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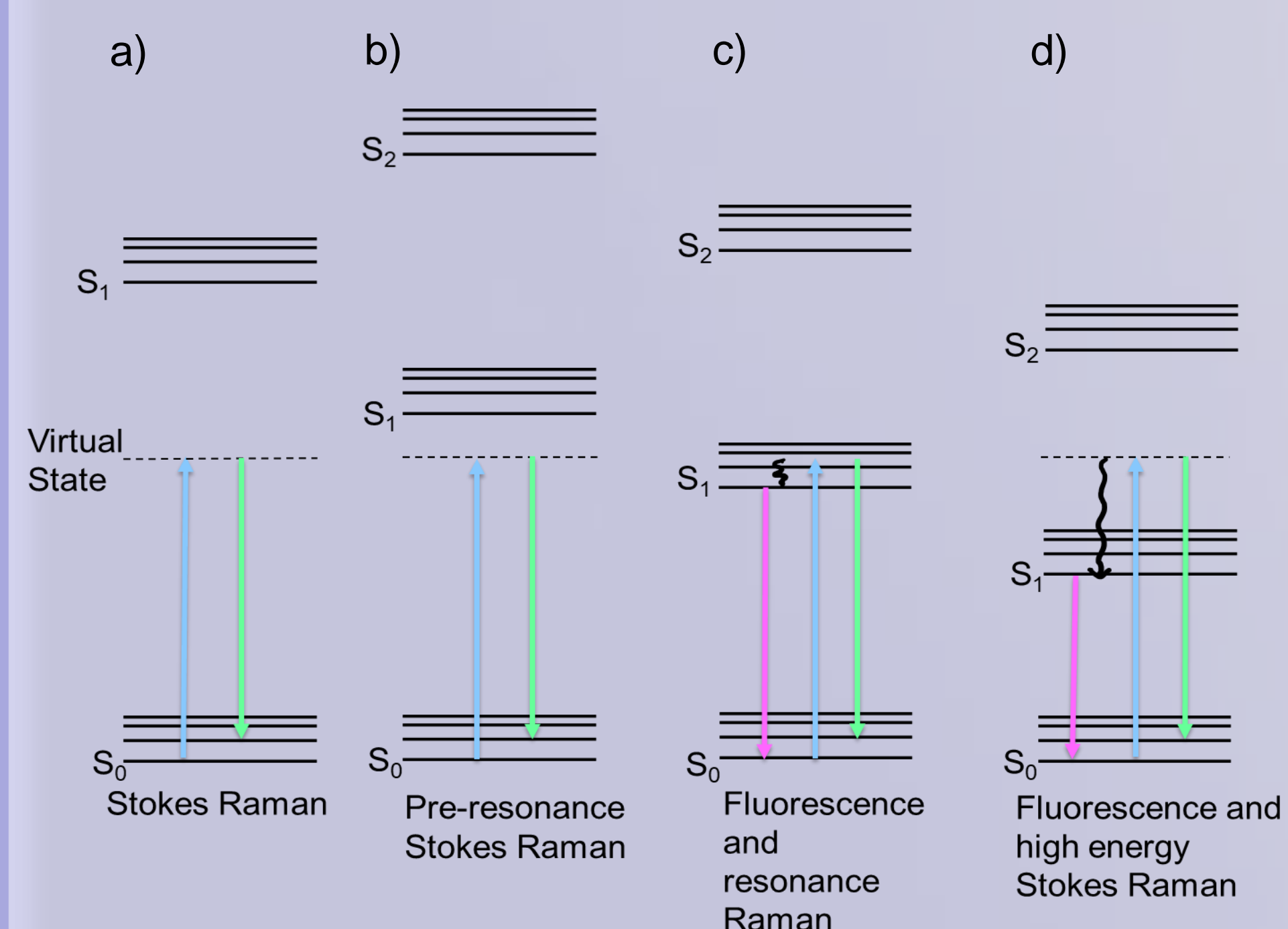
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## Introduction

Methods to detect hazardous or illicit materials accurately, rapidly, and at discreet distances, are needed for public safety. Monitoring mass transit facilities and luggage, the delivery of packages and letters, and participants at large scale events, without interfering with the progress of these normal operations is difficult.

