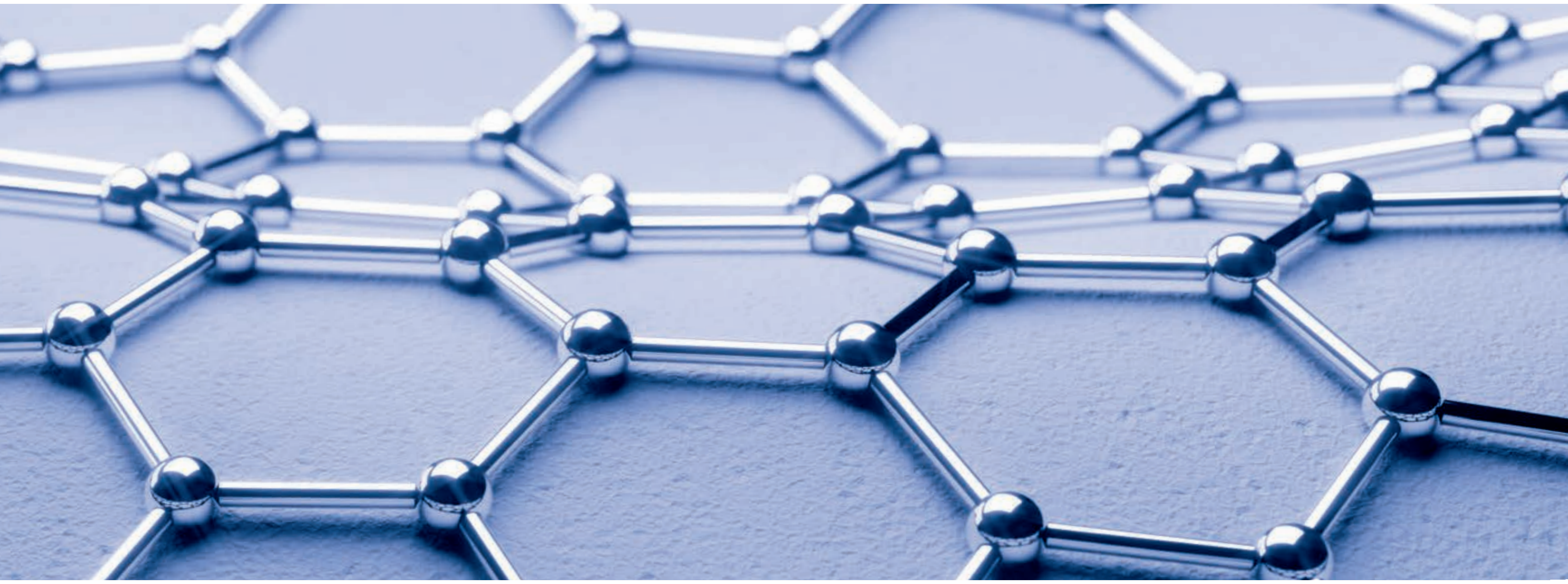
EXTENDING RAMAN into the THz DOMAIN



Delivering Both Chemical Composition and Structural Information in a Single Measurement

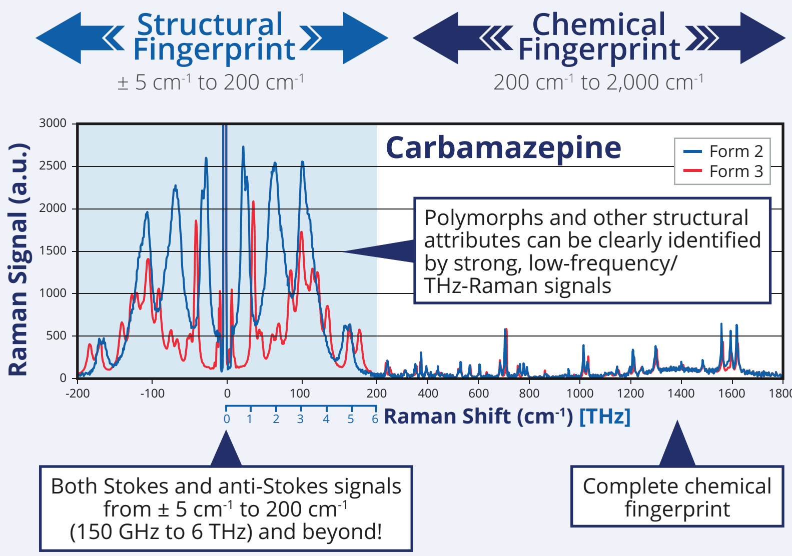
COHERENT®
Superior Reliability & Performance

