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UV RAMAN SPECTROSCOPY AS A POTENTIAL STANDOFF DETECTION TECHNIQUE

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Abstract

Standoff detection techniques are needed to allow hazardous materials to be identified rapidly from a safe distance. One potentially useful standoff technique utilizes UV-Raman spectroscopy. A novel experimental configuration was implemented to generate Raman spectra for samples as a function of distance away from the collection optic. With this configuration, Raman spectroscopy was conducted using 213-nm light on samples of several common solvents. Identifiable spectra were generated with single laser pulses at distances approaching 5 meters. The experiment revealed an intensity drop off in collected Raman scatter inversely proportional to the distance between the sample and the collection optics. In order for spectra to be generated at 10 m, the target distance of the project, numerous pulses were averaged to achieve the desired signal-to-noise ratios. To improve on this performance the arrangement of the collection optics, the laser pulse intensity and the type of detection system were manipulated. The inclusion on a telescoping lens may prove to amplify the intensity of the signal. The project is supported by the National Science Foundation Research Experience for Undergraduates (REU) Award No. CHE-1460653.

Fig. 1: A sample of cyclohexane subjected to 213nm light in an effort to generate a Raman spectrum.

Background

An efficient standoff detection technique has significant advantages over contact detection methods especially when analysis of hazardous materials is desired. Standoff detection is defined as the ability to remotely detect trace materials. Two competing candidates for a viable standoff technique include Raman spectroscopy and florescence. Florescence is a highly sensitive technique, capable of signal molecule detection, but it has low selectivity; characterizing a molecule based on florescence alone is difficult. On the other hand, Raman spectroscopy is a highly selective, although low-sensitivity, technique. Raman scatter is on the order of one billion times less intense than that of florescence. However, the high selectivity of Raman can make it a potential candidate for standoff detection since a single Raman spectrum is enough to characterize a known molecule when referencing a database. Overcoming the low sensitivity of the Raman scatter could establish Raman spectroscopy as a valuable standoff detection technique.

Specifically, UV-Raman spectroscopy was the topic of study for this research project due to its advantages over traditional, visible light based Raman. For instance, ultraviolet light scatters 40-50 times more efficiently than visible light; implying the Raman scatter evoked by UV light is more intense than that of its visible counterpart. Enhanced resonance effects are also expected up UV excited Raman spectroscopy. If resonance enhancements were to be observed, the intensity of scatter would be amplified by a factor of about up to one million. These two methods signal enhancements may prove to increase Raman scatter enough to make Raman spectroscopy viable as a standoff detection technique.

