

Resonance Raman measurements utilizing a deep UV source

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ABSTRACT

Raman scattering techniques have long been used as unique identifiers for spectral fingerprints of chemical and biological species. Raman lidar has been utilized on a routine basis to remotely measure several constituents in the atmosphere. While Raman scattering is very reliable in uniquely identifying molecules, it suffers from very small scattering cross sections that diminish its usefulness at increased ranges and decreased concentrations of the species of interest. By utilizing a resonance Raman technique, where the laser excitation is tuned near an electronic absorption band, it is possible to increase the Raman scattering cross section. An optical parametric oscillator (OPO) with a UV tuning range of ~220 nm – 355 nm has been utilized to explore the wavelength dependence of Raman scattering for diamond, water, benzene, and toluene. Resonance enhancements of the Raman spectra have been studied.

Keywords: Resonance Raman, tunable ultraviolet laser, benzene, toluene, diamond, resonance scatter

1. INTRODUCTION

The need for improved monitoring techniques for measuring chemical species has never been more important. The problems in need of attention include monitoring air pollutants, additional evidence for increases in global warming and the requirements for measurements of toxins and explosive materials due to the precarious situation caused by international terrorism. Improvements are also needed in the measurement and detection of greenhouse gas pollutants. These materials are most commonly found in small concentrations either spread throughout the atmosphere in the case of pollutants, or found in low concentrations around a small source such as an explosive or toxic chemical release. Raman spectroscopy has been used in the laboratory as a reliable means to measure most chemical species, however Raman scattering cross sections are quite small and these signals are directly proportional to the number of scatterers. In the case of small number densities it becomes extremely difficult to detect, let alone quantify, the trace concentrations of chemical species of interest. With the advent of more powerful and lower cost tunable ultraviolet sources it is now possible to consider using the resonance Raman effect on a more routine basis. The resonant enhancement of the scattering cross section occurs when the excitation frequency approaches the energy corresponding to an electronic state of a molecule. This phenomenon has been found to enhance the Raman scattering cross section between 3-8 orders of magnitude [1]. With this huge increase in scattering cross section it is possible to detect and possibly quantify significantly smaller concentrations of chemical and biological species, particularly trace pollutants, bio-contaminants, and explosives.

2. EXPERIMENT

Our experiments were performed at the North Carolina State University Optics Lab. The Raman scattering experiment used a tunable pulsed laser for excitation, and it was tuned over electronic absorption bands of several selected species. Samples were held in a teflon container with fused silica windows, and the incident radiation strikes the input window at ~45° before scattering into a matched optical collection system. The lens coupling system focused the light through the entrance slit into a triple monochromator for analysis.

2.1 Tunable Laser

A tunable optical parametric oscillator (OPO) from U-Oplaz was utilized as the laser of excitation. The OPO was pumped with the 3rd harmonic of the Nd:YAG laser at 354.7 nm (Spectra Physics INDI, 10Hz). This laser beam served as the pump beam, which is then split within the OPO cavity into two other beams a signal and an idler. In our case the signal beam is a tunable laser in the visible from 420 nm – 710 nm. This visible output is then doubled after the OPO cavity to create a tunable ultraviolet source from 210 nm to 355 nm. This ultraviolet laser became the tunable source of excitation for the resonance Raman experiments. The phase matching conditions for our OPO, and the associated laser output are summarized Table 1. A schematic of the excitation laser setup including the pump laser, OPO and ultraviolet doubling crystals is shown in Figure 1. The tunable output of the OPO in the visible is shown in Figure 2.

Table 1. Examples of phase matching angle of OPO using a 354.7 nm pump.

Phase Matching Angle (Deg)	Signal (nm)	Idler (nm)
25.1	423	2200
27.4	450	1682
30.1	500	1224
31.7	550	1001
32.5	600	869
32.9	650	782
33.1	700	720

