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Technology note from the Spectroscopy Products Division

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Advantages of dispersive Raman over FT-Raman

FT-Raman spectroscopy

Fourier transform (FT) Raman spectroscopy systems have been available since 1987. Commercial systems use a Nd: YAG laser (1.064 μm) with a near-infrared (near-IR) interferometer coupled to either a liquid nitrogen cooled germanium (Ge) or indium gallium arsenide (InGaAs) detector.

When it was introduced, FT-Raman had three main advantages over the dispersive Raman systems available:

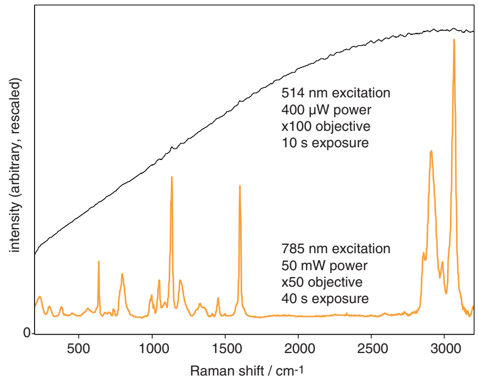
- reduction in the number of samples that exhibit laser-induced fluorescence
- ease of operation as with an FT-IR spectrometer
- high spectral resolution with good wavelength accuracy

Dispersive Raman spectroscopy

In the early 1990s Renishaw revolutionised the design of commercial dispersive Raman systems by combining a charge-coupled device (CCD) array detector with a single-grating spectrograph.

These systems, like FT-Raman systems, use filters to suppress the dominant Rayleigh scattering; this enables the much weaker Raman scattering to be detected.

inVia Reflex Raman microscope



Raman spectra of poly(sodium 4-styrenesulfonate) (514 nm and 785 nm excitation, 50x objective)

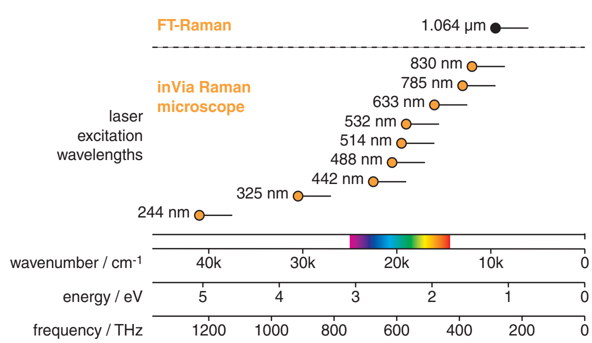
Renishaw's high power near-infrared lasers (available with 785 nm and 830 nm output) are ideal excitation sources for the Raman spectroscopy of most highly fluorescent materials.

inVia Reflex Raman microscope fitted with Class 1 microscope enclosure and triple laser baseplate with 785 nm (near-infrared), 514 nm (visible), and 325 nm (ultraviolet) lasers.

inVia advantages

Renishaw's inVia Raman microscopes comprise a single-grating spectrograph coupled to an optical microscope. This approach has many advantages over FT-Raman methods, including:

- inVia Raman microscopes can use near-IR diode lasers (785 nm and 830 nm). This largely overcomes fluorescence problems, as with FT-Raman (although a small subset of compounds may be more amenable to analysis using 1.064 µm excitation).
- inVia Raman microscopes use a multi-channel CCD detector, with extremely low intrinsic noise and a high quantum efficiency. This results in dispersive Raman being shot noise limited, whereas FT-Raman is detector noise limited. The benefits for dispersive Raman are far higher sensitivities (of the order of ×100) and far lower detection limits than FT-Raman.
- The shorter wavelengths of the near-IR lasers result in higher signal levels. For example, a 785 nm laser gives 3½ times increased sensitivity—when compared with the 1.064 µm laser of a FT-Raman system—because of the ν^4 scattering efficiency dependency. inVia Raman microscopes have demonstrated monolayer sensitivity, which is not achievable with relatively insensitive FT-Raman systems.
- Data acquisition times are much shorter than for FT-Raman methods, because of the high sensitivity and high efficiency of inVia Raman microscopes. Much lower laser powers ($^{1}/_{10}$ to $^{1}/_{100}$) can therefore be used, with benefits for light-sensitive samples.
- inVia Raman microscope systems offer great flexibility by supporting multiple excitation wavelengths on a single instrument. These can range from the deep-UV (244 nm) to the near-IR (830 nm), thus increasing the versatility of the instrument.



