Development of Methodologies for Wide Area Environmental Sampling

MTV Workshop, 2020

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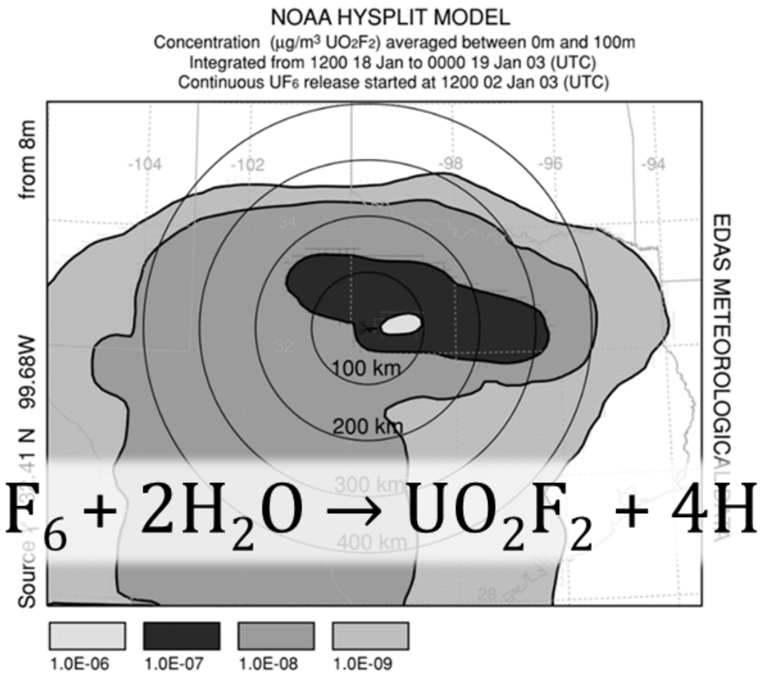
Introduction and Motivation

The National Academy identifies the prevention of nuclear attacks, with a focused interest on the detection of nuclear material at distances, as one of 14 Grand Challenges for Engineering in the 21st Century

Current Methods for monitoring declared and clandestine nuclear fuel cycle activities and weaponization programs include

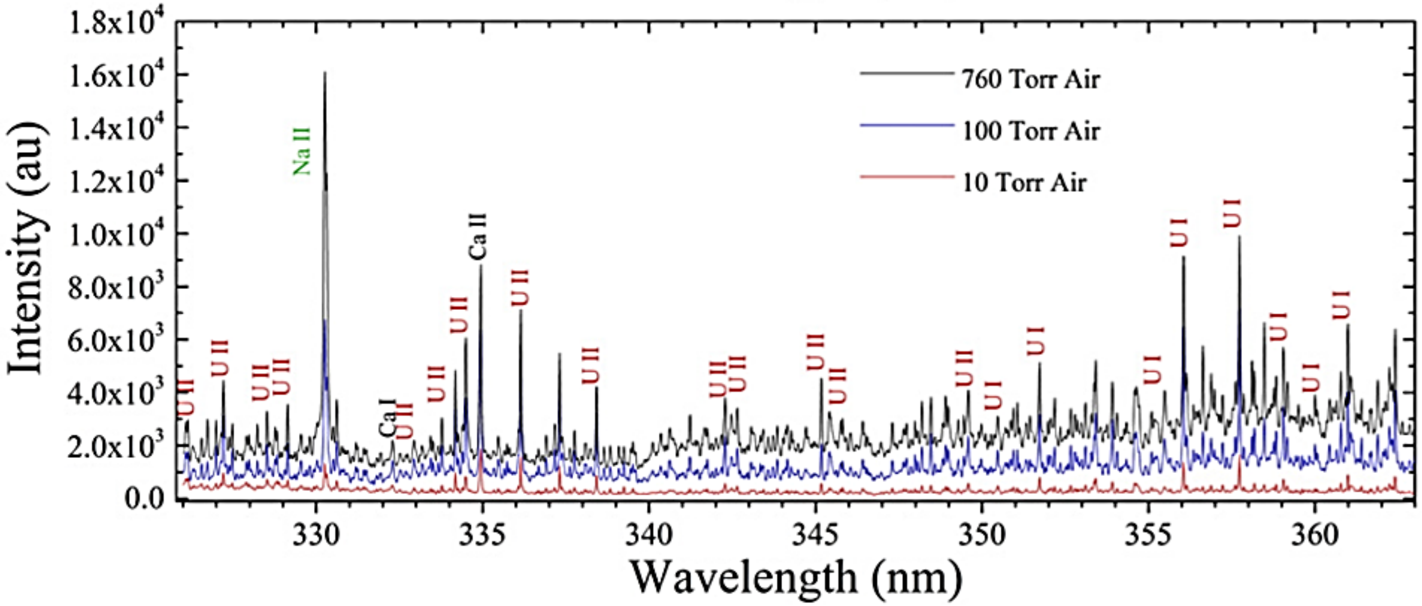
- Air sampling
- Swipe sampling with mass spectroscopy
    - Time Consuming – Requires sample preparation and transportation of radioactive samples to a laboratory
    - Costly



