Lightnovo

TECHNICAL NOTE

Low-Frequency Raman Spectroscopy

TeN-004

Key words

Raman spectroscopy, low-frequency Raman spectroscopy, phonon modes, intermolecular vibrations, materials science, pharmaceutical industry, polymer industry, RG Raman spectrometer

Introduction

Low-frequency Raman spectroscopy has emerged as a powerful technique for probing vibrational modes below ~200 cm^{-1}, offering valuable insights into lattice dynamics, interlayer interactions, and other collective excitations in materials. Traditionally obscured by Rayleigh scattering and limited by instrument design, access to the low-frequency region has improved significantly with advances in optical filtering and spectrometer performance. This technical note outlines the principles, challenges, and practical considerations associated with low-frequency Raman measurements. Emphasis is placed on instrumentation, sample preparation, and spectral interpretation, with the goal of enabling reliable acquisition and analysis of low-frequency Raman data for applications ranging from 2D materials and polymers to pharmaceuticals and solid-state systems.

Applications of Low-Frequency Raman Spectroscopy

Low-frequency Raman spectroscopy enables access to vibrational modes associated with long-range order, interlayer coupling, and collective motions within materials—making it a valuable tool across a broad range of scientific and industrial fields. Key application areas include:

- **2D Materials and Layered Structures**
  Low-frequency Raman is particularly well-suited for characterizing van der Waals materials such as graphene, MoS_2, and other transition metal dichalcogenides (TMDs). Shear and layer-breathing modes observed in the low-frequency range provide direct information about layer number, stacking order, and interlayer coupling, enabling precise structural analysis [1].
- **Polymorph Identification and Crystallinity**
  In pharmaceutical and materials science, low-frequency Raman can distinguish between different polymorphic forms of a compound, which may have identical chemical composition but distinct physical properties. These lattice modes are highly sensitive to crystal packing and long-range order, offering a non-destructive means of quality control and formulation development [2].
- **Phonon Dynamics and Lattice Vibrations**
  In solid-state physics and materials research, low-frequency Raman allows for the investigation of phonon modes and their interactions with other quasiparticles. This is crucial for understanding thermal conductivity, electron-phonon coupling, and phase transitions in complex materials [3].
- **Hybrid Organic-Inorganic Perovskites**
  The mechanical stability and optoelectronic performance of perovskite materials used in solar cells are closely tied to their lattice dynamics. Low-frequency Raman provides insights into structural disorder, phase stability, and ion migration, which are key to improving device reliability [4].

- **Colloidal Nanocrystals and Supramolecular Assemblies**

  In nanoscience, low-frequency modes can reveal information about particle–particle interactions, mechanical properties of assembled structures, and the rigidity or flexibility of molecular frameworks [5].

These examples highlight the unique value of low-frequency Raman spectroscopy in accessing vibrational information that complements conventional high-frequency Raman data. As instrumentation continues to improve, the range and resolution of these applications are expected to expand further.

Lightnovo RG Raman spectrometer

Experimental information

The Raman measurements were performed using a laser with a wavelength of 785 nm and at laser power of 44 mW. The spectrometer was equipped with middle distance probe. The exposure time varied depending on the sample to ensure optimal signal acquisition. For sulfur, polystyrene, and calcite, an exposure time of 500 ms was used, while for paracetamol and ibuprofen, a longer exposure time of 2000 ms was applied to enhance signal quality. This variation in exposure time reflects differences in Raman scattering efficiency and spectral characteristics among the samples.

Sulfur

Sulfur is commonly used as a reference material for calibrating low-frequency Raman shift measurements, in accordance with the ASTM E1840-96 standard. This standard specifies the use of elemental sulfur due to its well-defined and reproducible Raman-active lattice modes in the low-frequency region, typically below 200 cm^{-1}. These characteristic peaks make sulfur an ideal calibration standard for verifying the spectral accuracy and resolution of Raman spectrometers, particularly those optimized for low-frequency measurements. Using sulfur as a reference helps ensure consistency and reliability in low-frequency Raman data across different instruments and measurement conditions.

