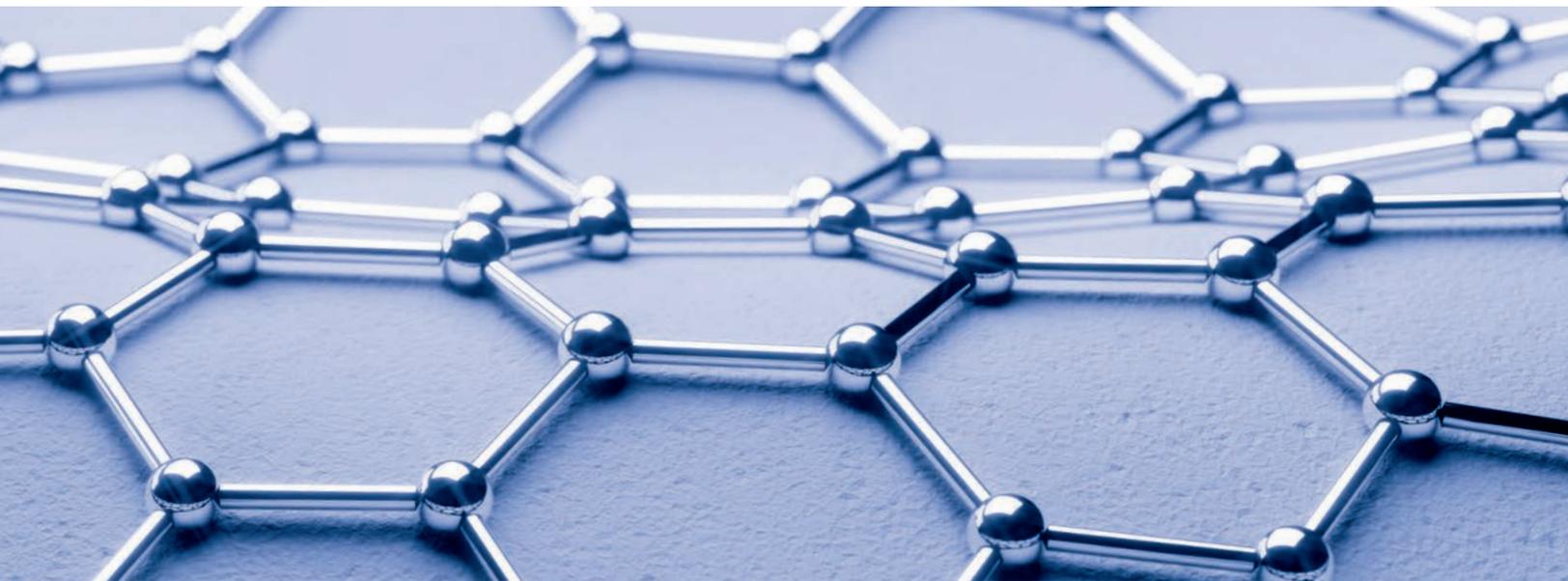


# EXTENDING RAMAN into the THz DOMAIN



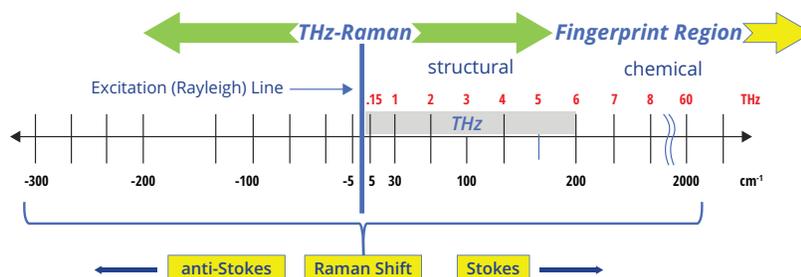
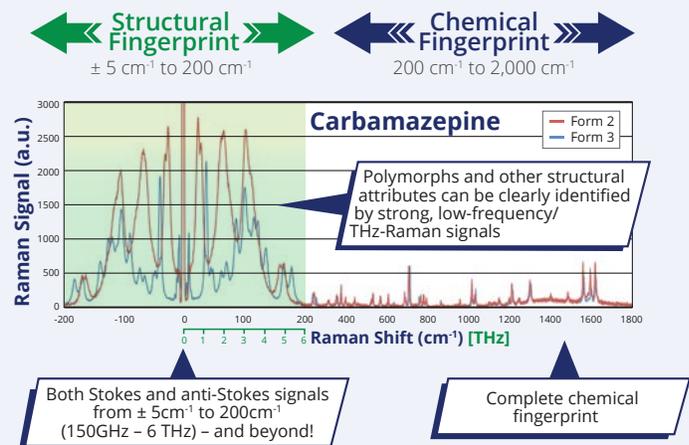
Delivering Both Chemical Composition and Structural  
Information in a Single Measurement

