Underwater Raman Sensor for Detecting High Explosives and Homemade Explosives (HMEs)

Shiv K. Sharma*
Hawaii Institute of Geophysics & Planetology,
*University of Hawaii (**UH**) at Manoa, Honolulu, Hawaii, USA*

***sksharma@soest.hawaii.edu**

Collaborators:
Bruce Howe
Anupam K. Misra
John N. Porter
Mark Rognstad

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Introduction

- **The marine environment can be affected by chemicals. Word-wide terroristic threats are also affecting coastal areas.**
- **Hydrocarbon benzene, toluene, ethyl benzene and xylenes isomers (BTEX) are present in gasoline (petrol). These BTEX compounds are ubiquitous contaminants in ground and surface waters. Because these compounds are known to be toxic to humans and aquatic life, their detection and identification is of critical importance.**
- **In recent years advances in solid state lasers, efficient spectrograph, CCD detectors and holographic optical filters and gratings have made it possible to develop small portable Raman systems which can also be used for measuring laser-induced native fluorescence (LINF). Fitting a Remotely Operated Vehicle (ROV) or glass bottom boat with a miniature telescopic Raman system could provide capability of investigating chemical pollution in deep and shallow waters.**

OUTLINE

- **Discuss briefly Raman spectroscopy**
- **Time-Resolved standoff Raman systems developed at the University of Hawaii (UH).**
- **Results of *in situ* remote Raman spectra of seawater as a function of depth in Snug Harbor, Oahu with a 203 mm (8-inch) diameter telescopic system.**
- **Results of TR Raman measurements of chemicals suspended in the ocean.**
- **Describe 76 mm (3-inch) diameter mirror lens (ML) based Raman Sensor has been developed at UH for underwater detection of HEs nd HMEs.**
- **Summary**

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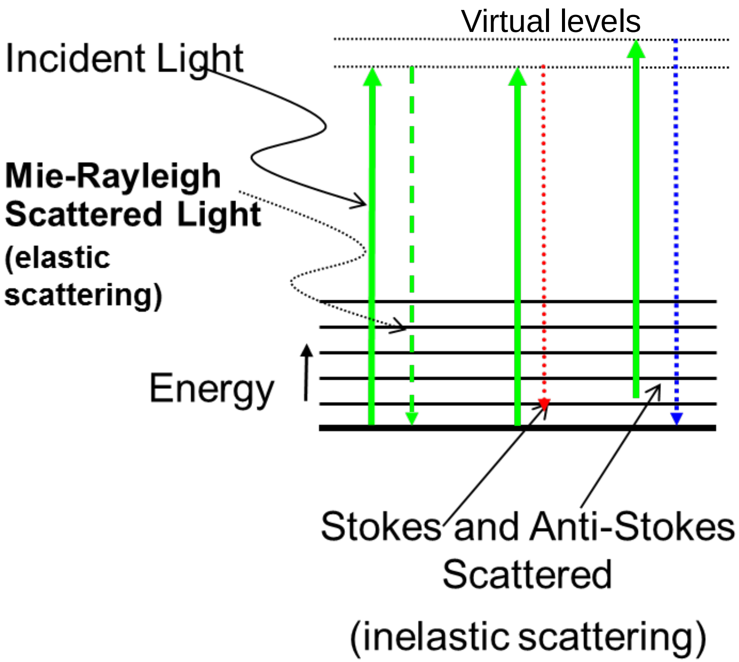
SCATTERING OF LIGHT



