

# Ultra-low frequency Stokes and anti-Stokes Raman spectroscopy at 785nm with volume holographic grating filters

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## ABSTRACT

We report the first results of ultra-low frequency Stokes and anti-Stokes Raman spectra at 785nm showing clearly resolved frequency shifts down to  $10\text{cm}^{-1}$  from the excitation line, using commercially available ultra-narrow band notch and ASE suppression filters, and a single stage spectrometer. Near infra-red (NIR) wavelengths are of particular interest for Raman spectroscopy due to the reduced fluorescence observed for most materials. Previously reported attempts to produce ultra-low frequency Raman spectra at 785nm with volume holographic notch filters were largely unsuccessful, due to the fact that these ultra-narrow line notch filters and the wavelength of the laser must be very well matched to be effective. Otherwise, if the filters have any manufacturing errors or the laser wavelength is unstable, insufficient suppression of the Rayleigh scattered light will allow it to overwhelm the Raman signal.

Recent improvements in both notch and ASE filters, wavelength-stabilized lasers, and optical system design have enabled low-frequency Raman spectra to be successfully taken at 785nm for several typical materials. Two ultra-narrow line notch filters formed as volume holographic gratings (VHG) in glass with individually measured optical densities of 4.5 were used to block the Rayleigh scattered light from a matched VHG wavelength stabilized laser. Five discrete peaks below  $100\text{cm}^{-1}$  were simultaneously observed for sulfur in both the Stokes and anti-Stokes regions at 28, 44, 52, 62, and  $83\text{cm}^{-1}$ . With no degradation in filter performance over time and extremely narrow spectral transition widths of less than  $10\text{cm}^{-1}$ , this relatively simple system is able to make ultra-low frequency Stokes and anti-Stokes Raman measurements at a fraction of the size and cost of traditional triple monochromator systems.

**Keywords:** Raman spectroscopy, notch filter, volume holographic grating, Stokes, anti-Stokes

## 1. INTRODUCTION

Raman spectroscopy has become an increasingly important tool for measuring and identifying the chemical composition and molecular structure of many materials. Traditional applications of Raman spectroscopy focus on signals that are hundreds of wavenumbers away from the excitation laser line due to the limitations of available filters for blocking the intense Rayleigh scattered laser light. Traditional notch filters tend to have bandwidths that are hundreds of wavenumbers wide and even the narrowest edge filters still block much of the Raman signal below  $100\text{cm}^{-1}$ . As a result, the study of ultra-low frequency Raman spectra in the  $<100\text{cm}^{-1}$  region could only be done by complex and high cost multi-stage spectrometer systems. Recent developments in volume holographic grating (VHG) filter technology have enabled ultra-low frequency Raman spectroscopy<sup>1,2</sup>. Armed with these new technologies, today's spectroscopist can explore uncharted territory that furthers the development of semiconductor materials, life sciences, pharmaceutical and homeland security fields to name a few.

Many important materials exhibit strong identifying ultra-low frequency Raman spectra as characteristics of their vibrational and rotational modes:

- Folded acoustic and shear modes of multilayer superlattice structures in advanced semiconductor devices<sup>3</sup> show strong signals below  $100\text{cm}^{-1}$ .
- Polymorphic structures such as organic semiconductors can be discriminated via their low frequency Raman spectra<sup>4</sup>.
- Radial breathing modes (RBM) of single and multi-wall carbon nanotubes exhibit Raman spectral components that depend on the tube diameter<sup>5,6</sup> and can be used to determine sample quality and composition.
- Vibrational modes of compounds that contain heavy atoms or radioactive isotopes<sup>7</sup>.

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- Relaxation mode measurements of various liquids and solutions<sup>8</sup> can help identify their dynamic structure.
- Rotational mode measurements of gases can be used to determine bond lengths.
- In situ measurements of rotational and vibrational temperatures in optical pumped gas cells<sup>9</sup> requiring simultaneous low frequency Stokes and anti-Stokes measurements.

### 1.1 Raman Measurements with VHG Notch Filters

The low interaction efficiency of typical materials exhibiting Raman shifts results in the majority of the light scattered by the sample (Rayleigh scattered light) remaining unshifted and can easily swamp the dynamic range of the spectrometer if it is not properly suppressed or blocked entirely. For larger frequency measurements, a thin film edge filter with optical density of  $\sim 8$  is typically sufficient but will block the low frequency components  $<100\text{ cm}^{-1}$  and will also block either the Stokes or anti-Stokes signal depending on whether the filter is low or high pass.

To meet the demands of ultra-low frequency Raman measurement applications, several different approaches have emerged as solutions:

- Triple spectrometers: such as the Princeton Instruments Trivista use three cascaded stages to first limit the spectral band pass and reject the excitation line, then perform signal dispersion.
- Near Excitation Tunable (NEXT) filters: from Renishaw introduce a double subtractive spectrometer to their standard InVia systems with a physical stop to block the laser line.
- Ultra-narrow band notch filters: such as the SureBlock filter from Ondax, use VHGs to create an ultra-narrow ( $<10\text{ cm}^{-1}$ ) spectral response compared to conventional thin film filters (see Figure 1) that selectively blocks only the excitation laser line and transmits all other components.