Comparison of the choice of excitation wavelengths available with inVia Raman microscopes and the excitation wavelength predominantly used in FT-Raman systems. The bars represent the typical range covered by the Stokes Raman spectrum.

FT-Raman disadvantages

Three classes of compound prove intractable to FT-Raman analysis:

- **Aqueous phase samples.** These may strongly absorb both the exciting laser radiation and the Raman scattered light
- **Samples at elevated temperatures.** Above 250 °C intense black body emission can mask the Raman signal
- **Black samples.** These can strongly absorb, heat up, and produce intense background emission, or even degrade

In contrast, inVia Raman microscopes using 785 nm or 830 nm excitation overcome all of these problems; water again becomes the ideal solvent for Raman studies; dynamic reaction systems may be studied above 250 °C; and black samples can be analysed with ease.

Resolution

Most importantly, the optical design of the inVia Raman microscope provides a spectral resolution of typically 1 cm^{-1} in the near-infrared, and its research-grade optical microscope provides a lateral spatial resolution better than 1 µm—far better than commercial FT-Raman microscopes (typical resolution worse than 5 µm). The encoded diffraction grating stage in the inVia Raman microscope also ensures absolute accuracy of better than ± 1 cm^{-1} across the whole of the near-infrared wavelength range.

Advantage inVia

The conclusion is that Renishaw's inVia microscope systems are faster, more sensitive, and provide better spatial resolution than FT-Raman systems - and at lower cost.

inVia Raman microscope using a custom adapter for the analysis of bulk aqueous samples

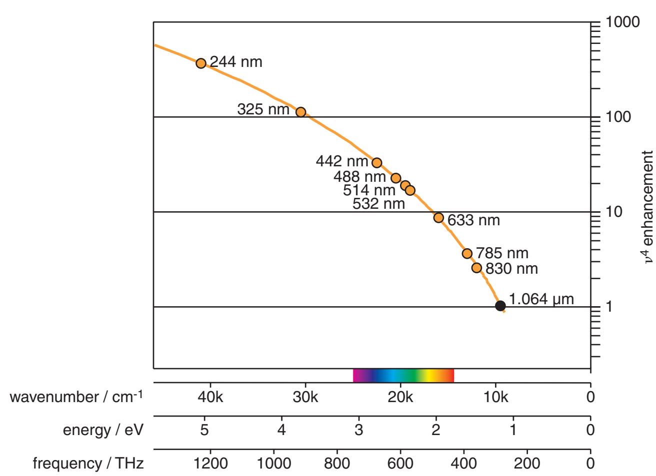


Diagram showing the effect of the ν^4 term on the efficiency of Raman scattering for a range of excitation wavelengths. Data are normalised to give 1.064 µm excitation an efficiency of 1.

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Comparison of performance: inVia vs. FT-Raman

Description	Renishaw's inVia Raman microscope	FT-Raman
Wavelength coverage	~ 10 cm^{-1} to 9000 cm^{-1} (depending on configuration)	~ 50 cm^{-1} to 3650 cm^{-1} (fixed)
Laser options	multiple, from 244 nm to 830 nm	1.064 µm (on >99% of systems)
Detector	Si CCD	Ge, InGaAs
Noise limitation	signal shot noise limited	detector noise limited
Detector sensitivity	excellent; CCD is detector of choice	poor, best available for 0.8 µm to 1.6 µm range
Elevated temperature	no problem even > 1000 °C	limited to < 250 °C
Aqueous samples	no problem (solvent of choice)	difficult; strong absorption of laser and Raman
Black samples	no problem	intense thermal emissions usually observed
Microscope spatial resolution	< 1 µm (depending on configuration)	> 5 µm
Spectral resolution	~ 1 cm^{-1} (depending on configuration)	0.5 cm^{-1}
Fluorescence suppression	good at 785 nm and 830 nm	optimum at 1.064 µm
Raman imaging	Sequential point imaging, line-focus imaging, True Raman Imaging™	Sequential point imaging only (very limited availability)
ν^4 scattering enhancement (785 nm relative to 1064 nm)	×3.5	×1