$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$$

R.S. Kemp, *Science and Global Security* **16**, 2008

Mission Relevance



P.J. Skrodzki *et al.*, *Spectrochimica Acta Part B* **125**, (2016)

Focused on the NNSA mission of preventing the proliferation of nuclear weapons and protecting against radiological terrorism through

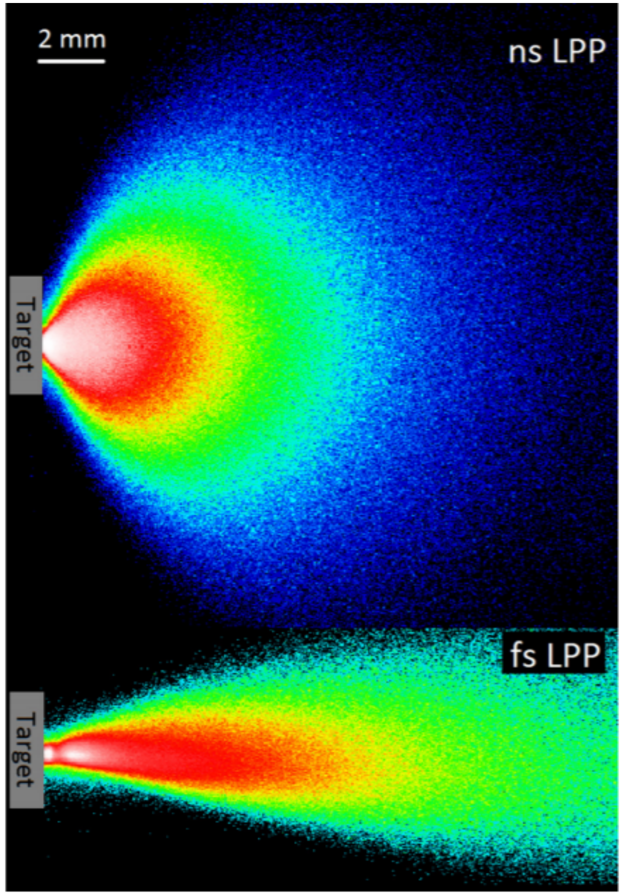
Wide-area Environmental Sampling using Optical Detection: Focused on developing optical techniques for the detection of actinides. Supports the NNSA mission by developing the next generation of robust detectors for (1) standoff, isotopically-resolved detection, (2) in-field, real-time measurements of nuclear materials with (3) no sample preparation.

Explosion Physics and LPP Chemistry: The physical and chemical properties of plasma produced by ultrashort laser pulses is representative of HE and nuclear fireballs. Provides a laboratory-scale method towards developing models and techniques to detect, characterize, and respond to nuclear explosion events.

