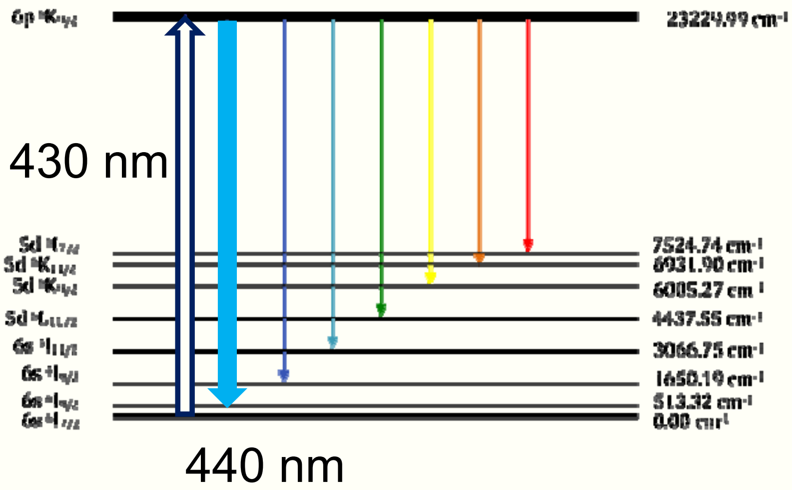


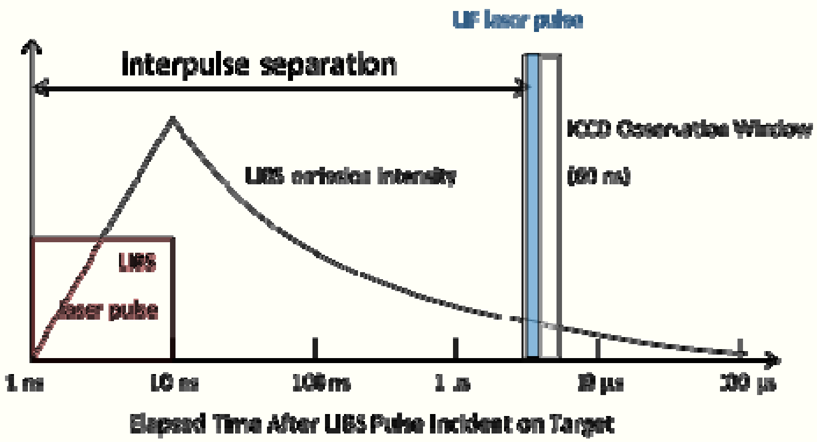


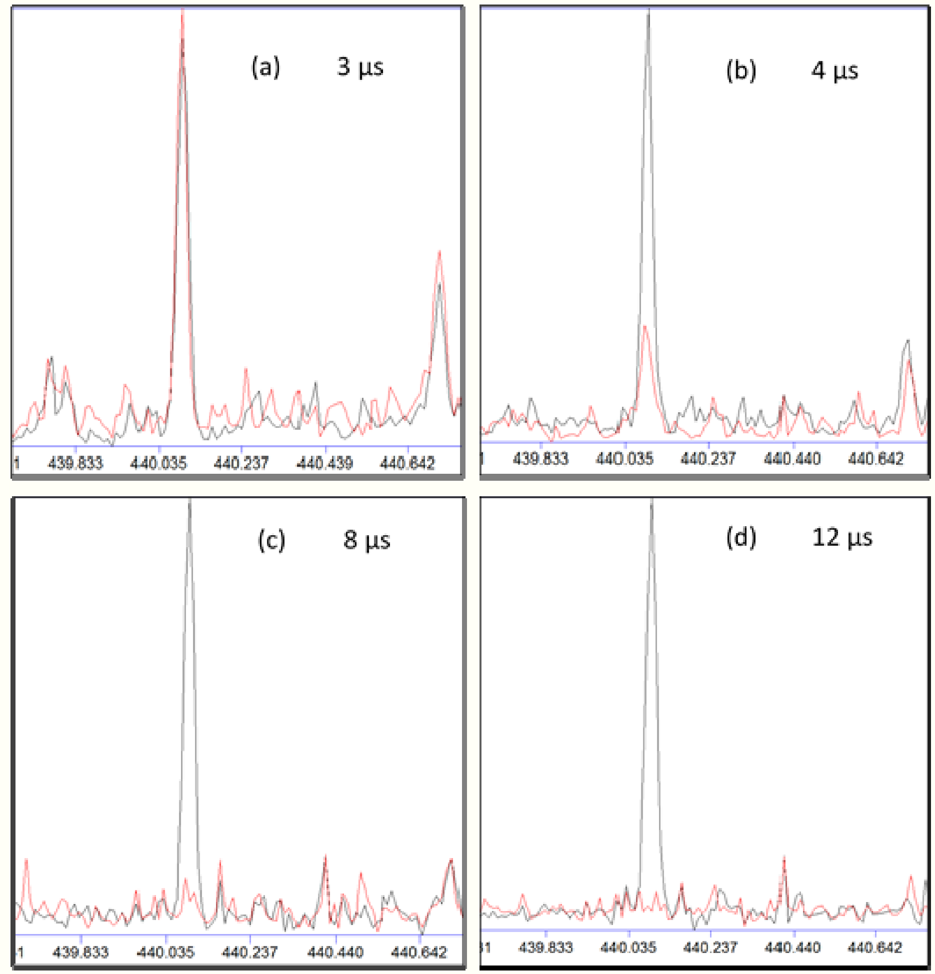


Partial Grotrian diagram of NdII. All transitions are observed in a LIBS plasma.