Among the most promising technologies poised to address this critical need is Raman spectroscopy. This technology requires no sample preparation and does not damage the sample. Raman also has the potential to identify chemicals in a single laser pulse and from distances far enough to keep the operator safe. These properties are especially advantageous for in-field applications.

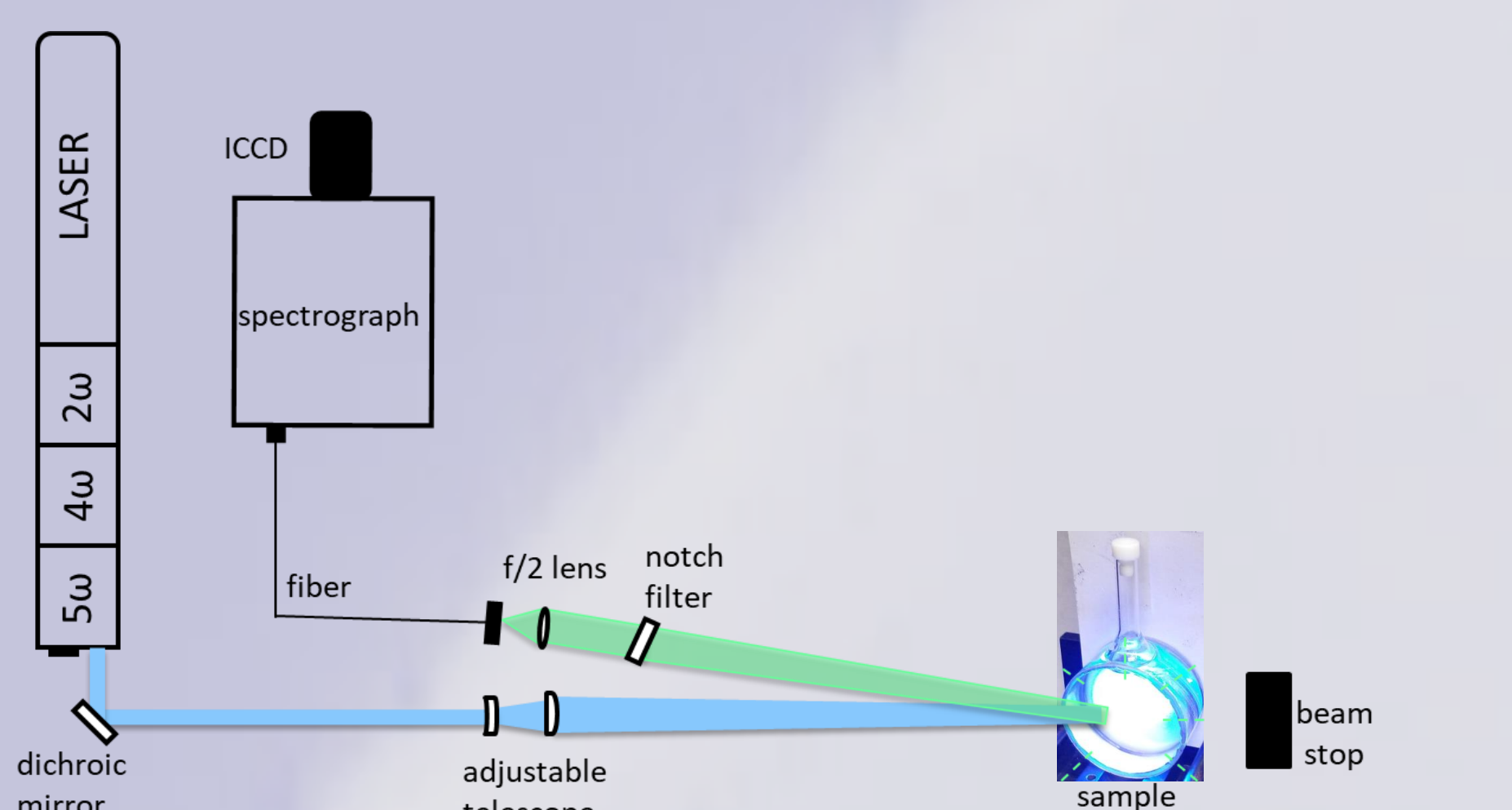
## Raman Background



**Figure 1.** Jablonski diagram of the Raman phenomenon. Excitation photons from the laser interact with electrons in the sample to promote them to a “virtual state”. When the electrons relax to a different vibrational level in the ground state, the photon emitted is called Raman scatter (a). The probability that this will occur is enhanced when the interactions have energies similar to the energy of an electronic transition (b and c). The main challenges associated with Raman spectroscopy are inherently weak signals and intense background from competing fluorescence (c). Fluorescence can be avoided by exciting these samples in the deep-uv (d).