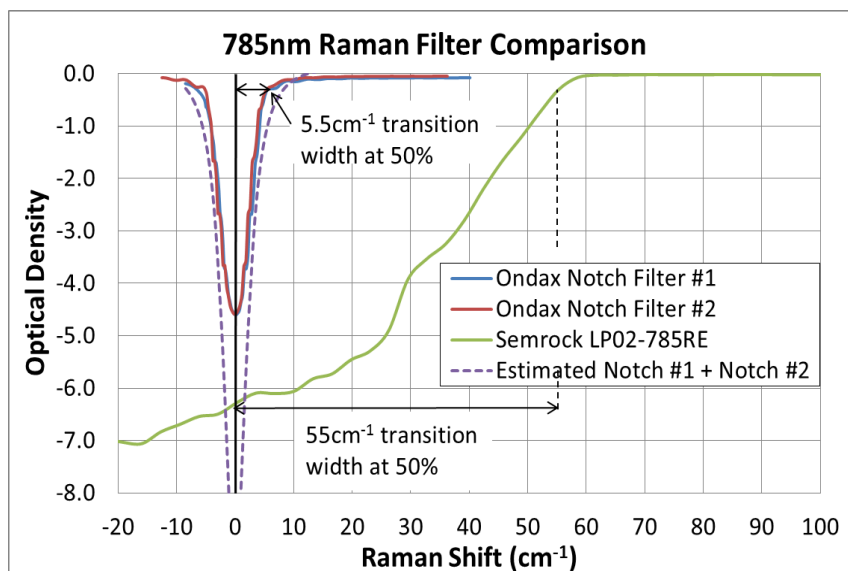


Figure 1. Comparison of VHG notch filter spectral response to conventional thin film edge filters.

The VHG notch filter approach offers the unique ability to simultaneously measure extremely low frequency Stokes and anti-Stokes Raman signals with a single stage spectrometer. Their high transmission efficiency on both sides of the notch filter results in an order of magnitude higher throughput than equivalent multi-stage spectrometers.

### 1.2 Benefits and Challenges of Raman Measurements with Near IR Excitation

Near IR excitation has many advantages for Raman spectroscopy that can enable new applications. For materials that are prone to fluorescence, longer wavelengths induce less of a response and leads to a larger signal to noise ratio. This can be particularly useful for many biological samples. Common diode lasers that are much more compact and less expensive than conventional visible and UV Raman lasers can be employed as excitation sources at these wavelengths. Lasers with relatively high powers in the hundreds of milliwatts are commonly available at these wavelengths with such

low power requirements, they can be battery powered. As a result, near IR excitation enables the development of compact, low cost portable Raman systems with low power consumption that can be battery powered and yet still have high signal to noise ratio capability.

Diode lasers present unique challenges for ultra-low frequency Raman measurements with VHG notch filters compared to conventional gas lasers. The ultra narrow-band transition width of the notch filters requires them to be well matched to the wavelength of the excitation laser. Standard diode lasers can often emit in multiple modes simultaneously or hop between modes. In both cases, the wavelength change between modes can easily be larger than the transition width of the filters, limiting the filter's ability to block the Rayleigh scatter for the both modes simultaneously. The additional mode will also broaden the Raman signal (or create twin signals) for each line by the difference in frequency between the two modes thus reducing the effective resolution of they system. Therefore an important requirement of Raman spectroscopy with diode lasers is to ensure the laser is wavelength stabilized.

Even with a wavelength stabilized laser, it is important to ensure that back reflections do not make it back to the laser cavity. Feedback to the laser can destabilize the laser output wavelength or even damage the laser facet. Ensuring that surfaces are anti-reflection coated and not aligned to retro-reflect the incident beam back to the laser during alignment of the system is critical to achieving good performance.

Diode lasers will also typically emit broadband amplified spontaneous emission (ASE) that can act as background noise in Raman measurements. While the signal level is typically on the order of 40dB or more below the peak emission wavelength (see Figure 2), this can still swamp any weak Raman signals in this region if it is not blocked. Conventional thin film ASE filters generally have a much broader spectral profile that still passes ASE that is close to the laser wavelength. Including an ASE suppression filter in the system that is well matched to the corresponding notch filter spectral profile effectively cleans up the laser emission by reflecting only the wavelength of interest.

