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Advanced Ultrafast Spectroscopy for Chemical Detection of Nuclear Fuel Cycle Materials

The development of new signatures and observables from processes related to proliferation activities are often related to the development of technologies. In our physical world, the intensity of observables is linearly related to the input drivers (light, current, voltage, etc.). Ultrafast lasers with high peak energies, opens the door to a new regime where the intensity of the observables is not necessarily linear with the laser energy. Potential nonlinear spectroscopic applications include chemical detection via remote sensing through filament generation, material characterization and processing, chemical reaction specificity, surface phenomena modifications, X-ray production, nuclear fusion, etc. The National Security Directorate laser laboratory is currently working to develop new tools for nonproliferation research with femtosecond and picosecond lasers. Prior to this project, we could only achieve laser energies in the 5 nano-Joule range, preventing the study of nonlinear phenomena. To advance our nonproliferation research into the nonlinear regime we require laser pulses in the milli-Joule (mJ) energy range. We have procured and installed a 35 fs-7 mJ laser, operating at one-kilohertz repetition rate, to investigate elemental and molecular detection of materials in the laboratory with potential applications in remote sensing. Advanced, nonlinear Raman techniques will be used to study materials of interest that are in a matrix of many materials and currently with these nonlinear techniques we can achieve greater than three orders of magnitude signal enhancement. This work studying nuclear fuel cycle materials with nonlinear spectroscopies will advance SRNL research capabilities and grow a core capability within the DOE complex.
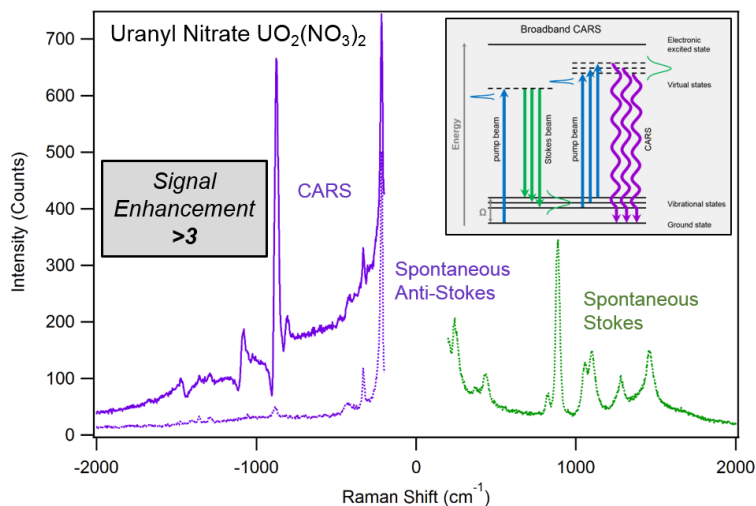
SRNL Legal Signature

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Signature   **Date**

Advanced Ultrafast Spectroscopy for Chemical Detection of Nuclear Fuel Cycle Materials

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Thrust Area: NS

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Project End Date: September 30, 2017

The development of new signatures and observables from processes related to proliferation activities are often related to technological advancements. In our physical world, the intensity of observables is linearly related to the input drivers (light, current, voltage, etc.). Ultrafast lasers with high peak energies, opens the door to a new regime where the intensity of the observables is not necessarily linear with laser energy. Potential nonlinear spectroscopic applications include chemical detection via remote sensing, material characterization and processing, surface phenomena modifications, nuclear fusion, etc. Currently, we can achieve laser energies in the 5 nano-Joule range, preventing the study of nonlinear phenomena. To advance our nonproliferation research into the nonlinear regime we require laser pulses in the milli-Joule (mJ) energy range. We have procured and installed a 35 fs-7 mJ laser, operating at one kilohertz repetition rate, to investigate elemental and molecular detection of materials in the laboratory with potential applications in remote sensing. Advanced, nonlinear Raman techniques will be used to study materials of interest that are in a matrix of many materials and currently with these nonlinear techniques we can achieve >3 orders of magnitude signal enhancement.