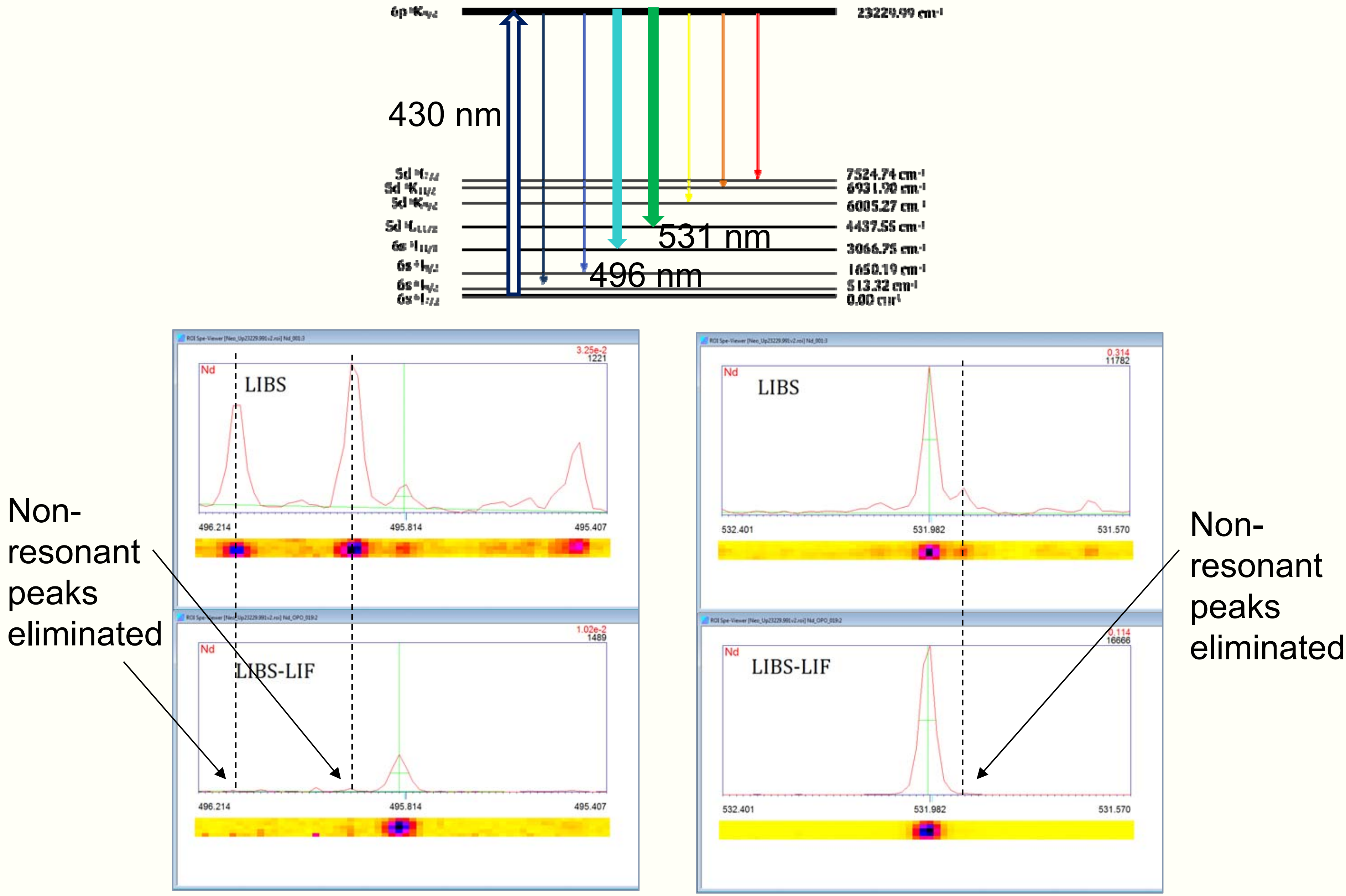
Investigation of LIBS-LIF in low-pressure lanthanide plasmas
Dependence on interpulse timing



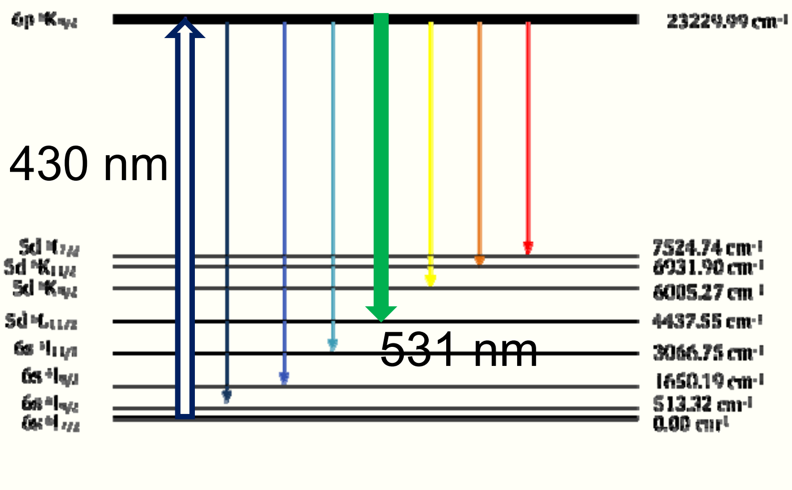


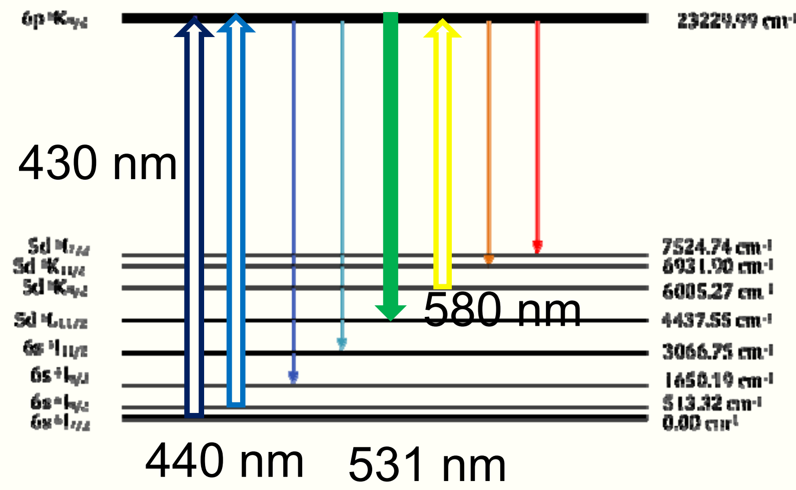


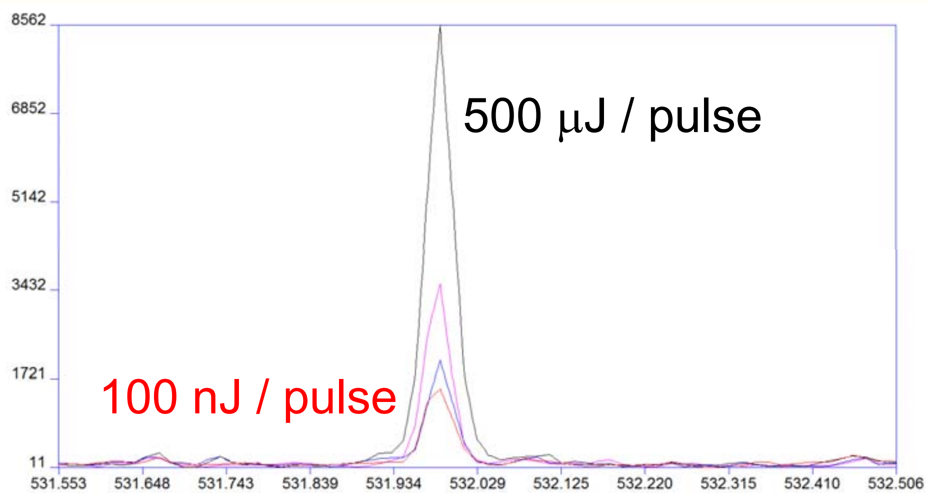
Investigation of LIBS-LIF in low-pressure lanthanide plasmas

