New Opportunities in Low-Frequency
Raman Spectroscopy

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Raman spectroscopy is an increasingly important tool for measuring and identifying the chemical composition and molecular structure of many materials.

Technological advances in volume holographic grating filters allow ultralow-frequency Raman spectroscopy for homeland security, pharmaceuticals, life sciences research and more.

Typical applications focus on signals that are hundreds of wave numbers away from the excitation laser line because of the limitations of available filters for blocking the intense reflected laser light.

Traditional notch filters tend to have bandwidths that are hundreds of wave numbers wide, and even the narrowest edge filters still block much of the Raman signal below 100 cm^{-1}. As a result, the study of ultralow-frequency Raman spectra in the <100-cm^{-1} region has been largely overlooked.

Recent developments in volume holographic grating (VHG) filter technology have enabled ultralow-frequency Raman spectroscopy. Today's spectroscopist now can explore uncharted territory that furthers the life sciences, pharmaceutical, homeland security and other fields.

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

- Radial breathing modes of single- and multiwall carbon nanotubes exhibit Raman spectral components that depend on the tube diameter and that can be used to determine sample quality and composition.
- Folded acoustic modes of multilayer superlattice structures in advanced semiconductor devices show multiple strong signals below 100 cm^{-1}.
- Vibrational modes of compounds that contain heavy atoms – such as the halides used in incandescent lights – also exhibit ultralow-frequency signals.
- Relaxation mode measurements of various liquids and solutions can help identify their dynamic structure.
- Rotational mode measurements of gases can be used to determine bond lengths.

