

WHITE PAPER

Comparison of Raman Spectroscopy and Fourier Transformed Infrared (FTIR) Spectroscopy for Advanced Technology R&D and Quality Control

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Motivation

Increasing complexity in device and packaging materials requires a thorough understanding of the chemistry of the materials at hand. Identifying unknown materials, quantifying differences between research samples, mapping homogeneity of composition, and characterizing surface chemistry can all be paramount in the design and manufacturing processes. To meet these growing demands, a diversified group of characterization techniques is often required. Two instrumental techniques – Fourier Transform Infrared (FTIR) Spectroscopy and Raman Spectroscopy, present effective methodologies for characterizing chemistry in both organic and inorganic systems.

Overview:

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR is a measurement of transmitted or reflected infrared light from a sample, and typically provides information about the rate of light absorption at a range of infrared wavelengths (Fig. 1). Those absorption events are characteristic of the resonant vibrational frequencies of the molecules in the sample. With control samples, reference libraries, or knowledge about the fundamental relationships between molecular vibrations and e.g. temperature, symmetry, crystallinity, or composition (Harris & Bertolucci, 1989), FTIR can be highly informative about the

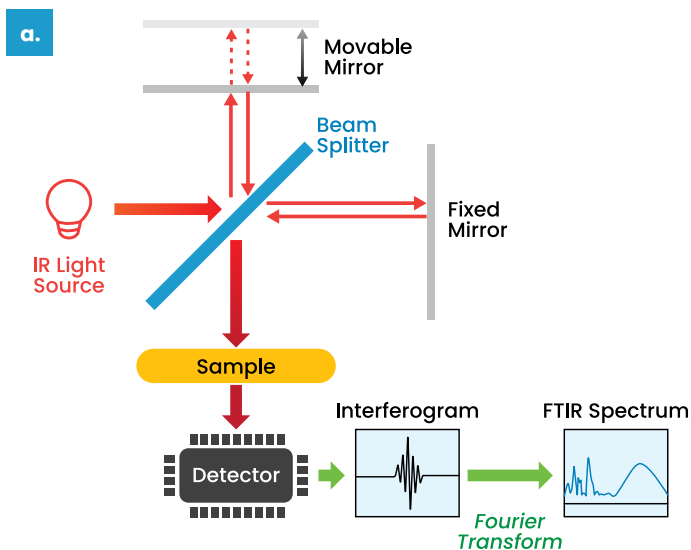


Figure 1a. Michelson FTIRs use a movable mirror to create variable path lengths of the light going into the sample. That modulation causes a change in the frequency distribution of the light incident on the sample. Upon interacting with the sample and reaching the detector, signal is gathered in the time domain as an interferogram, which is then Fourier transformed into a FTIR signal used for analysis.

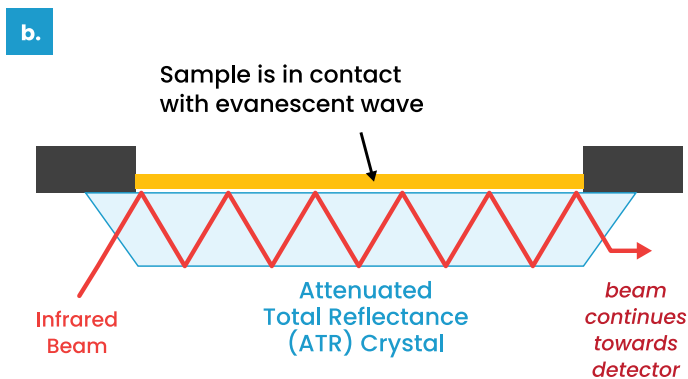


Figure 1b. FTIR can also be conducted in a contact mode called attenuated total reflectance (ATR), in which the standard (Michelson) light probe interacts with the sample not just once, but multiple times before reaching the detector. The sample is placed on a crystal with high refractive such that the light undergoes total reflectance from the sample surface except for evanescent wave effects at characteristic vibrational frequencies. The multiple interactions caused by ATR result in enhanced signal-to-noise, and the total reflection physics create high degrees of surface sensitivity.

structure and dynamics of a samples constituent chemistry. With transmittance, reflectance, and total attenuated reflectance (ATR) contact modes, nearly all samples can be handled and measured with FTIR.