# Simultaneous Measurement of Both Chemical and Structural Properties

On dax patented<sup>1</sup> THz-Raman<sup>®</sup> systems boost both the efficiency and reliability of materials characterization, in a single, real-time, non-destructive measurement. By unveiling the low-frequency (low wavenumber) range of the Raman spectrum, often referred to as a secondary “structural fingerprint,” it is possible to directly observe and differentiate key structural properties of materials, while preserving the complete chemical fingerprint.

## Key Applications include:

- Differentiation and screening of polymorphs
- Monitoring and quantifying degree of crystallinity
- Characterizing and observing co-crystal formation
- Process monitoring and analysis of chemical reactions
- Characterizing thickness and orientation of few-layer nanomaterials
- Structural characterization of polymers
- Explosives detection and analysis, including determination of formulation methods



The THz-Raman<sup>®</sup> region (± 5 cm<sup>-1</sup> to 200 cm<sup>-1</sup>) corresponds to the THz-energy vibrations (150 GHz to 6 THz) of inter-molecular/intra-molecular vibrations, including phonon modes, lattice modes, and rotational modes. These are often 5 to 10 times stronger than normal vibrational modes, significantly boosting signal strength. By capturing both Stokes and anti-Stokes signals, spectral features can be validated and the excitation wavelength (0 cm<sup>-1</sup>) can be precisely determined due to signal symmetry, eliminating the need for system re-calibration.

<sup>1</sup> US Patents 7,986,407 and 8,184,285.

<sup>2</sup> Data taken using SureBlock™ notch filters and a single-stage spectrometer at 785 nm.

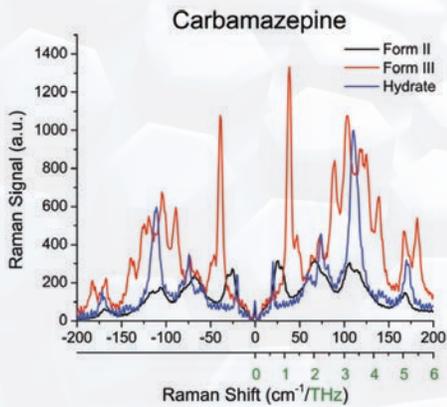
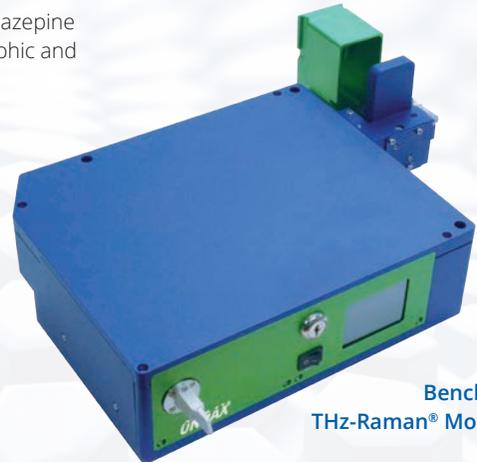


Fig. 1: THz-Raman spectra of Carbamazepine shows clearly differentiated polymorphic and hydrated forms?



Benchtop THz-Raman® Module

THz-Raman® Spectroscopy Modules are designed as integrated, ultra-compact, plug-and-play solutions to upgrade your existing Raman spectrometer. Comprising an ultra-narrowband ASE-free laser source, NoiseBlock™ 90/10 beamsplitter, and dual-stage SureBlock™ notch filters, the system delivers >OD9 Rayleigh attenuation and signal capture of both Stokes and anti-Stokes signals down to 5 cm<sup>-1</sup>. (Fig 1)

