

Compact Raman spectrometer system for low frequency spectroscopy

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ABSTRACT

We report low frequency Stokes and anti-Stokes Raman spectra resolving frequency shifts down to 15 cm^{-1} using a standard commercial Raman spectrometer with ultra-narrow band notch filters. The ultra-narrow band notch filters were fabricated holographically in a glass material with optical densities ranging from 4 to 6 per notch filter at the standard Raman laser lines of 488 nm, 532 nm, 633 nm and 785 nm. The notch filters have greater than 80% transmission at 15 cm^{-1} away from the laser line. This simple notch filter-based system provides high performance low frequency Raman spectroscopy as a low cost alternative to bulky and expensive triple spectrometer Raman systems.

Keywords: low frequency, volume grating, Raman, compact, triple spectrograph, notch filter, Stokes, anti-Stokes

INTRODUCTION

Notch rejection filters, also called wavelength blockers are an essential component in Raman instruments. The purpose of the notch filter is to greatly attenuate the backscattered Rayleigh light from the laser illuminating a sample under test, while letting the faint Raman spectrally shifted signature pass through. Two non-dispersive filter technologies are currently used for notch filters: 1) holographic (thin polymer material) and 2) thin film. Both can achieve 3dB rejection bandwidth of less than approximately 350 cm^{-1} . The Raman signal in the low frequency shift region ($\sim 5\text{-}200 \text{ cm}^{-1}$), i.e near the frequency of the excitation laser, contains critical information about the molecular structure. For example, carbon nanotubes exhibit vibration modes in the range of 150 cm^{-1} to 200 cm^{-1} depending on their size [1,2]. Relaxation in liquids, solutions and biological samples exhibit Raman shift, in the range between 0 and 400 cm^{-1} [3].

We have demonstrated a non-dispersive holographic notch filter technology capable of observing the Raman signal near the excitation wavelength (15 cm^{-1}). The novelty of the approach is the compactness of the notch filter (same size as a standard thin film/holographic notch filter) realized by bonding individual notch filters without creating spurious multiple diffractions [4]. Such ultra-narrow-band notch filters can thus be used in standard compact Raman instruments and help bring high-end research to a greater number of users. Figure 1 below illustrates graphically the relative bandwidth of notch filters fabricated with thin film deposition (Semrock), thin holographic polymer (Kaiser Optical System) and thick holographic glass (Ondax).

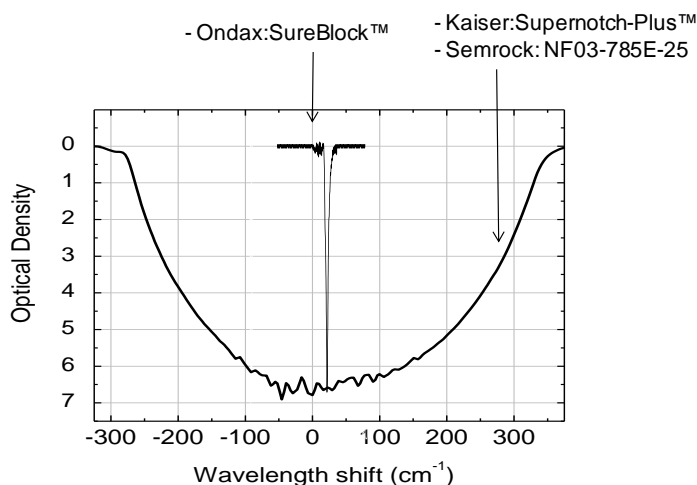


Figure 1: bandwidth comparison between notch filters manufactured by Kaiser Optical System (holographic, supernotch™), Semrock (thin film, NF03-785E-25) and Ondax (holographic, SureBlock™).

2. NOTCH FILTER PERFORMANCE

Notch filters at the typical Raman wavelengths 488 nm, 532 nm, 633 nm and 785 nm were fabricated following the method described in [4]. The notch filter spectral shape is shown in figure 2 for the wavelengths of 785 nm and 488 nm. The transmission data includes 8% of reflection losses from the uncoated interfaces. With appropriate AR coating, the transmission is more than 85% for the 785 nm notch filter and more than 65% for the 488nm notch filter.