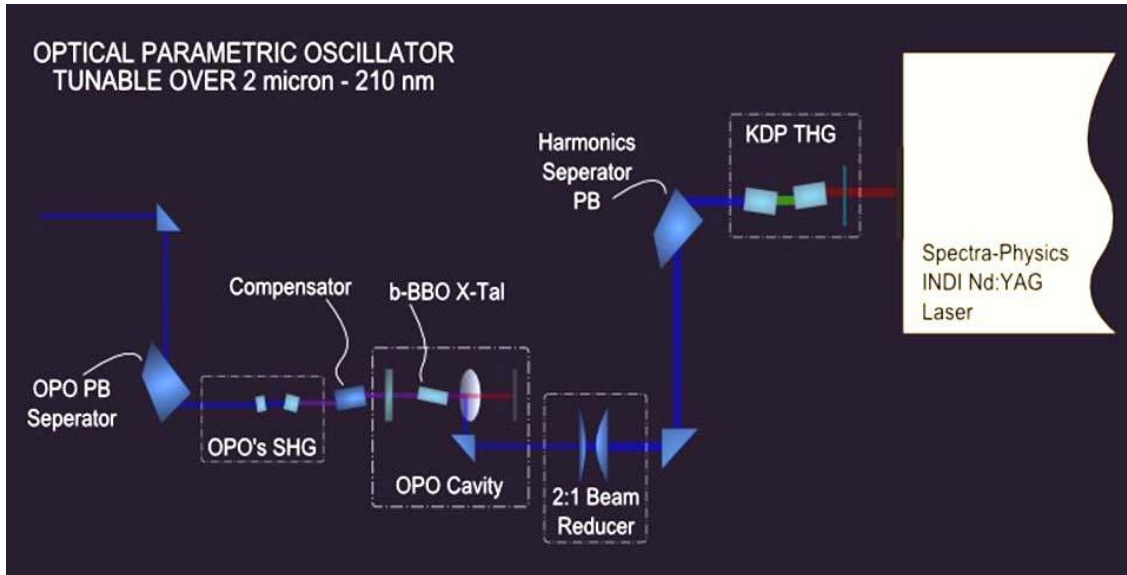


Figure 1. Excitation laser for Raman scattering setup.

2.2 Experiment Arrangement

A 90⁰ optical scattering setup was utilized to collect the Raman spectra. The incident light illuminates the sample at approximately 45⁰ with respect to the window normal, and then is scattered at 45⁰ completing a 90⁰ optical scattering arrangement. The phenomena of Raman scattering is the result of a collection of randomly oriented dipole scatterers resulting in near isotropic scattering. The collection of the scattered radiation is via a matched lens system to collimate and focus the scattered light into the spectrometer's entrance slit. Since the beam is coupled through a slit into the spectrometer the most critical direction for optimal beam alignment is perpendicular to the input slit. In order to optimize coupling into the spectrometer a UV (fused silica) right angle prism was mounted on a multi-axis mount allowing a micro-adjustment of the beam position.

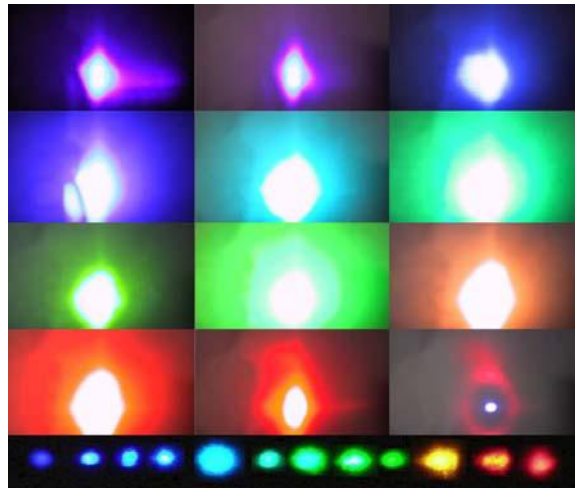


Figure 2. OPO laser output showing the 420-710 nm (white center portions due to saturation of digital camera).

2.3 Spectrometer

In many Raman scattering experiments, the extremely strong Rayleigh scattering is removed via a holographic notch filter. However, when using a tunable source it is not feasible to utilize the extremely large number of filters spanning the tuning range of the laser. In lieu of holographic notch filters a three stage spectrometer was utilized, the triple Spex Jobin Yvon Horiba 1877 spectrometer. With the first two stages utilized as a filter to remove any stray light and the much stronger Rayleigh (elastic) scattering from the optical path. The final third stage is the traditional spectrometer dispersal stage to separate the Raman scattered light. By narrowing the filter stage's slit width, it is possible to have out of band blocking on the order of 10^{14} . In our case the Raman scattered light was imaged onto a UV EM-CCD (Electron Multiplying Charge Coupled Device). The minimum filter slit width is limited by the field of view of the camera. As the filter slit is diminished in size the stray light rejection becomes more effective, however the field of view of the camera becomes constricted.