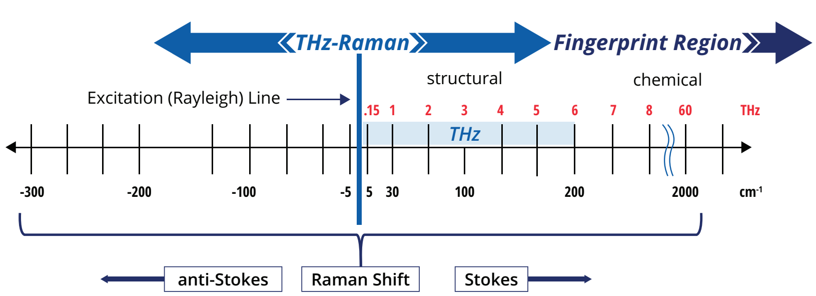
Simultaneous Measurement of Both Chemical and Structural Properties

Coherent-patented[1] **THz-Raman**® 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





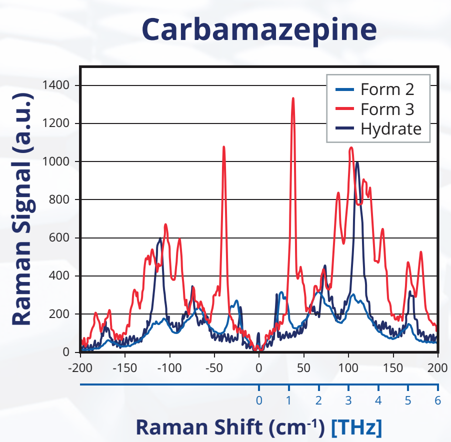
The THz-Raman® region (±5 cm-1 to 200 cm-1) corresponds to the THz-energy vibrations (150 GHz to 6 THz) of inter-molecular/intra-molecular vibrations, including phonon modes, lattice modes, and rotational modes. These are often 5 to 10 times stronger than normal vibrational modes, significantly boosting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

1 US Patents 7,986,407 and 8,184,285.
2 Data taken using SureBlock™ notch filters and a single-stage spectrometer at 785 nm.

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^{-1}. (Fig 1)

Fig. 1: THz-Raman spectra of Carbamazepine shows clearly differentiated polymorphic and hydrated forms.[2]



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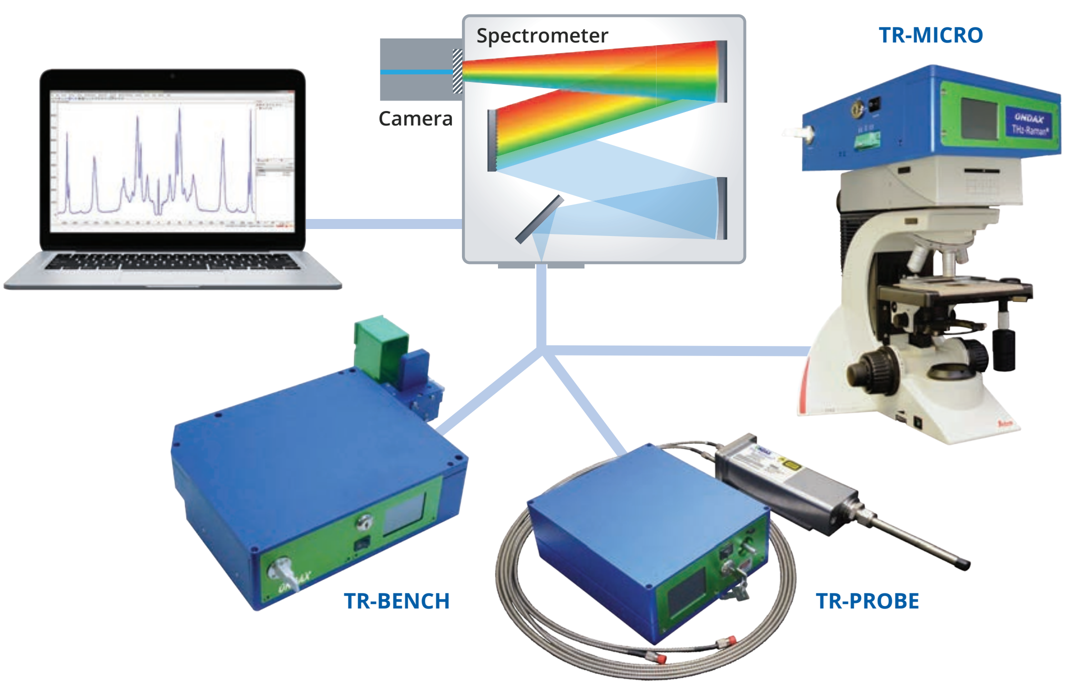
System Configurations

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.