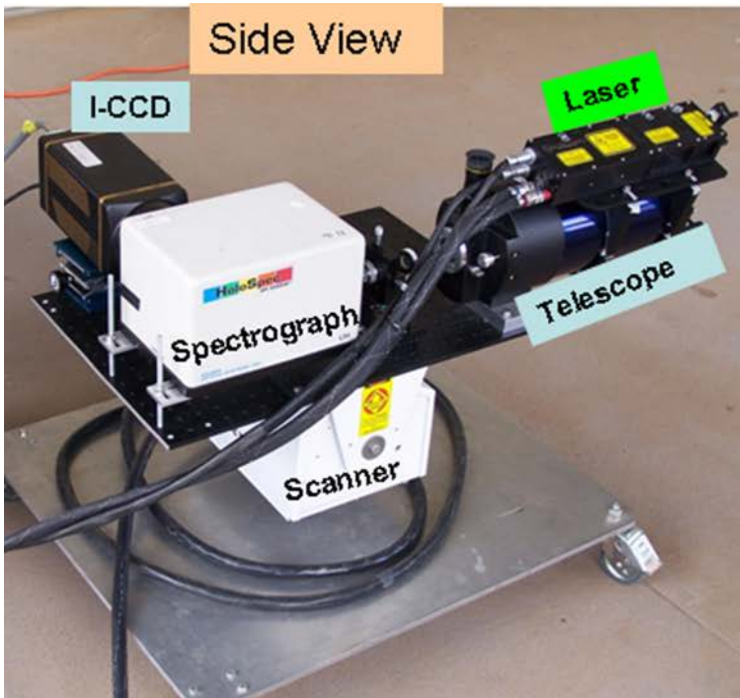
Raman Scattering

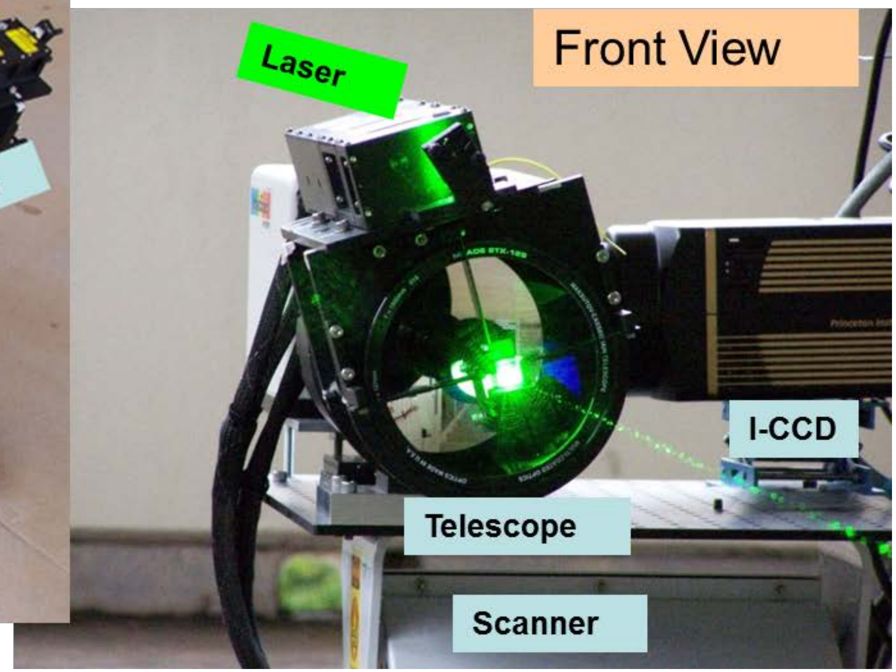
- involves polarizability of a molecule (induced dipole)
- the electric field of the molecule oscillates at the frequency of the incident wave (emits E.M. Radiation)
- if induced dipole is constant, scattering is elastic (Rayleigh-Mie)
- if induced dipole is not constant, inelastic (Raman) scattering is allowed
- Lifetime Raman process ~10^{-13} s

In the Raman spectra the information about vibrations of molecules is obtained in visible part of the spectrum as a difference from the energy of the visible laser excitation.

Raman spectra is complementary to IR spectra but the selection rules are different. For IR activity requires change in the permanent dipole moment.

Photographs of a Combined Remote Raman & LINF System in Coaxial Geometry

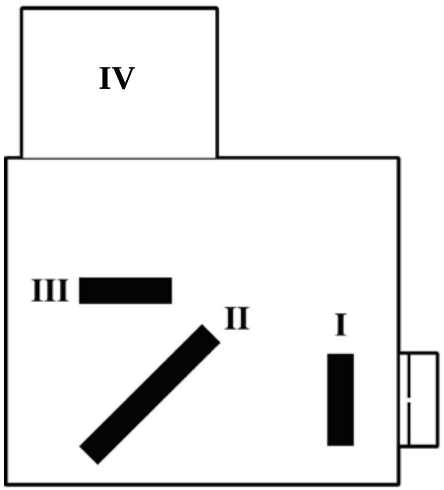


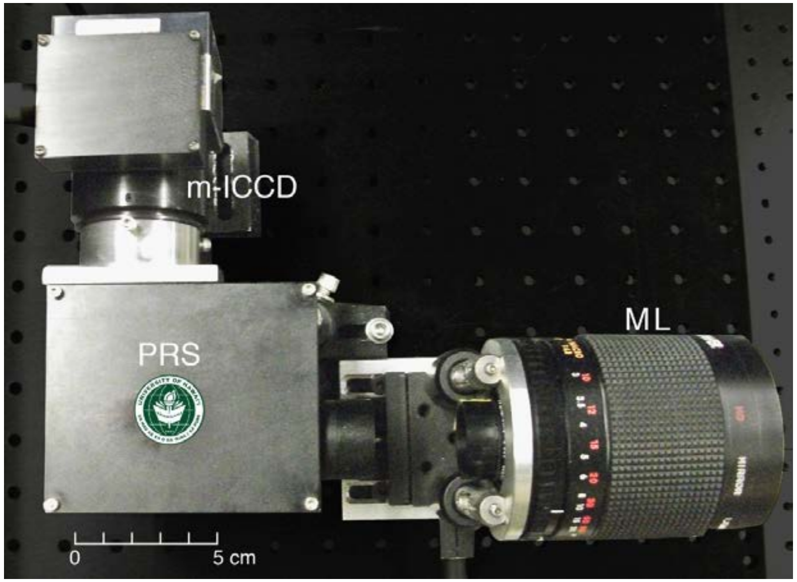


Laser: pulsed Nd:YAG 1064 nm, doubled to 532 nm, 20 Hz, 35 mJ/pulse
Spectrograph: Kaiser HoloSpec commercial spectrograph
Telescope: Meade ETX-125 125 mm Maksutov Cassegrain
Detector = Princeton Instruments' Intensified charge coupled device (ICCD)

Sharma,S. K. et al (2002) *Appl. Spectrosc.,* 56, 699-705.

Photograph of 76 mm (3-inch) Diameter Mirror Lens based Remote Raman Sensor





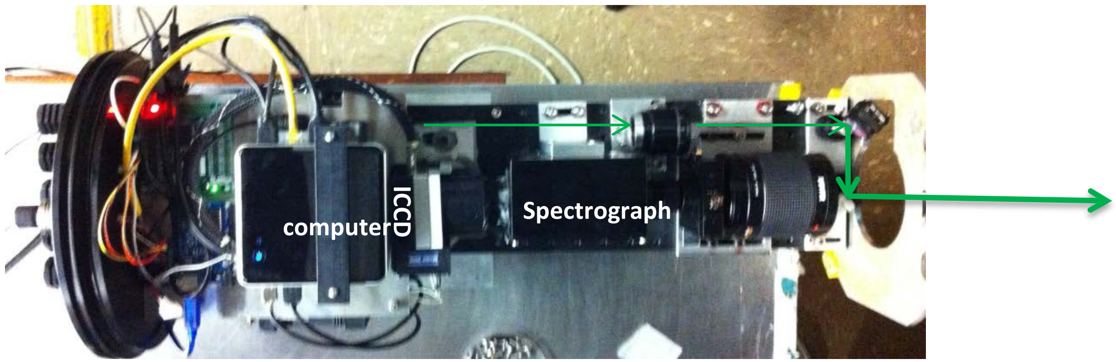
I = Lens; II = Holographic transmission grating; III = lens; and IV = miniature ICCD detector

Spectral resolution 15 cm^{-1} (0.43 nm) in the 100-2400 cm^{-1} and 13 cm^{-1} (0.37) in 2400-4000 cm^{-1} region;
LINF spectral range 533-700 nm
Spectrograph wt. = 631 g & ICCD wt. = 620 g (fabricated with aluminum body)
dimension 10 cm (length) x 8.2 cm (width) x 5.2 cm (high)

