Standoff Time-resolved (TR) Raman Spectroscopy for Detecting Home-Made Explosives (HMEs) and High-Explosives (HEs)

Shiv K. Sharma
Hawaii Institute of Geophysics & Planetology
University of Hawaii

Team Members:
Anupam Misra, John Porter & Barry Lienert

First published observation:
"A new type of Secondary Radiation"
C. V. Raman and K. S. Krishnan
Nature, March 31, 1928

Nobel Prize in Physics 1930

Raman spectra

Vibrational modes of molecules

\[ \omega = \sqrt{\frac{k}{\mu}} \]

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

Unique spectrum for each molecule

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Advancements in lasers, spectrographs and notch filters led to development of lab-based and field portable systems.

(i) Micro-Raman spectrometers
(830 nm; 785 nm; 514.5 nm, 488 nm, 244 nm)

(ii) Stand-off Raman spectrometers with pulsed lasers

(iii) Lifetime of scattering is $\sim 10^{-13}$ s

(iv) Raman intensities $\propto 1/\lambda^4$ (i.e., shorter excitation wavelengths stronger Raman spectra). If molecule absorbs excitation wavelength, one get resonance Raman enhancement up to $\sim 10^3$)

Raman spectra of molecules in solid, liquid and gas phase provide complementary information to infrared spectra but contain much sharper lines and the selection rules are different for Raman and infrared activity. It is possible to identify chemicals from their Raman fingerprints.
Standoff Time-Resolved Raman Systems
Pulsed Lasers: 785nm; 532 nm; UV: 355 & 266 nm; and 248 nm (KrF)

(A) The custom pan-tilt system allows us to scan a distant region collecting standoff Raman spectra over a user specified area. The final result will be the spatial distribution of Raman signatures of chemical residue and an image of the distant object. (B) Front view of Scanning Stand-Off Raman (SSOR) System
Single Shot TR-Raman detection of Potassium Perchlorate, Ammonium & Potassium Nitrates at 120 m

* Good reproducibility (showing 5 measurements- as measured)

Target at 120 m
Single shot excitation
100 mJ, 532 nm, 50 μm slit,
laser spot size 1 cm (diameter).

Raman Shift (cm⁻¹)

Intensity (Counts x 10⁴)

KClO₄

NH₄NO₃

KNO₃
Raman spectra of aqueous solutions of TNT, urea, KClO₃, KClO₄, and KNO₃ in various concentrations as marked. Exposure time: 60 s (10 pulses, 60 accumulations), 266 nm laser excitation, 105 mW at the sample. ICCD camera gain 255, 290 ns delay, 50 ns gate width. The band at 1354 cm⁻¹ corresponds to TNT. Broad bands centered around 680, 1650 and 2100 cm⁻¹ correspond to water. Bands at 787, and 1063 cm⁻¹ correspond to silica glass.

UV Raman Detection Limits in water: TNT (1 ppm); RDX (5 ppm); PETN (5 ppm)