HORIBA Scientific

200 YEARS 1819-2019 HORIBA JOBIN YVON

Raman Spectroscopy

Ultra-Low Frequency Raman With the LabRAM HR

Technical Note

RA TN-02

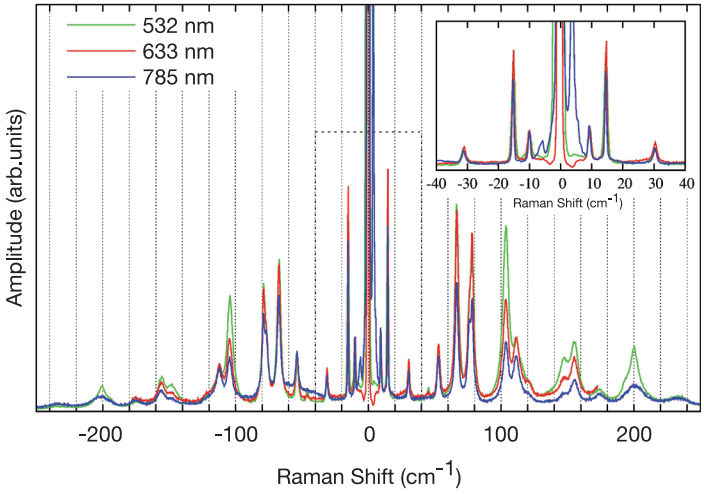
Introduction

With the introduction of the Ultra-Low Frequency (ULF) module, HORIBA Scientific now gives access to ultra-low frequency down to 5 cm-1 on the LabRAM HR.

Recent advances in photo-thermo-refractive (PTR) glass technology allows the design of low scattering, high optical density, and narrow bandwidth volume Bragg gratings (VBG). These new types of notch and bandpass filters have bandwidths of 5 to 10 cm-1 and offers 50% transmission at positions less than 3.5 cm-1 from the central filter position.

Field of applications

- Pharmaceutical polymorphs
- LA modes of polymer
- Semiconductor lattices and superlattices
- Material phase/structure
- Metal Halides
- Gases
- Carbon nanotubes
- Micro-crystallites
- Protein

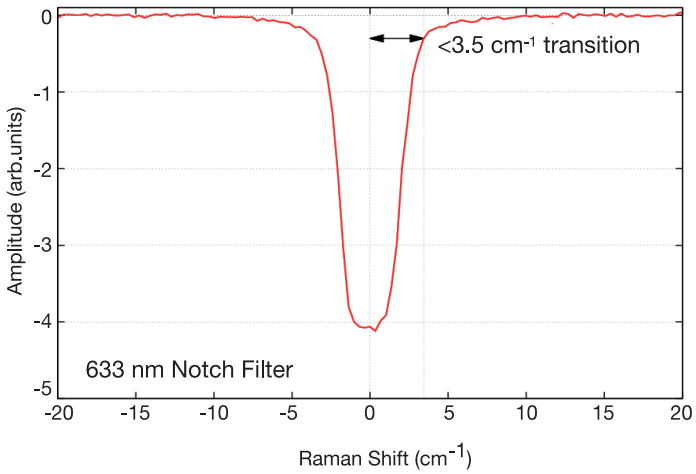


***ULF Raman measurements of L-Cystine at 532, 633, and 785 nm wavelengths**. Stokes and Anti-Stokes bands at 9 cm-1 are clearly resolved at all wavelengths.*

Key Features

- Access to Raman frequencies down to 5 cm^{-1} with a single stage monochromator.
- Preserves high throughput advantage of single stage spectrographs (favouring sensitivity, mapping speed…): transmission >70% at 633 nm.
- Allows measuring the entire Raman/PL range (from 400 to 2500 nm).
- Stokes and Anti-Stokes frequencies readily available simultaneously.
- Unlimited lifetime, environmentally stable (high temperature operations, no humidity effects), no degradation of optical performance (even with high-power laser sources).
- Available wavelengths: 488, 514.5, 532, 633 and 785 nm.