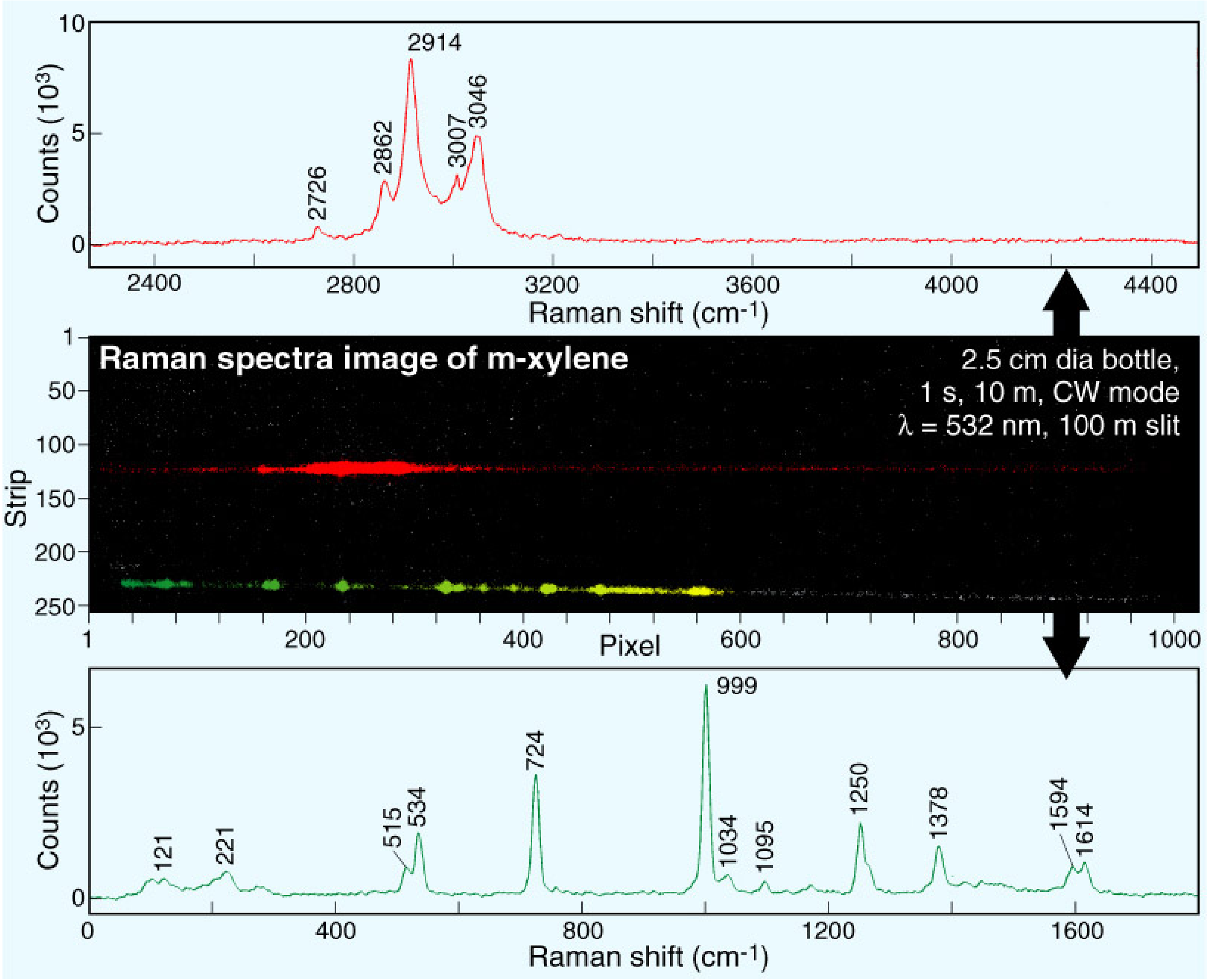
Miniaturized Raman-LINF spectrometer developed for Mars exploration is 1/14 in volume as compared to commercial Kaiser Raman spectrometer.