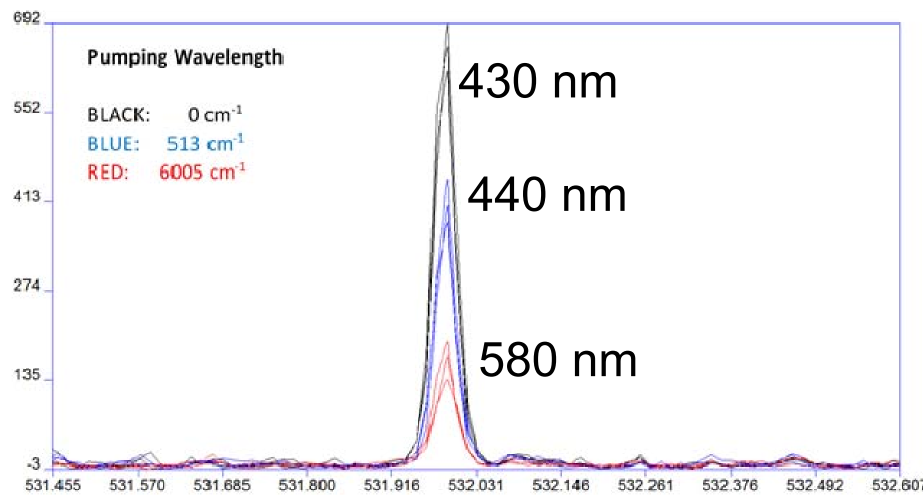


Investigation of LIBS-LIF in low-pressure lanthanide plasmas
Effect of LIF pulse energy and pumping transition

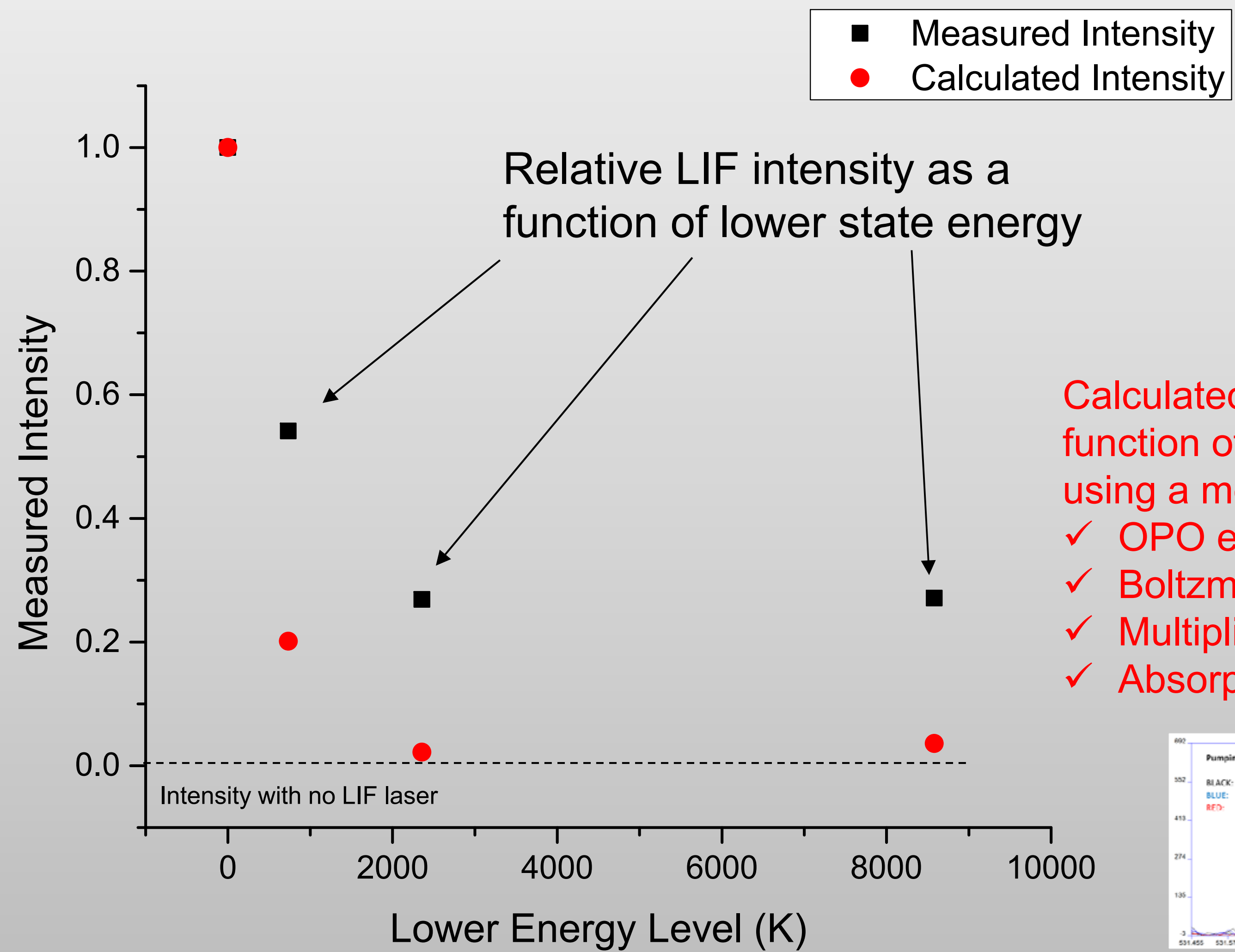






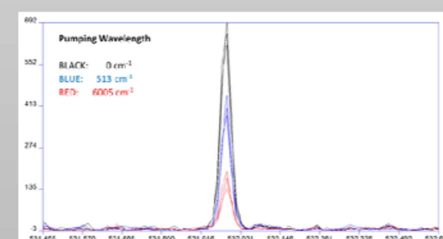


Investigation of LIBS-LIF in low-pressure lanthanide plasmas
Things we cannot yet explain