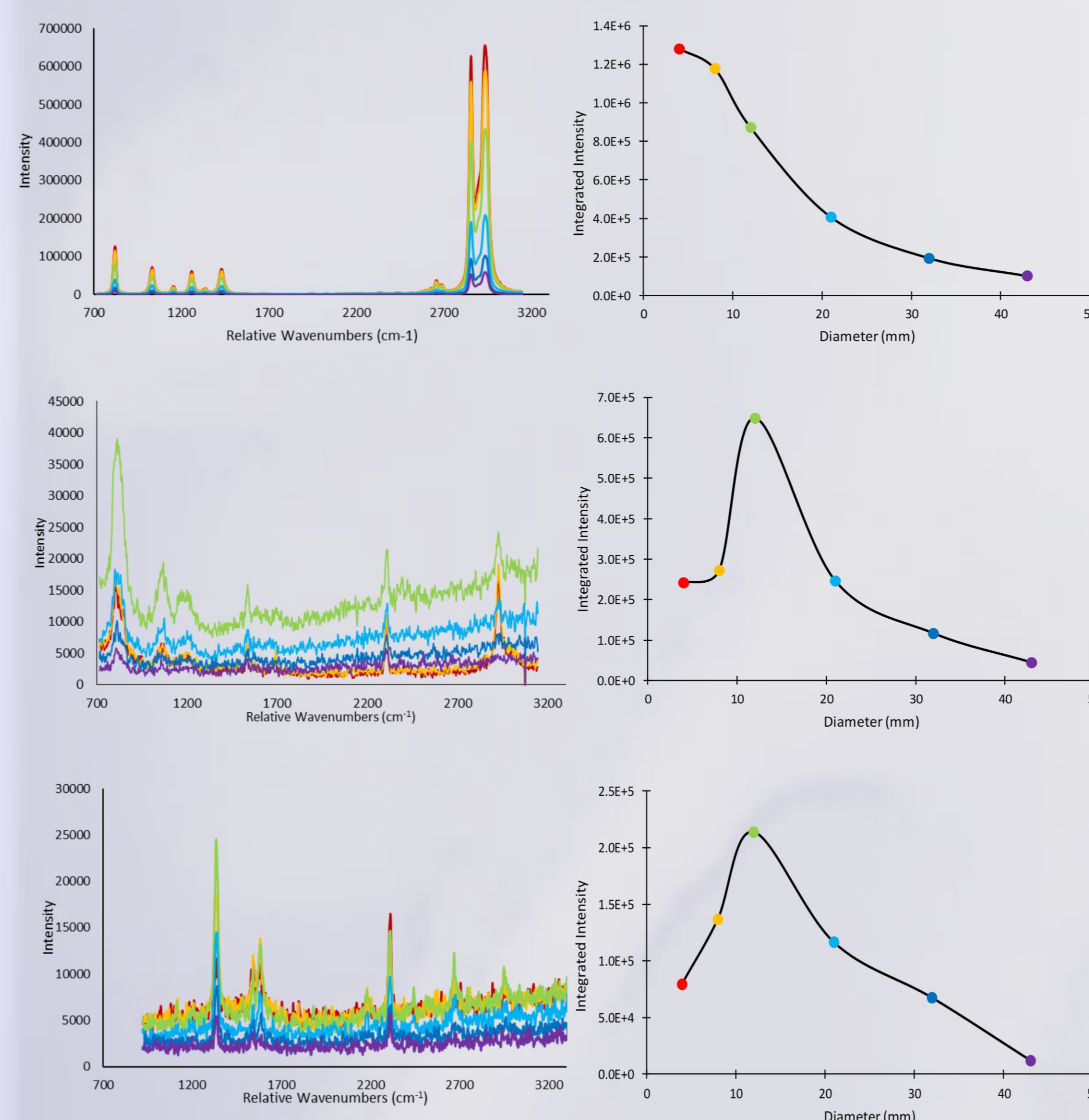
## Methods and Theory

By using intense laser pulses at 213 and 266 nm along with gated detection this experiment aimed to mitigate the appearance of fluorescence in the spectral region being observed. Furthermore, excitation spot size of the laser on the sample was manipulated with the goal of allowing more molecules to scatter from the surface and not requiring deep penetration into the sample to observe Raman spectra. The spot size was varied using a beam expanding telescope. Comparisons between excitation wavelengths, excitation spot size, and sample presentation were carried out. The experimental setup is shown below.