With these advances driving research

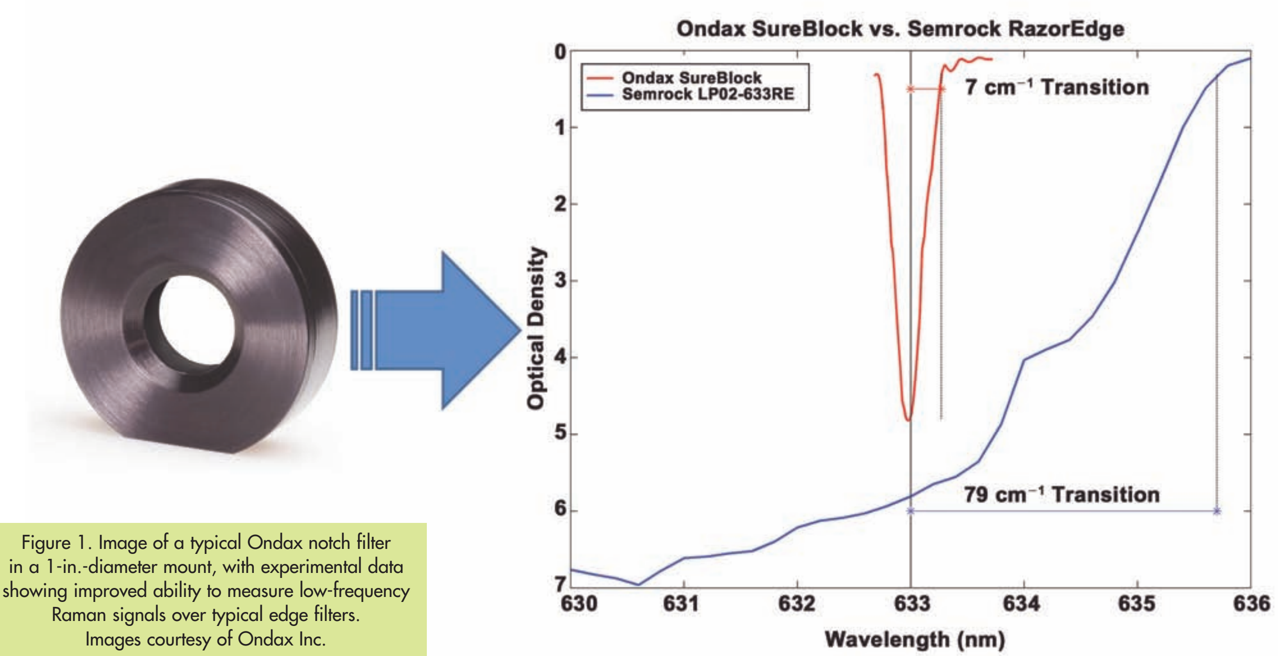

Figure 1. Image of a typical Ondax notch filter in a 1-in.-diameter mount, with experimental data showing improved ability to measure low-frequency Raman signals over typical edge filters. Images courtesy of Ondax Inc.

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and development efforts, the world of ultralow-frequency Raman spectroscopy is just beginning to unfold.

Signal generation, measurement

When a sample that exhibits Raman activity is illuminated by a laser source, a small fraction of photons (typically $<10^{-7}$) from the laser will interact with the atomic and molecular structure of the sample. In the process, a phonon is either emitted (Stokes) or absorbed (anti-Stokes), and a photon with a different energy, directly corresponding to the amount of energy gained or lost through the phonon interaction, is emitted. The change in energy of the scattered signal determines the frequency shift of the reflected light. By measuring the relative strength of each spectral component, information about the material's rotational and vibrational modes – which provide the phonon transport mechanism – can be derived.

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

To meet the demands of ultralow-frequency Raman measurement applications, several approaches have emerged:

- Triple spectrometers, such as Princeton Instruments' TriVista, use three cascaded stages to limit the spectral bandpass, reject the excitation line and then perform signal dispersion.
- Multiple edge filters can be used to measure as low as 30 to 50 cm^{-1} with good throughput.
- Near Excitation Tunable (NExT) filters from Renishaw plc of New Mills, Wotton-under-Edge, UK, introduce a double subtractive spectrometer to standard InVia systems, with a physical stop to block the laser line.
- Ultranarrowband notch filters such as the SureBlock filter from Ondax use VHGs to create an ultranarrow ($<10\ cm^{-1}$) spectral response compared with conventional thin-film filters (Figure 1) that selectively block only the excitation laser line and transmit all other components.

Ultralow-frequency Raman measurement

Each approach to taking ultralow-frequency Raman measurements has its advantages and limitations. See Table 1 for a summary comparison of each approach.

The triple spectrometer approach is very flexible. "The TriVista is completely tunable from below 200 nm to the IR, rendering it ideal for use with tunable lasers or in multilaser facilities," said Ed Gooding, spectroscopy product manager at Princeton Instruments. "In the subtractive mode of the TriVista, the first two stages act as a tunable edge filter to reduce the Rayleigh scattered light to negligible levels, enabling Raman data to be taken to within 4 cm^{-1} of the laser line."

When used in additive mode, "the TriVista can achieve extremely high resolution or, in conjunction with a baffle, acquire simultaneous Stokes and anti-Stokes data," Gooding said. Historically, however, triple spectrometers can be expensive and can require complex alignments and operation. They also can have lower throughput efficiency.

Multiple edge filters can be an economical option for measuring signals closer to 100 cm^{-1}. The Semrock RazorEdge filter can achieve OD 6 within a 79-cm^{-1} transition at 633 nm, with high transmission over a large wavelength range away from the edge response. Adding several of these