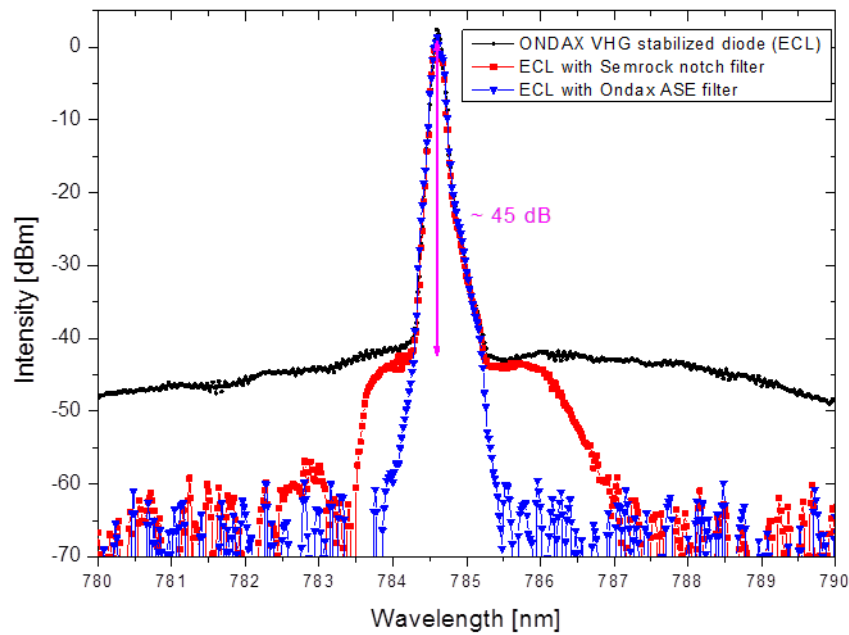


Figure 2. Comparison of 785nm laser diode emission with and without filtration to eliminate ASE using a standard Semrock notch filter and an Ondax NoiseBlock ASE suppression filter. The noise floor for these measurements is at -60 to -70 dBm.

## 2. NEAR IR ULTRA-LOW FREQUENCY RAMAN SYSTEM

Each of the previously described techniques required to achieve high quality ultra-low frequency Raman measurements were incorporated into the system shown in Figure 3. An Ondax SureLock 785 nm wavelength stabilized laser with 80mW output power and measured center wavelength of 784.38nm was used as a stable source. The output from this

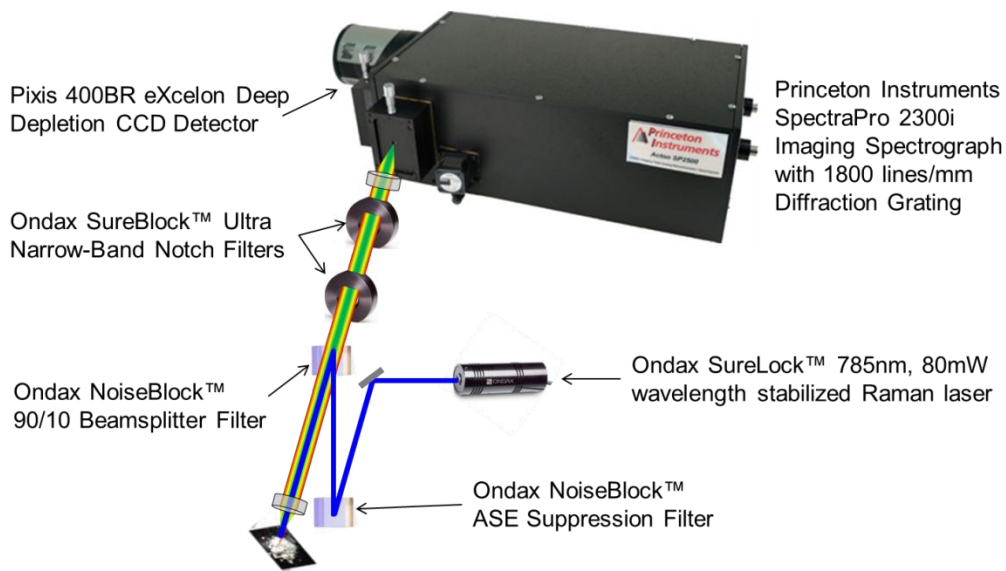


Figure 3. Measurement setup used to capture ultra-low frequency Raman signals.

laser was directed towards an Ondax NoiseBlock ASE suppression filter that was designed to match the wavelength of the laser with a  $\sim 4$  degree angle of incidence relative to the surface normal. The diffracted beam was directed toward an Ondax NoiseBlock 90/10 beamsplitter filter with matching angle of incidence that reflected the beam through an objective lens towards the sample. The objective lens re-collimated the scattered light from the sample and directed it back to the 90/10 beamsplitter. Approximately 90% of the Rayleigh scatter fulfilled the Bragg condition and was diffracted by the filter while all of the Raman signal and only  $\sim 10\%$  of the Rayleigh scatter was transmitted. Two Ondax SureBlock ultra narrow-band notch filters were used to block the remaining Rayleigh scattered light for an estimated total optical density of  $\sim OD 8$  while again transmitting  $\sim 90\%$  of the Raman signal through each filter. The filtered Raman signal was then focused onto a variable width slit at the entrance port of a Princeton Instruments SpectraPro 2300i imaging spectrograph. An 1800 lines/mm diffraction grating was used to disperse the light within the spectrometer and a Princeton Instruments Pixis 400 BR eXcelon deep depletion CCD detector captured the resulting Raman signal.