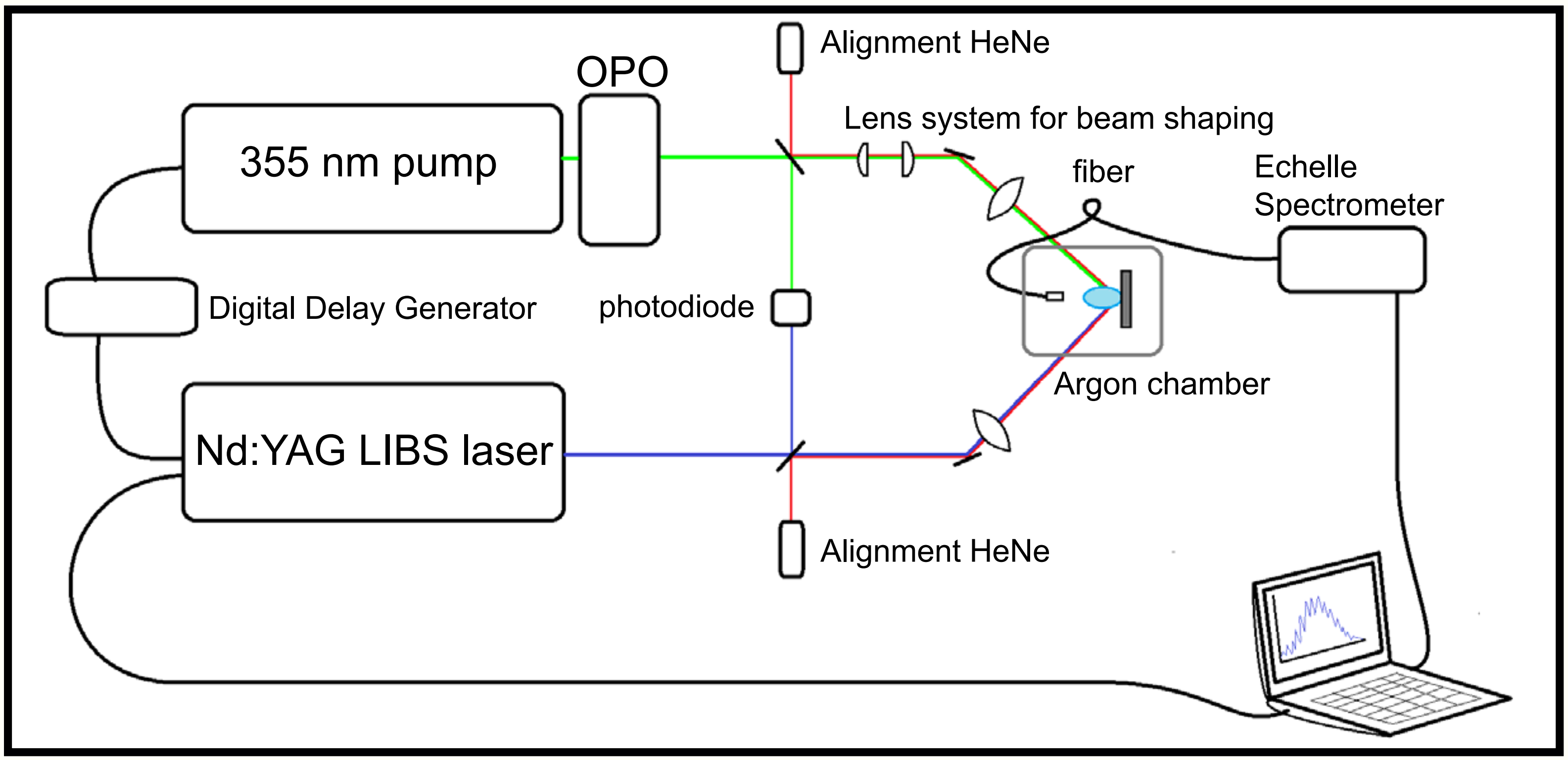


Calculated LIF intensity as a function of lower state energy using a model which includes:

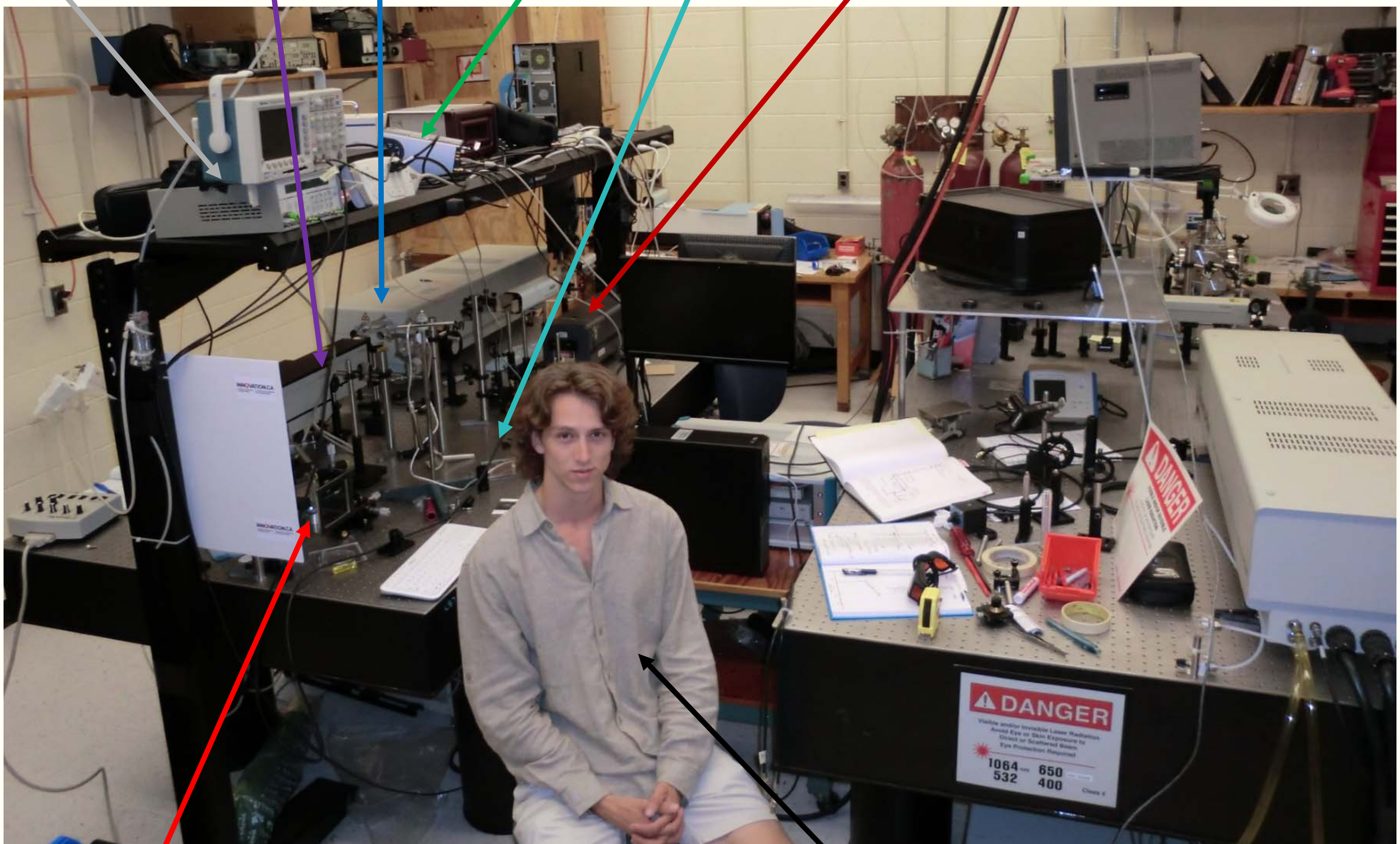
- ✓ OPO energy
- ✓ Boltzmann population
- ✓ Multiplicity of lower state
- ✓ Absorption oscillator strength