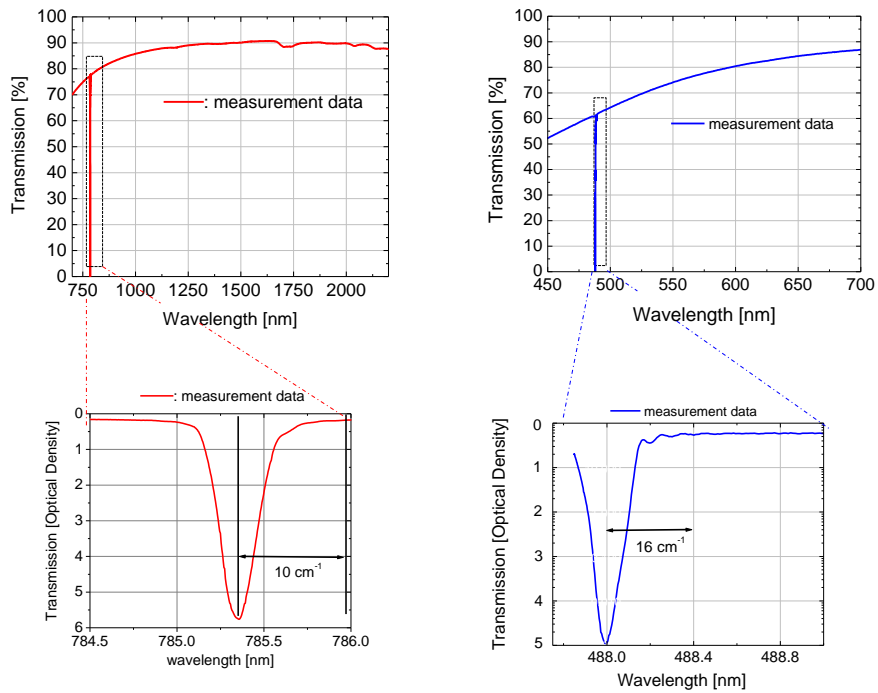


Figure 2: filter performance of 785 nm notch filter (left) and 488 nm notch filter (right).

The alignment sensitivity of the notch filter is of the order of 0.5 degrees in order to obtain better than optical density 4. Figure 3 shows the angular sensitivity of the 488 nm notch filter.

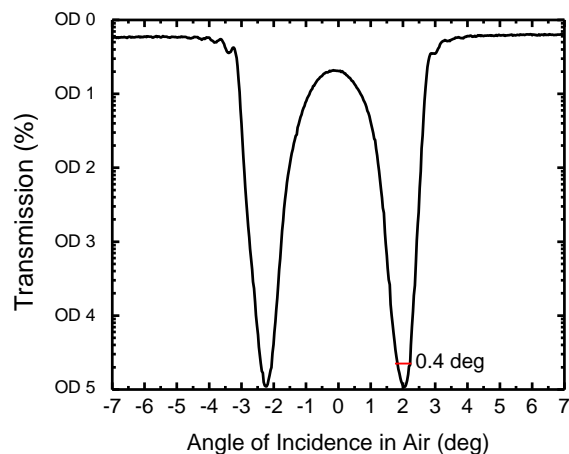


Figure 3: angular sensitivity of the 488 nm notch filter. The plot shows the positive and negative angles.

The table below summarizes the performance of the ultra-narrowband notch filters. The notch filter at 632.8 nm is used in the Raman system discussed in section 2.

	488 nm	532 nm	632.8 nm	78X nm
50% notch bandwidth	0.4 nm 16 cm ⁻¹	0.45 nm 16 cm ⁻¹	0.6 nm 15 cm ⁻¹	0.8 nm 13 cm ⁻¹
Laser line blocking (O.D)	4.5	4.5	4.5	5.5
Transmission (%)	65%	70%	75%	85%

Table 1: Summary performance of the holographic glass notch SureBlock™ filters.

2. LOW FREQUENCY RAMAN SYSTEM

Figure 4 illustrates the Raman system. The collimated laser light is incident on a reflective volume holographic glass filter (NoiseBlock™) that acts as an ultra-narrow band mirror to re-direct the light towards the objective. The incident light makes an angle of approximately 10 degrees in air with the NoiseBlock™ filter. The filter has a 3dB bandwidth of 8 cm⁻¹ and directs approximately 90% of the light towards the objective and transmits 90% of the spectrally shifted Raman signal. The objective focuses the laser light onto the sample. The Raman and Rayleigh backscattered light is collimated by the objective. The Rayleigh light is attenuated 90% (optical density, O.D = 1) by the NoiseBlock™ filter, however the Raman signal is only attenuated 10%. Two SureBlock™ notch filters are placed in series in the path of the backscattered collimated light. Each notch filter has two angular adjustments (yaw and pitch) to maximize the optical density.

A first lens placed after the last notch filter focuses the light onto the slit of the spectrometer box. The slit of the spectrometer determines its spectral resolution.