FY2017 Objectives

- **Installation of an ultrafast, femtosecond laser system and an optical parametric amplifier (OPA).**
- **Programming of a spatial light modulator (SLM) to control the phase and amplitude of laser pulses.**
- **Design of microscope and optical components required to couple laser light to samples of interest.**
- **Measure various materials with different advanced Raman techniques.**

Introduction

The National Security Directorate (NSD) has supported the DOE NA-22 Uranium Program via characterization of UO_2F_2 particulates and aged products with Raman, luminescence and infrared spectroscopic techniques. These techniques were used to study the behavior of particulates in the laboratory under different humidity and lighting conditions. Other U-bearing compounds (UO_2, U_3O_8 and UO_3) were also studied in order to understand the oxidation process of uranyl samples in the environment. NSD has also conducted particulate matter collection campaigns from different U-based sources. Particulate collections were made during campaigns dedicated to the detonation of devices with depleted uranium, U-bearing compounds from conversion and enrichment plants and other facilities dedicated to the production of materials from the nuclear fuel cycle. Our collections have resulted in the identification of unique signatures from different processes.

Similarly, pre-screening of environmental samples for anthropogenic uranium and fluoride compounds is important in order to identify proliferation activities. The hydrolysis of UF_6 results in the formation of UO_2F_2 and its aged products. Luminescence of the environmental soil matrix overwhelms the

spectroscopic signals of interest originating from the anthropogenic compounds. The weak spontaneous Raman scattering signal requires long integration times for analysis and is one of the major limiting factors of large-scale sample analysis. Ultrafast lasers have opened new doors in research to enhance detection sensitivity. The expected several orders of signal enhancement (i.e. up to 10^6 orders of magnitude)[1] with advanced, nonlinear spectroscopic techniques are a game changer for detection of chemical species related to proliferation activities.

The recent acquisition of femtosecond and picosecond lasers, a deep ultraviolet laser and an ultrafast-gated imager for picosecond Raman spectroscopy has opened the door to conduct advanced linear and nonlinear spectroscopic research. Currently, the laser systems helped to secure additional funding from DOE NA-22 to study plutonium particulates. The laser systems are also being used in different research projects funded by DOE NA-22 and LDRD programs. One goal of the current LDRD project is to demonstrate remote detection of U-bearing compounds in soil samples using Stimulated Raman Scattering (SRS) and Coherent Anti-Stokes Raman Scattering (CARS) in a standoff configuration, which has successfully been shown in literature for the detection of explosive residues.[2] Data from this project will be used to write new work with NA-22 for improved detection sensitivity for U and Pu. In another project, a gated imager will be used to gate Raman scattering from particulates generated from laser ablation of targets within a 300 picosecond window, therefore eliminating/reducing the strong luminescent background interfering with the signal of interest. We are also exploring CARS to identify microscopic particles embedded in bulk material and in airborne material. These projects are providing technological seeds to grow a core capability within the DOE weapons complex that will facilitate increased ROI through future proposals to other government agencies.

Approach

Our research approach for this LDRD includes completing the assembly and installation of an ultrafast Ti:Sapphire laser system with modules for an optical parametric amplifier (OPA) to access the infrared to the deep ultraviolet spectral regions. Following installation of the ultrafast laser system, advanced Raman methodologies will be developed (i.e. stimulated Raman scattering (SRS) and coherent anti-Stokes Raman scattering (CARS)) to measure and analyze samples of interest (i.e. nuclear fuel cycle materials), processes shown in Figure 1. Additionally, software will be written to manipulate the energy (spectral regime) and
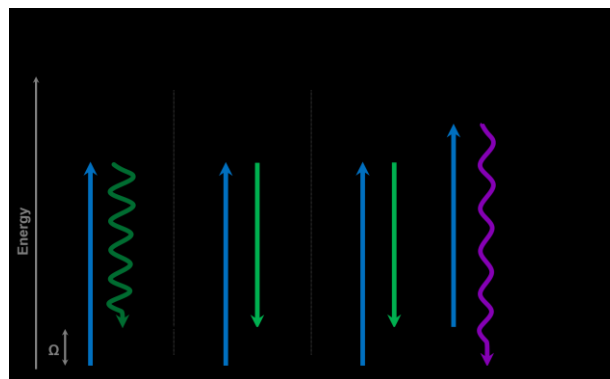
**Figure 1.** Schematic energy level diagrams for Raman processes.