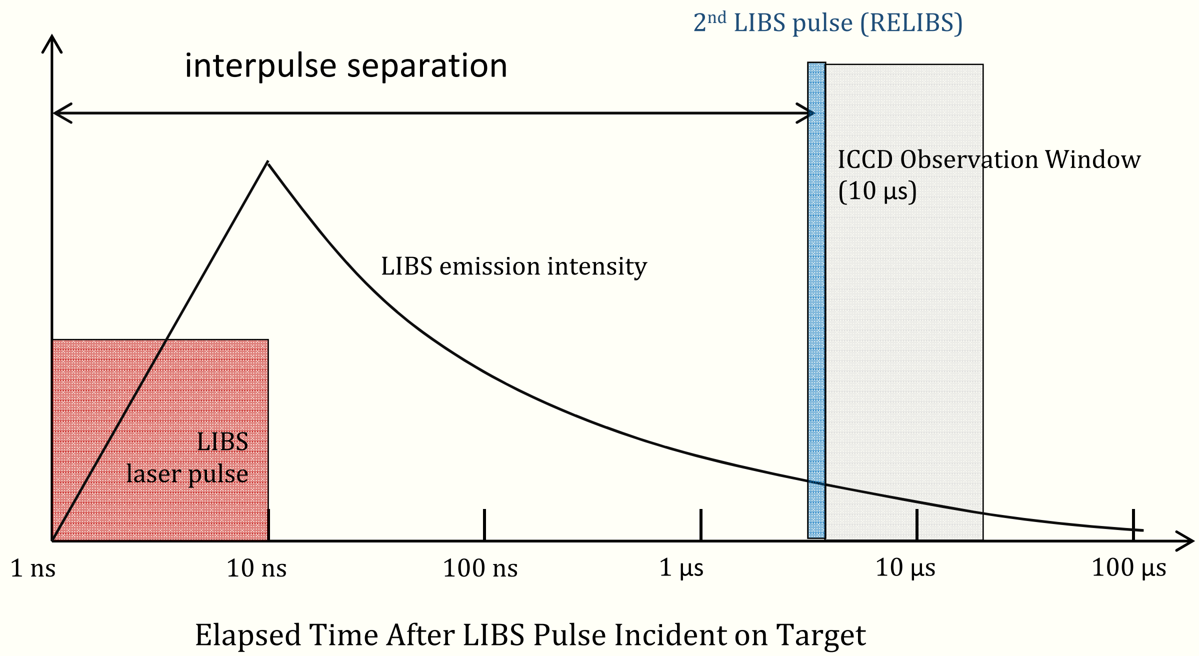
To begin investigations in biomedical specimens at atmospheric pressure we constructed a new system



Investigation of RELIBS in atmospheric pressure lanthanide plasmas



Investigation of RELIBS in atmospheric pressure lanthanide plasmas



1. 120 mJ 1064 nm laser creates first LIBS plasma.
2. OPO pulse is fired into the first plasma at varying times after the LIBS pulse.
3. The resulting emission is observed for 10 microseconds after second pulse.

<u>Three experiments were performed:</u>

- With OPO laser on Nd resonance
- With OPO laser slightly off-resonance
- With no LIBS pulse at all

An important definition difference!

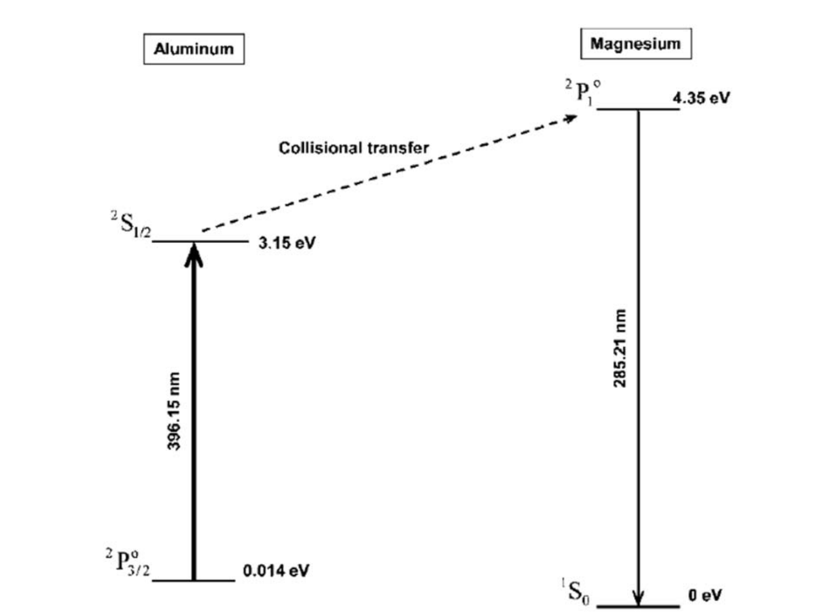


Fig. 2 Partial Grotrian diagram for excitation of magnesium from selective excitation of aluminium atoms.

J. Anal. At. Spectrom., 2010, **25**, 635–644 | 637

From *Goueguel et al. JAAS 2010* which is Mohamad Sabsabi's group at NCR Canada.

