

. Raman Spectroscopy

By

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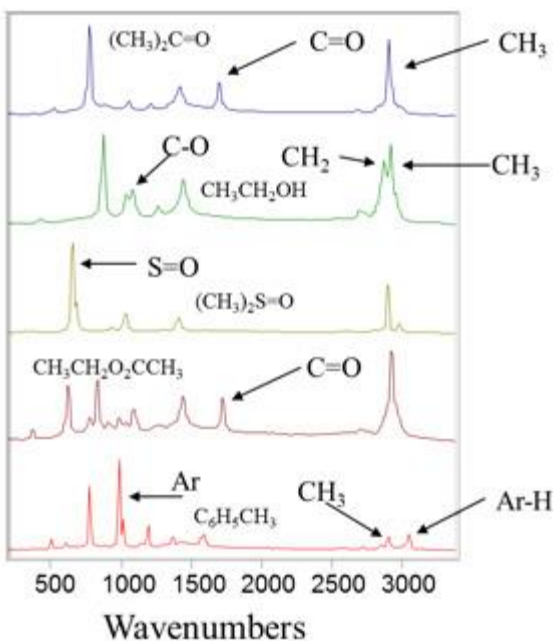
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Raman spectroscopy is a molecular spectroscopic technique that utilizes the interaction of light with matter to gain insight into a material's make up or characteristics, like FTIR. The information provided by Raman spectroscopy results from a light scattering process, whereas IR spectroscopy relies on absorption of light. Raman spectroscopy yields information about intra- and inter-molecular vibrations and can provide additional understanding about a reaction. Both Raman and FTIR spectroscopy provide a spectrum characteristic of the specific vibrations of a molecule ('molecular fingerprint') and are valuable for identifying a substance. However, Raman spectroscopy can give additional information about lower frequency modes, and vibrations that give insight into crystal lattice and molecular backbone structure.

Inline Raman spectroscopy is used to monitor crystallization processes and reveal reaction mechanisms and kinetics. Combined with analysis tools, this data enables informed reaction understanding and optimization.

Raman spectroscopy, a molecular spectroscopy which is observed as inelastically scattered light, allows for the interrogation and identification of vibrational (phonon) states of molecules. As a result, Raman spectroscopy provides an invaluable analytical tool for molecular fingerprinting as well as monitoring changes in molecular bond structure (e.g. product formation; state changes and stresses & strains; crystalline form and crystallinity).