Underwater Raman Sensor

Underwater Raman Sensor

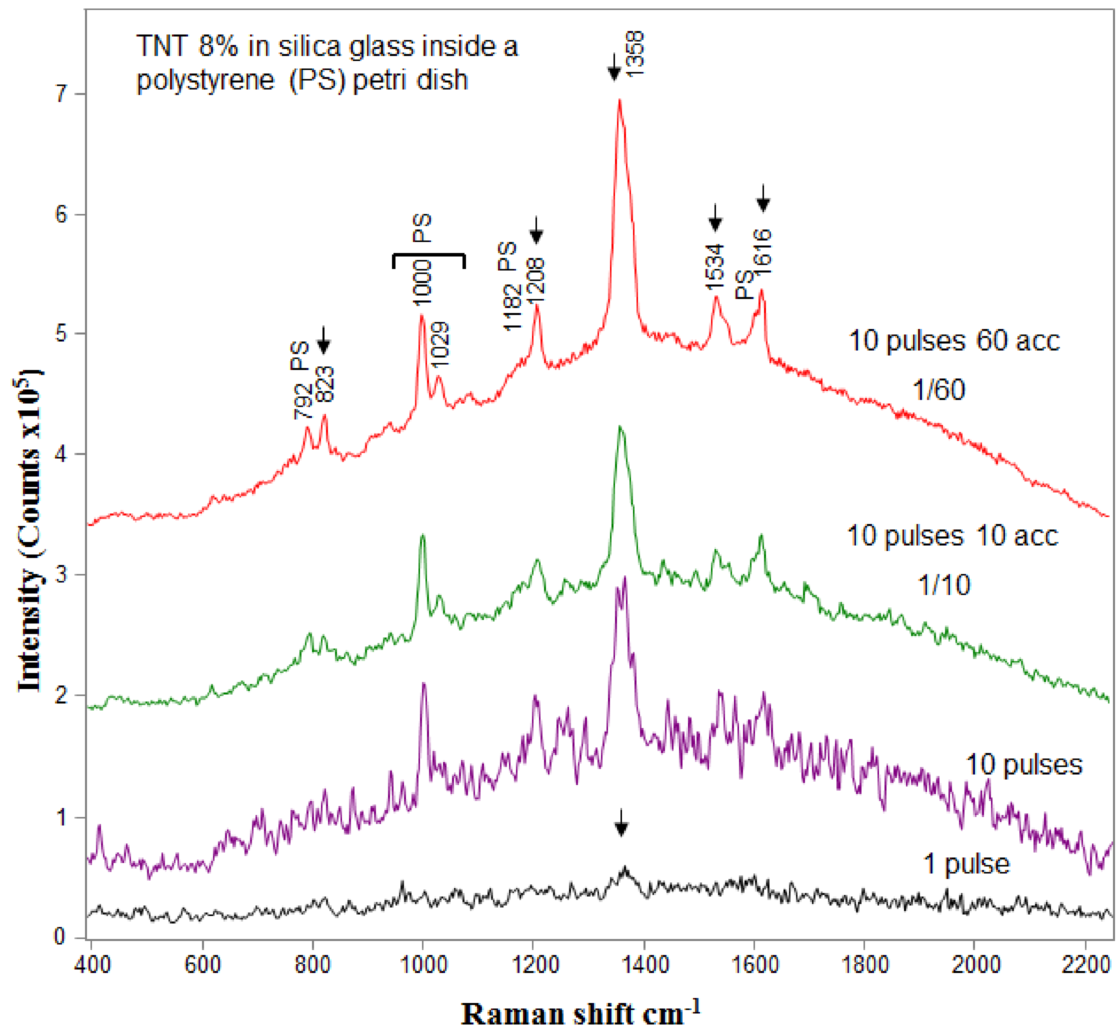


TR-Remote Raman Spectra of m-Xylene at 10 m

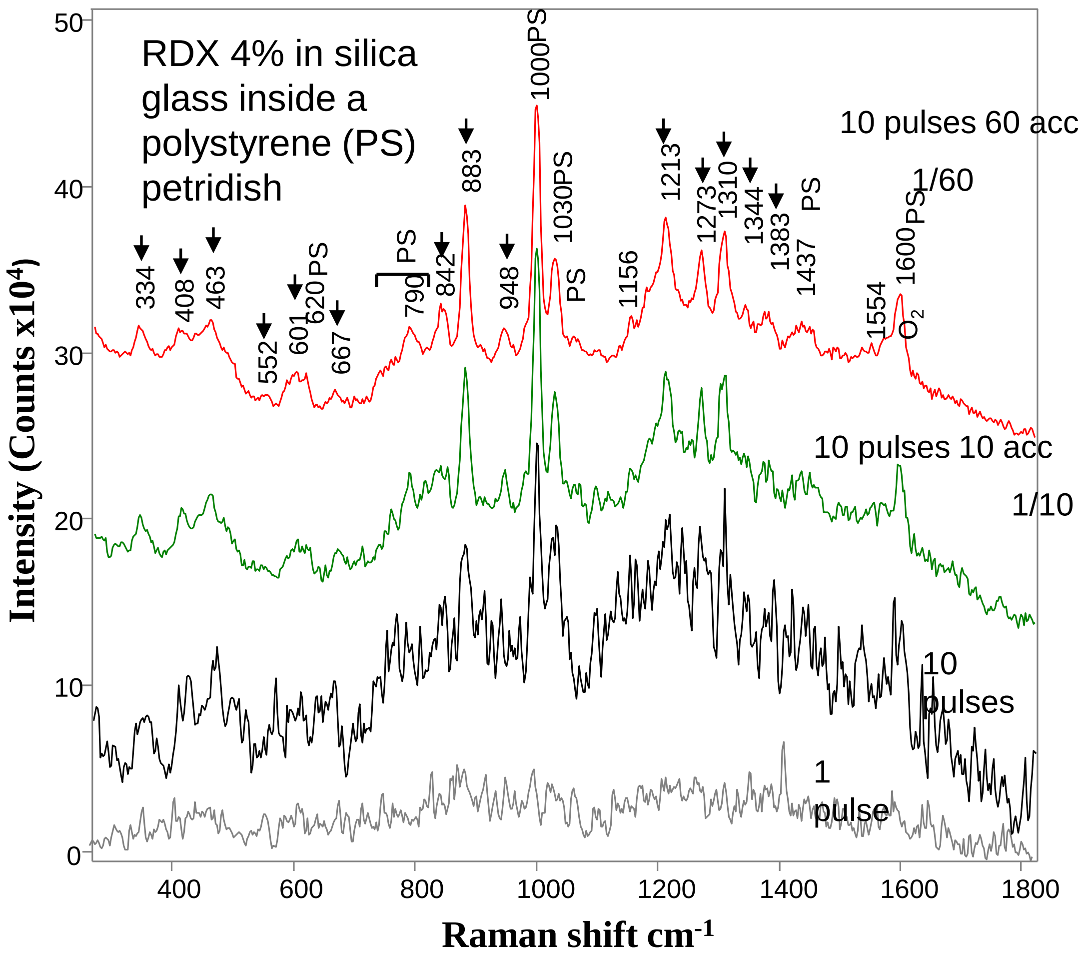


HoloPlex grating contains two holographic gratings that project spectrum in low- and high-frequency regions on ICCD.