Table 1. Sulfur Raman lines

Tabulated line position	Measured line position	Deviation
26.9 cm^{-1}	28 cm^{-1}	1.1 cm^{-1}
50.0 cm^{-1}	48 cm^{-1}	-2 cm^{-1}
85.1 cm^{-1}	83 cm^{-1}	-2.1 cm^{-1}
153.8 cm^{-1}	152.6 cm^{-1}	-1.2 cm^{-1}
219.1 cm^{-1}	218 cm^{-1}	-1.1 cm^{-1}

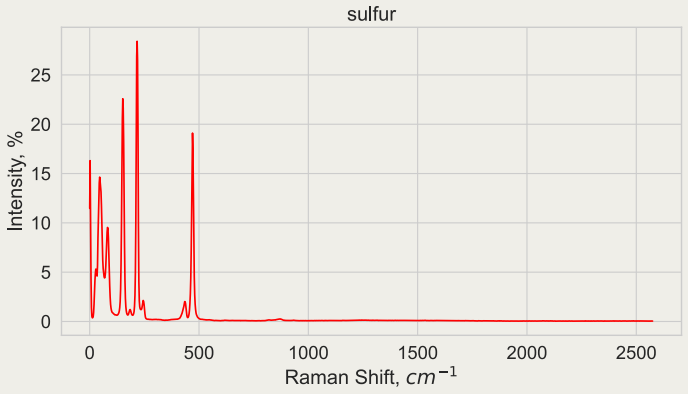


Figure 1. Raman spectrum of sulfur.

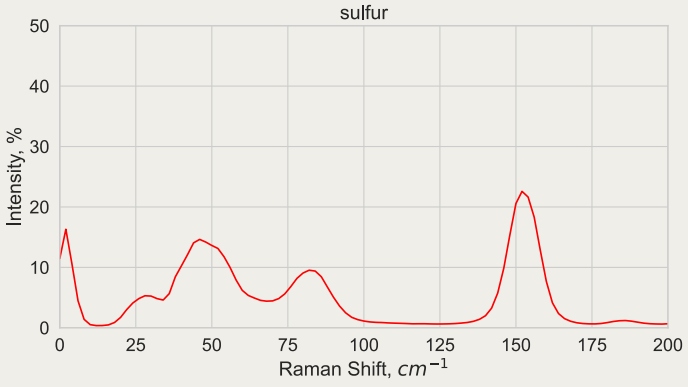
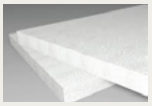


Figure 2. Low frequency Raman spectrum of sulfur.



Polystyrene

Polystyrene is widely recognized as a standard reference material for Raman shift calibration, as outlined in the ASTM E1840-96 standard as well as the European Pharmacopoeia 10.7, Section 2.2.48. Its well-characterized and sharp Raman peaks, particularly in the mid-frequency range (e.g., near 1001 cm^{-1}), make it ideal for verifying both the spectral accuracy and resolution of Raman spectrometers. Polystyrene's stable and reproducible spectral features serve as reliable benchmarks for aligning the Raman shift axis and ensuring consistent instrument performance over time. Its inclusion in both U.S. and European regulatory standards reflects its importance in maintaining the traceability and quality of Raman measurements, whether in research, quality control, or pharmaceutical applications.

Table 2. Polystyrene Raman lines

Tabulated line position	Measured line position	Deviation
620.9 cm^{-1}	619.1 cm^{-1}	-1.8 cm^{-1}
1001.4 cm^{-1}	1000.9 cm^{-1}	-0.5 cm^{-1}
1031.8 cm^{-1}	1031.1 cm^{-1}	-0.7 cm^{-1}
1602.3 cm^{-1}	1603.2 cm^{-1}	0.9 cm^{-1}

As it can be seen from the position of polystyrene lines, the Lightnovo RG Pro spectrometer provides excellent calibration in both low frequency range (as demonstrated above on the example of sulfur) as well as in the fingerprint region.

The low-frequency Raman spectral region of polystyrene provides information on the supramolecular structure of the material, as it is sensitive to collective vibrational modes associated with chain packing, intermolecular interactions, and morphological organization. Changes in these low-frequency features can reflect variations in polymer structure, such as differences in molecular ordering, crystallinity, or processing history. This information is highly relevant for quality control in the polymer industry, where consistent supramolecular structure is critical for ensuring reproducible mechanical, thermal, and optical properties of the final product.