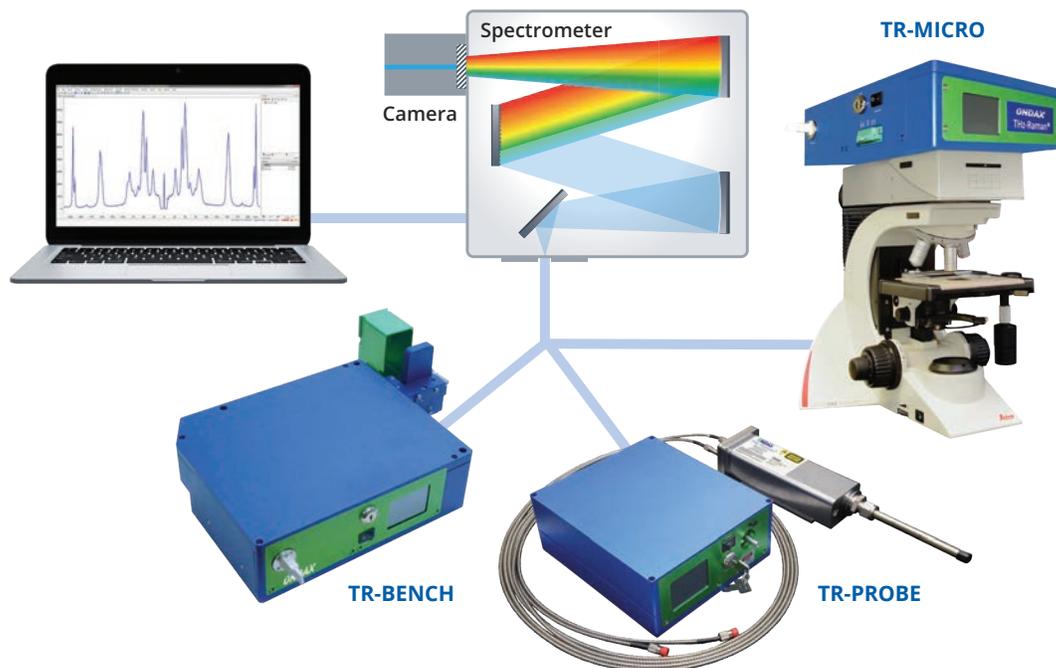
# System Configurations

All **TR-Series** THz-Raman® modules are ultra-compact and simple to connect via fiber to almost any spectrometer or Raman system. A high-power, wavelength-stabilized, single-frequency laser source is precisely matched to the ultra narrow-band ASE, beamsplitter and notch filters to assure maximum throughput and exceptional attenuation (>OD 9) of the excitation source. Systems are available in 532 nm, 633 nm, 785 nm, 808 nm, 976 nm and 1064 nm excitation wavelengths.

The **TR-PROBE** is a compact, robust THz-Raman® probe that enables in-situ reaction or process monitoring, and can also be flexibly configured with a variety of sample interface accessories, including immersion or contact probe tips, a convenient vial/tablet holder, a Transmission Raman adapter, a microscope mount, or a steerable non-contact optic (see options below). A separate CleanLine™ laser provides ASE-free excitation via a multimode fiber, enabling the probe to operate in harsher environments where electrical connections are not permitted.

The **TR-BENCH** is configured for benchtop use and offers a similar range of interchangeable sample interface accessories holder for fast, easy measurements. The system also comes with a standard cage mounting plate (centered on the collimated output beam) to allow for customized collection optics or easy integration into a customized system. Options include circular polarization or a dual-port/dual polarization output for simultaneous measurement of both S and P polarizations.

The **TR-MICRO** mounts directly to a broad range of popular microscope platforms and micro-Raman systems, and can be easily switched in and out of the optical path. Linear polarization is standard, circular polarization is optional.

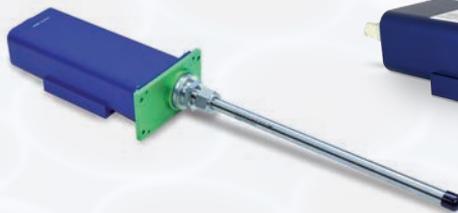


THz-Raman® modules are compatible with virtually any commercial Raman system or spectrometer, and Coherent can recommend or integrate an appropriate spectrometer and deliver as a complete turnkey system.

Probe with  
Vial/Tablet Holder



Probe with  
Non-Contact Optic



Probe with Contact/Immersion  
Probe Tip



A variety of sample interface accessories enable the TR-PROBE and TR-BENCH to be easily configured to match a broad range of applications. Immersion or contact probe tips may be mounted with either a fixed SwageLok mount, or for longer probes that may need alignment, an adjustable tip/tilt probe mount. The Vial/Tablet Sample Holder incorporates an adjustable steering mirror, interchangeable focusing lens, and safety shutter, and the Steerable Non-contact Optic Mount allows for projection and steering of the output beam with precision alignment and interchangeable focusing optics, for applications requiring long-range collection paths. New accessories include a Transmission Raman adapter (Probe only) which is ideal for bulk sampling of tablets or vials, and a Microscope mount with in/out optical switching and beam steering adjustments.