TR-Remote Raman Spectra of 8% TNT at 8 m



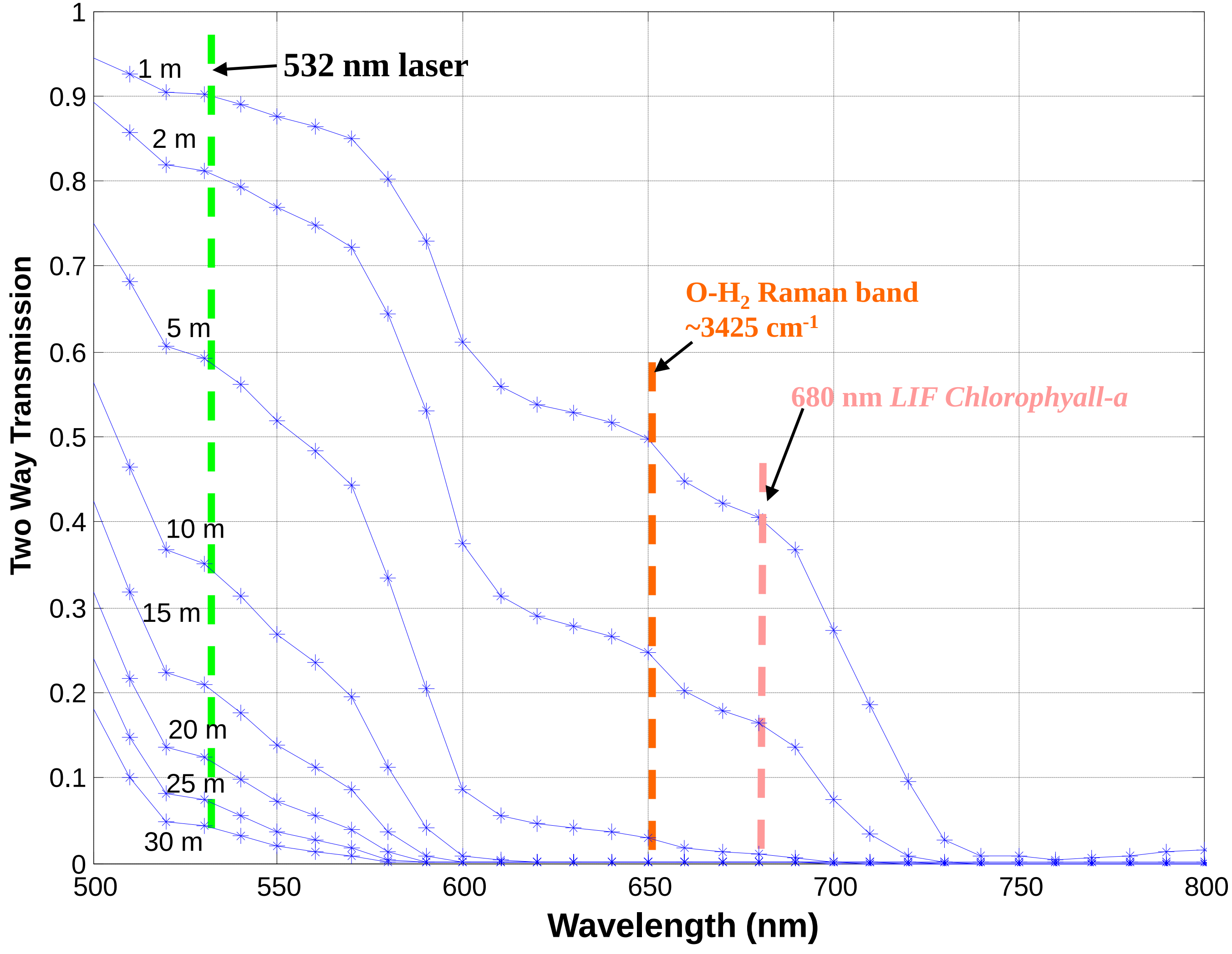
TR-Remote Raman Spectra of 4% RDX at 8 m



Remote Raman Spectroscopy of Seawater

- Detection of HEs and HMEs and Hazardous Chemicals in seawater.

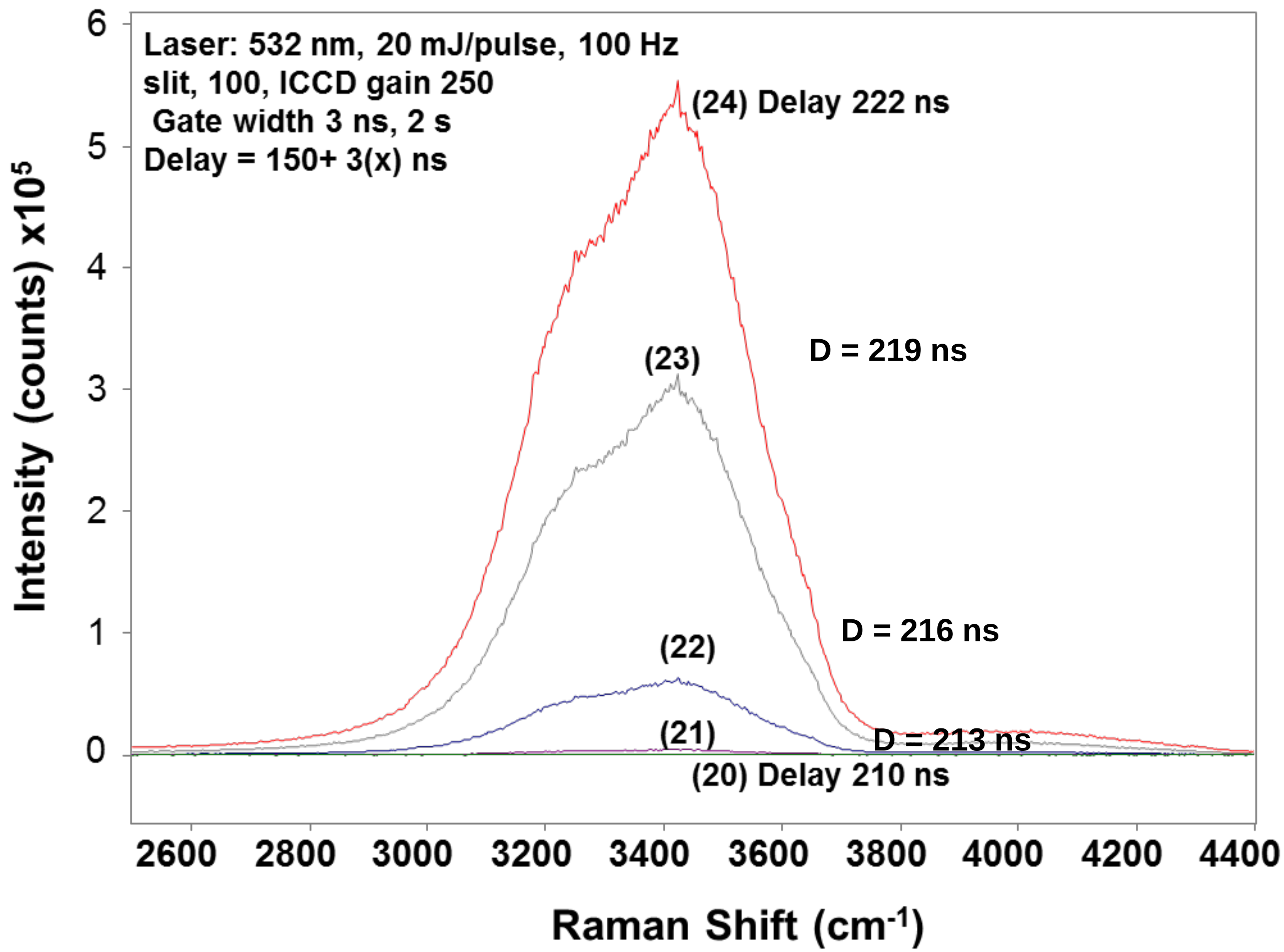
Two Way Light Transmission in water (500-800 nm)