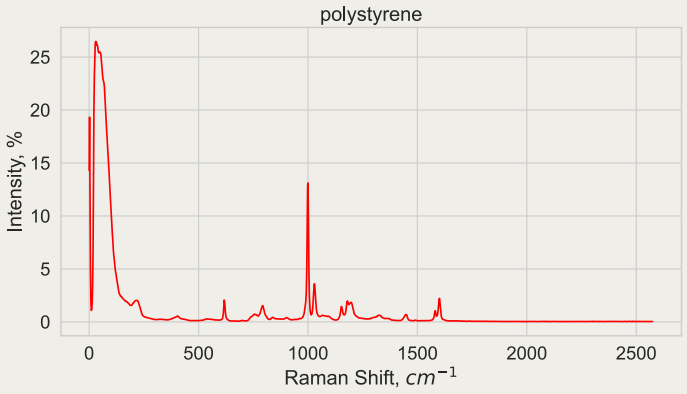


Figure 3. Raman spectrum of polystyrene.

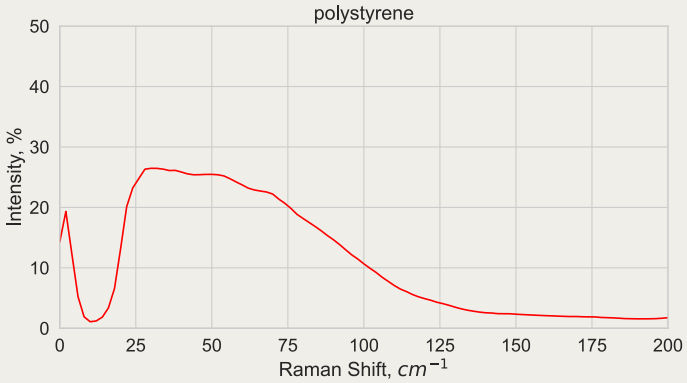


Figure 4. Low frequency Raman spectrum of polystyrene.

Calcite

Calcite is widely used as a reference material for evaluating the spectral resolution of Raman instruments, as described in the ASTM E2529-06 standard. This standard provides guidelines for assessing the performance of dispersive Raman spectrometers, particularly in terms of spectral resolution and peak shape. Calcite is well-suited for this purpose due to its distinct and narrow Raman peaks, most notably the strong peak at 1085 cm^{-1}, which corresponds to the symmetric stretching mode (ν_1) of the carbonate group. This peak is sharp and well-defined, making it an excellent marker for testing an instrument's ability to resolve fine spectral features.

In addition to the 1085 cm^{-1} band, calcite also exhibits lower frequency lattice modes, such as the one near 155 cm^{-1}, which can further support resolution assessment, especially in the low-frequency region. Measuring the full width at half maximum (FWHM) of these peaks allows users to evaluate the spectrometer's resolution and ensure consistent performance for applications requiring high spectral fidelity.

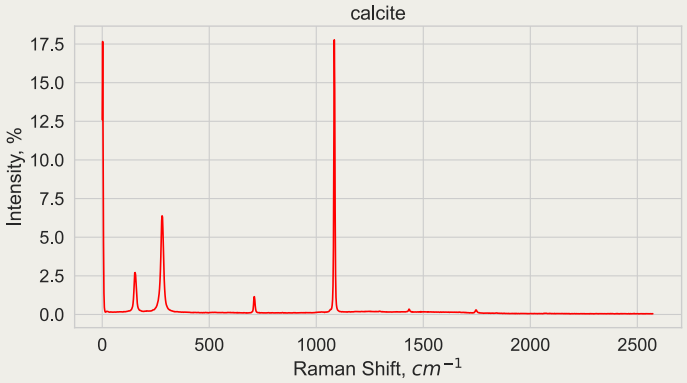


Figure 5. Raman spectrum of calcite.

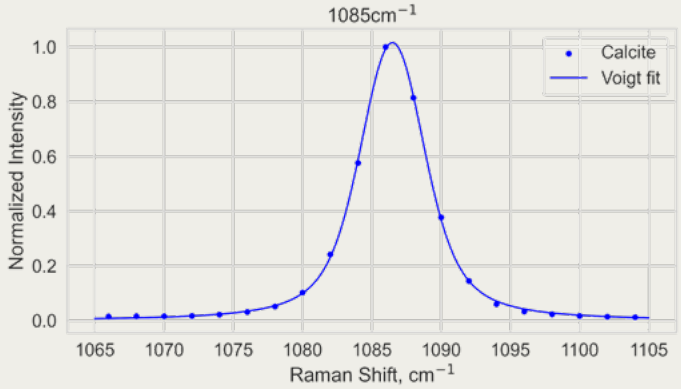


Figure 6. Profile of 1085 cm^{-1} Raman line of calcite.