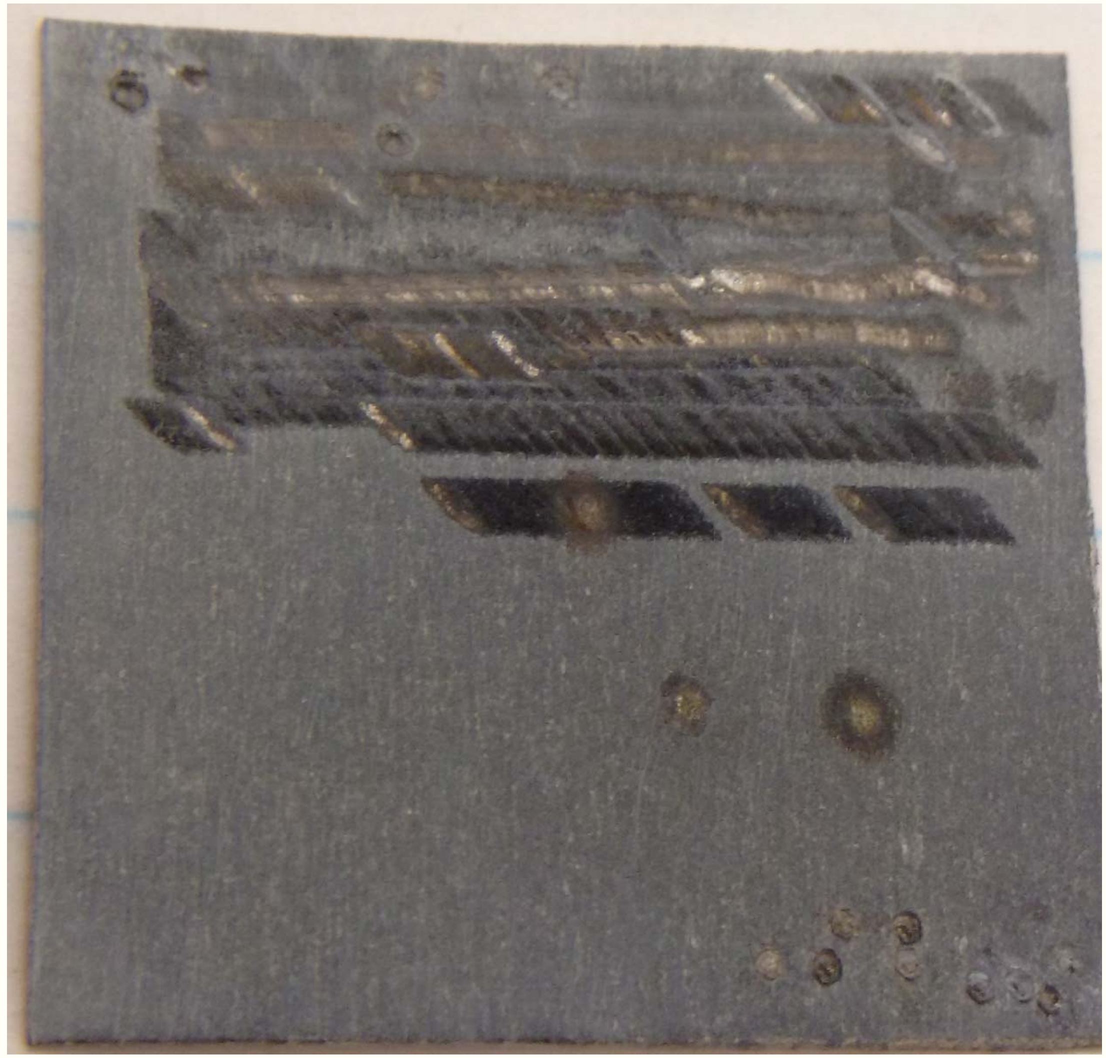
"*The OPO laser, excites the Al neutrals…the higher level of Mg is excited either by free electrons having undergone superelastic collisions with the excited Al neutrals (i.e., collisions in which the incident electrons gain the excitation energy of the excited Al atoms) or by direct collisions of the Mg atoms with the excited Al atoms*."

"*It is worth noting that selective excitation can also be performed using a single laser pulse via the resonant laser ablation (RLA) scheme. In RLA the ablation wavelength is tuned either on a resonant transition of the analyte, as in LIBS-LIF, or of the matrix atoms, as in RELIBS.*"

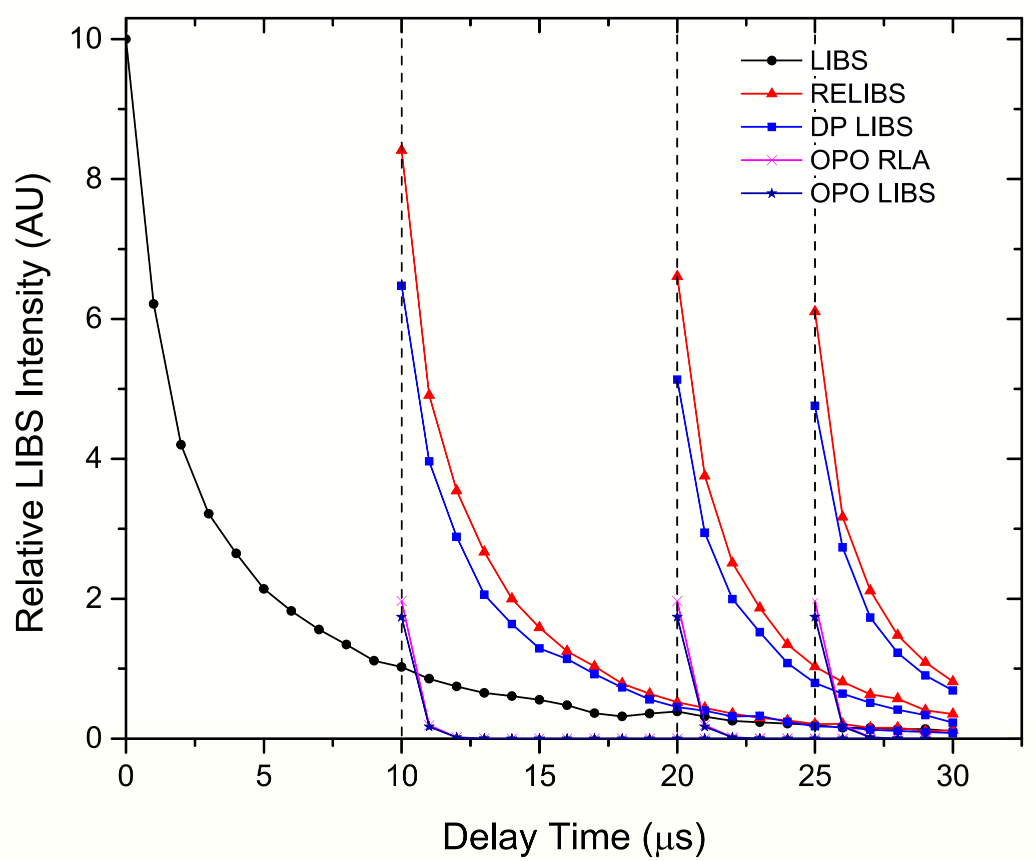
Because our target is pure Nd metal foil (shown at right) there is no matrix.

We are tuned into a resonance of the analyte with our second pulse (which doesn't fit either the definition of RLA or RELIBS).

But it is tuned into the dominant species in the plasma, so we still refer to it as RELIBS.