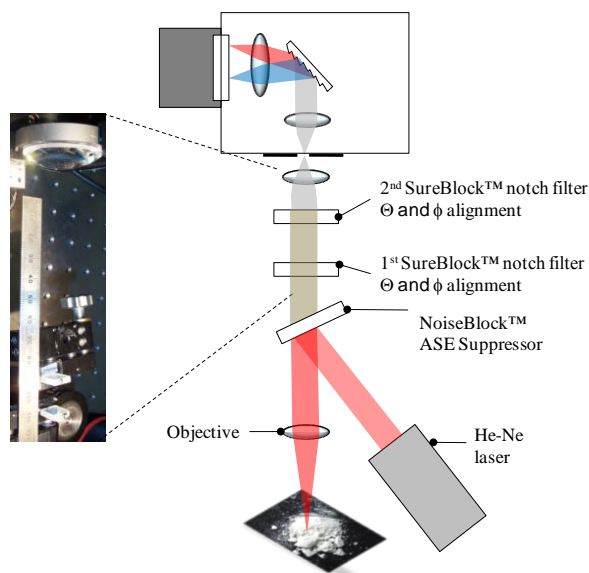


Figure 4: Schematic of the Raman system with two ultra-narrowband notch filters in series providing low frequency (10 cm^{-1}) Raman spectroscopy capability.

For the experiments, a raw beam from a He-Ne laser (Melles Griot 05-LHP-141-15, 632.8 nm) with 2 mW optical power illuminating the sample through a 5X objective lens. The backscattered light is collimated by the objective and has a diameter of 6 mm. The NoiseBlock™ and SureBlock™ filters have an aperture of 9 mm. The distance between the two notch filters is 15 mm. The distance between the 2nd notch filter to the first lens is 120 mm. The spectrometer slit size is 20 micrometers (Acton SP2356 Princeton Instruments, 300mm focal length). The exposure time can be varied from milliseconds to several minutes on the TEC-cooled back-illuminated deep depletion camera (Pixis 400BR, Princeton Instruments). The total effective optical density at the laser line obtained with this system is approximately 8 to 9.

With the apparatus illustrated in figure 4, various compounds exhibiting low frequency Raman responses were analyzed. Figure 5 shows the Raman spectrum of Sulfur. Sulfur is a strong Raman scatterer as the intensity of the Raman peaks compared with the attenuated laser signal show. The Raman spectrum is obtained with a 2 second integration time on the camera. This spectrum demonstrates the low frequency as well as the Stokes and anti-Stokes capability of this simple Raman system.

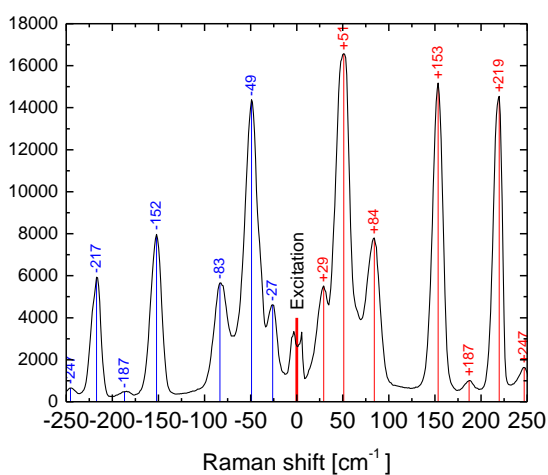


Figure 5: Raman spectrum of Sulfur obtained with the Raman system of figure 4. The Stokes and anti-Stokes low frequency peaks at 29 cm^{-1} are clearly visible.

The Raman instrument was aligned and optimized with Sulfur as a sample. Other compounds such as L-Cystine have a low scattering cross-section yielding a very weak Raman signal surrounded by strong stray-light detrimental to resolve the low-frequency component in the Raman spectrum. L-Cystine (reagent grade, powder form, Sigma-Aldrich C8755) was chosen to show the excellent performance of the low-frequency Raman system. Figure 6 shows the Stokes Raman spectrum of L-Cystine. The exposure time was 5 minutes with an incident power on the sample of 4 mW at the He-Ne wavelength.