FTIR is best suited for measurements of organic or polymer systems. Inorganic systems present two common barriers to molecular vibrational spectroscopy:

1. Conductors absorb light by elevating a free electron to a higher energy, which happens at high rates and broad frequency bands. Typically, this will result in high reflectivity at metal surfaces, but little to no information about bonding.
2. Semiconductor crystal unit cells often have the property of inversion symmetry. Most of these are FTIR inactive (including all single-element crystals like pure Si), due to their inability to generate uncompensated dipole moments.

By contrast, organic and polymer systems are generally not conducting or centrosymmetric. Large libraries have been produced to document the vibrational signature of polymer systems (Wiley Science Solutions, 2023), which can also be implemented to highlight alterations in polymer sample chemistry. Metal oxides and other insulating, non-centrosymmetric systems can also make good targets for FTIR, but low wavenumber detection ranges (which require the right optical windows and detectors, as in Covalent Metrology's ThermoFisher iS50 diamond ATR unit) are often required to make positive identifications.

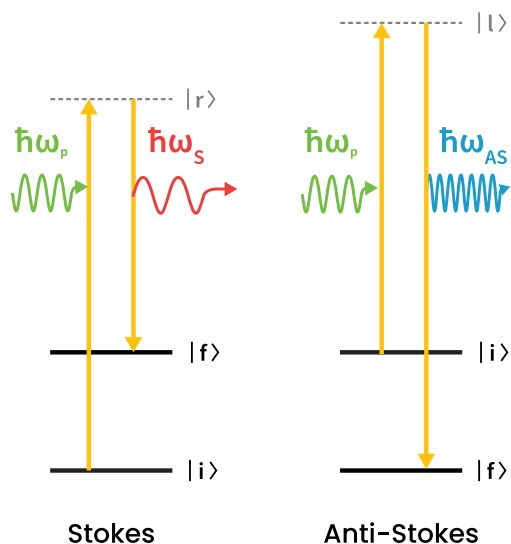


Figure 2. Raman scattering can result in either decrease of energy in the scattered wave (Stokes shifting) or increase of energy in the scattered wave (Anti-Stokes shifting). In conventional Raman experiments, Stokes shifted light is gathered, and the degree of energy downshifting is measured.

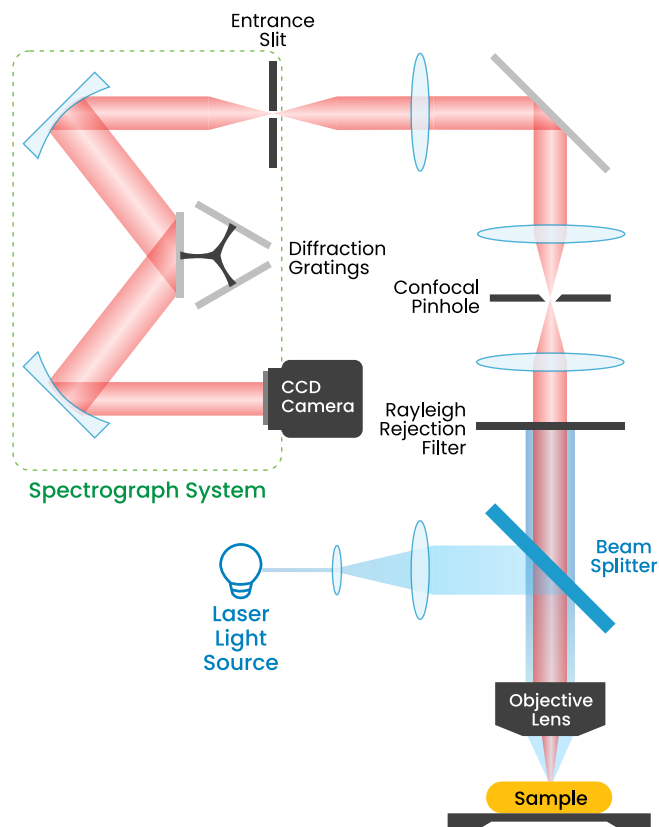


Figure 3. Modern Raman confocal microscopes are composed of laser sources, elastic (Rayleigh) scattering rejection filters, confocal pinholes, and spectrometers. The spectrometer separates light of different Stokes shifts (from different vibrational excitation events), and signal is read by a CCD device.