Standoff Raman Testing in the Lab with 532 nm Laser

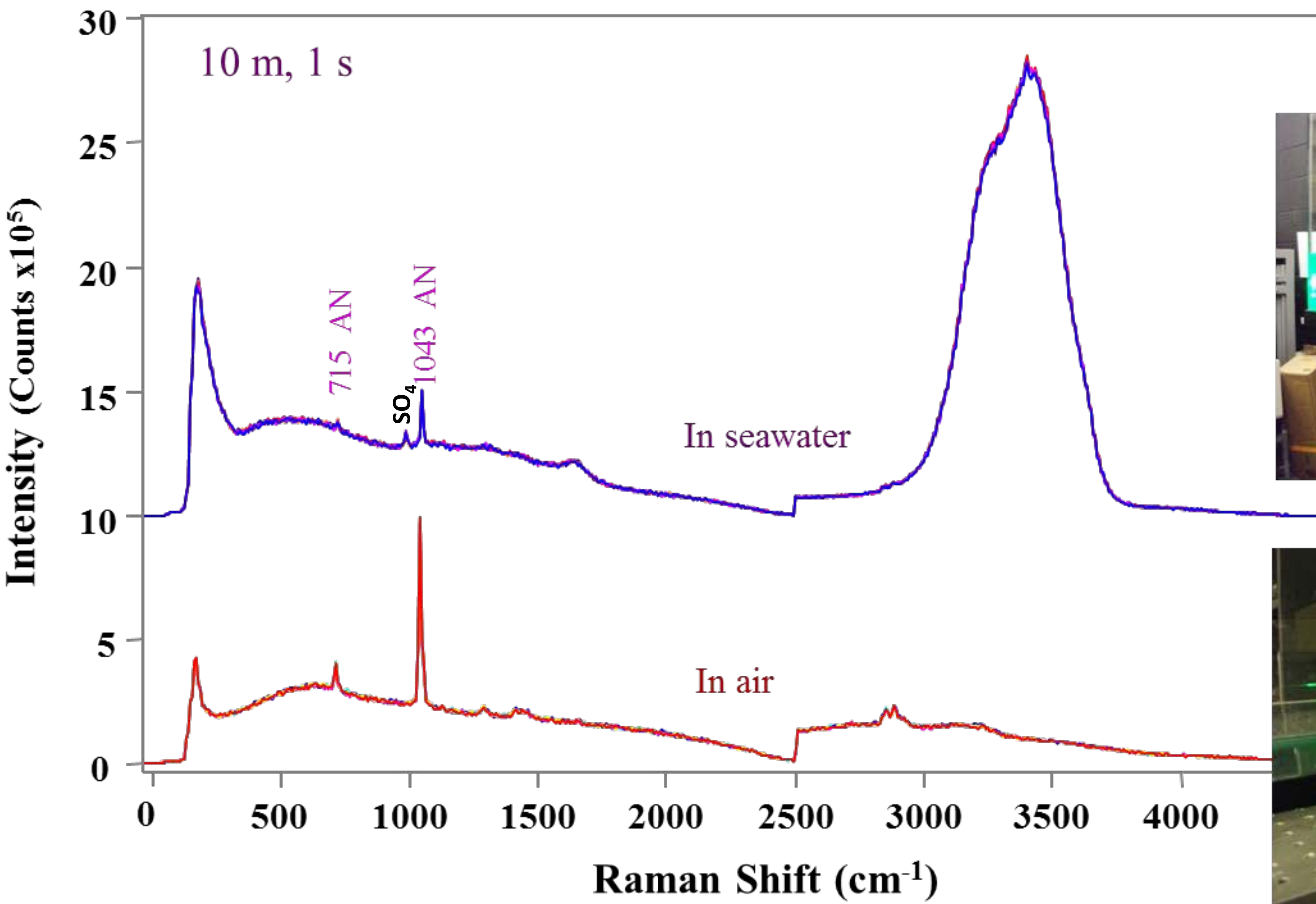
Standoff Raman Sensor Lab Setup
* 10 m distance
* all lights on
* 1 m fish tank with seawater at far end

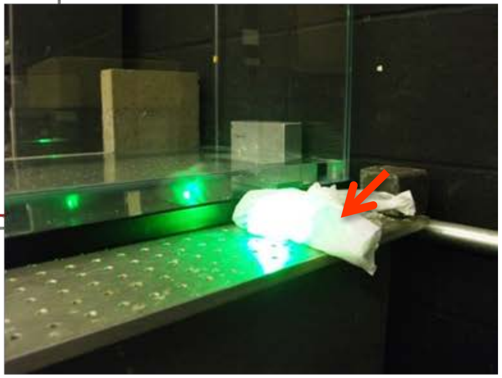
Remote TR-Raman Spectra of Seawater (2320-4480 cm^{-1}) in Snug Harbor, Honolulu, Hawaii



Raman Detection of Ammonium Nitrate (NH_4NO_3, AN) Through Seawater and 3 Plastic Bags