2.4 Detector

The data was taken utilizing an EM-CCD camera from Andor. The EM-CCD was chosen for 2 primary reasons; the camera has extremely low dark count background, and has very high quantum efficiency ($\approx 35\%$) through the ultra-violet region. Figure 3 shows the Andor IXON back illuminated EM-CCD camera quantum efficiency curve.

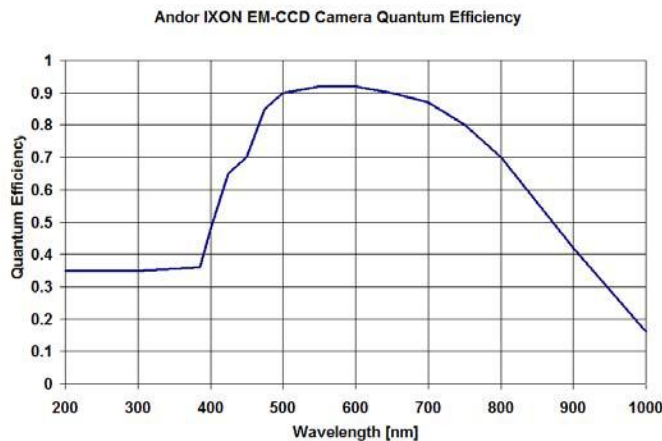


Figure 3. Andor Ixon EM-CCD quantum efficiency.

2.5 Instrument Calibration

The spectrometer was calibrated using a low pressure mercury vapor lamp. The lamp is chosen because of its strong ultraviolet emission lines in the wavelength region of interest. By utilizing the mercury vapor emission lines it is quite simple to calibrate the spectrometer to an accurate wavelength scale. Figure 4 shows four lines from the mercury lamp, each of which is ~ 0.2 nm apart. A separate confirmation of calibration was performed using a known laser wavelength and a diamond. Diamond is commonly used as a reference spectrum because of its strong single Raman scattering component at 1331 cm^{-1} . Figure 5 shows the rough cut diamond, the bluish color observed is due to fluorescence. Shown in Figure 6 is the Raman scattering component of the diamond when excited by 260 nm. It should also be noted that throughout the experimentation process many other chemicals (heptane, Teflon, naphthalene, beta-carotene, water) were tested with known and well documented Raman spectra. Each Raman line from these chemicals was located in its proper position giving more confidence in a well calibrated spectrometer throughout the duration of the experiment.

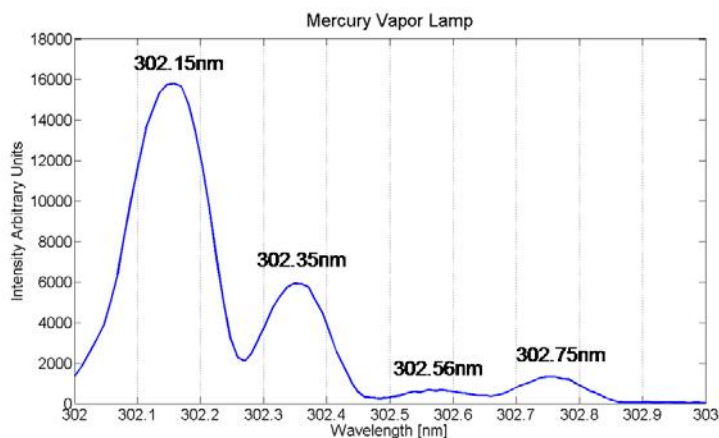


Figure 4. Mercury vapor lamp spectra 2400 gr/mm triple spex spectrometer.



Figure 5. Rough diamond for calibration, color observed is due to fluorescence.

3. RESULTS

The wavelength spectra of Raman scattering of several samples were explored and recorded within the ultraviolet region (220 nm – 300 nm). Pre-resonance enhancements were examined in diamond and resonance enhancements were studied in both benzene and toluene.

3.1 Diamond Pre-resonance Spectra

A pre-resonance enhancement in diamond was measured by tuning the laser from 245 nm to 215 nm. A maximum in the pre-resonance found near an excitation wavelength of 235 nm. This pre-resonance enhancement is shown in Figure 7. However, when approaching 225 nm, the band gap of diamond (~ 5.5 eV), the Raman scattering was found to diminish and completely disappear. Since the band gap in diamond is so large it was not possible to find a full resonance enhancement within the tuning range of our OPO.