Data

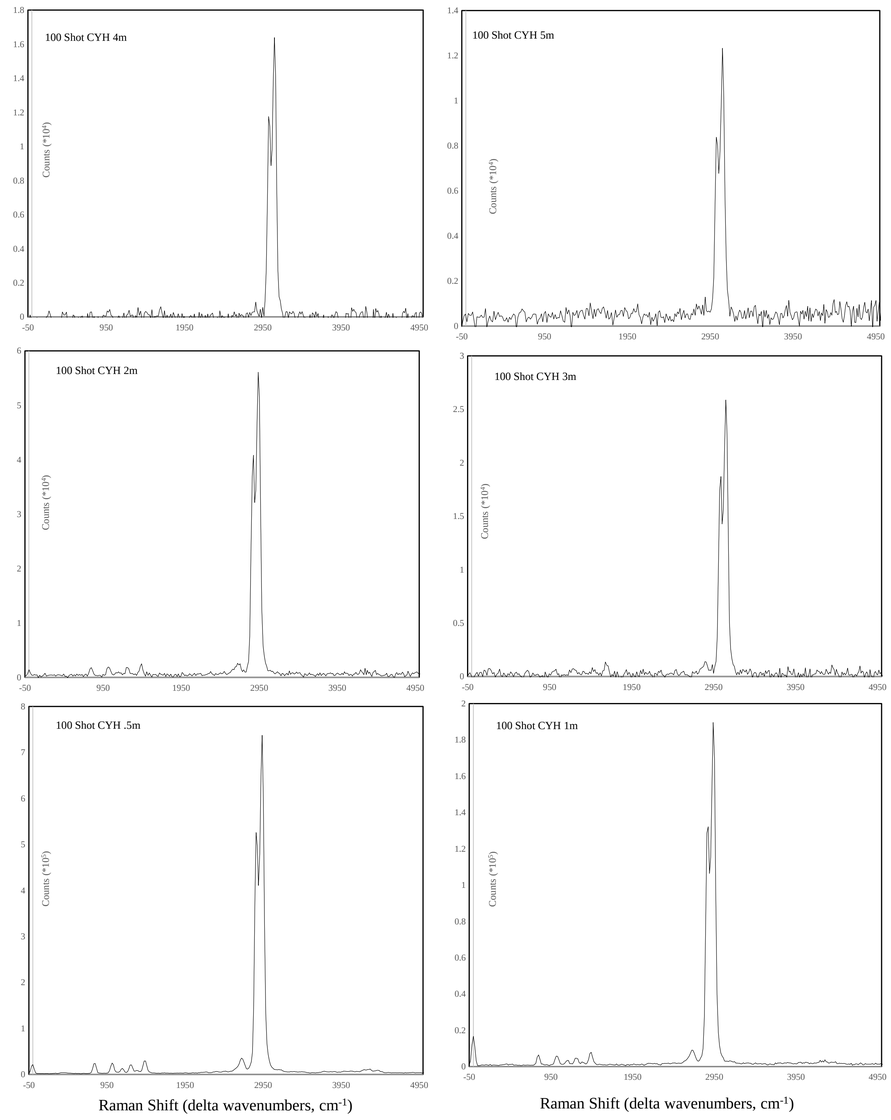


Figure 3:

100 accumulation (10s) Raman spectra of cyclohexane taken from distances between .5-5m are shown above. The Raman Shift is relative to 213-nm light. The Raman bands between 801 – 1443 cm^{-1} reside in what is known as the fingerprint region. In general, bands existing in the fingerprint region of a Raman spectrum are characteristic to the compound being studied. The large band centered at 2950cm^{-1} is indicative of the carbon-hydrogen (C-H) stretch.

As can be seen, the signal-to-noise ratio of each spectrum decreases with increasing distance between the sample and the collection optic. The fingerprint region becomes indistinguishable from noise at distances greater than or equal to 4m. However, the C-H band was observable throughout the entire series.

Experimental

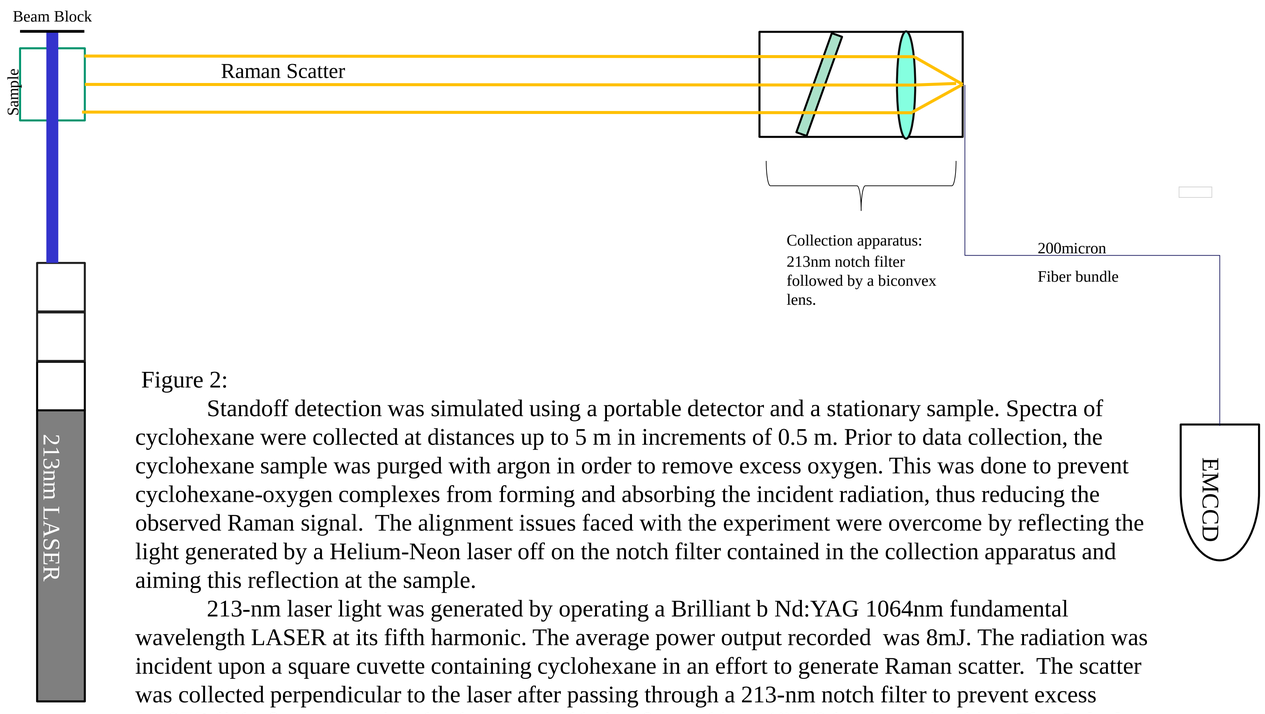
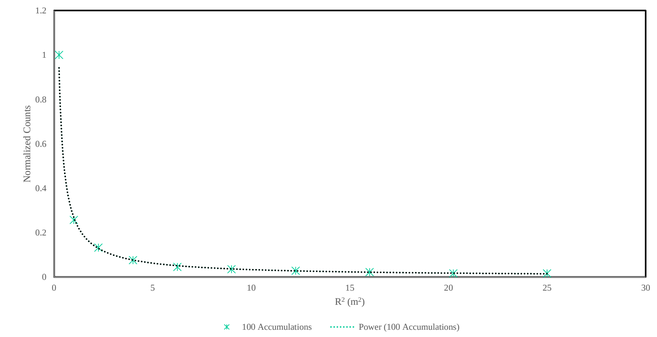