Optical Spectroscopy and Detection

Objectives:

- Developing optical signatures of actinide isotopes for standoff detection and remote sensing
  - Well-defined initial conditions of laser parameters
  - Environmental and atmospheric conditions
- Characterizing and developing models of the spatio-temporal evolution of LPP plumes following laser ablation in ambient conditions. Optical spectra are highly sensitive to the plasma conditions
- Actinide plasma chemistry and formation of atomic and molecular species post-detonation



Verhoff *et al.*, *J. Appl. Phys.* **112**, 093303 (2012)

Collaborators: Dr. Laura Tovo and Dr. Eliel Villa-Aleman at SRNL, Dr. Batikan Koroglu and Dr. Chad Durrant at LLNL

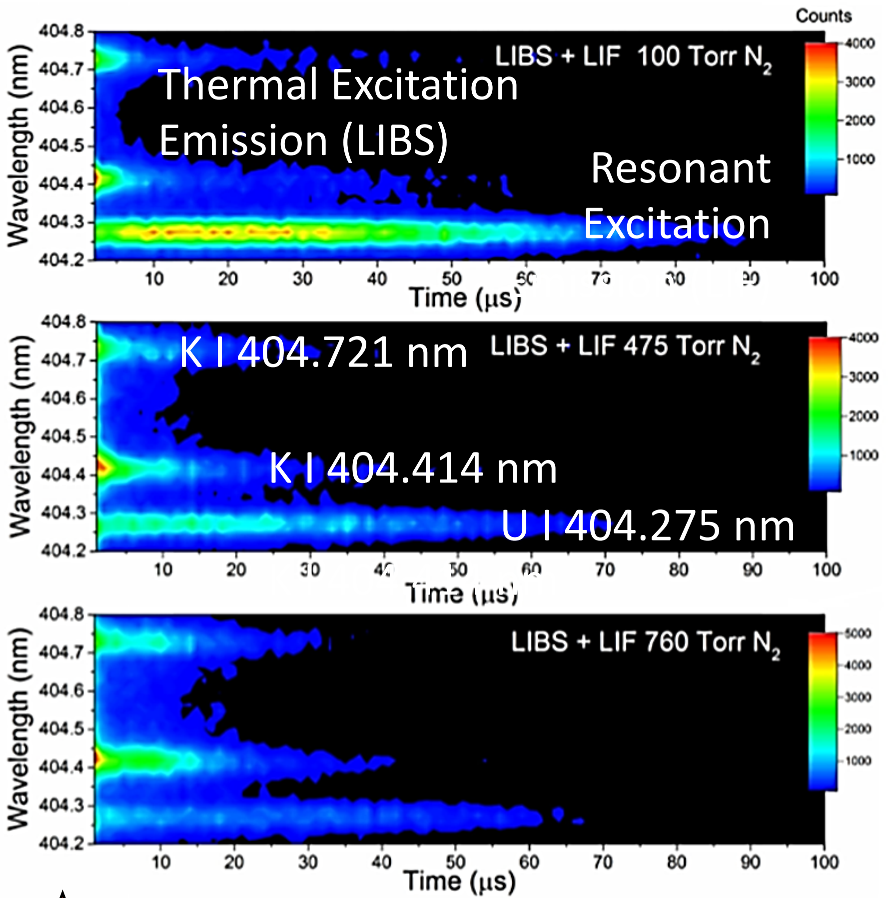
Optical Spectroscopy

<u>Changes in Pressure:</u> Affect fundamental LPP properties (e.g. density, temperature evolution, plume hydrodynamics, etc.)

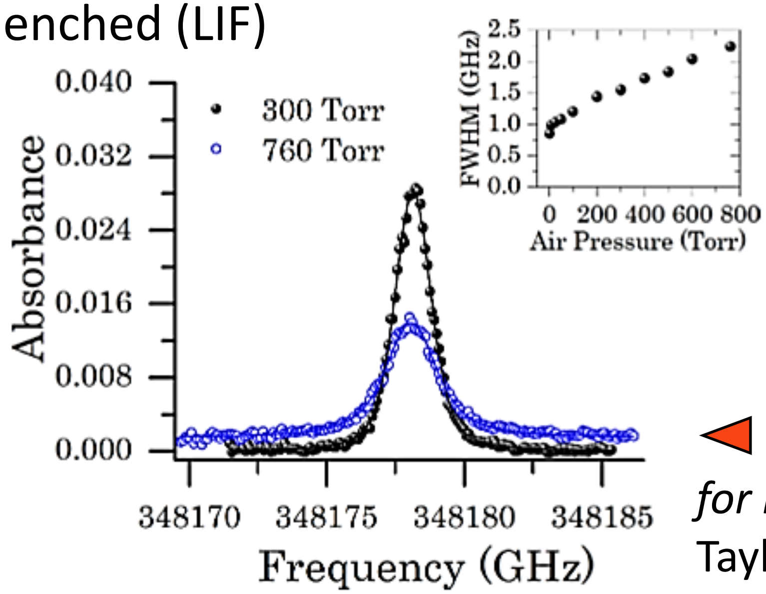
- **Emission Spectroscopy:** Due to stronger confinement and collisional effects in the plasma
  - Thermal emission is enhanced (LIBS)
  - Lifetime of thermally excited species is extended (LIBS)
  - Resonant emission is quenched (LIF)
- **Absorption Spectroscopy:**
  - Absorption path length decreases as the absorption coefficient increases (LAS)