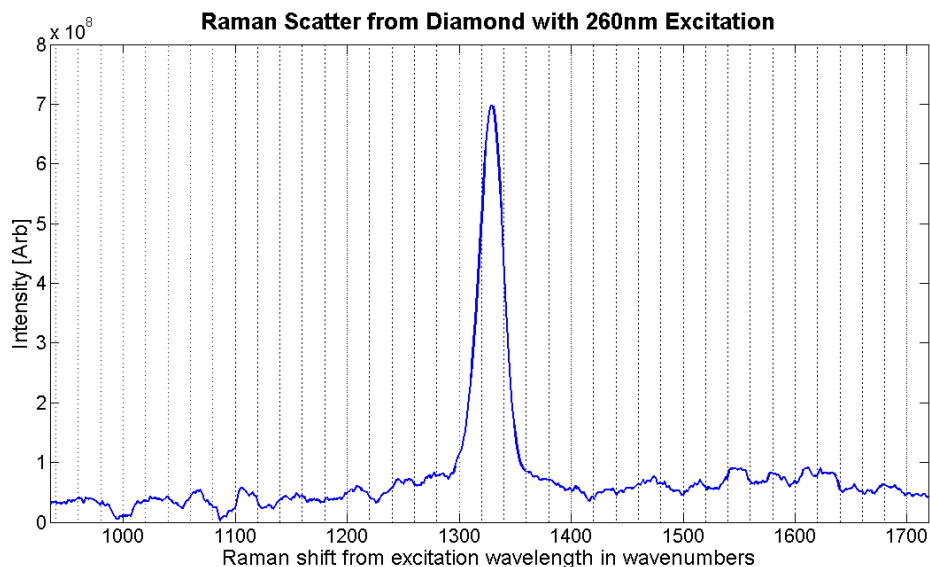


Figure 6. Raman scatter from diamond with 260 nm excitation.

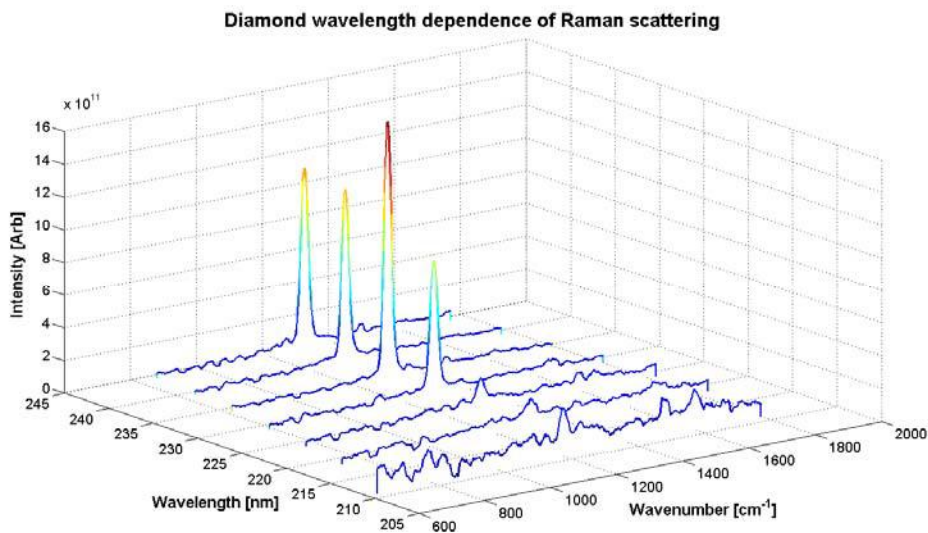


Figure 7. Excitation wavelength dependence of Raman scatter intensity in diamond.

3.2 Benzene Resonance

Resonance enhanced Raman scattering was studied in liquid benzene when tuning through the forbidden ${}^1B_{2u}$ absorption band. This ultraviolet absorption band has a ‘fingerlike’ fine structure from 230 nm to 270 nm, see Figure 8. The resonance enhancement within liquid benzene produced a significant increase in the Raman scattered signal intensity compared with the expected in the visible region. Resonance Raman scattering in liquid benzene was found to enhance the ν_2 (Herzberg notation) vibration. Our measurements and calculations show enhancements of 2- to 4-orders of magnitude. In addition to the enhancement of the ν_2 vibration, an array of combination and overtones modes are found that are similar modes to those seen by Zeigler and Hudson [2]. A comparison of the resonance enhanced Raman scattering and the non-resonance enhancement in benzene is shown in Figure 9.