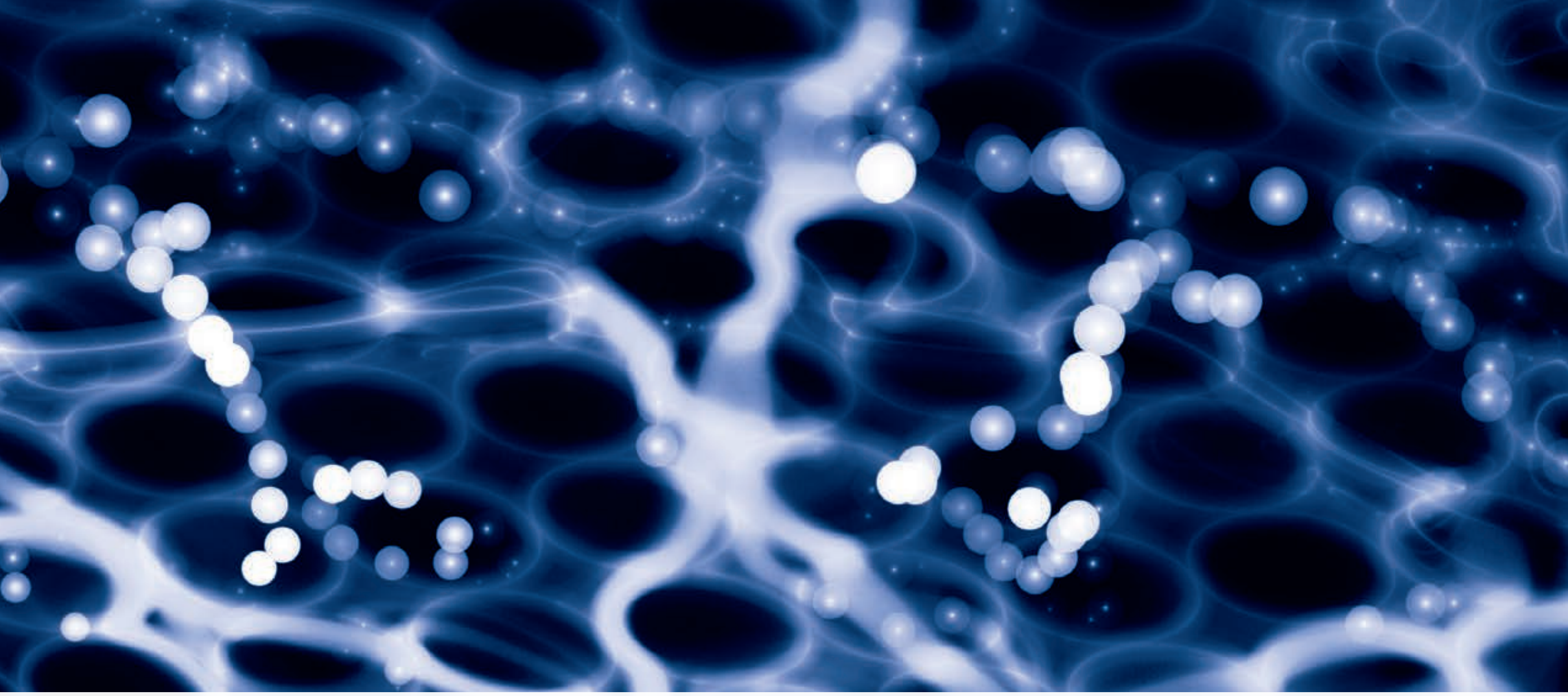
The **TR-PROBE** is a compact, robust THz-Raman® probe that enables in-situ reaction or process monitoring, and can also be flexibly configured with a variety of sample interface accessories, including immersion or contact probe tips, a convenient vial/tablet holder, a Transmission Raman adapter, a microscope 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.

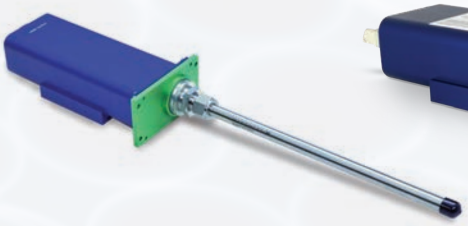


THz-Raman® modules are compatible with virtually any commercial Raman system or spectrometer, and Coherent can recommend or integrate an appropriate spectrometer and deliver as a complete turnkey system.