Overview: Raman Spectroscopy

Raman spectroscopy, on the other hand, capitalizes on the phenomenon of inelastic scattering, which shifts incident light to slightly lower energy when molecular vibrational states are excited (Fig. 2). Raman tools typically use higher powered laser sources to offset the relatively low signal created by its secondary emissions, and to ensure interpretability of light shifts with a highly monochromated (usually visible range) source (Fig. 3). That shifted light is characteristic of the bonds in the system, and can provide similar information about composition, crystallinity, strain, etc. of a sample. Because the technique uses monochromated visible laser sources, Raman spectrometers often also utilize confocal microscope objectives, can target features down to 1 μm , and excel at mapping of near-surface chemistry.

Like FTIR, there are some materials that don't produce significant Raman signal, although they are more rare. Raman relies on changes in dielectric polarizability in samples, which can generally be viewed as changes of shape or size of the electron cloud surrounding the bonded atoms during vibration. Among these are SiO₂ and distilled water, which enable chip measurements through passivation and aqueous measurements, respectively.

Smooth and ordered materials, like crystals, can produce high levels of characteristic Raman signal. For 2D materials, Raman has become

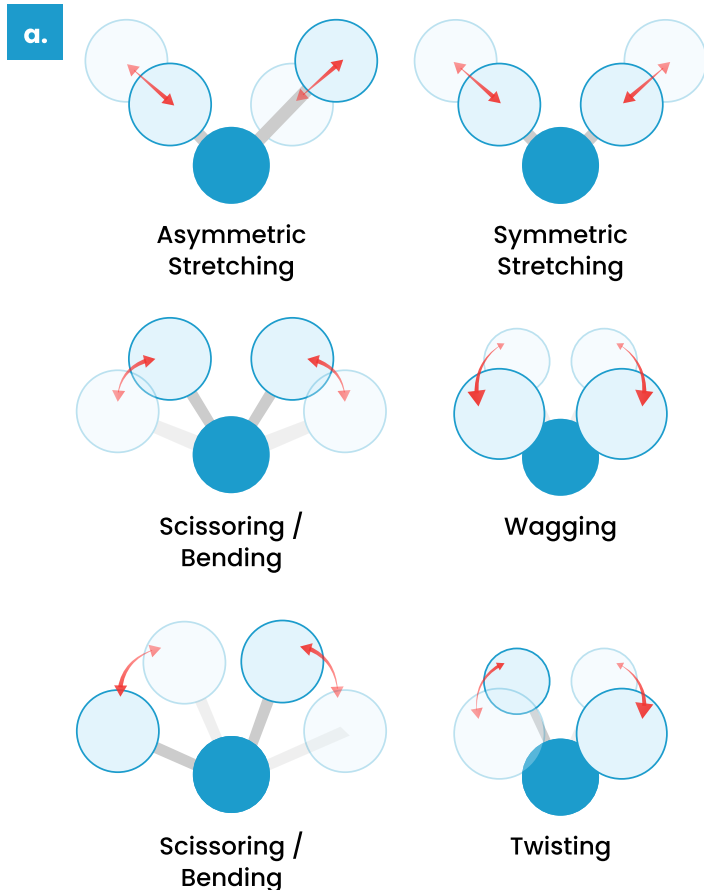


Figure 4a. Diagram of the various bond vibrations detectable with Raman spectroscopy.

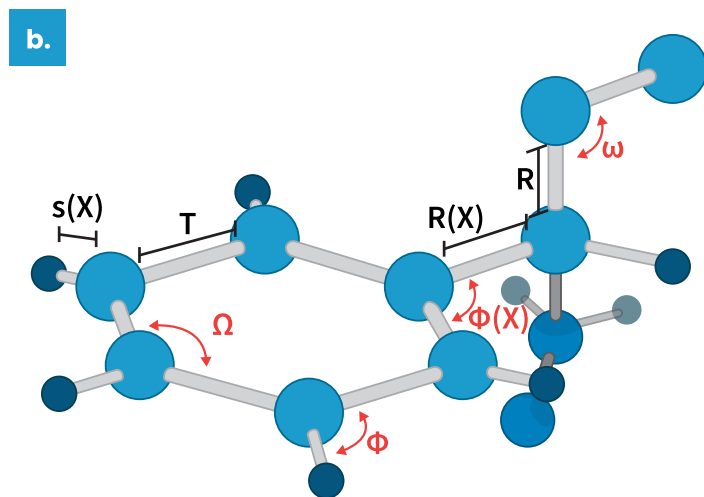


Figure 4b. Atomic structure of the polystyrene monomer.

