Remote Raman & Fluorescence Capabilities for Chemical Detection at University of Hawaii

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* Daytime Operation
* Long Detection Range (no sample collection)
* Fast Response
* Portable

- 5” system (532 nm) (fiber optic coupled)
- 5” system (532 nm) (direct coupled)
- 8” system (532 nm)
- 8” UV system (248 nm)
- 16” UV system (248 nm)
- 8” Raman+LIBS system
- 8” Raman (785 nm)
- 2” system (532 nm)
- 3.5” system (tunable UV)
- 2.5” Raman+LIBS+LINF+LIDAR (532 nm)
- 12” UV system (248 nm, 266 nm)
What is Raman spectroscopy? Why need Raman spectra?

Vibrational modes of molecules

Depends on atomic mass, bond lengths, bond strength, configuration, etc...

Unique spectrum for each molecule

* Raman Fingerprints: Chemical detection with very high confidence level
Example of Raman Spectra:

- Raman spectroscopy can distinguish between very similar chemicals

Always the same unique spectrum for a chemical !!!
* Good technique for detecting chemicals you don’t want to handle.
* No sample preparation

(Chemical waste sites, airport)

Single pulse Raman detection of **Conc. Sulfuric Acid** from 10 m

$\text{H}_2\text{SO}_4$, single pulse excitation, 10 m

* 5 as-measured spectra shown

55 mJ/pulse, gate width 100 ns, slit 50 µm
**Integrated Remote Raman+LIBS System**

Key Components:
(a) Dual Pulse Laser, 532 nm, 15 Hz, 100 mJ/pulse
(b) One gated intensified detector (ICCD)
(c) One high resolution, high throughput spectrograph
(d) 8-inch Telescope
Single shot Raman detection of Potassium chlorate & Potassium perchlorate at 120 m

* Good reproducibility  
  (showing 5 spectra as measured)  
* Good quality (High S/N)

100 mJ, 532 nm, 50 µm slit, laser spot size 1 cm (diameter).
Single shot Raman detection of Ammonium Nitrate & Potassium Nitrate at 120 m distance through sealed glass bottles

* Good reproducibility (showing 5 measurements- as measured)

Target at 120 m
Single shot excitation
Detection time = 0.5 µs
Single shot detection of 8% TNT on silica (NESTT sample) at 120 m distance

* Good reproducibility (showing 5 measurements - as measured)

8% TNT on silica at 120 m
Single shot excitation
Detection time = 0.5 µs
Single shot Raman detection of Urea and Sugar at 120 m distance through sealed glass bottles

* Good reproducibility (showing 5 measurements- as measured)

![Graph showing Raman shift for Urea and Sugar](image)

Target at 120 m
Single shot excitation

- 100 mJ, 532 nm, 50 µm slit, laser spot size 1 cm (diameter).
**Significant improvement in Raman signal (1 s)**

* Good reproducibility (5 measurements shown)

**Gypsum at 120 m**

![Graph showing Raman signal improvement with 1 second integration time](attachment:image.png)

- Intensity (Counts)
- Raman Shift (cm⁻¹)
- 1 s (= 15 pulses)
- 1 pulse

- Significant improvement in Raman signal
- Good reproducibility (5 measurements shown)
Raman Detection of Mixed grains of chemicals at 120 m distance

* 1 s detection time
* Good reproducibility (5 measurements shown)

100 mJ/pulse, 15 Hz, 532 nm, 50 micron slit, laser spot size 1 cm.
Detection of atmosphere, target mineral and both (as measured spectra)

Target (Gypsum CaSO₄·2H₂O) at 50 m

- **Target**
  - 1136 cm⁻¹
  - 1556 cm⁻¹
  - 2331 cm⁻¹

- **Atmosphere**
  - 3405 cm⁻¹
  - 3496 cm⁻¹
  - 3652 cm⁻¹

- **Target + atmosphere**
  - 414 cm⁻¹
  - 493 cm⁻¹
  - 619 cm⁻¹
  - 616 cm⁻¹

Raman Shift (cm⁻¹)
2” compact Raman+LIBS system

Minerals at 9 m, 1 s (3 measurements shown for each mineral)