Probe with
Vial/Tablet Holder

Probe with
Non-Contact Optic



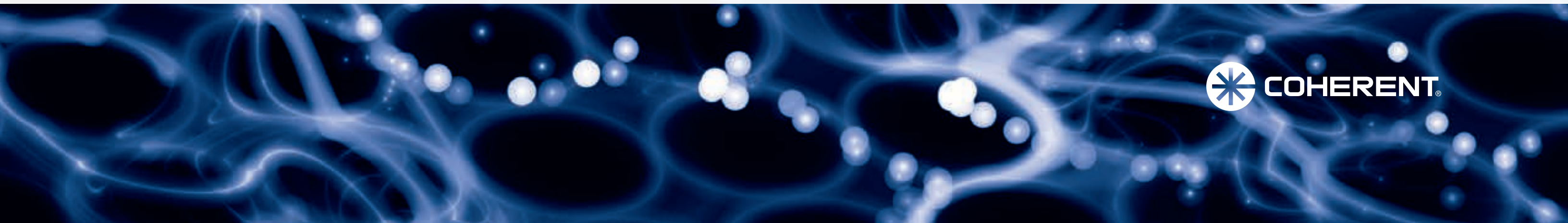
Probe with Contact/Immersion
Probe Tip

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



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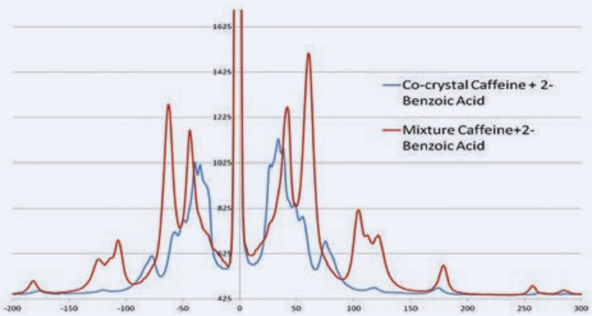
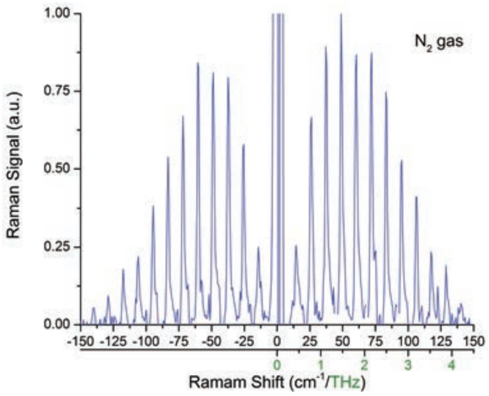
THz-Raman® Applications Examples



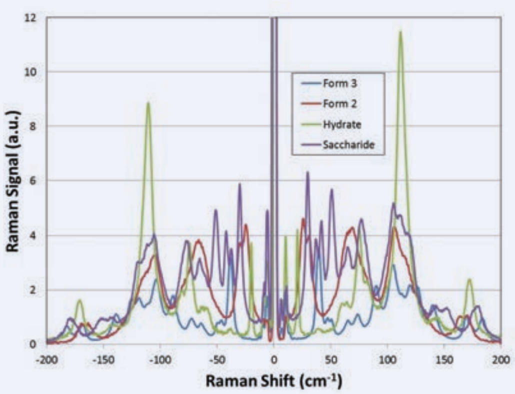
Crystal Monitoring and Analysis

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.



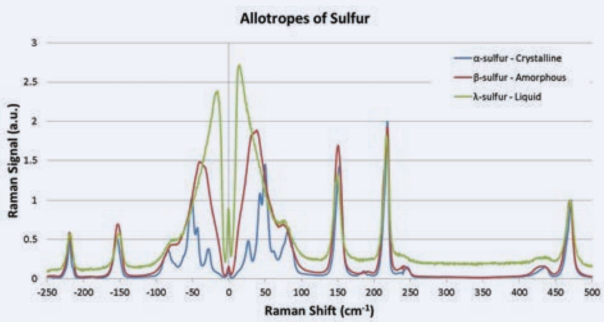
Gas Sensing

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.