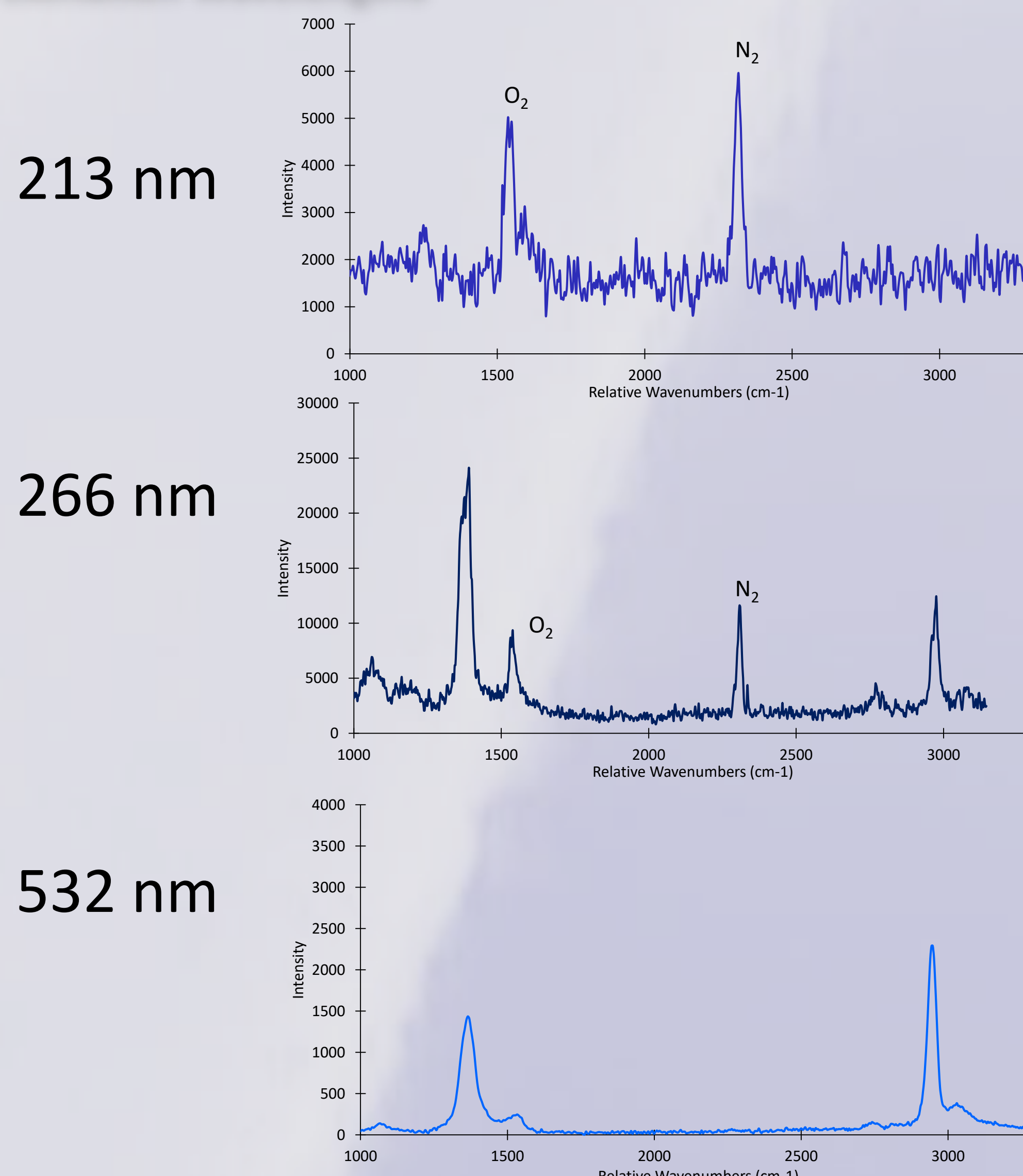
**Figure 2.** 266 and 213 nm laser light was generated by operating a Brilliant b Nd:YAG 1064nm fundamental wavelength laser at its fourth and fifth harmonic, respectively. The average power output recorded was 5 mJ. The scatter was collected nearly co-linearly to the laser after passing through a notch filter to prevent excess laser light from saturating the detector, and was focused by a 1” F/2 lens contained in a ThorLabs laser cage on to a 200 micron fiber bundle. The signal was sent to an Intensified Charge Coupled Device (ICCD) in order to generate Raman spectra.