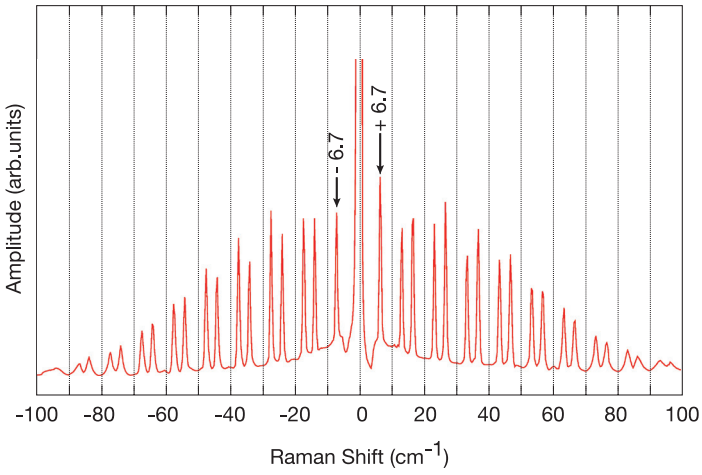
HORIBA Scientific has implemented VBG filters in the LabRAM HR allowing key measurements of important materials to be made, including analysis of lattice modes in pharmaceutical polymorphs, longitudinal acoustic modes (LAM) in polymers or superlattice modes of semiconductors. For the first time, these measurements are available in routine analytical instruments, without the need to move to larger, more complex instrumentation.



Notch filters curve at 633 nm.
Transition to 50% transmission is shown here.

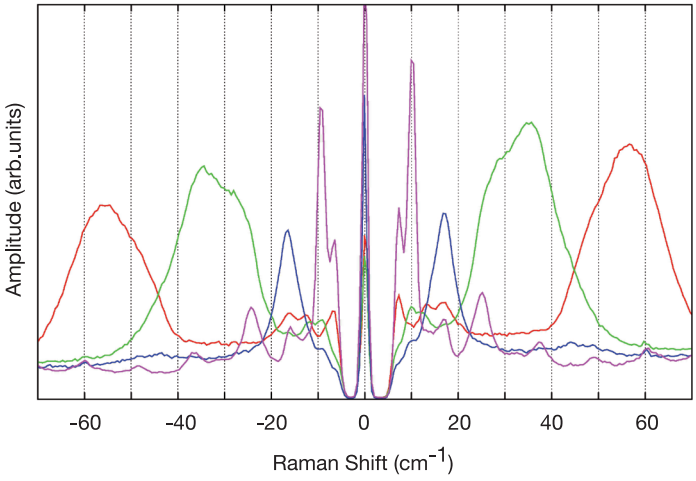
Semiconductor superlattices are composed of alternate layers of two different semiconductors. Superlattices have a lot of applications in electronic (diode, …) and in optic (laser, detector, …).

One of remarkable effects is the folding of acoustic branches related to the periodicity of the superlattices. These folded acoustic phonon modes are observed in the low-frequency region of Raman spectrum and give information about the structural quality of the superlattices.

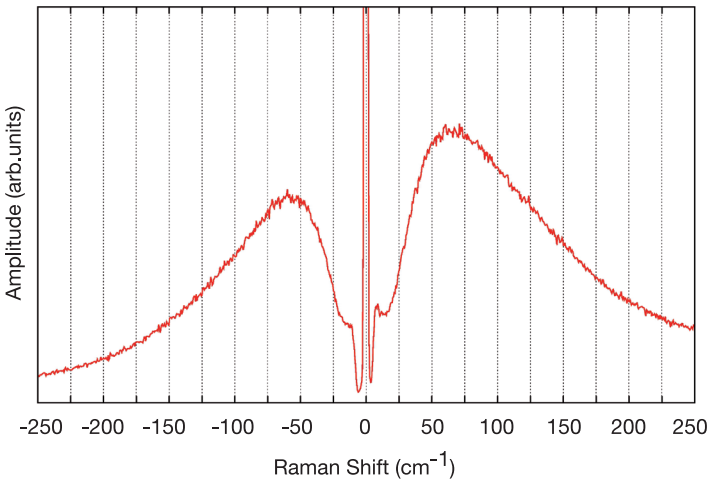


Semiconductor superlattices.