Probe with  
Microscope Mount



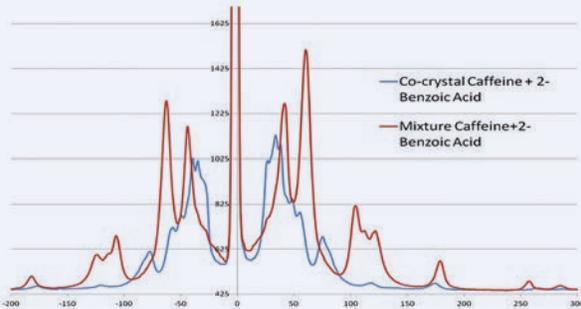
Probe with Transmission Raman Adapter  
and Sample Tablet/Vial Holders



Probe without Accessory –  
Collimated Beam Output

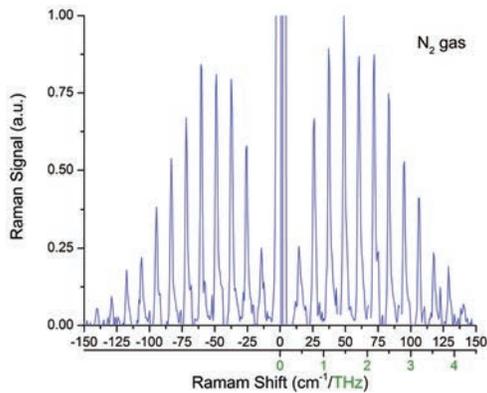


# THz-Raman® Applications Examples



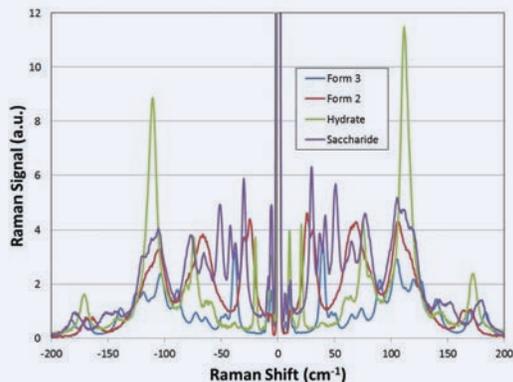
## Crystal Monitoring and Analysis

Identifying and monitoring the formation of cocrystals is also improved using THz-Raman spectra. The figure above shows the clearly recognizable peak shifts that occur when cocrystals are formed in a mixture of Caffeine and 2-Benzoic acid.



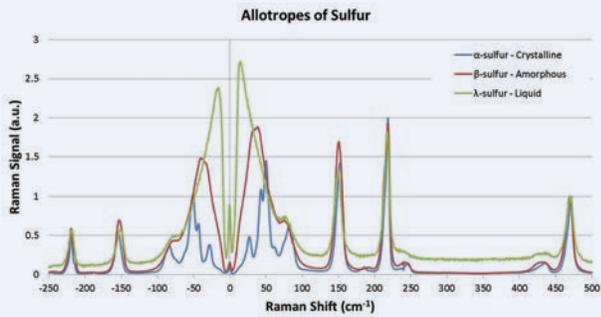
## Gas Sensing

Rotational modes of many gases can be clearly seen in the THz-Raman region. Signal intensities can be up to 10x those in the fingerprint region, opening up the possibility of using Raman for extremely sensitive gas sensing applications. The Stokes/anti-Stokes ratios can also be used for in-situ sensing of temperature.



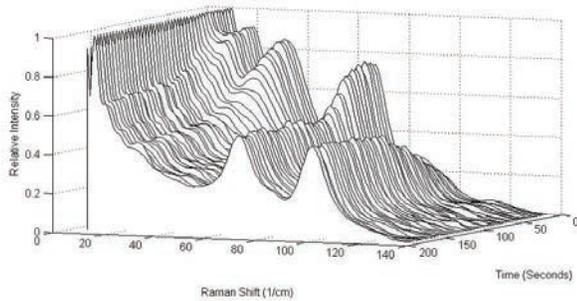
## Polymorph Identification

Polymorphic forms and hydrates of pharmaceuticals can easily be distinguished in raw materials analysis, finished goods, process monitoring, and QC applications.