Table 3. Calcite 1085 cm-1 Raman line and spectral resolution

Tabulated line position	Measured line position	Deviation	FWHH	Resolution
1085 cm^{-1}	1086.5 cm^{-1}	1.5 cm^{-1}	5.7 cm^{-1}	5.0 cm^{-1}

Paracetamol

Paracetamol is recognized as a standard reference material for Raman shift calibration in accordance with both the ASTM E1840-96 standard and the European Pharmacopoeia 10.7, Section 2.2.48. It exhibits a well-defined and reproducible Raman spectrum with several sharp, prominent peaks—particularly in the fingerprint region—which makes it suitable for verifying the spectral accuracy and performance of Raman spectrometers. These characteristic vibrational modes, arising from the molecular structure of paracetamol, provide reliable reference points for calibrating the Raman shift axis and ensuring instrument consistency. The inclusion of paracetamol in both American and European regulatory standards highlights its relevance for pharmaceutical quality control, analytical method validation, and routine instrument qualification across laboratory and industrial settings.

Table 4. Paracetamol Raman lines

Tabulated line position	Measured line position	Deviation
797.2 cm^{-1}	797.4 cm^{-1}	0.2 cm^{-1}
857.9 cm^{-1}	857.9 cm^{-1}	0
1168.5 cm^{-1}	1169.0 cm^{-1}	0.5 cm^{-1}
1236.8 cm^{-1}	1237.3 cm^{-1}	0.5 cm^{-1}
1323.9 cm^{-1}	1325.3 cm^{-1}	1.4 cm^{-1}
1648.4 cm^{-1}	1650.0 cm^{-1}	1.6 cm^{-1}

The low-frequency Raman spectrum of paracetamol provides valuable insight into the supramolecular structure of the material, as this spectral region is sensitive to lattice vibrations and weak intermolecular interactions within the crystal. Variations in low-frequency Raman features can be directly correlated with different polymorphic forms, enabling reliable identification and differentiation of crystalline phases. This capability is of particular importance for the pharmaceutical industry, where polymorphism can significantly influence key properties such as solubility, bioavailability, mechanical behavior, and long-term stability of drug products.

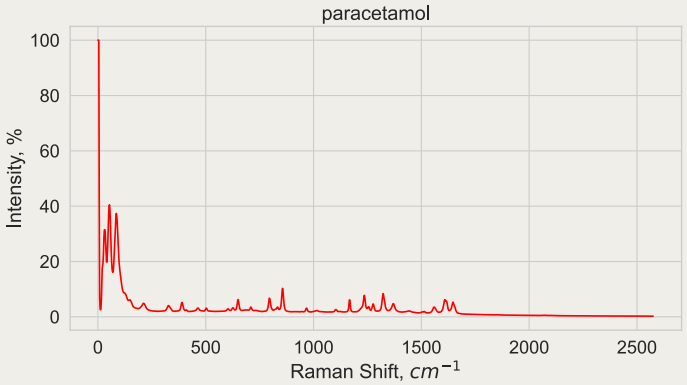


Figure 7. Raman spectrum of paracetamol.

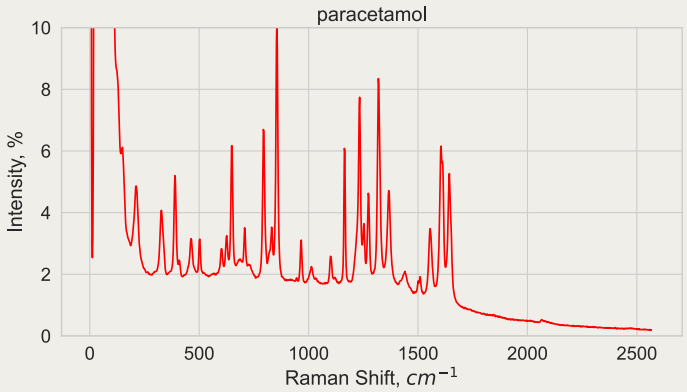


Figure 8. Raman spectrum of paracetamol in fingerprint region.