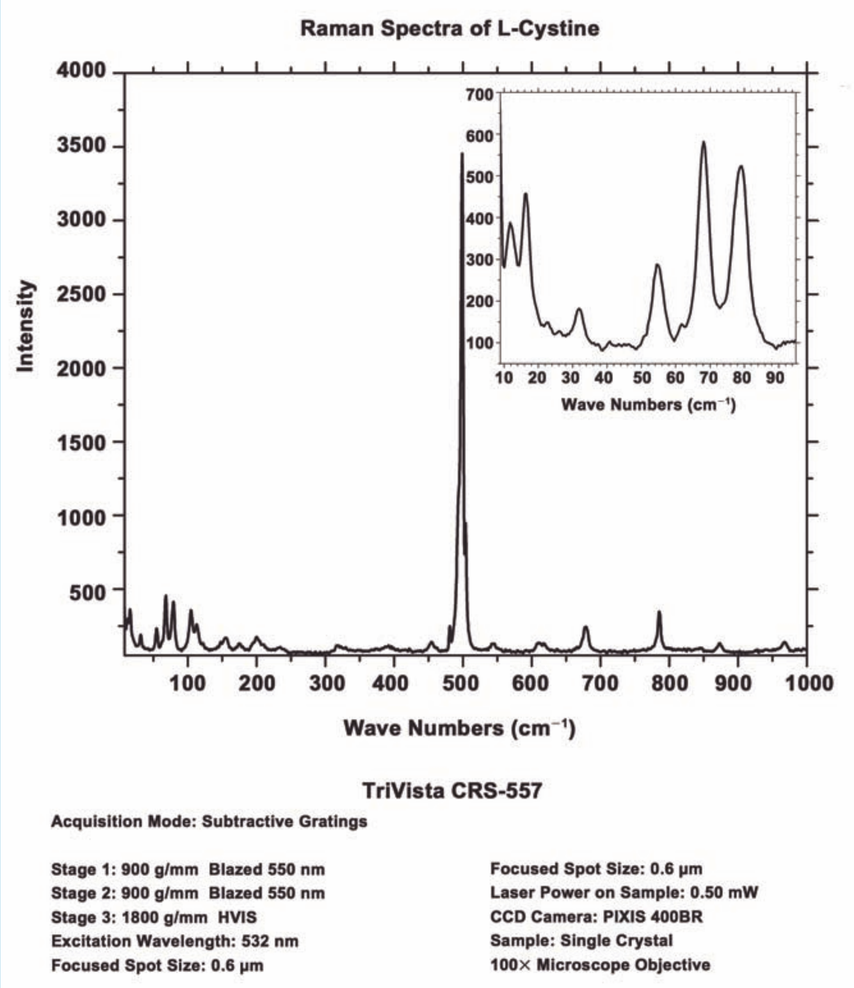

Figure 2. Raman spectra measurement of L-Cystine using a Princeton Instruments' TriVista triple spectrometer at 532 nm.

	Triple Spectrometer	Multiple Edge Filters	NExT Filter Assembly	Ultranarrow VHG Notch Filters
Measure 10-cm⁻¹ Signals	✓	✗	✓	✓
Tunable/Multiple Wavelengths	✓	✗	✓	✗
Relatively Low Cost	✗	✓	✗	✓
Measure Stokes and Anti-Stokes Simultaneously	✓	✗	✗	✓
High Throughput	✗	✓	✓	✓
UV-Capable	✓	✓	✓	✗
Compact	✗	✓	✓	✓

Table 1. Comparison of benefits and limitations of various methods for measuring ultralow-frequency Raman signals.

filters into the system can effectively increase the optical density value and reduce the effective transition width required to achieve the minimum suppression of Rayleigh scatter to take low-frequency measurements.

These filters can be wavelength-tuned by angular adjustments to position the edge as close to the laser line as possible. Even with multiple filters added to the system, the transition width still limits the useful measurement range to 30 to 50 cm^{-1}.

When using edge filters, only Stokes or anti-Stokes measurements can be taken, and the filters are designed to work at only one wavelength.

The NExT filter assembly has many traits in common with the triple spectrometer approach, with good throughput and low wave number measurement ability down to ~10 cm^{-1}. It is flexible and relatively more compact than a triple spectrometer because it can be configured directly into the standard InVia system. The filter alignment procedure can be complex, and it has limited wavelength tunability. Also, because a knife edge is used to block the laser line, only Stokes shifted spectra can be measured.