* 5 as-measured spectra shown



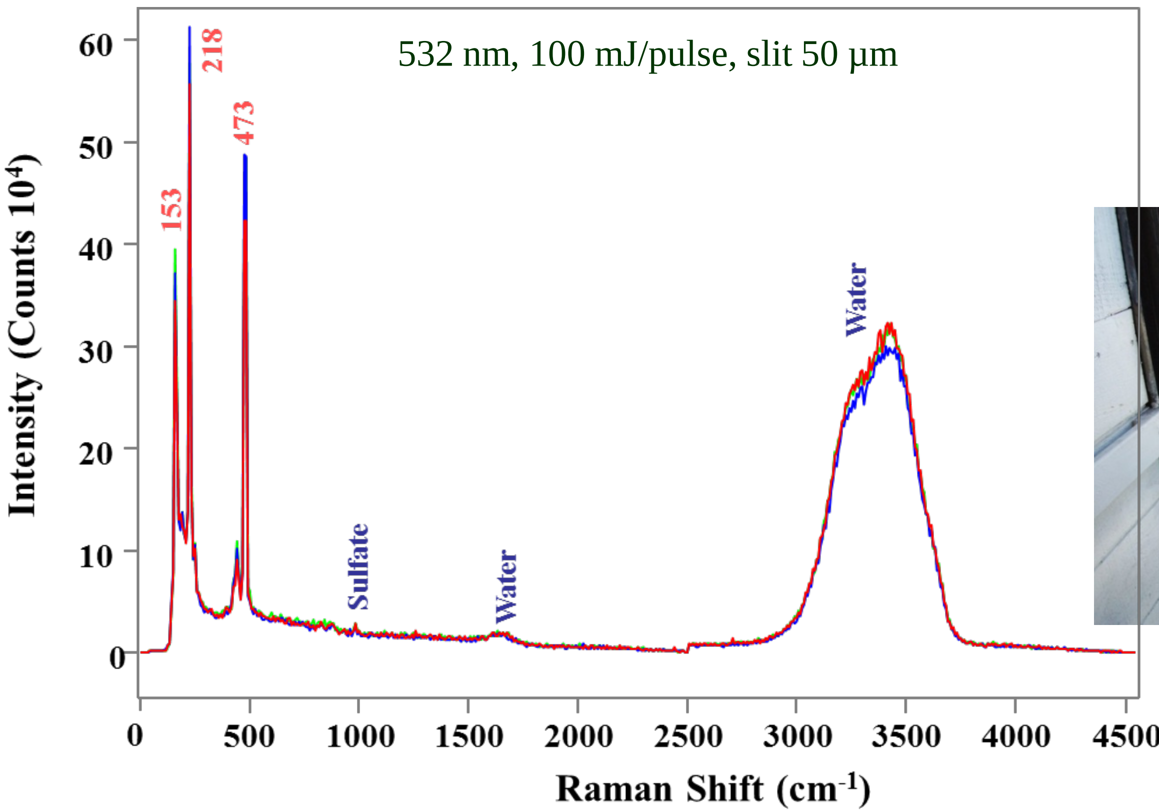


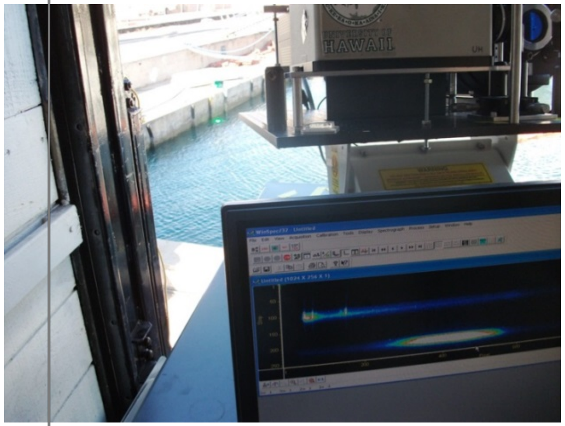
532 nm, 50 mJ/pulse, 15 Hz, gate width 100 ns, slit 50 µm