temporal properties of a femtosecond laser pulse with a spatial light modulator (SLM).[3] We will then demonstrate detection of particles of interest in soil samples, as well as detection of samples up to 5 meters away. Other spectroscopic and material processing applications will also be conducted and demonstrated, including surface modification through laser desorption and ablation, chemical characterization within the desorbed material pulse, hydrogen and deuterium detection, etc.

Results/Discussion

The Astrella ultrafast Ti:Sapphire laser from Coherent that produces <35 fs pulses at >7 mJ/pulse at a repetition rate of 1 kHz and an optical parametric amplifier (OPA), the OPerA Solo from Coherent that

extends the wavelength range from 190 nm to 20 μm were both installed in the National Security Directorate laser laboratory in March 2017. However, the laser system has been "down" following installation due to defective internal components of the laser system. These multiple components within the laser system need to be replaced by Coherent, but these components may not be available for installation until 2018.
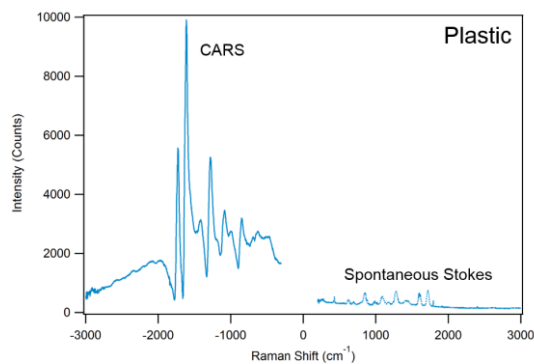
Advanced, nonlinear Raman spectroscopy setups were assembled, which included coherent anti-Stokes scattering, stimulated Raman scattering and quantum coherent control, shown in Figure 2. An optical microscope setup was designed and built to couple laser light to our samples of interest. Software to control the dual-mask transmission SLM was written and tested to control both the phase and amplitude of laser pulses within the spectral range of 488-900 nm, for quantum coherent control.
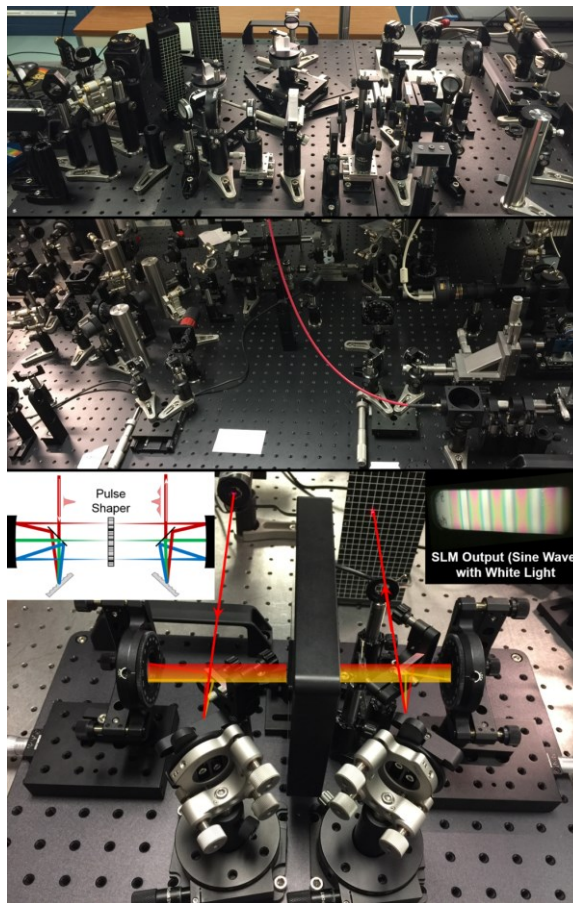
Figure 2. Experimental setups of stimulated Raman scattering (top), coherent anti-Stokes Raman scattering (middle) and quantum coherent control (bottom).
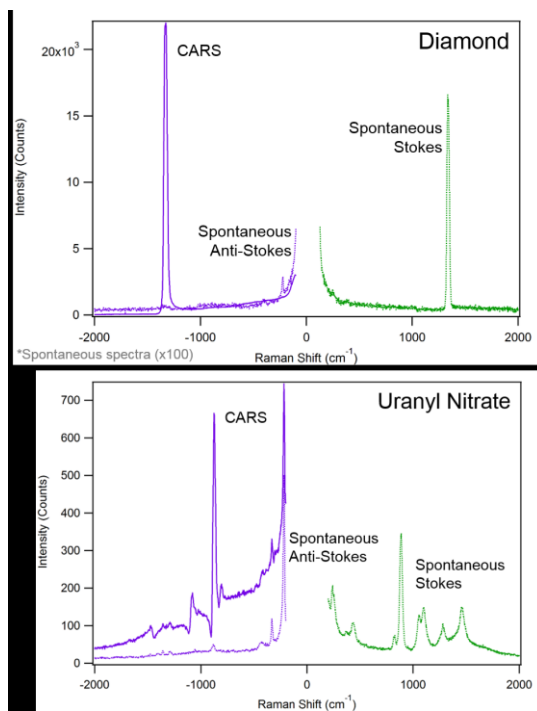
Figure 3. Coherent anti-Stokes Raman scattering, spontaneous Stokes and anti-Stokes spectra of (top) diamond, and (bottom) uranyl nitrate.