$$T = \frac{I}{I_0} = e^{-kx}$$

$$A = -\log T$$



***LIBS & LIF:** 2D Contours of K I and U I emission for increasing pressure*
Harilal *et al.*, *Opt. Exp.* **25**, 273181 (2017)

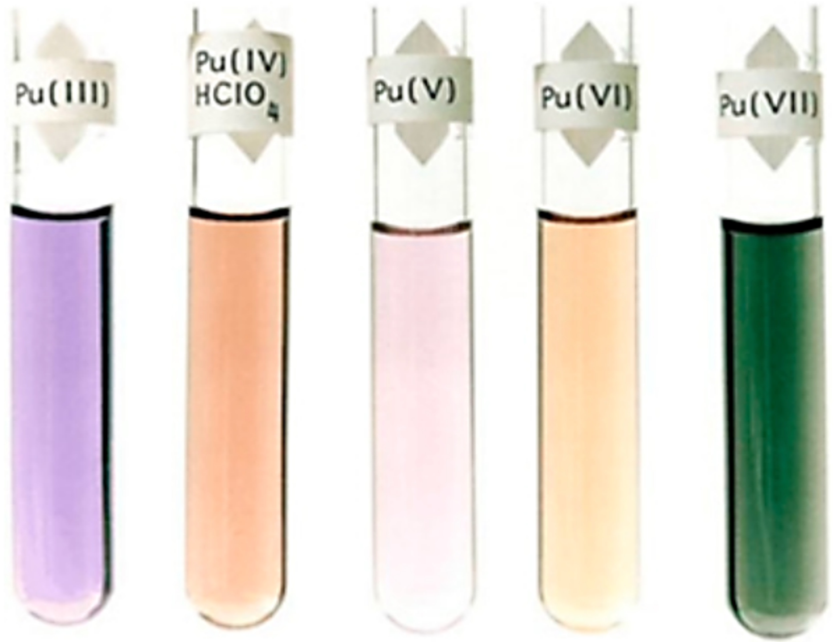


***LAS:** Absorbance of ^{238}U transition (861 nm) for increasing pressure*
Taylor and Phillips, *Opt. Lett.* **39**, 594 (2014)

Plutonium vs Uranium Chemistry

<u>The behavior of Pu with its environment is very different than that of Uranium</u>

- Pu has 5 oxidation states: Pu(III), Pu(IV), Pu(V), Pu(VI), Pu(VII)
- Oxidation states of U: U(III), U(IV), U(V), U(VI)
  - U(V) is unstable and readily reacts with itself to form 4+ or 6+ oxidation states
- PuO_2 is chemically stable and does not oxidize with air
  - Lower reactivity in optical spectra to increases in ambient pressure (air)
- Pu metal will oxidize quickly in moist air
  - Oxidation rate decreases when alloyed with Gallium