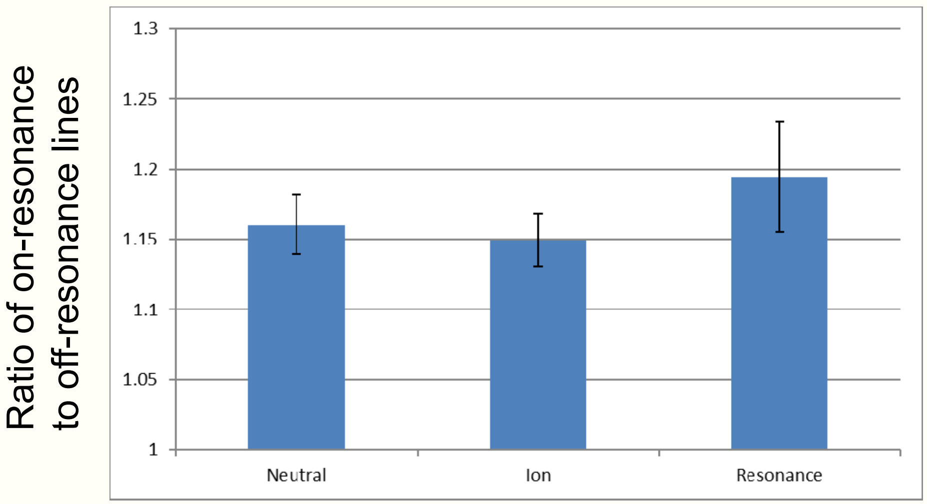
Enhancement of LIBS Emission when OPO pulse is On-Resonance vs. Off-Resonance



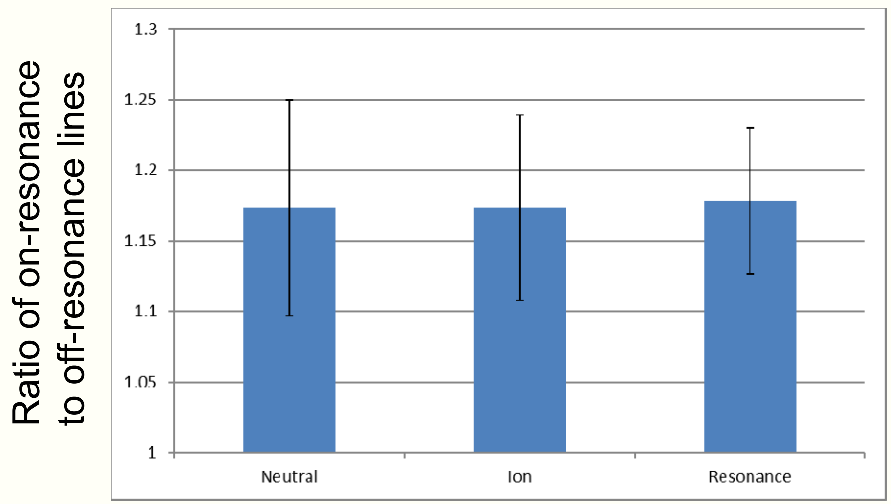
Relative LIBS intensity is the sum of 22 ion lines and 22 neutral lines (normalized to the 1064 nm LIBS emission)

Enhancement of LIBS Emission when OPO pulse is On-Resonance vs. Off-Resonance

0 μs after OPO pulse



1 μs after OPO pulse



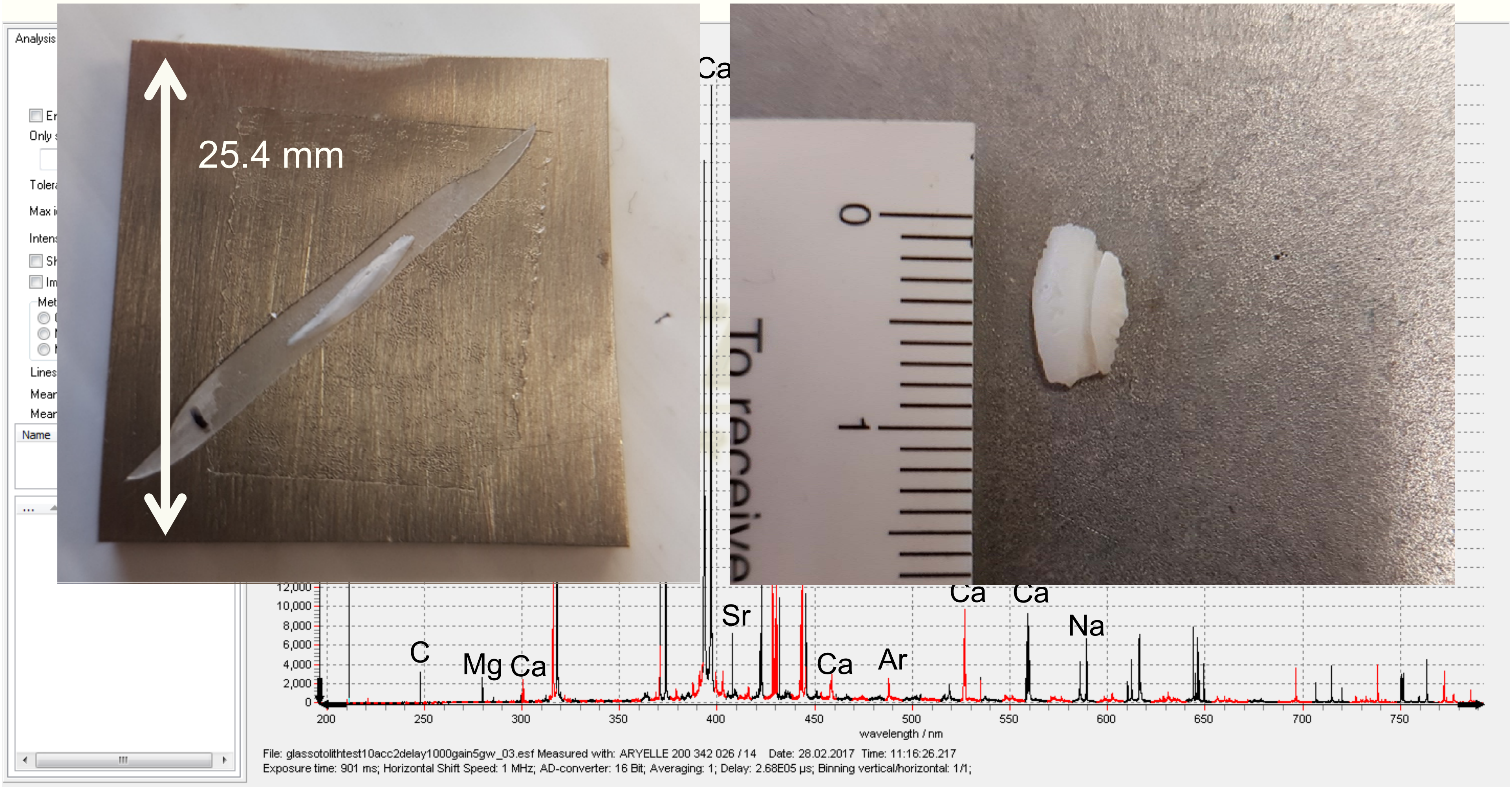
Neutral: Average of 22 NdI lines

Ion: Average of 22 NdII lines

Resonance: Average of 8 NdII lines, all originating in upper state of resonance transition

