

Raman Concatenation

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In previous blogs, the basics of Raman Spectroscopy have been explained along with various trade-offs that exist when selecting the laser type ([Multi-mode vs. Single-mode Lasers for Raman Spectroscopy](#)) and laser wavelength ([The Influence of Laser Wavelength on Raman Spectroscopy](#)) for a particular sample. In this blog the concept of “Raman Concatenation” is explained, which is a measurement technique that can be utilized to overcome many of the trade-offs previously outlined.

In general, many Raman measurements suffer from fluorescence, which forces the use of longer excitation wavelength (lower photon energy) lasers to prevent the fluorescence signal overwhelming the Raman signal. However, this results in reduced sensitivity of low-cost silicon CCD detectors at longer wavenumbers, making it difficult or impossible to observe the “stretch” portion of the Raman spectra (i.e. 2000 – 4000 cm^{-1}). This is particularly true for excitation wavelengths > 760 nm. In addition, longer wavelength excitation lasers result in a reduced Raman excitation cross-section which can make it difficult to observe and perform quantitative analysis in the “fingerprint” portion of the Raman spectra (i.e. 0 – 2000 cm^{-1}). Raman concatenation overcomes these difficulties and allows a user to visualize the entire Raman spectra from 0 to 4000 cm^{-1} by utilizing two lasers with a single-grating-spectrometer and single probe. As an added benefit, since a shorter wavelength (higher photon energy) laser is utilized to collect the “stretch” portion of the spectrum, an enhanced signal is observed in this region which allows for greater quantitative accuracy.

The first longer wavelength laser is selected to avoid fluorescence in the sample and to probe the “fingerprint” region of the spectrum. For the case of a 785 nm excitation laser, 0-2000 cm^{-1} corresponds to a single-grating-spectrometer detection wavelength of 785 nm to ~950 nm. The second shorter wavelength laser is selected to probe the “stretch” region of the spectrum using the same spectrometer detection wavelengths. In this example, a 680 nm excitation laser corresponds to a 2000-4000 cm^{-1} Raman shift. The probe filters are selected to allow excitation and collection at both wavelengths. In operation, each portion of the Raman spectra is collected sequentially and then the composite spectrum is “concatenated” or stitched together. Figure 1 below shows an example of a concatenated spectrum collected on cyclohexane using a 680 nm / 785 nm laser pair. Note, the significant enhancement and improved peak discrimination of the Raman signal strength in the stretch portion of the spectrum.

The ~ 10X enhanced signal and signal-to-noise ratio in the stretch region of the spectrum [Fig 2] makes Raman concatenation ideal for quantitative process control of CH, OH, and NH molecules in many applications. Finally, it should be noted that longer wavelength laser pairs can also be selected if fluorescence is still an issue at 680 / 785 nm. For example, a 735 / 830 nm laser pair can be utilized with a silicon-based spectrometer while an 830 / 1064 nm laser pair can be utilized with an InGaAs-based spectrometer. The Raman concatenation system is patented by Innovative Photonic Solutions under US 10,359,313 and is patent pending in the EU.

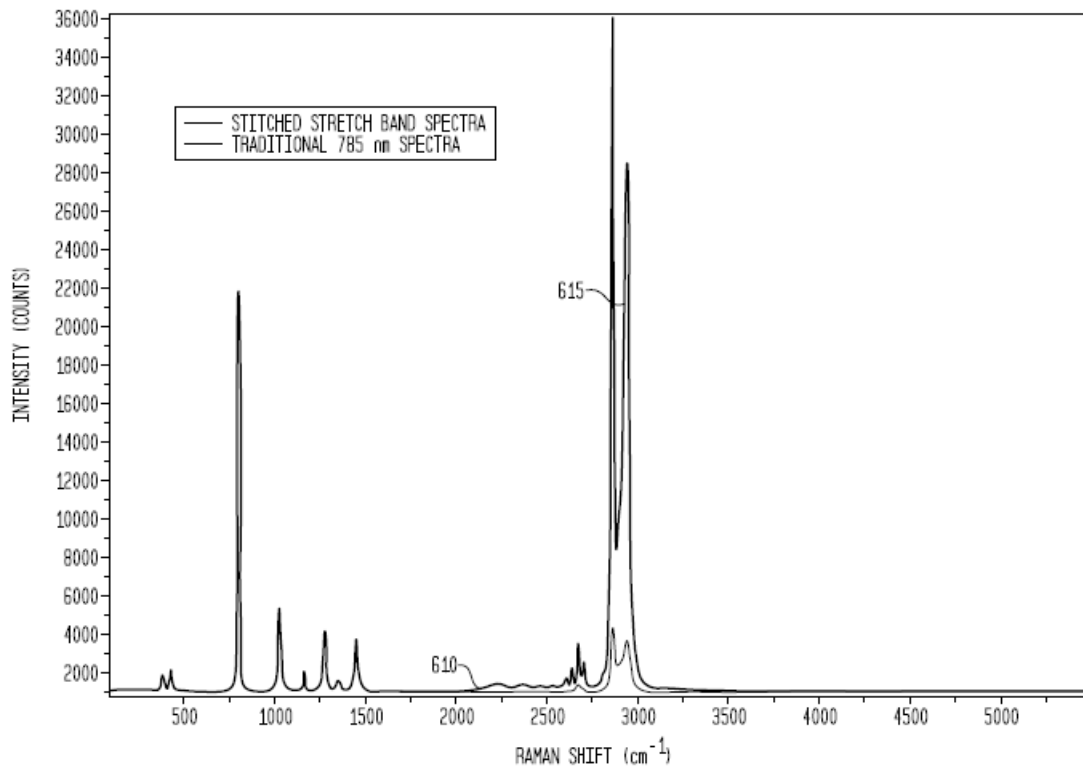


Figure 1 – Concatenated Raman spectra for cyclohexane obtained with a 680 nm / 785 nm laser pair.

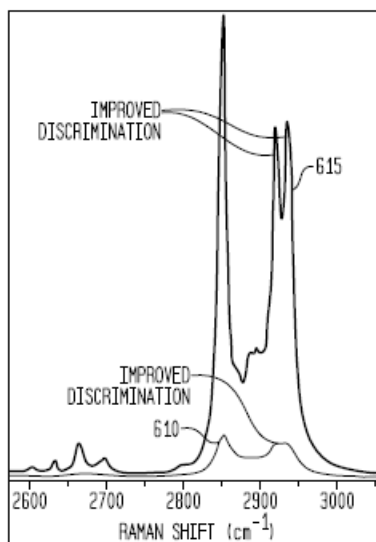


Figure 2 – Enhanced stretch-band signal and discrimination obtained with Raman concatenation.