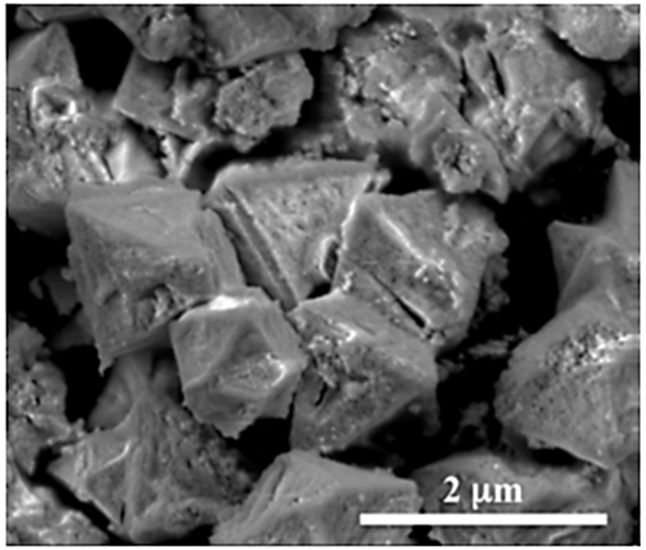


D.L. Clark, *Los Alamos Science* **26**, 373 (2000)

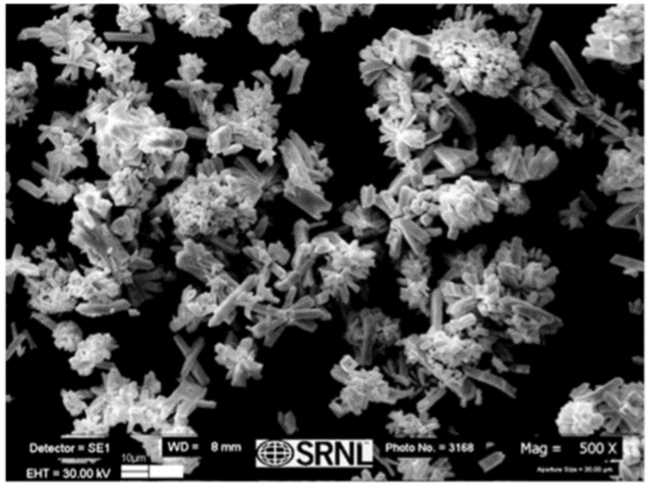
Plutonium Chemistry

Research on Pu and its compounds in regards to optical spectroscopy and plasma chemistry is limited

- Complex chemistry due to polyvalency (large number of oxidation states)
- Many morphologies depending on production process and calcination temperature
- Formation and persistence of molecular species in the plasma plume in response to
  - Oxidation state and type of Pu compound (e.g. powder, metal, Ga-doped, etc.)
  - Material surface roughness and morphology
  - Initial conditions of the laser and resultant plasma temperature



M. Goldberg, "Plutonium Processing and Pu Signatures," DHS DNDO, 5 Oct 2017, University of Michigan, Ann Arbor, MI



E. Villa-Aleman *et al.*, *J. Nucl. Materials* **515**, 2019

SEM Images of PuO_2

Surrogate for Plutonium

- CeO_{2-x} as a surrogate for PuO_{2-x} because of similarities in
    - Thermodynamic and mechanical properties
    - Ionic radii dimensions for oxidation states 3+ and 4+
    - Non-symmetrical crystal structures
    - Gallium solubility
    - Oxygen diffusivity
    - Phase transformation characteristics due to degree of localization of f electrons
    - Low melting temperature
- Ga_2O_3-doped CeO_{2-x} as a surrogate for weapons-grade PuO_{2-x}
    - Ga is added to weapons-grade Pu to stabilize its delta-phase
    - Ga is an embrittling agent, and therefore, removed from Pu used in reactors