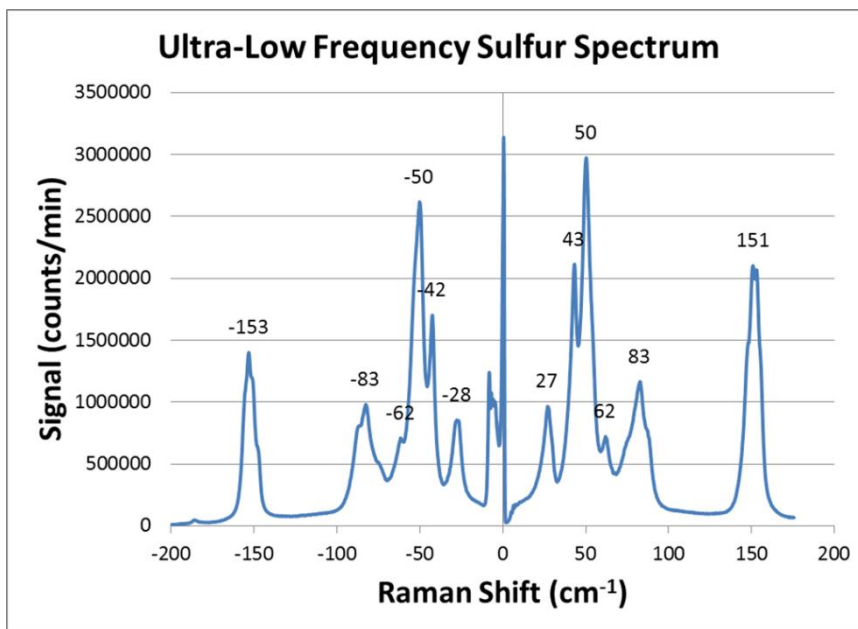


Figure 4. Low frequency Raman spectrum of sulfur showing high SNR for both Stokes and anti-Stokes signals.

### 3. EXPERIMENTAL RESULTS

Sulfur was chosen as the first sample to test because of its strong scattering capability and the well-known presence of numerous low frequency signals. Figure 4 shows the experimental results obtained for powdered sulfur with clearly identifiable low frequency peaks located at  $83\text{cm}^{-1}$ ,  $62\text{cm}^{-1}$ ,  $50\text{cm}^{-1}$ ,  $43\text{cm}^{-1}$  and  $27\text{cm}^{-1}$ . The Rayleigh scattered light was quite effectively blocked by the VHG notch filters to a level that is comparable to the Raman scattered signal. In addition, the residual background away from any Raman signal peaks is very low down to much less than  $25\text{cm}^{-1}$ , indicating the ASE filter effectively eliminated all of the background ASE light from the excitation laser.

#### 3.1 L-Cystine Measurements

To test the limitations of the VHG notch filter method, L-Cystine was also measured as an excellent example of a very weakly scattering material with well-characterized low frequency signals. Figure 5 shows the Raman spectra from  $-200\text{cm}^{-1}$  to  $1000\text{cm}^{-1}$  using this system. There is one strong peak at  $\sim 500\text{cm}^{-1}$  in the observed portion of the traditional “fingerprint” region but several peaks with roughly half the signal in the ultra-low frequency region ( $<100\text{cm}^{-1}$ ) represented by the dashed lines. The Rayleigh scattered signal is now much larger than the Raman signals due to the low

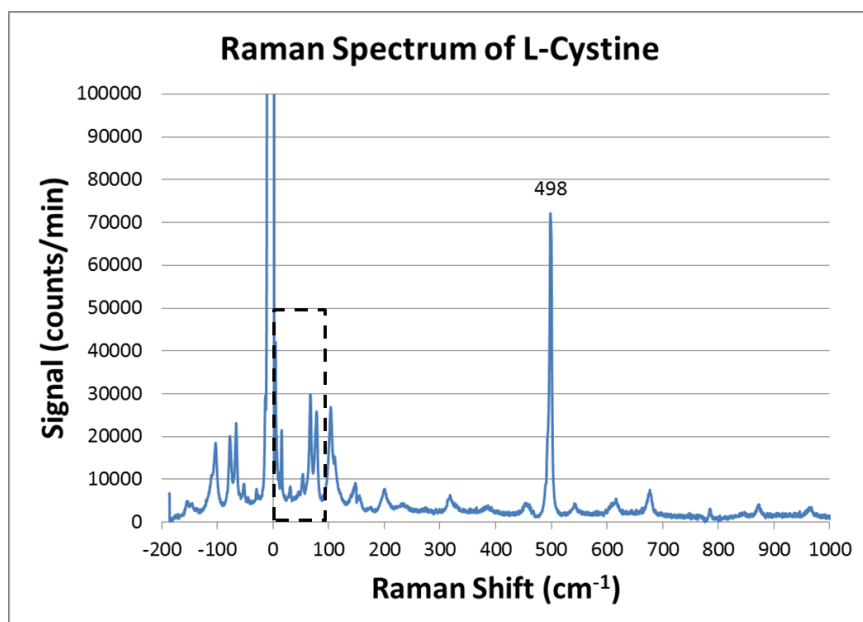


Figure 5. Raman spectrum of L-Cystine showing both Stokes and anti-Stokes signals at 785nm with VHG notch filters.

scatter properties of L-Cystine, but absolute counts on the CCD camera are comparable to the levels observed for sulfur. The integration time of 1 second was chosen to ensure the Rayleigh scatter did not saturate the camera at any time.