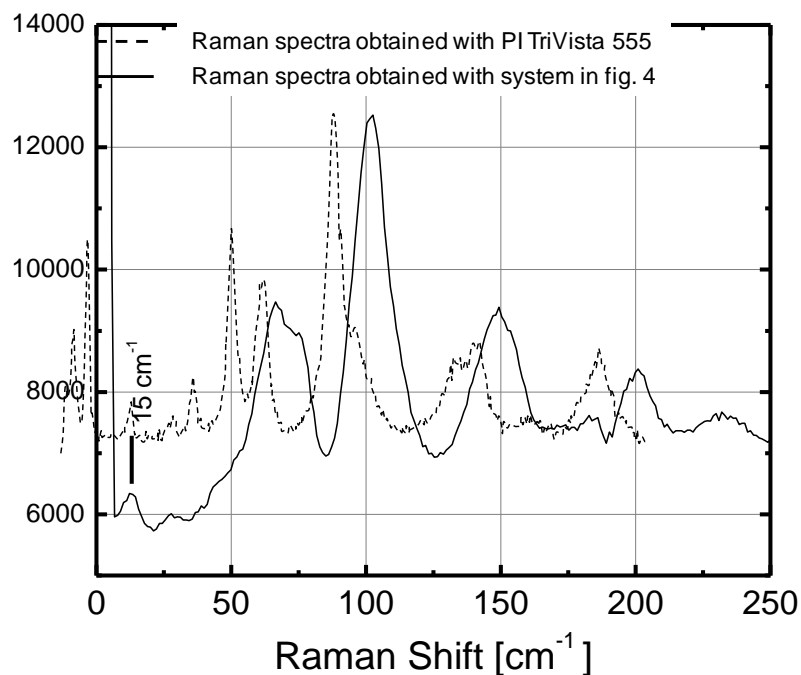


Figure 6: Raman spectrum of L-Cystine obtained with the Raman system of figure 4 (plain curve). The low frequency peak at 15 cm^{-1} is distinguishable.

The solid curve of the Raman spectrum in figure 6 is obtained with the Raman system in figure 4 (single spectrometer, Acton SP2356 Princeton Instruments, 300 mm focal length). As a reference, the dashed curve in figure 6 is obtained with a Princeton Instrument TriVista 555 (2 stages in subtractive mode, 500mm focal length each stage). Both curves show the main Raman peaks of L-Cystine from 15 cm^{-1} .

The L-Cystine spectrum demonstrates that two notch filters in series can block the backscattered laser light effectively to resolve the Raman peak at 15 cm^{-1} . From the notch filter shape graphs in figure 2, we can expect to distinguish Raman peaks down to 8 cm^{-1} . However, the spectrometer resolution is 2.7 cm^{-1} per pixel and thus not enough to distinguish the other peak of L-Cystine at 10 cm^{-1} . With a higher resolution spectrometer (750 mm focal length), the fine spectral structure could be resolved.

The Raman system was also tested on two pharmaceutical tablets of Tylenol and Advil. The Raman spectra in figure 7 show strong low frequency Raman lines below 100 cm^{-1} .

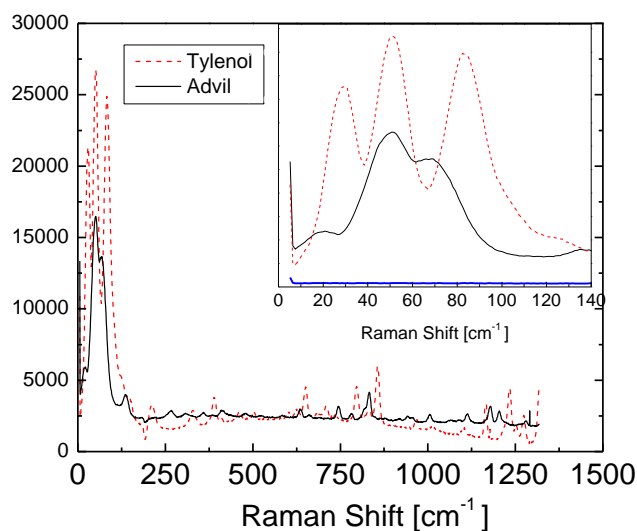


Figure 7: Raman spectrum of pharmaceutical tablets Tylenol and Advil obtained with the Raman system of figure 4. The insert shows that the low frequency peaks below 100 cm^{-1} are intense and easily distinguishable.

5. CONCLUSIONS

A simple Raman system with two cascaded ultra-narrowband notch filters has been demonstrated to yield Stokes and anti-Stokes low frequency Raman spectrum with resolved features down to 15 cm^{-1} on the most challenging samples (L-Cystine). The novelty of this high-end Raman system lies in the ultra-narrowband notch filter technology. Low frequency Raman spectra of Sulfur, L-Cystine and tablets of Tylenol and Advil have been presented. The SureBlock™ notch filter technology has been demonstrated at other Raman wavelengths such as 488 nm, 532 nm and 785 nm. Because the Raman system presented in this paper is based on narrowband notch filters with a standard format, other Raman systems currently using wider band notch filters can be transformed into a high performance low frequency Raman instruments by simply retrofitting the notch filters.

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