a first line of characterization, providing critical defectivity and substrate interaction information (L.M. Malard, 2009). Optimum applications for Raman spectroscopy extend to a wide variety of sectors including mineralogy, semiconductor & solar industries, polymers & plastics characterization, pharmaceuticals, and forensic analysis (Sharma, 2016). The non-destructive nature of this technique, combined with its spatial mapping capabilities, and its minimal interference from water molecules, makes it an exceptional choice for investigations of a wide range of material systems.

FTIR vs Raman Spectroscopy: An Inter-technique Utilization

While both FTIR and Raman Spectroscopy can individually identify certain chemical systems, in concert, they can be used to characterize wide arrays of materials. The data they produce can help researchers and process designers understand organics and inorganics, solids and liquids, homogeneous bulks and mixed materials, and more materials from the applications listed above. Even for single-component samples, such as polystyrene films, they provide complimentary information, making for more complete pictures of conditions of the molecule's constituent bonds (Fig. 4).

For centrosymmetric systems, the complementarity is especially pronounced, as vibrations in those systems can be either IR active or Raman active, but not active in both regimes (Jones, 2019). By integrating the insights generated by the two techniques, one can garner a more complete picture of surface and bulk chemistry.

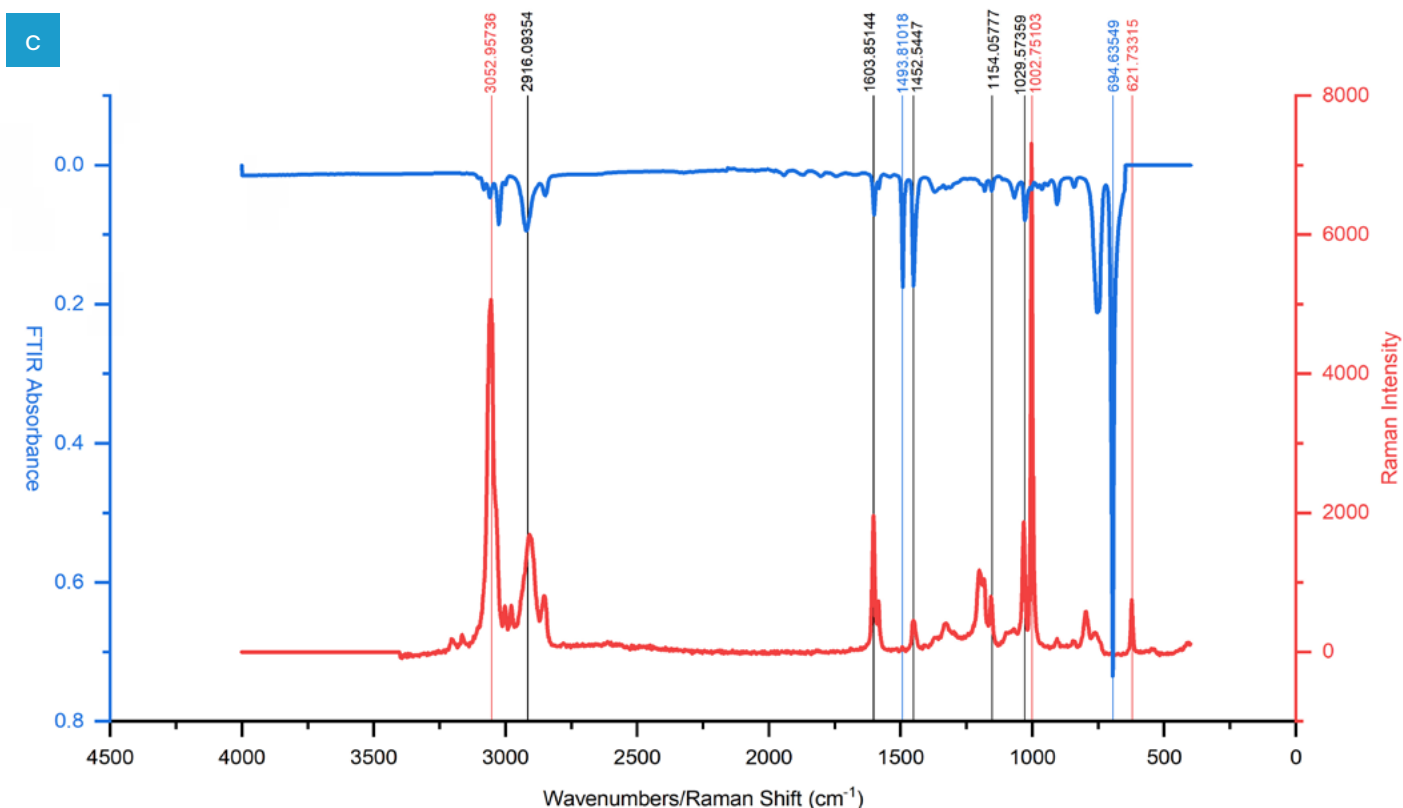


Figure 4c. Overlay of the FTIR and Raman spectra collected on polystyrene. Highlighted in blue are peaks uniquely detectable with FTIR. Highlighted in red are those that are unique to Raman. In addition to the signals unique to each technique, one should also observe the difference in peak intensity among those vibrational modes which both FTIR and Raman can detect.

d	FTIR	Raman	Vibrational Mode
		621.7	Ring deformation: $C_{ring}-C_{ring}$ bending, $C_{ring}-H$ bending