Raman Shift (cm$^{-1}$)

Intensity (Counts x 10$^6$)

532 nm, 30 mJ/pulse
Remote Raman at 430 meters
1 s detection time, daytime

\[
\begin{array}{c|c}
\text{Raman Shift (cm}^{-1}\text{)} & \text{Intensity (Counts)} \\
\hline
200 & 0 \\
400 & 0 \\
600 & 0 \\
800 & 0 \\
1000 & 0 \\
1200 & 0 \\
1400 & 0 \\
1600 & 0 \\
1800 & 0 \\
2000 & 0 \\
\end{array}
\]

- **NH}_4\text{NO}_3**
- **KNO}_3**
- **KClO}_3**
- **Urea**
Standoff Raman (532 nm) detection through sealed containers

A: borosilicate glass vial (20 ml)
B: polypropylene (PP) vial (30 ml)
C: high-density polyethylene (HDPE) bottle (60 ml)
D: amber glass bottle (75 ml)
E: dark brown glass bottle (500 ml)

A B C D E
T= 81% 54% 18% 5.6% 1.7%

HDPE Water bottle Bubble wraps containing 20 ml glass vials
Single pulse Raman detection of Ammonium Nitrate at 10 m distance through sealed bottles

* 3 as measured spectra shown for each target

532 nm, 55 mJ/pulse, gate width 100 ns, slit 50 µm
Raman detection of hidden glass vial of Ammonium Nitrate through plastic bubble wrap

* 5 as-measured spectra shown

532 nm, 55 mJ/pulse, 15 hz, gate width 100 ns, slit 50 µm
Raman detection of AN through fluorescent label on HDPE bottle

10 m, 10 s

HDPE bottle
AN in HDPE bottle
Yellow tape (center)
Yellow tape (off set)
X 10
Raman+LIBS Spectrograph with 5 spectral images on one ICCD detector

ICCD Image (1024 x 256 pixels)

Wavelength Range
532.5 – 612.7 nm
457.3 – 530.9 nm
604.1 – 697.9 nm
736.5 – 869.4 nm
645.2 – 745.7 nm

Steel, at 9 m, 1 double pulse LIBS, Pulse separation 1 µs, 100 mJ/pulse, gate delay 1 µs, gate width 4 µs. ICCD Gain 25
Single pulse and double pulse LIBS spectra of Aluminum sheet at 9 m.

* Spectra showing good reproducibility (4 measurements shown)
* LIBS signal enhancement in double pulse excitation

Gate delay 1 µs, Gate width 20 µs, ICCD gain 10%, Double pulse separation 1 µs, 100 mJ/pulse, spot size 1 mm (dia)
There are small shot to shot variations.
Raman and Fluorescence Imaging LIDAR (RFI-LIDAR) for sea mine detection

Issues:
* No detection in the top 1-2 m surface layer
* Glint problem
* Signal from fishes, plants, air bubbles…

Ocean LIDAR (532 nm)
Single Shot Detection of AN inside HDPE plastic bottle at 2 m Seawater Depth with 532 nm Laser

*3 as-measured spectra shown

- Single pulse excitation
- 100 ns detection

* Can detect explosives in plastic bags underwater
* Metals have no Raman signal
Detection of both opaque metal object and also the transparent plastic dish using the image contrast.

**Raman Image**
Single pulse detection, detection time 300 ns
Detection in presence of bio-fluorescence

Detection of oil spill

One drop (0.1 ml) of crude oil in 2000 ml of water (50 ppm)

• Oil film is few micron thick
Current projects:

1. NASA Mars2020 mission: Los Alamos National Lab
   SuperCam Instrument

2. NASA EPSCoR: Standoff biofinder+Chemical analyzer

3. NASA PICASSO: Standoff Raman Line Scanner

4. NASA STTR: Q Peak Inc.: Small laser for remote Raman+LIBS (phase I)

5. ONR: Underwater Raman system

6. ONR (code 30): Long range (~km) Raman system (low cost drone)

Thank you.