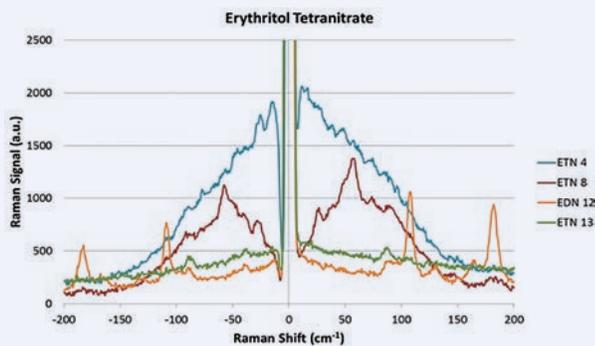
### Phase Monitoring

Phase changes of Sulfur observed when heated from room temp.( $\alpha$ ) to 95.2°C ( $\beta$ ) and then to the melting point of 115.21°C ( $\lambda$ ). Note the clearly recognizable changes in peak location, shape and magnitude in the THz-Raman® region. Crystalline phases result in sharp peaks, which broaden and dissipate as the sulfur liquifies.



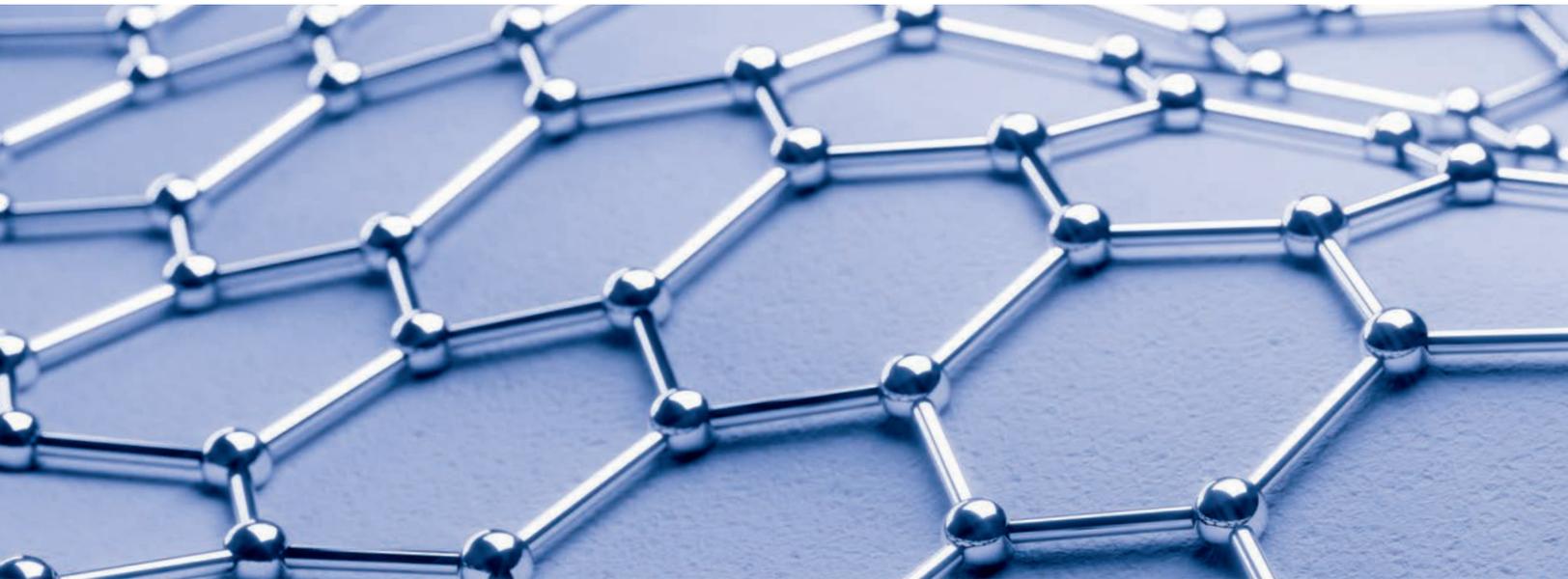
### Phase Monitoring

Low frequency spectra can be used to monitor transformation of polymorphs. The waterfall plot above shows anhydrous theophylline before and after its transformation into a flocculated slurry, over a period of approximately 100 seconds. (data courtesy Clairret Scientific Ltd.)



### Synthetic Pathway Analysis: Explosives Forensics

Multiple samples of ETN (Erythritol Tetranitrate), representing systematic variations of ingredients and preparation routes, show distinctive differences.



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