Figure 6 shows an enlarged view of just the ultra-low frequency region of the Stokes signal to better illustrate the resolution capability of this method. The data shown in Figures 5 and 6 is an average of 100 discrete 1 second measurements. Even at very low signal levels, the SNR remains high enough to easily observe the characteristic low frequency peaks at  $78\text{cm}^{-1}$ ,  $67\text{cm}^{-1}$ ,  $54\text{cm}^{-1}$ ,  $46\text{cm}^{-1}$ ,  $31\text{cm}^{-1}$ ,  $15\text{cm}^{-1}$  and  $10\text{cm}^{-1}$ . Detection of the peak at roughly  $5\text{cm}^{-1}$  is more challenging. The large peak in this region is likely an alignment artifact of the system.

These extreme low frequency measurements were previously only measurable via multi-stage spectrometer systems. Figures 7 and 8 show comparable measurements taken respectively with a Princeton Instruments TriVista triple spectrometer and a Renishaw InVia spectrometer configured with the NExT filter system. In both cases, the measured spectra are quite comparable to the results shown in Figures 5 and 6 despite the fact that they were measured at visible wavelengths that do not typically exhibit strong ASE background signatures. The throughput for multi-stage spectrometer systems is typically an order of magnitude or more less than the comparable single-stage spectrometer with

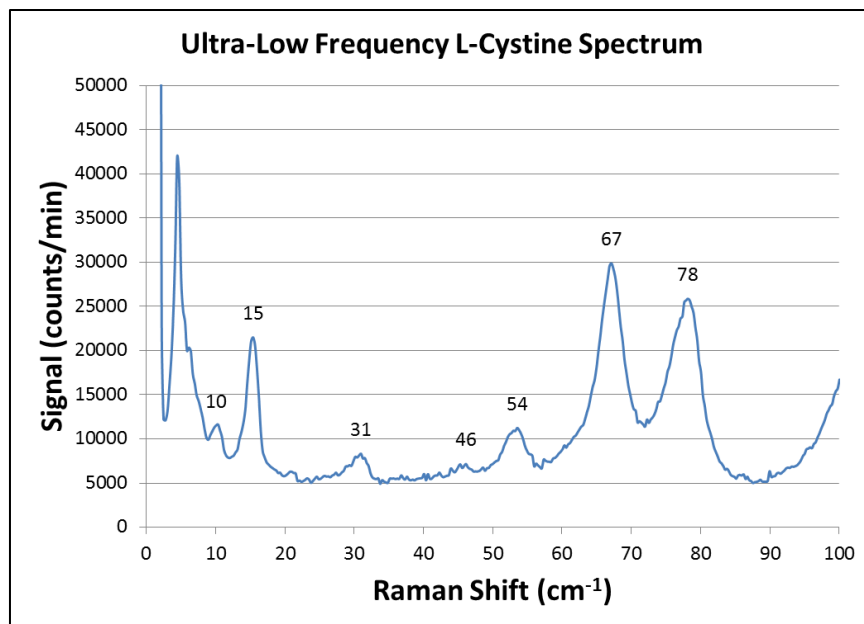


Figure 6. Low frequency spectrum of L-Cystine corresponding to the dashed region of Figure 5.

VHG filters. Multi-stage spectrometers are also generally more complex to align and use for measuring Raman signals. The fact that comparable performance can be obtained from a single-stage system represents a significant opportunity to bring ultra-low frequency Raman spectroscopy into main stream usage for many applications.