Data courtesy of P. H. Tan, State Key Laboratory for SL and Microstr., Institute of Semiconductors, Beijing, 100083, P. R. China and K. Brunner, University Wuerzburg, EP 3, Am Hubland, D-97074 Wuerzburg, Germany.



Longitudinal acoustic modes in bulk PE crystals.



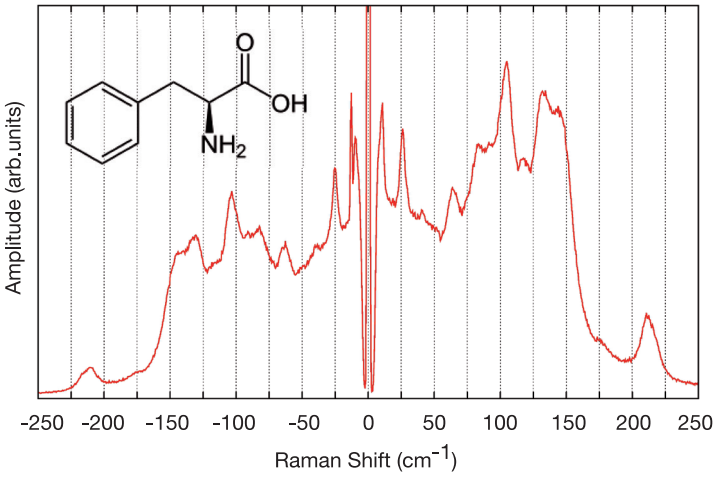
ULF at 514 nm: Borate glass spectrum.
Structural properties of borate glasses can be studied by following the low-energy vibrational modes (Boson Peak) in the 20 - 100 cm^{-1} range.

Data courtesy of Barbara Fazio, CNR - Istituto Processi Chimico-Fisici Messina (Italia)

The ULF module allows Raman spectroscopic information in the sub-100 cm^{-1} region, with measurements down to 5 cm^{-1} routinely available. It retains the high throughput of the single spectrometer, and measurements are obtained in just a few seconds or minutes without any limitation in the higher wavenumber region. Stokes and Anti-Stokes spectral features can be simultaneously measured, providing additional information to the user.

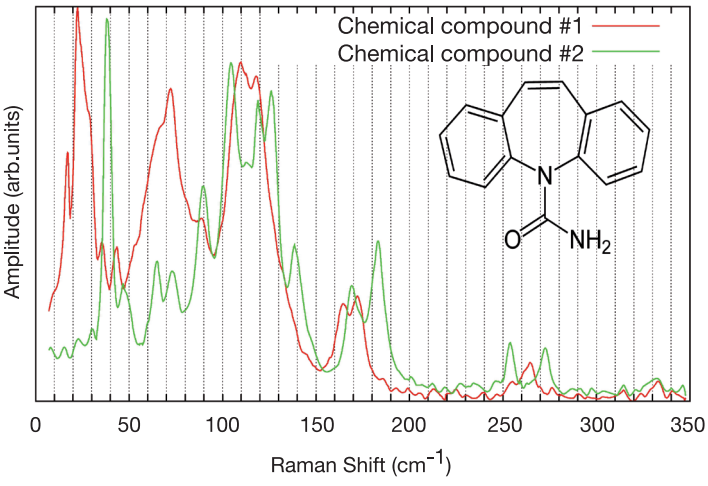
Traditionally, low frequency analysis has been confined to large research systems or complex and expensive instruments such as far IR, terahertz spectrometers or triple monochromator. Thus, the module opens up new areas of research for routine Raman microscopy.

ULF provides important information on a range of sample types, from pharmaceutical polymorphs or carbon nanotubes to heavy metal halides and semiconductors. The ULF mode can give details on conformational changes, subtle changes in lattice structure and even gaseous phase bond length, parameters not easily accessible on traditional benchtop equipment.