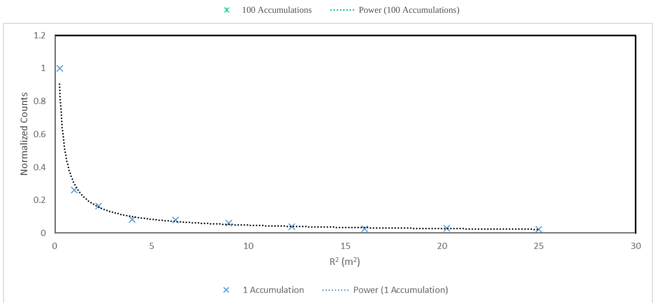
Figure 2:

Standoff detection was simulated using a portable detector and a stationary sample. Spectra of cyclohexane were collected at distances up to 5 m in increments of 0.5 m. Prior to data collection, the cyclohexane sample was purged with argon in order to remove excess oxygen. This was done to prevent cyclohexane-oxygen complexes from forming and absorbing the incident radiation, thus reducing the observed Raman signal. The alignment issues faced with the experiment were overcome by reflecting the light generated by a Helium-Neon laser off on the notch filter contained in the collection apparatus and aiming this reflection at the sample.

213-nm laser light was generated by operating a Brilliant b Nd:YAG 1064nm fundamental wavelength LASER at its fifth harmonic. The average power output recorded was 8mJ. The radiation was incident upon a square cuvette containing cyclohexane in an effort to generate Raman scatter. The scatter was collected perpendicular to the laser after passing through a 213-nm notch filter to prevent excess LASER light from saturating the detector, and being focused by a 1" F/2 lens contained in a ThorLabs laser cage on to a 200micron Fiber bundle. The signal was sent to an Electron Multiplying Charge-Coupled Device (EMCCD) in order to generate Raman spectra. At each point in the series, 1, 10 and 100 accumulation spectra were generated.

Results





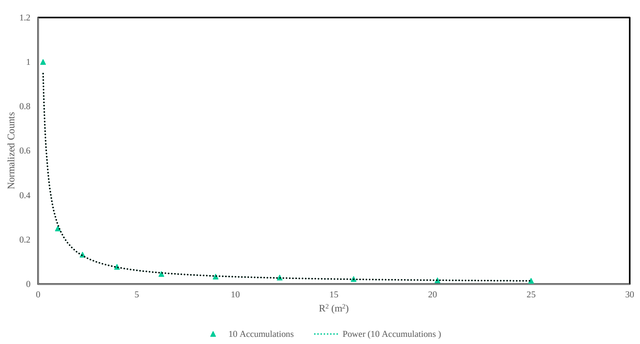


Figure 4:

Distance dependence plots for the 1,10, and 100 accumulation series are shown. Each plot was normalized against the highest intensity point (.5m) of the series. The experimental evidence suggests an inversely proportional relationship between the distance the Raman signal travels before detection and the intensity of the observed signal.

Conclusions

- The Raman scatter signal drops off inversely proportional to the distance traveled.
- UV-Raman spectroscopy may be a viable standoff detection technique if a stronger Raman signal can be collected. To accomplish this collection, modifications to the experimental set-up need to be made. One potential change is the inclusion of a telescoping lens to collect and focus a large area of scatter on to a single point.
- In the next phase of the research, solid state nitroaromatic compounds will be tested for their capability of producing a Raman signal. This series of experiments will simulate the in field detection of trinitrotoluene (TNT), a common explosive encountered by military personal.

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