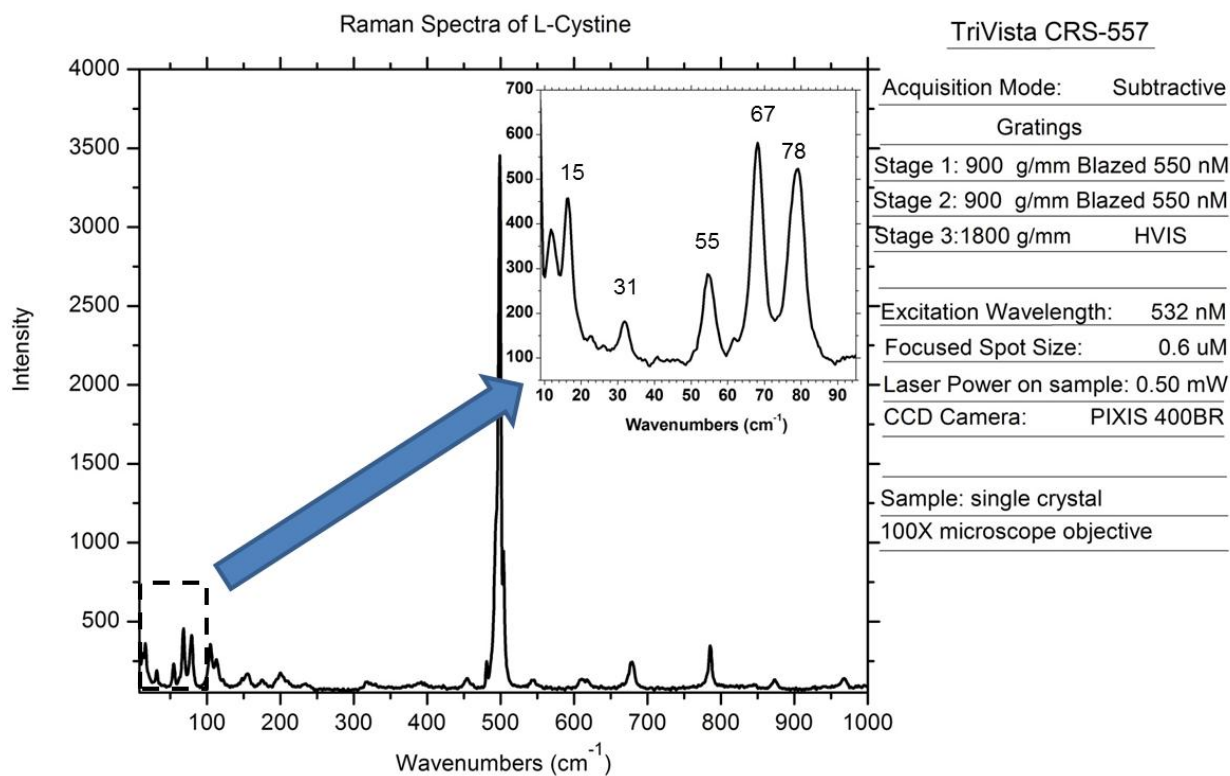


Figure 7. Experimental results for L-Cystine taken with a Princeton Instruments TriVista triple spectrometer, in subtractive mode and measured at 532nm courtesy of Princeton Instruments.



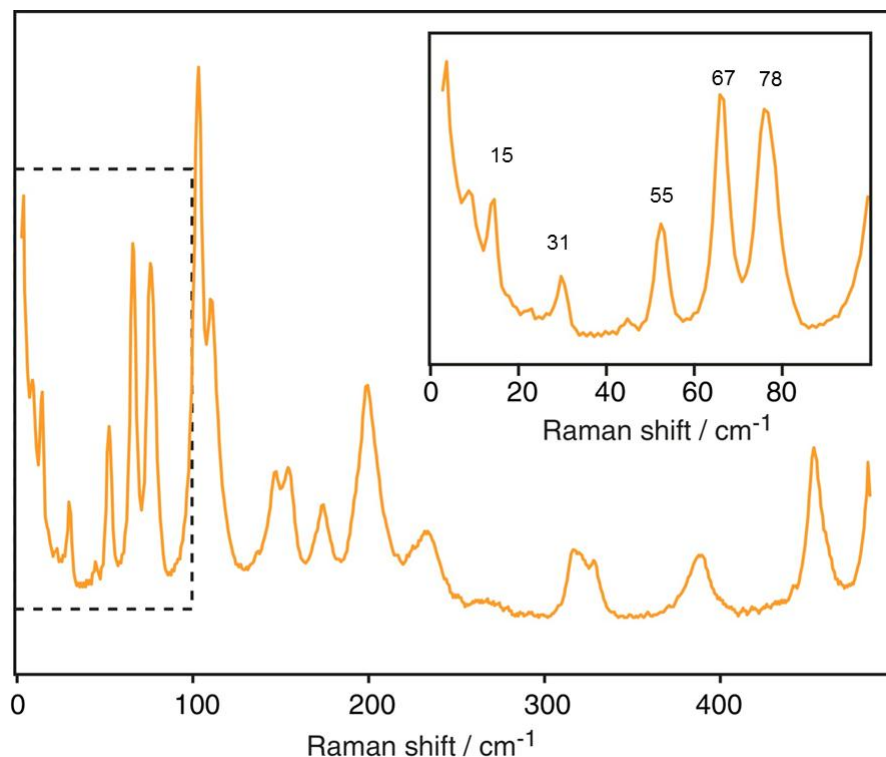


Figure 8. Experimental results for L-Cystine taken with a Renishaw InVia spectrometer, configured with the NExT filter system and measured at 633nm courtesy of Renishaw.

### 3.2 Low Frequency Raman Measurements of Common Pharmaceuticals

Additional measurements using the previously described Raman system were performed for some commonly found pharmaceutical tablets that are known to have low frequency signatures<sup>10</sup>. Ibuprofen, Aspirin, Acetaminophen and Vicodin (a combination of 5mg Hydrocodone with 500mg Acetaminophen) were all measured and compared. The resulting signals are shown in Figure 9. In each case, the samples were measured using a 1 second integration time and plotted with the same scale to compare relative signal strengths between samples. All four tablets demonstrated numerous low frequency Raman peaks extending well below 50cm<sup>-1</sup>.