## Excitation Spot Size



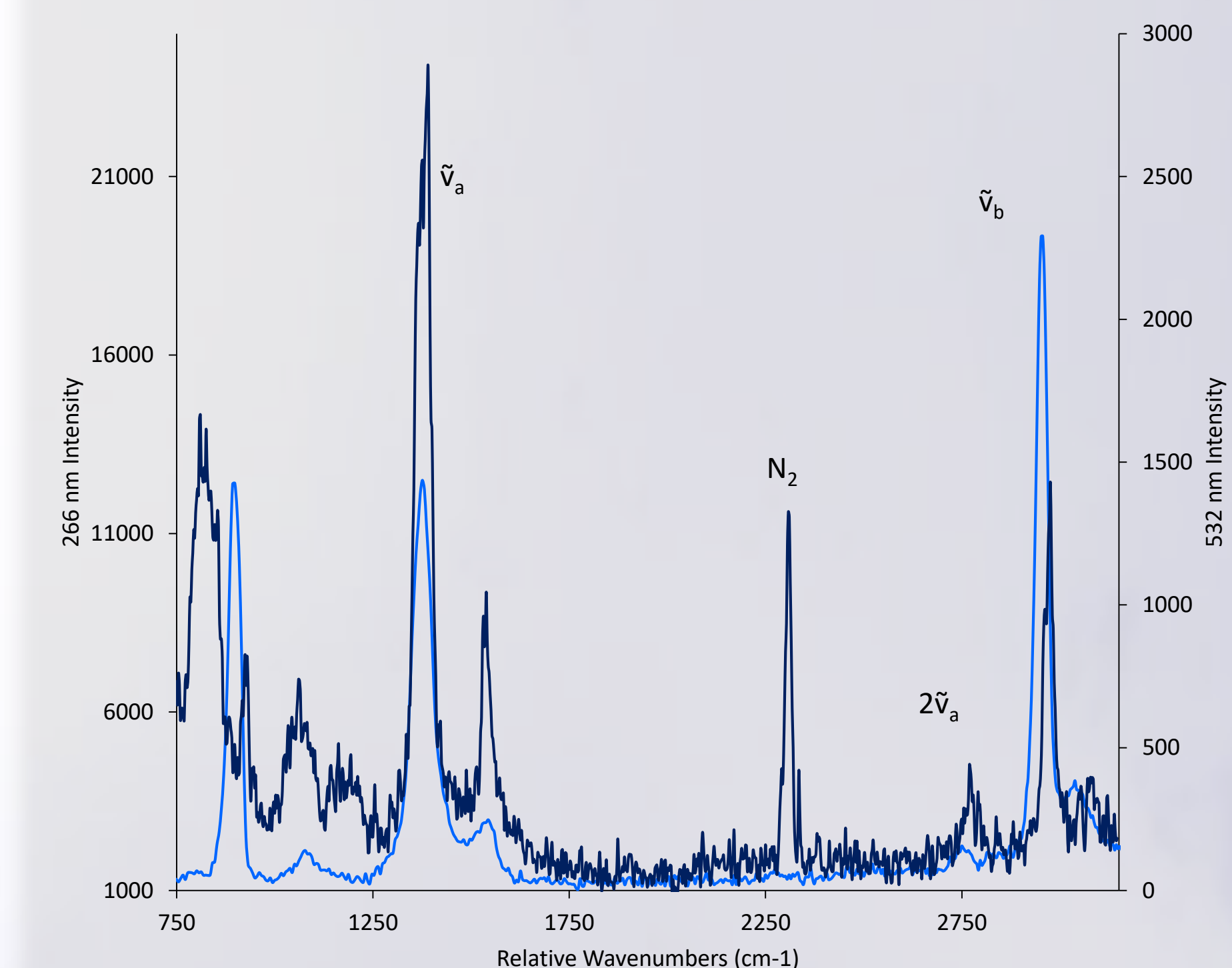
**Figure 3.** Left, from top to bottom: 266 nm Raman spectra of cyclohexane, acetone, and 4-nitrotoluene with the excitation spot size varied. Right column, corrected integrated intensities of a given peak by spot size. Cyclohexane does not absorb 266 nm light. Acetone and 4-nitrotoluene strongly absorb 266 nm light. For this experimental configuration the 12 mm spot size shows the most efficient scattering for the absorbing samples that were examined.