Field Testing at Snug Harbor, Hawaii with 532 nm Standoff TR-Raman System

Single Shot Detection of Sulfur at 2 m Seawater Depth with 532 nm Laser

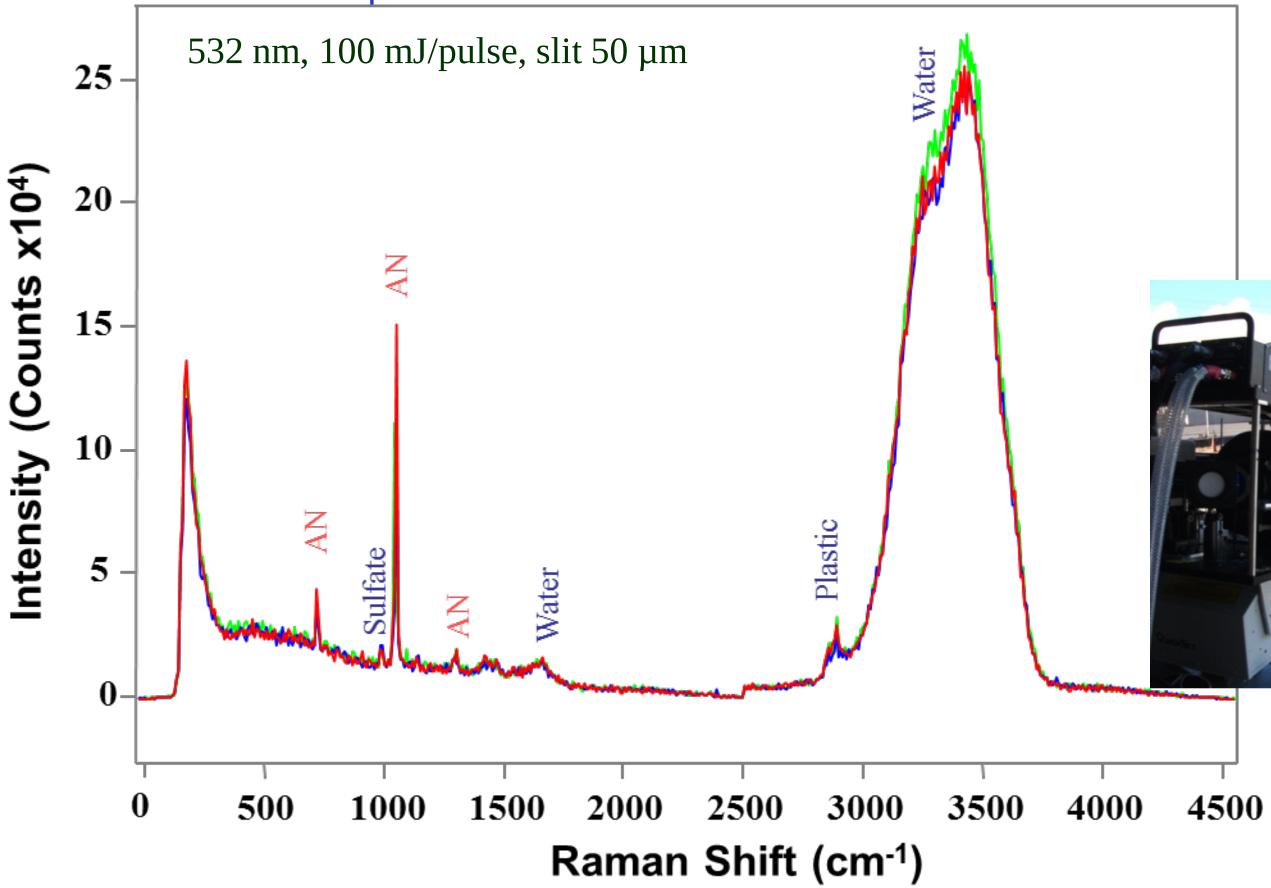
* 3 as measured spectra shown





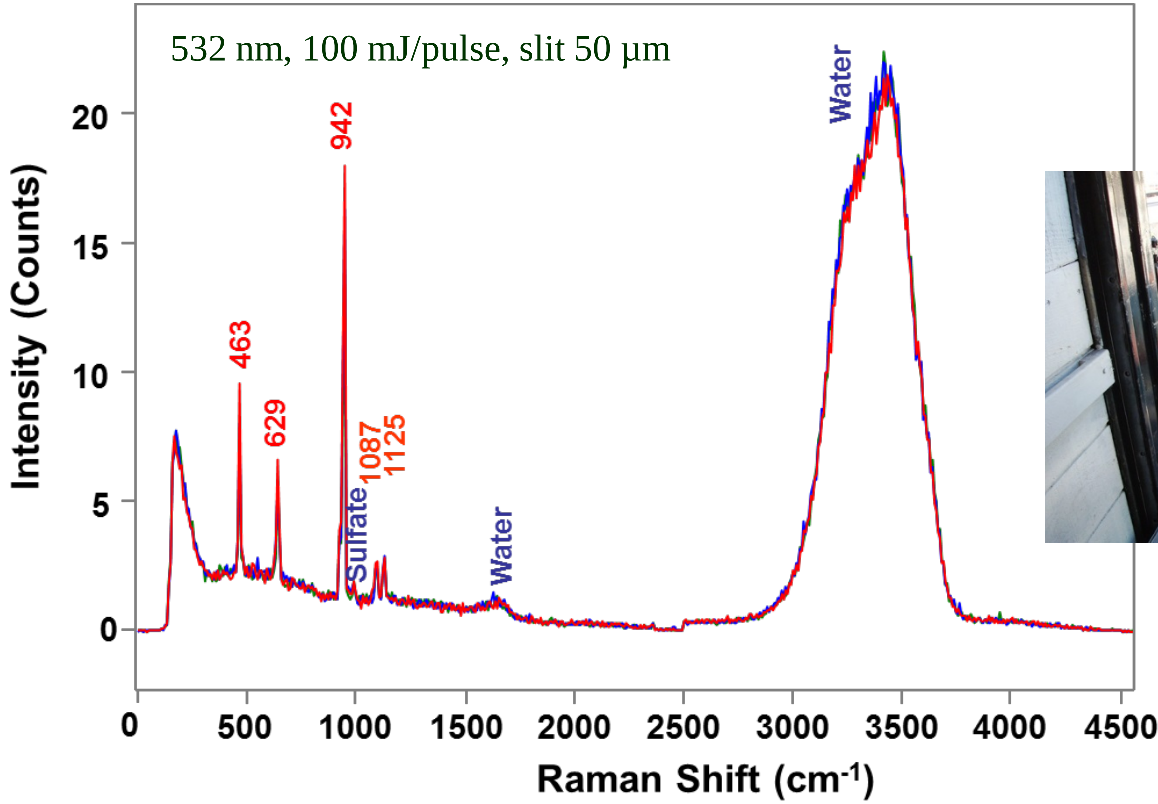
Single Shot Detection of AN inside HDPE bottle at 2 m Seawater Depth with 532 nm Laser

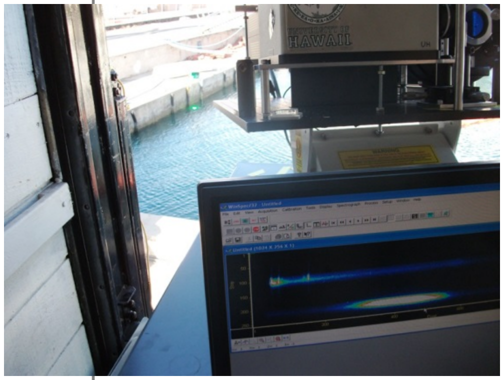
* 3 as measured spectra shown



Single Shot Detection of $KClO_4$ inside Glass at 2 m Seawater Depth with 532 nm Laser-excited TR Raman system

* 3 as measured spectra shown





Summary

* Described capability of TR- remote Raman systems for detecting Hes and HMEs chemicals
* Developed compact time-resolved remote Raman sensor with 3-inch optics
* It has range of detection in air to 50 m
* Unambiguous detection of various chemicals both organic and inorganics
* 2 m detection range for most chemicals in coastal seawater
* Daytime/nighttime detection
* The Raman Sensor will find applications in many DoD and Homeland Security as well as in marine environmental monitoring

Thank You for Your Attention