A comparison with the signals in the 100cm<sup>-1</sup> to 1000cm<sup>-1</sup> region indicates that these ultra low-frequency signals are often an order of magnitude or more larger in signal strength, making them relatively easier to detect. Figure 10 shows an enlarged view of the low frequency regions of all four samples, overlaid for direct comparison. Ibuprofen, Aspirin and Acetaminophen all show distinctly different Raman signatures at this scale, suggesting that identification of these materials could also be performed based on ultra low-frequency Raman measurements. Examination of the Acetaminophen and Hydrocodone + Acetaminophen samples shows virtually identical signatures with only a difference in magnitude of the peaks. This suggests that the majority of the Raman signal in both samples is due to the predominant Acetaminophen component and any exhibition of low frequency structure by the Hydrocodone compound is negligible in comparison.

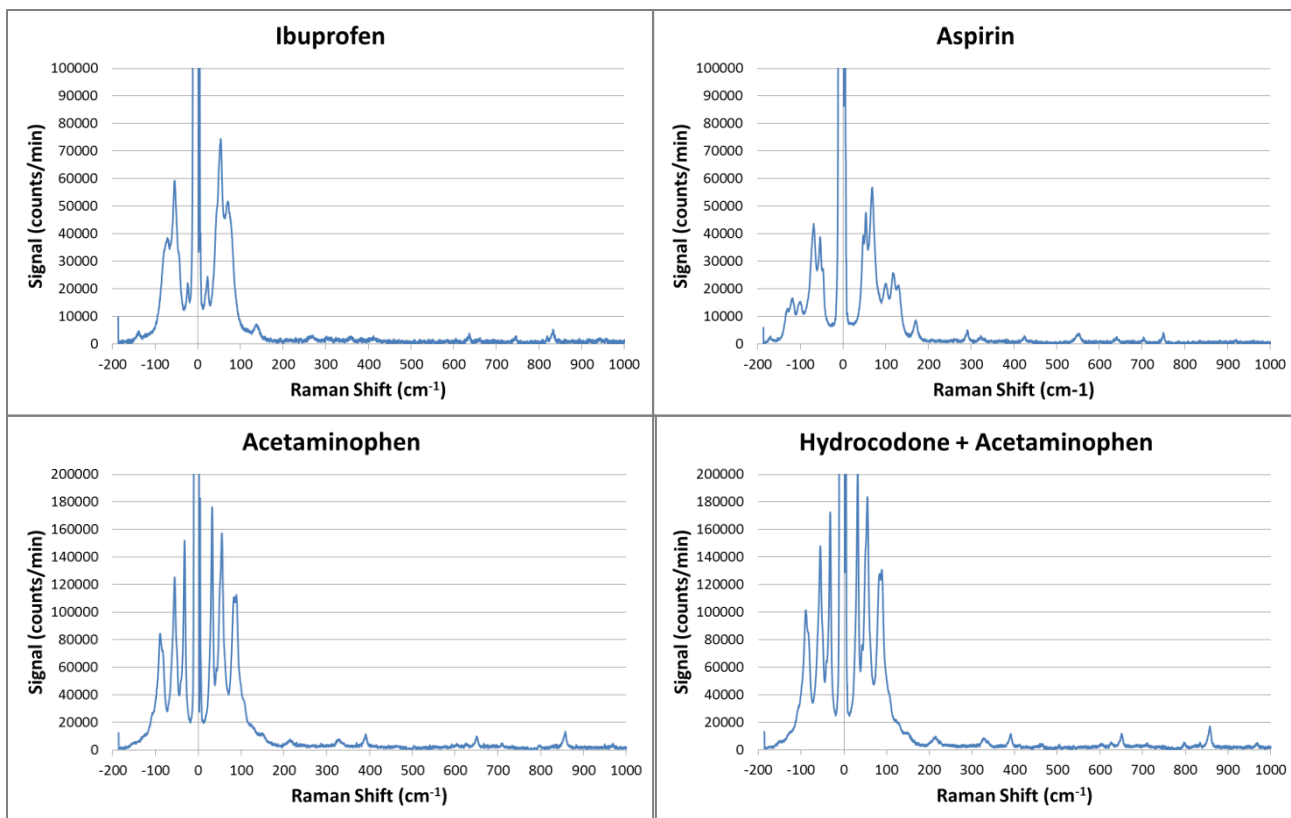


Figure 9. Low frequency Raman measurements of common pharmaceutical tablets.