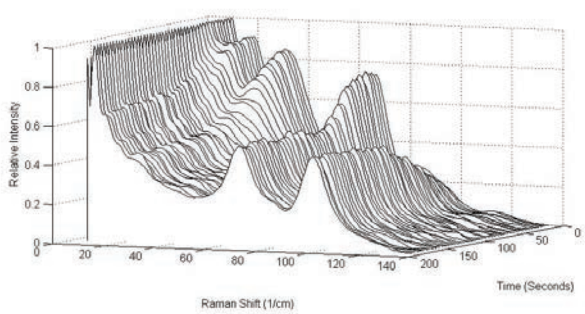
Polymorph Identification

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



Phase Monitoring

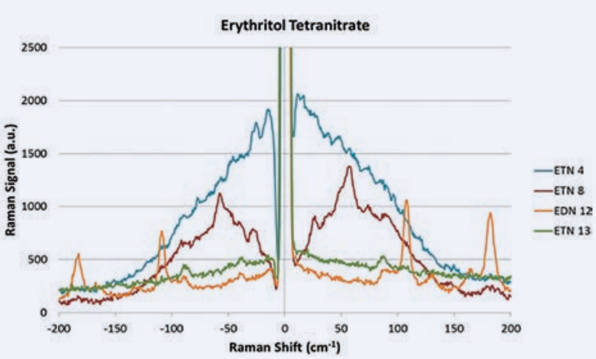
Phase changes of Sulfur observed when heated from room temp.(α) to 95.2°C (β) and then to the melting point of 115.21°C (λ). Note the clearly recognizable changes in peak location, shape and magnitude in the THz-Raman® region. Crystalline phases result in sharp peaks, which broaden and dissipate as the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



Phase Monitoring

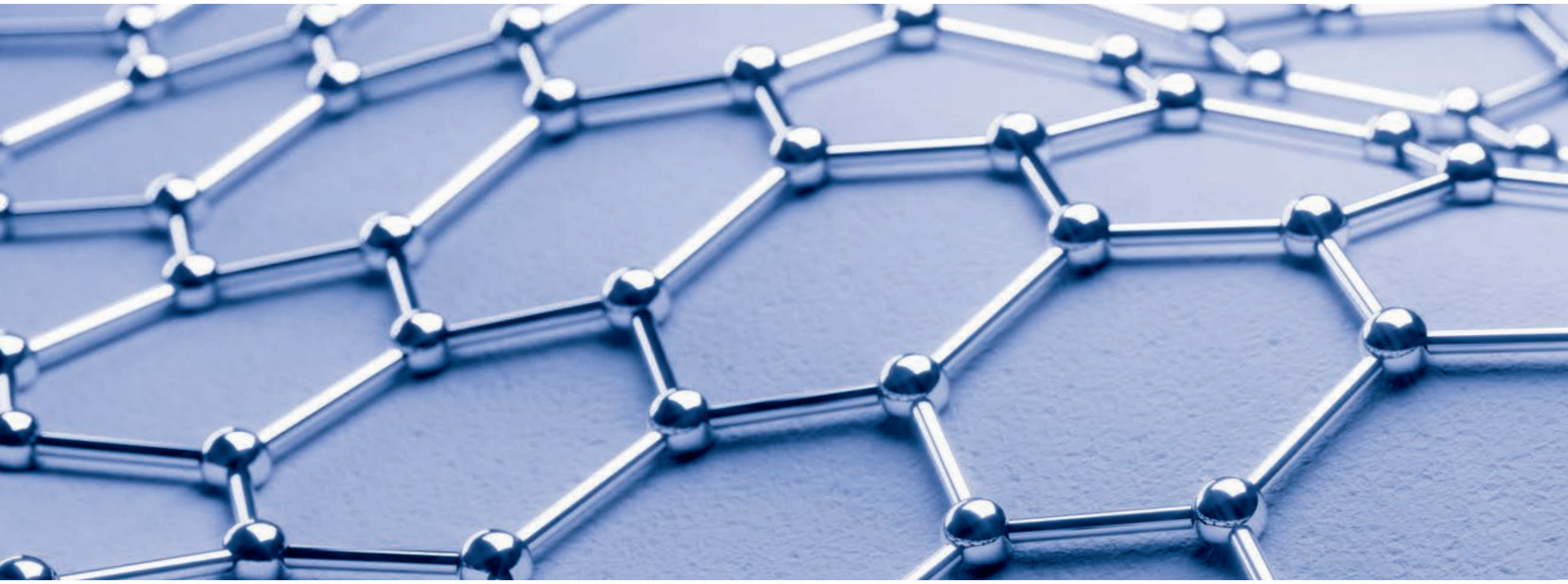
Low frequency spectra can be used to monitor transformation of polymorphs. The waterfall plot above shows anhydrous theophylline before and after its transformation into a flocculated slurry, over a period of approximately 100 seconds.

(data courtesy Clairet 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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