Ultranarrowband notch filters are the newest approach to ultralow-frequency Raman spectroscopy. Volume holograms can be designed to have a spectral response of <10 cm^{-1}, which blocks only the laser line but passes all other spectral components so both Stokes and anti-Stokes signals can be measured simultaneously.

With typical OD values of 4 to 4.5, only two filters are required to achieve enough optical density to block the Rayleigh scattered light. They can be retrofitted to replace edge filters in commercially available Raman systems or used directly with single-stage grating spectrometers, making them a powerful and cost-effective approach for measuring both low and standard wave number signals.

The filter must be designed to match the specific wavelength of the laser that is used, so multiple wavelength applications require multiple filter sets. The ultranarrow linewidth also means that the laser must be wavelength-stabilized because drifts of >0.1 nm would cause the Rayleigh light to be transmitted.

The transmission properties of the filters away from the design wavelength are very good throughout the visible and IR regions (>70 percent transmission from 550 to >1200 nm), but absorption in the UV limits their performance below 400 nm.

“These new narrowband volume holographic grating filters are the next quantum step in Raman technology, enabling single-stage grating spectrometers to do something that was only realized using a double or triple grating spectrometer,” said Andrew King, West Coast sales manager for Renishaw. “These VHG filters will empower scientists and engineers with the ability to analyze low-wave-number Raman bands and phonon modes in many areas of materials and nanotechnology research.”

Comparison of experimental results

One of the best means of comparison for these methods is looking at a relatively weak Raman scatterer with known signals below 100 cm^{-1}. L-Cystine, a common amino acid, can be synthesized by the body and is necessary for wound healing and the formation of white and red blood cells. It has six easily distinguishable peaks below 100 cm^{-1}, with three occurring below 30 cm^{-1}.

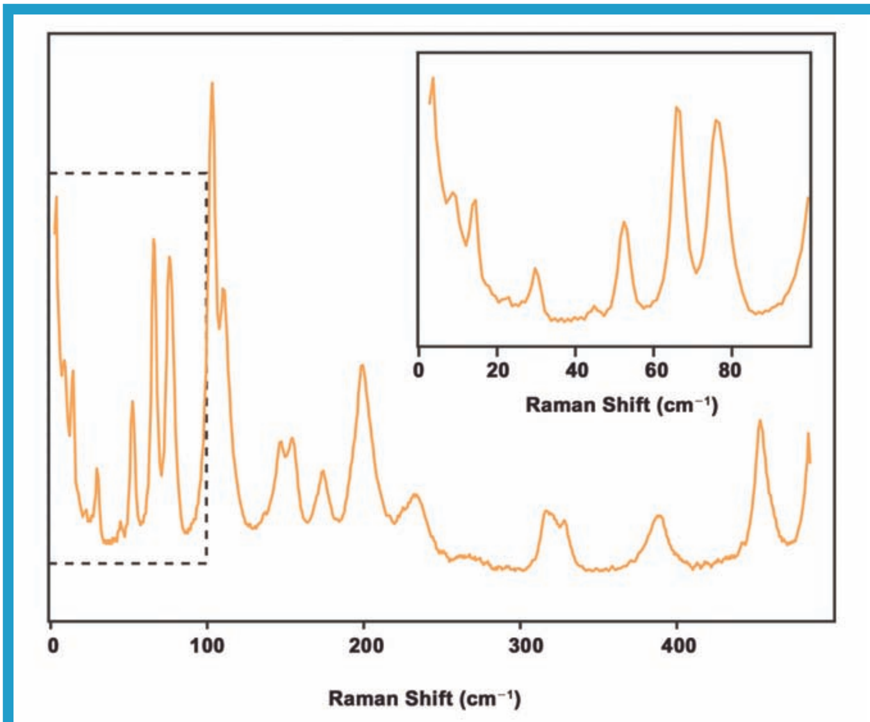

Figure 3. Raman spectra measurement of L-Cystine using a NExT filter configured Renishaw InVia system at 633 nm.