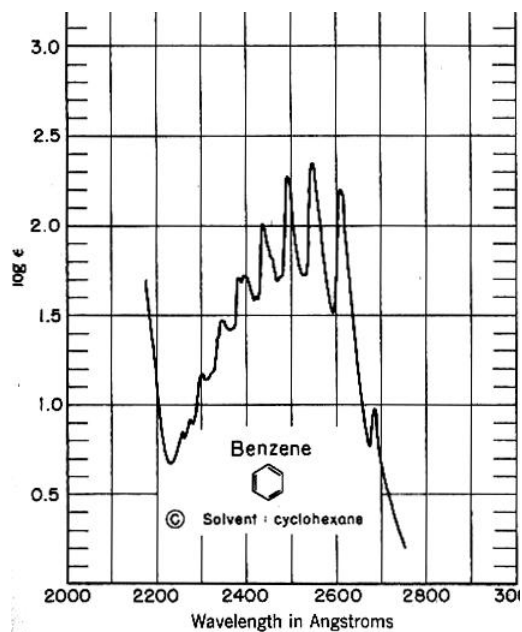


Figure 8. Liquid benzene absorption in cyclohexane [3].

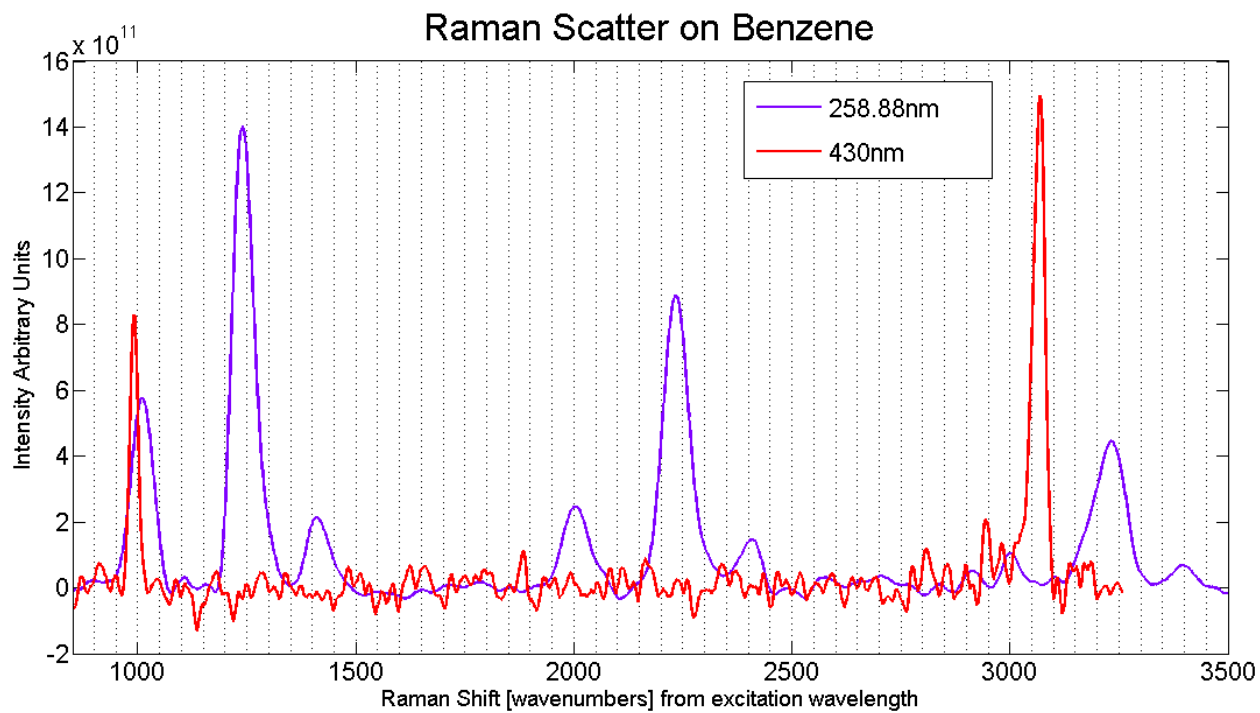


Figure 9. Resonant and non-resonant Raman scattering in benzene.

3.3 Toluene Resonance

Resonance enhanced Raman scattering was observed in toluene when tuning through the absorption features in the region between 260 nm and 270 nm, as seen in Figure 10. Similar to benzene the resonance enhancement in toluene

resulted in a number of combinational modes and overtones. Initial calculations show the resonant enhancement in toluene to be approximately 3-orders of magnitude. A comparison of the resonance enhanced Raman scattering in toluene with the non-resonant spectra is shown in Figure 11.