Future Work

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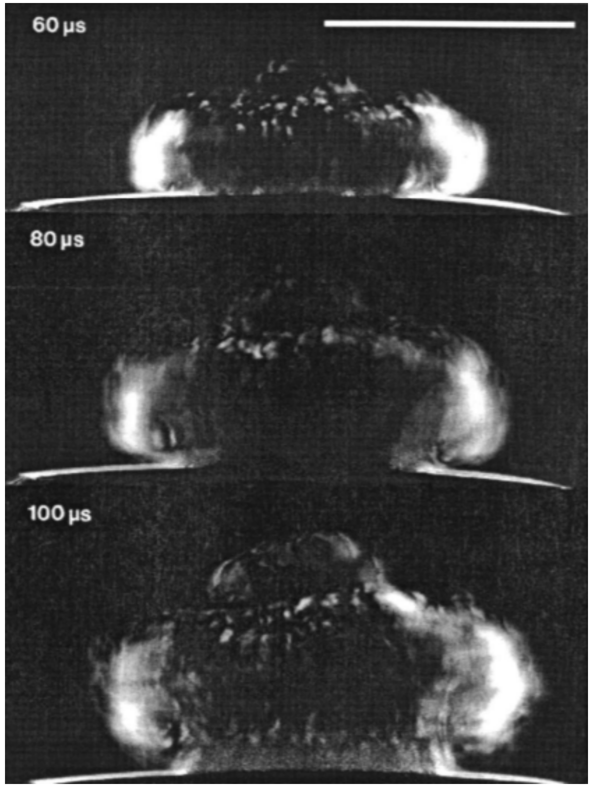
- At SRNL during Summer 2020 will study
  - Breakdown mechanisms of PuO_2 and Pu metal using ultrafast laser ablation
  - Pu laser-produced plasma plumes under inert and ambient atmospheric conditions
    - Elucidate the significance of ambient conditions on absorption and emission features of Pu LA plasmas
- Possible approaches
  - Laser-induced Breakdown Spectroscopy (LIBS)
  - Laser Ablation Molecular Isotope Spectroscopy (LAMIS)
- **Goal:** Understand elemental composition and evolution of molecular species in the LPP due to the different Pu precursors used to synthesize PuO_2 and metal
  - 2-3 journal publications of results and analysis

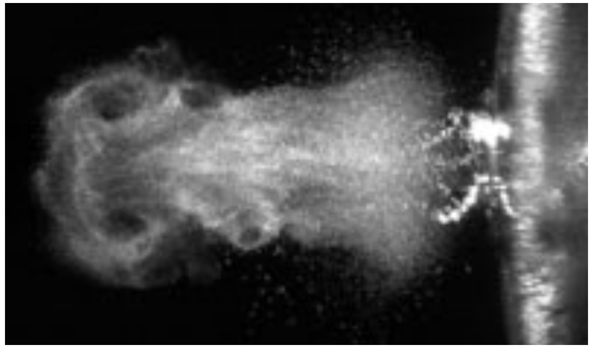
Expected Impact

- If successful, will gain an informed understanding of the fundamental physical and chemical properties of LPP Pu plumes in relation to monitoring nuclear explosives
- Improved understanding of the formation of atomic and molecular species in LPP plumes and their effect on plume evolution
- Models of actinide plasma plumes will be developed that capture the impact of oxidation and ambient atmospheric effects on absorption and emission spectra of actinides



Laser ablation dynamics of water

K. Nahen & A. Vogel, *J. Biomedical Optics* **7**(2), 2002



Laser ablation dynamics of glycerol at 24 μs

K. Murray, Louisiana State University

MTV Impact

- Professional Development Opportunities for Students
  - **BNL** Graduate Course: *Nuclear Nonproliferation, Safeguards, and Security in the 21st Century*
  - **PNNL** Graduate Course: *Radiation Detection for Nuclear Security Summer School*
- Internships
  - Past internships at **PNNL**, **BNL**, and **NNSS**
  - Upcoming graduate internships at **SRNL**, **LLNL**, **AFRL**, and **NNSS**
- Conferences: **ANS**, **INMM**, **COLA**, **CLEO**, and **SCIX**
- Collaborations with MTV co-PIs: Dr. Igor Jovanovic (**UM**), Dr. Andreas Enqvist (**UF**)
- Collaborations with National Labs: **SRNL**, **LLNL**, **ORNL** (planned)

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Conclusion

- This work supports the NNSA mission in treaty verification, monitoring of declared nuclear activities, and detection of undeclared activities by advancing technologies towards the wide-area environmental sampling of actinides
- Graduate students will be involved in developing optical detection techniques towards remote sensing of nuclear materials. This will involve
  - Participation in internships and research at national laboratories
  - Publishing technical papers and presenting at conferences
  - Expected that students will obtain full-time employment at national laboratories or in government following graduation
- Undergraduate students will be given the opportunity to experience research in academia and at national laboratories in the exciting field of nuclear security

Acknowledgements

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