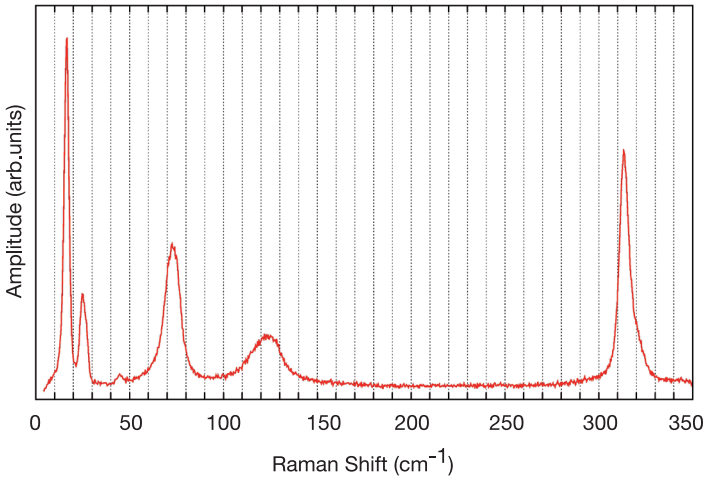


L-Phenylalanine spectrum at 514 nm.
L-Phenylalanine is a natural form of phenylalanine, who is an essential amino acid, found in most foods that contain protein and also in aspartame. It is also a constituant of some antidepressant and diet drugs.

Data courtesy of Pietro G. Gucciardi, CNR - Istituto Processi Chimico-Fisici Messina (Italia)

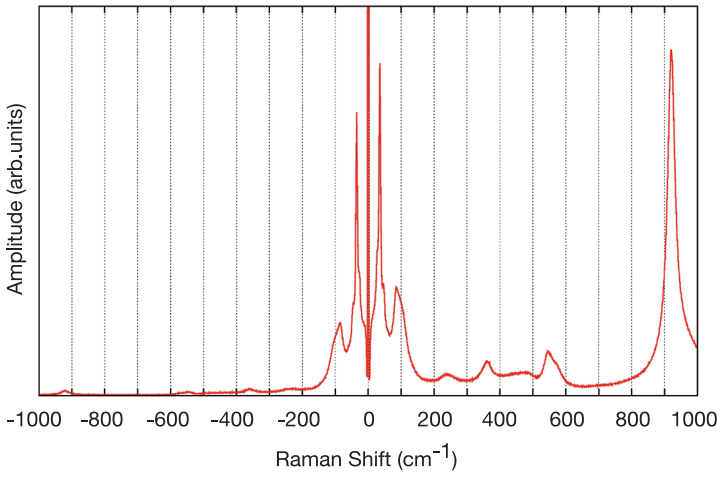


Pharmaceutical polymorph (carbamazepine) spectrum at 633 nm.
Carbamazepine is an anticonvulsant and mood stabilizing drug used primarily in the treatment of epilepsy and bipolar disorder.



ULF spectrum at 514 nm: $HgCl_2$.

Data courtesy of Dr. Bellot-Gurlet, Laboratoire de Dynamique, Interactions et Réactivité, Université Pierre & Marie Curie, Paris (France)



ULF spectrum at 514 nm: TlH_2PO_4.

Data courtesy of Dr. Bellot-Gurlet, Laboratoire de Dynamique, Interactions et Réactivité, Université Pierre & Marie Curie, Paris (France)

References

- A. Rapaport, B. Roussel, H.-J. Reich, F. Adar, A. Glebov, O. Mokhun, V. Smirnov, and L. Glebov, "Very Low Frequency Stokes and Anti-Stokes Raman Spectra Accessible with a Single Multichannel Spectrograph and Volume Bragg Grating Optical Filters," ICORS 2010, AIP Conf. Proc. 1267, 808-809 (2010).
- J. Ibáñez, A. Rapaport, C. Boney, R. Oliva, R. Cuscó, A. Bensaoula, and L. Artús, "Raman scattering by folded acoustic phonons in InGaN/GaN superlattices," Journal of Raman Spectroscopy (published online July 14th 2011).

Web links

- http://www.raman-scattering.eu/raman/texts/046_text_36.php
- https://www.horiba.com/en_en/products/detail/action/show/Product/ultra-low-frequency-raman-module-1642/
- http://www.laboratoryequipment.com/product-ss-horiba-scientific-ulf-labram-raman-system-030111.aspx

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