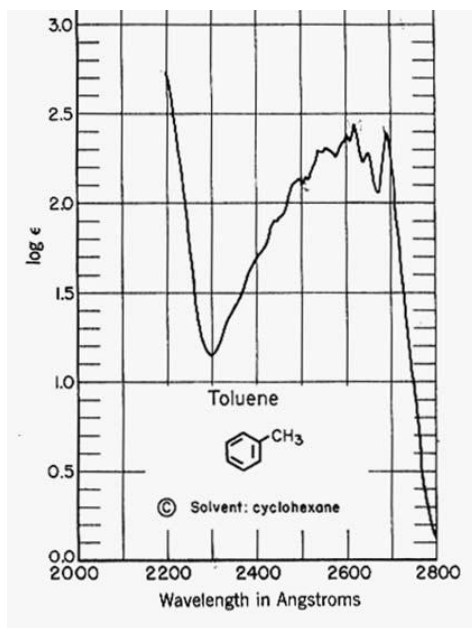


Figure 10. Liquid toluene absorption in cyclohexane[3]

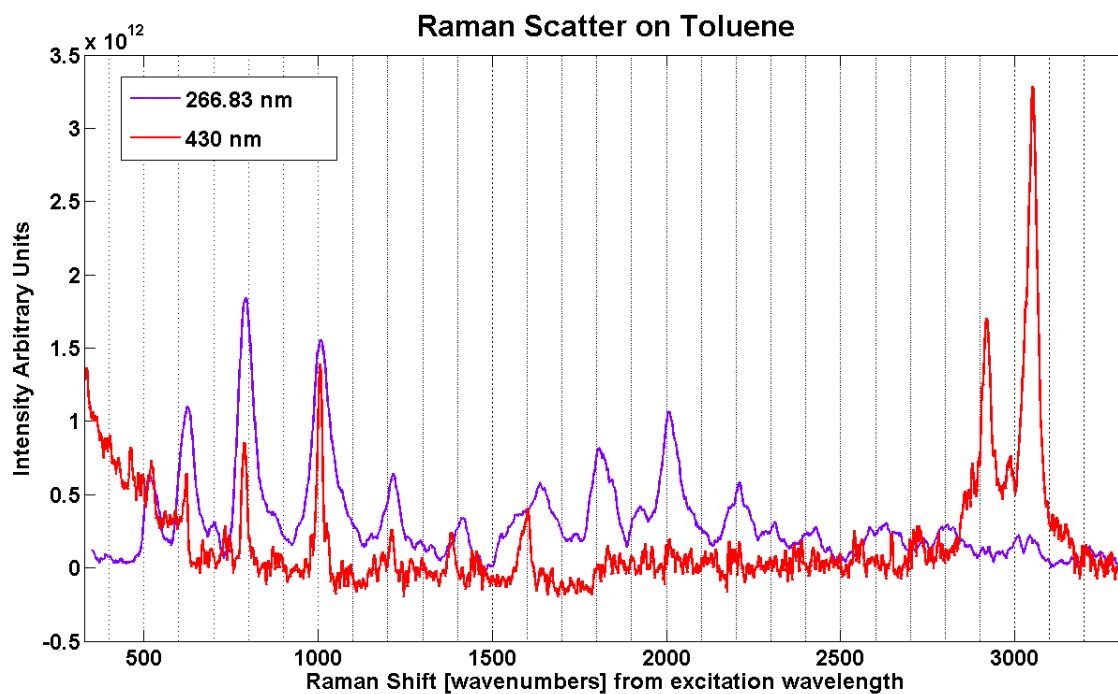


Figure 11. Resonant and non-resonant Raman scattering on toluene.

4. CONCLUSIONS

The resonance enhanced Raman scattering was explored in diamond, benzene and toluene and initial results are presented. A pre-resonance enhancement within diamond is seen on the long-wavelength side of the band gap. As the wavelength of excitation is tuned deeper into the band gap the enhancement is seen to disappear, and all of the Raman scattered signal within diamond is lost. The resonance enhancement in benzene and toluene are quite significant with increases in the Raman scattered signal to be approximately 2- to 4-orders of magnitude. Both benzene and toluene not only show increases in the Raman scattered signal but also show many combination and overtones. The resonance Raman technique is expected to provide new capabilities for measurements of trace concentrations of molecular species, and may prove applicable to detection of explosive materials, toxics, and air pollution species. Our goal in pursuing the resonance scattering processes is to increase the sensitivity of lidar for remote detection of trace concentrations of chemical species.

5. REFERENCES

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