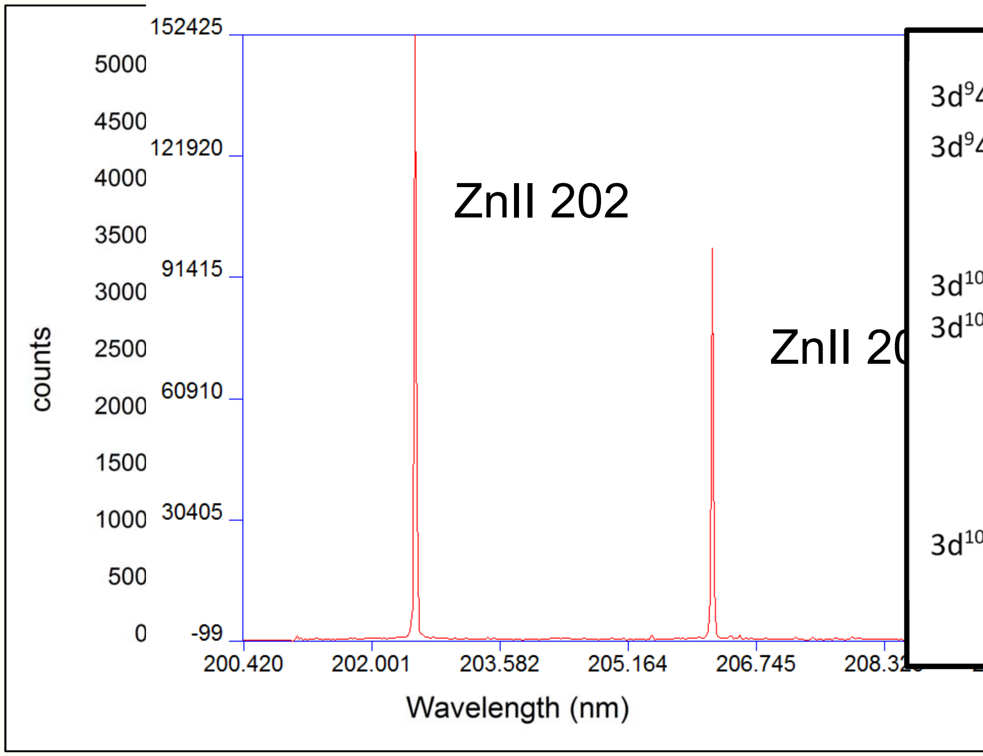
Salmon otoliths (ear bones)

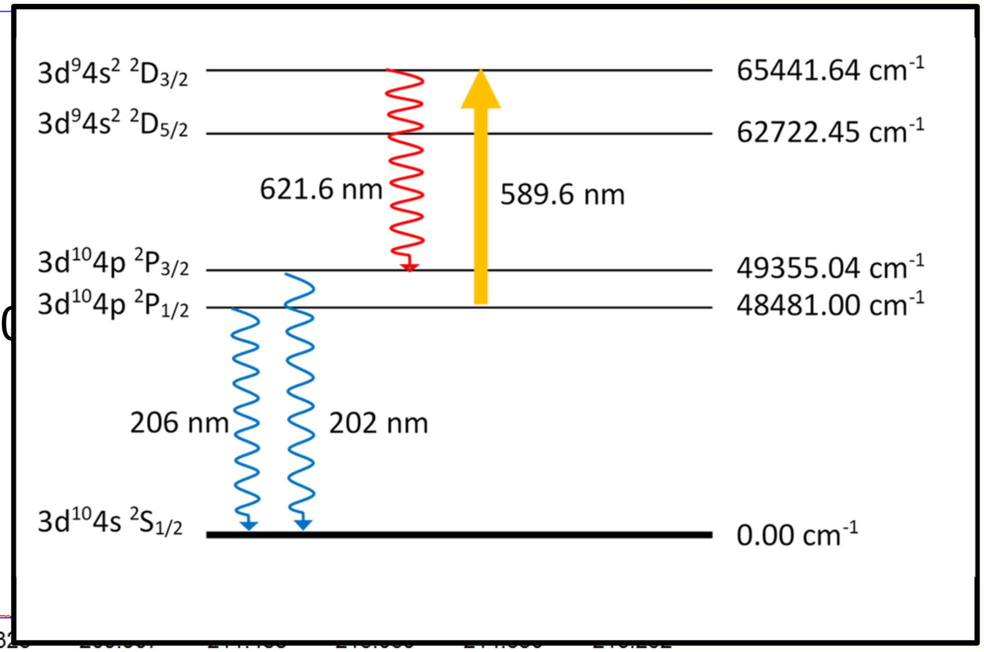
Salt/inorganic composition is reflective of growth environment → point sampling required



Fingernail zinc

Fingernail zinc is reflective of dietary zinc (related to neurodevelopment)





- ✓ Apply OPO pulse at 589.6 nm (excellent OPO energy)
- ✓ Pump atoms to the $^2P_{3/2}$ state
- ✓ Observe change in 202 nm vs. 206 nm emission

Conclusions

- Demonstrated LIBS-LIF in low pressure lanthanide plasmas
  - Elimination of overlapping lines observed
  - LIF laser energy dependence observed
  - Dependence on LIF laser wavelength unexplained

- RELIBS in atmospheric pressure lanthanide plasmas significantly enhanced emission at longer times
  - 15% improvement when on-resonance
  - Ions and neutrals enhanced identically
  - Decay of RELIBS plasma is on a different time scale

- System is in place to start investigating biomedical/biological specimens

Work continues, with generous help from:

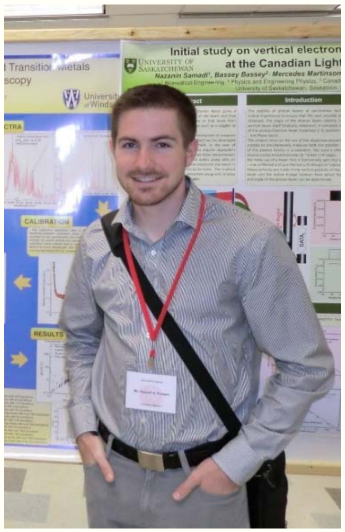
University of Windsor

NSERC Discovery Grant

CFI-LOF grant

All Credit to the Students

Russell Putnam



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