Figure 4. Coherent anti-Stokes Raman scattering and spontaneous Stokes spectra of plastic.

Various liquid and solid samples were analyzed with advanced, nonlinear Raman techniques. The measured CARS and spontaneous Raman spectra of diamond and uranyl nitrate are shown in the top and bottom of Figure 2, respectively. Plastic was also successfully measured with CARS and spontaneous

Raman in Figure 3. The signal enhancements we were able to achieve with the advanced, nonlinear Raman techniques exceeded three orders of magnitude enhancement compared to spontaneous Raman.

FY2017 Accomplishments

- The Astrella ultrafast laser (<35 fs at >7 mJ/pulse and 1 kHz) and an optical parametric amplifier (OPA) covering the 190 nm to 20 μm spectral range were delivered at the end of FY16 and were installed in March 2017. Following laser installation, the laser system was "down" until the end of August 2017 due to components in the system needing replacement once available from Coherent.
- Software was written and tested to control the transmission SLM (CRi SLM-128-D-VN, Meadowlark Optics) that has a dual-mask configuration for simultaneous phase and amplitude pulse shaping (spectral range of 488-900 nm).
- Completed designing and building an optical microscope setup to couple laser light to our samples of interest.
- Measured various solid and liquid samples with advanced Raman techniques, including Uranium-bearing compounds and plastics.
- Signal enhancement >3 orders of magnitude using advanced Raman techniques.

Future Directions

- Demonstrate detection of samples up to 5 meters away.
- New technologies developed during this project have the potential to lead to applications in the fields of chemical detection via remote sensing, material characterization, surface decomposition, isotropic composition, etc.

References

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2. M. T. Bremer and M. Dantus, "Standoff Explosives Trace Detection and Imaging by Selective Stimulated Raman Scattering," *Appl. Phys. Lett.*, vol. 103, pp. 061119, 2013.
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Acronyms

CARS – Coherent Anti-Stokes Raman Scattering
fs – femtosecond
mJ – milli-Joule
NSD – National Security Directorate
OPA – Optical Parametric Amplifier
ROI – Return on Investment
SLM – Spatial Light Modulator
SRS – Stimulated Raman Scattering
U – Uranium