	694.6		$C_{ring}-H$ out-of-plane bending
		1002.7	Ring breathing mode: $C_{ring}-C_{ring}$ bending, $C_{ring}-C_{ring}$ stretching
	1029.6		$C_{ring}-C_{ring}$ bending, $C_{ring}-C_{ring}$ stretching, $C_{ring}-H$ bending
	1154.1		$C_{ring}-H$ bending, $C_{ring}-C_{ring}$ stretching
	1452.5		$C_{chain}H_2$ scissoring, $C_{ring}-H$ bending
	1493.8		$C_{ring}-H$ bending, $C_{ring}-C_{ring}$ stretching
	1603.8		Ring-skeletal stretch: $C_{ring}-C_{ring}$ stretching
	2916.1		$C_{chain}-H$ stretching
		3052.9	$C_{ring}-H$ stretching

FTIR gives Ring C-H Out-of-Plane Bend

Both give Chain C-H Stretch

Raman gives Ring C-H Stretch

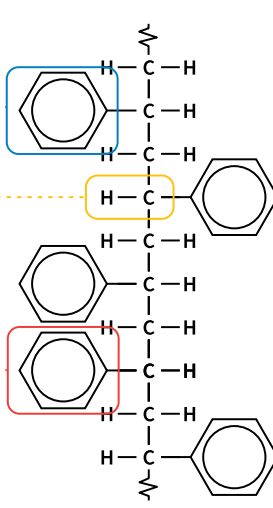


Figure 4d. Description of the specific Vibrational Modes corresponding to each peak in the FTIR and Raman spectra.

Conclusion

Understanding the chemical landscape of samples, be it in tech R&D or manufacturing quality control, is of the utmost importance. Advanced spectroscopic techniques such as FTIR and Raman spectroscopy present a conducive means of performing this characterization while also remaining minimally invasive. By considering their distinctive advantages and areas for complement, an organization can not only deploy these technologies for singular investigations but work towards streamlining quality control and product development into a future of consistent precision and reliability.

Choosing the correct tool requires a strong understanding of both Raman and FTIR spectroscopy, working with an experienced measurement services partner is critical to ensuring the allocation of resources matches the needs of your specific goals. Accurate, measurable results are the lifeblood of development and quality control processes, and these tools help those results be more accurate, and yet easy to interpret.

References

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To learn more about Raman and FTIR Spectroscopy, or to request a quote for these services, visit us online at

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