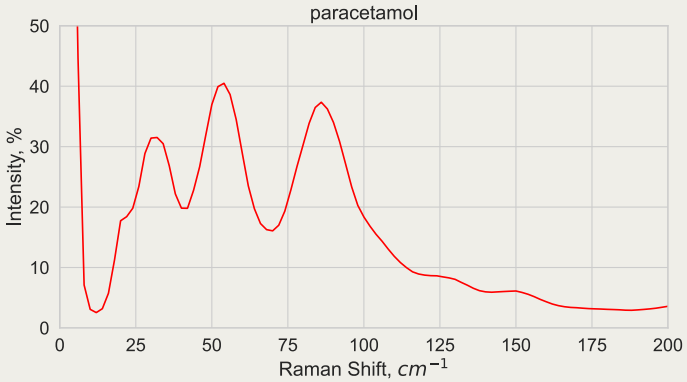


Figure 9. Low frequency Raman spectrum of paracetamol.

Ibuprofen

Low-frequency Raman spectroscopy offers valuable insight into the structural and crystalline properties of ibuprofen, a widely used non-steroidal anti-inflammatory drug (NSAID). In the low-frequency region (typically below 200 cm^{-1}), ibuprofen exhibits lattice vibrational modes that are highly sensitive to intermolecular interactions and crystal packing. These modes can be used to distinguish between different polymorphic forms of ibuprofen, detect changes in crystallinity, or monitor phase transitions during processing. Such information is crucial in pharmaceutical development and quality control, where the physical form of a drug can significantly influence its solubility, stability, and bioavailability. The ability of low-frequency Raman to capture subtle changes in solid-state structure makes it a powerful, non-destructive tool for characterizing ibuprofen in both research and industrial environments.

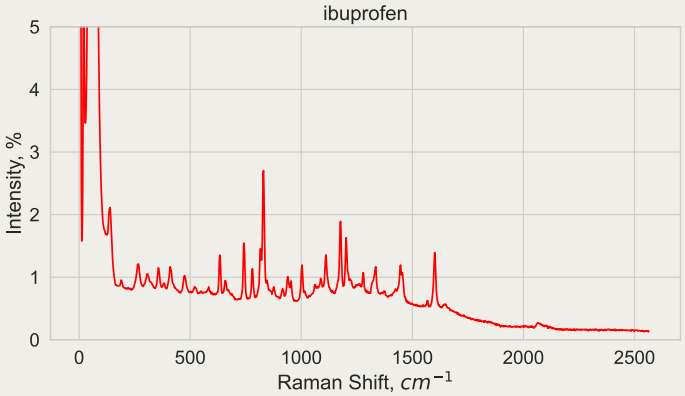


Figure 10. Raman spectrum of ibuprofen.

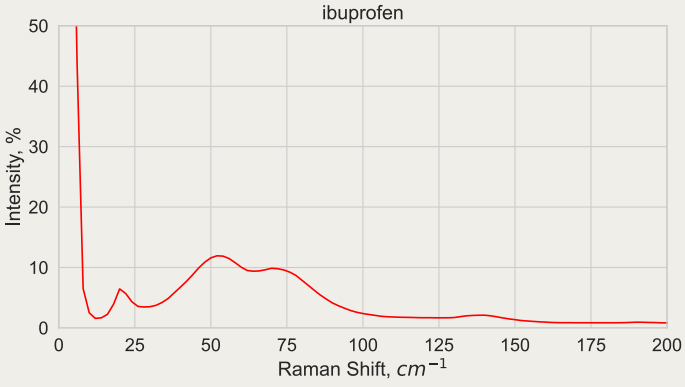


Figure 11. Low frequency Raman spectrum of ibuprofen.

Conclusions

To summarize, in this technical note we have demonstrated the performance of the Lightnovo low-frequency Raman setup through the measurement of several well-established reference materials, including sulfur, polystyrene, calcite, and paracetamol. Each of these samples provided distinct spectral features across both low- and mid-frequency ranges, enabling validation of the system's spectral accuracy, resolution, and sensitivity in accordance with relevant standards. To further showcase the capabilities of the system, we also measured ibuprofen—while not a formal reference material, it serves as a representative pharmaceutical compound with characteristic low-frequency modes. The successful detection of these subtle features reinforces the system's ability to resolve fine structural details below 200 cm^{-1}. Collectively, these results highlight the Lightnovo system as a powerful and reliable tool for both routine analysis and advanced research applications in low-frequency Raman spectroscopy.

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