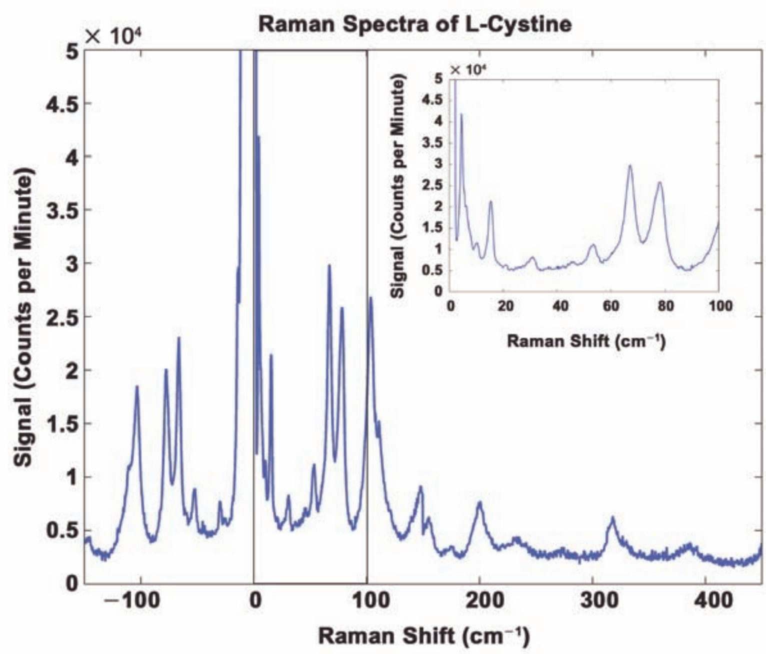

Figure 4. Raman spectra measurement of L-Cystine using Ondax SureBlock ultranarrow-band notch filters and a single-stage SpectraPro 2300i spectrograph at 785 nm.

Figure 2 shows experimental results for L-Cystine taken with a TriVista, using a Princeton Instruments PIXIS 400BR eXcelon deep-depletion CCD detector in subtractive mode and measured at 532 nm. All six peaks are clearly distinguished in the inset image, with significant signal-to-noise ratio for each signal.

Figure 3 shows similar experimental results for L-Cystine taken with a NExT filter system at 633 nm. Once again, all six peaks are clearly distinguished with comparable performance to the TriVista measurements.

Figure 4 shows L-Cystine measurements taken with two Ondax SureBlock filters designed for 785 nm and each having OD 4.5. A total of 8 mW of light was focused on the L-Cystine sample from a wavelength-stabilized Ondax 785-nm laser source with an optical isolator to prevent any destabilizing feedback and Ondax NoiseBlock ASE filters to remove extraneous spontaneous emission background. A single-stage Acton series SpectraPro 2300i imaging spectrograph, equipped with a PIXIS 400BR eXcelon deep-depletion CCD detector and an 1800-lines-per-mm diffraction grating, was used to collect the Raman signal data. The high throughput of this system allowed clear signals to be detected from this weak scatterer after only 1 s of integration. The data is an average of 100 discrete 1-s measurements, and all six peaks are clearly distinguished.

Measuring ultralow-frequency Raman signals has never been easier, enabling new discoveries of applications in a variety of research areas. Each of the depicted methods shows comparable ability to measure ultralow-frequency Raman signals across a wide range of wavelengths. The choice of which approach is best depends upon the conditions under which measurements will be taken.

For measuring signals in the 50- to 100-cm^{-1} range on a budget, multiple cascaded edge filters may be sufficient. For lab environments where tunability is important, or for samples that work best with UV illumination, the triple spectrometer or NExT filter configuration may be better choices. And the VHG notch filter configuration is a versatile, compact and cost-effective option that can retrofit existing single-stage spectrometer systems simply by changing the existing edge filters.

Meet the author

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