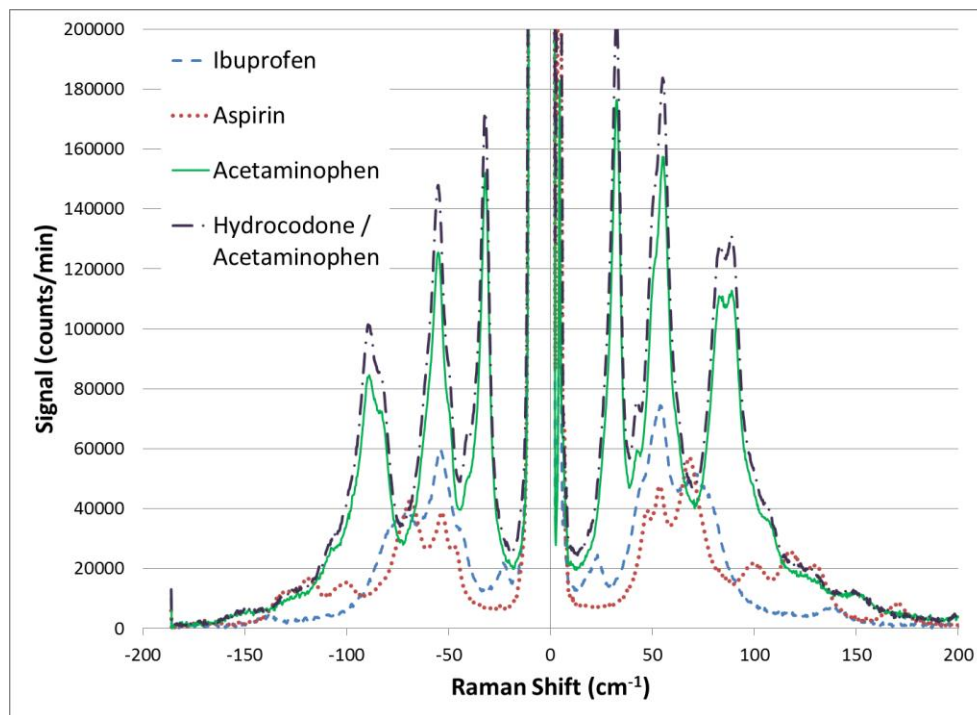


Figure 10. Low frequency Stokes and anti-Stokes signals of the pharmaceutical tablets.



## 4. SUMMARY

Measuring ultra low-frequency Raman spectra in the near IR with holographic filters has historically been difficult to achieve. By using a wavelength stabilized diode laser in combination with a narrow-band ASE suppression filter, we were able to produce a clean, stable wavelength excitation source required for these measurements. By matching the spectral profile of the VHG notch filters to that of the wavelength stabilized laser, ultra low-frequency Raman measurements were taken on a single-stage spectrometer with comparable quality to much larger and more costly multi-stage spectrometer systems. The reported system had an order of magnitude higher throughput than typical multi-stage spectrometers, allowing measurements of low scattering materials such as L-Cystine to be taken with a short integration time of only 1 second. High transmission on either side of the VHG notch filter profile enabled simultaneous measurement of both Stokes and anti-Stokes signals. The examination of several common pharmaceutical samples showed the presence of numerous ultra low-frequency peaks that could be used for sample identification and purity measurements. This new capability enables ultra low-frequency Raman spectroscopy systems to be developed that are much more compact, portable and lower cost for a variety of applications the life sciences, pharmaceutical and homeland security fields to name a few.

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## REFERENCES

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- [1] Moser, C., Havermeier, F., "Ultra-narrow band tunable laserline notch filter", *Applied Physics B: Lasers and Optics* **95**(3), pp. 597-601 (2009).
  - [2] Moser, C., Havermeier, F., "Compact Low Frequency Raman Spectroscopy System", *XXII Int. Conf. Raman Spectroscopy*, AIP Conf. Proc. 1267, pp. 794-795 (2010).
  - [3] Tan, P.H., Han, W.P., Zhao, W.J., Wu, Z.H., Chang, K., Wang, H., Wang, Y.F., Bonini, N., Marzari, N., Savini, G., Lombardo, A. and Ferrari, A.C., "The Shear Mode of Multi-Layer Graphene", arXiv:1106.1146v1 [cond-mat.mes-hall] (2011).
  - [4] Ranzieri, P., Girlando, A., Tavazzi, S., Campione, M., Raimondo, L., Bilotti, I., Brillante, A., Della Valle, R. G. and Venuti, E., "Polymorphism and Phonon Dynamics of  $\alpha$ -Quaterthiophene", *ChemPhysChem*, **10**, 657–663 (2009).
  - [5] Iliiev, M.N., Litvinchuk, A.P., Arepalli, S., Nikolaev, P. and Scott, C.D., "Fine structure of the low-frequency Raman phonon bands of single-wall carbon nanotubes", *Chem. Phys. Lett.* 316 (3-4), pp. 217-221 (2000).
  - [6] Poretzky, A., Geohegan, D. and C. Rouleau, "Narrow and intense resonances in the low-frequency region of surface-enhanced Raman spectra of single-wall carbon nanotubes", *Phys. Rev. B* **82**, 245402 (2010).
  - [7] Pakhomov, P., Khizhnyak, S., Galitsyn, V., Rogova, E., Hartmann, B. and Tshmel, A., "Application of the Low Frequency Raman Spectroscopy for Studying Ultra-High Molecular Weight Polyethylenes", *Macromolecular Symposia*, **305**, 63–72 (2011).
  - [8] Galvin, M. and Zerulla, D., "The Extreme Low-Frequency Raman Spectrum of Liquid Water", *ChemPhysChem*, **12**, 913–914 (2011).
  - [9] Walter, D.K., Griffith, W.M. and Happer, W., "Energy Transport in High-Density Spin-Exchange Optical Pumping Cells," *Phys. Rev. Lett.* **86**, 3264-3267 (2001).
  - [10] Moser, C., Havermeier, F., "Compact Raman spectrometer for low frequency spectroscopy", *Proc. SPIE* 7598, 7598OS (2010).