## Excitation Wavelengths



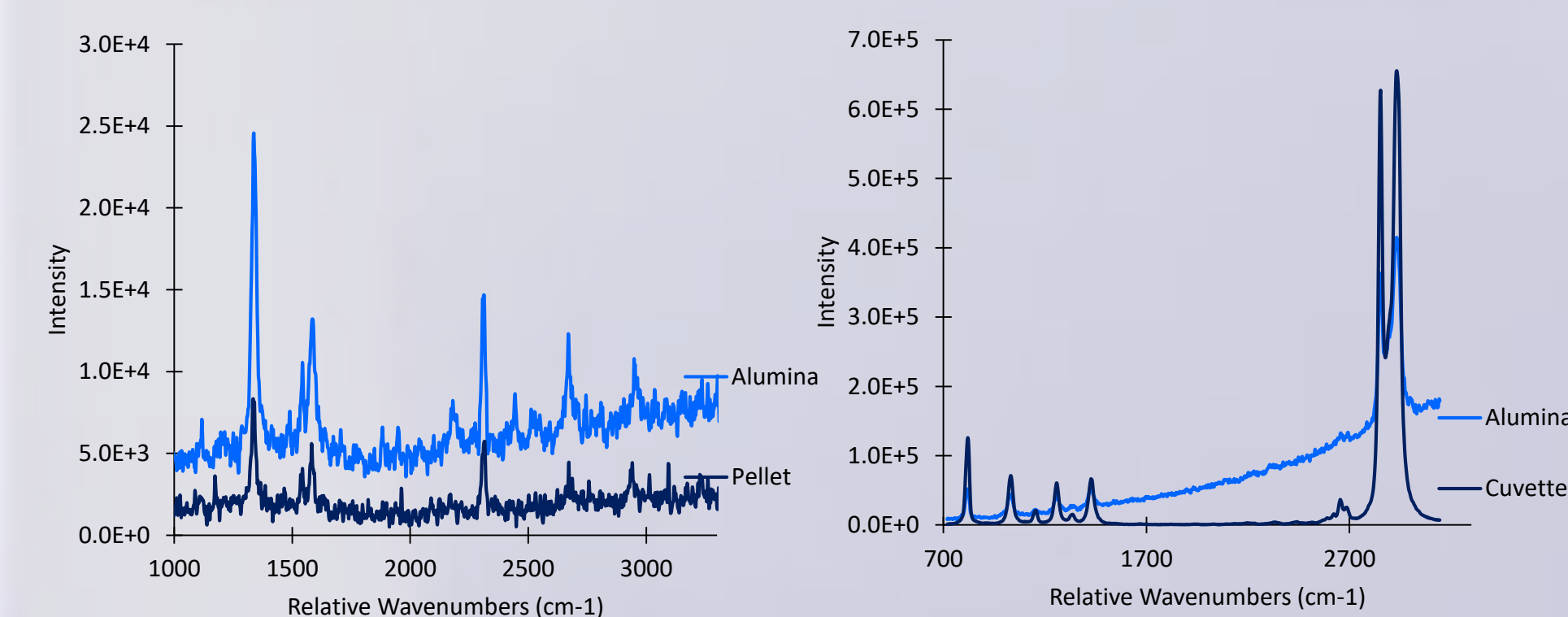
**Figure 4.** Raman spectra of nitromethane using 213, 266, and 532 nm excitation wavelengths. Because nitromethane absorbs strongly at 213 nm, only N<sub>2</sub> and O<sub>2</sub> from air are visible. A well resolved spectrum can be obtained using 266 nm as shown above.

## Resonance Enhancement



**Figure 5.** Raman spectra of nitromethane taken using 532-nm excitation (light blue) and 266 nm excitation (navy blue). The bands labelled  $\tilde{\nu}_a$  and  $\tilde{\nu}_b$  clearly demonstrate a change in relative intensities, indicating resonance enhancement of  $\tilde{\nu}_a$ . Furthermore, the band labelled  $2\tilde{\nu}_a$  is an enhanced overtone of  $\tilde{\nu}_a$ .

## Sample Presentation



**Figure 6.** Raman spectra of 4-nitrotoluene (left) and cyclohexane (right) presented in their pure forms and on an alumina coupon. The alumina increases the surface area of the sample, allowing absorbing species, such as 4-nitrotoluene, to scatter more efficiently. Cyclohexane is transparent at the excitation wavelength and the fluorescence of the alumina is observed as the rising baseline.

## Conclusions

- 266 nm excitation showed resonance enhancement in overtones and combination bands.

- In excitation absorbing samples, 12 mm laser spot size showed the greatest signal.

- Distinct spectra can be obtained from liquid samples, solid samples, and samples dispersed on an alumina coupon further proving this setup as a viable in-field technique.

- The increased surface area of sample on the alumina coupons improved signal for some excitation absorbing compounds.

## Acknowledgements

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