Figure R-1 Example Raman Spectra of Various Molecules

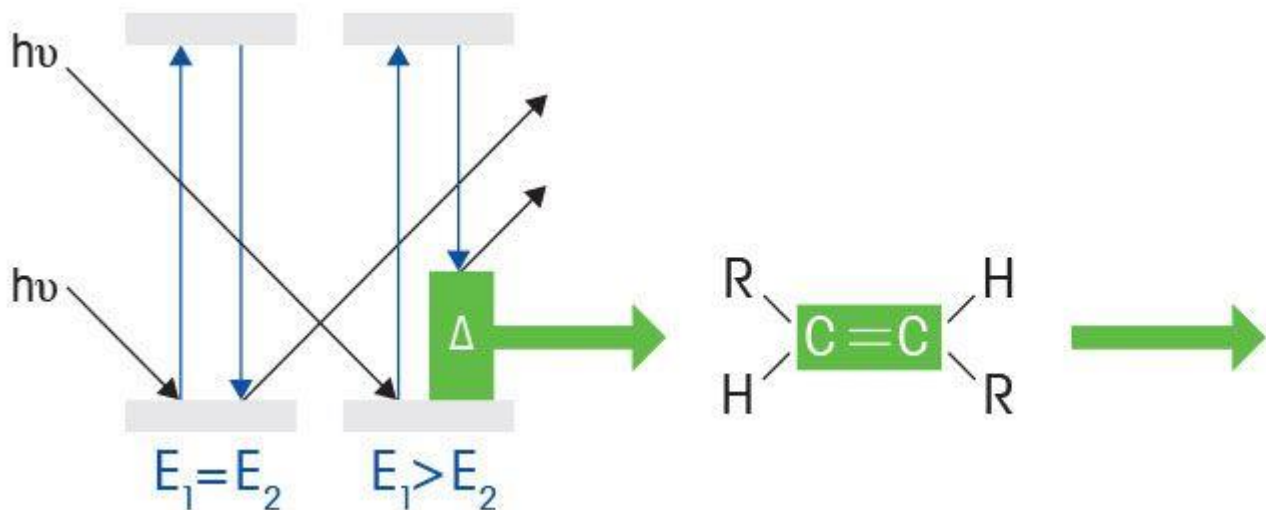


In comparison to other vibrational spectroscopy methods, such as FTIR and NIR, Raman has several major advantages. These advantages stem from the fact that the Raman effect manifests itself in the light scattered off of a sample as opposed to the light absorbed by a sample. As a result, Raman spectroscopy requires little to no sample preparation and is insensitive to aqueous absorption bands. This property of Raman facilitates the measurement of solids, liquids, and gases not only directly, but also through transparent containers such as glass, quartz, and plastic.

Raman spectroscopy is highly selective, as is the complementary method of FTIR, which allows it to identify and differentiate molecules and chemical species that are very similar, and measure small changes in samples. An example of five molecules - Acetone, Ethanol, Dimethyl Sulfoxide, Ethyl Acetate, and Toluene, with peaks from specific functional groups marked. Although these organic solvents have similar molecular structure, their Raman spectra are clearly differentiable, even to the untrained eye.

The Raman Spectroscopy Principle

When light interacts with molecules in a gas, liquid, or solid, the vast majority of the photons are dispersed or scattered at the same energy as the incident photons. This is described as elastic scattering, or Rayleigh scattering. A small number of these photons, approximately 1 photon in 10 million will scatter at a different frequency than the incident photon. This process is called inelastic scattering, or the Raman effect, named after Sir C.V. Raman who discovered this and was awarded the 1930 Nobel Prize in Physics for his work. Since that time, Raman has been utilized for a vast array of applications from medical diagnostics to material science and reaction analysis. Raman allows the user to collect the vibrational signature of a molecule, giving insight into how it is put together, as well as how it interacts with other molecules around it.



Raman Scattering Process

The Raman Scattering Process, as described by quantum mechanics, is when photons interact with a molecule, the molecule may be advanced to a higher energy, virtual state. From this higher energy state, there may be a few different outcomes. One such outcome would be that the molecule relaxes to a vibrational energy level that is different than that of its beginning state producing a photon of different energy. The difference between the energy of the incident photon and the energy of the scattered photon is the called the Raman shift.

When the change in energy of the scattered photon is less than the incident photon, the scattering is called Stokes scatter. Some molecules may begin in a vibrationally excited state and when they are advanced to the higher energy virtual state, they may relax to a final energy state that is lower than that of the initial excited state. This scattering is called anti-Stokes.

Raman Spectroscopy Basics

How Does Raman Spectroscopy Work?

Unlike FTIR Spectroscopy that looks at changes in dipole moments, Raman looks at changes in a molecular bonds polarizability. Interaction of light with a molecule can induce a deformation of its electron cloud. This deformation is known as a change in polarizability. Molecular bonds have specific energy transitions in which a change of polarizability occurs, giving rise to Raman active modes. As an example, molecules that contain bonds between homonuclear atoms such as carbon-carbon, sulfur-sulfur, and nitrogen-nitrogen bonds undergo a change in polarizability when photons interact with them. These are examples of bonds that give rise to Raman active spectral bands, but would not be seen or difficult to see in FTIR.

Because Raman is an inherently weak effect, the optical components of a Raman Spectrometer must be well matched and optimized. Also, since organic molecules may have a greater tendency to fluoresce when shorter wavelength radiation is used, longer wavelength monochromatic excitation sources, such as solid state laser diodes that produces light at 785 nm, are typically used.

Key Raman Spectroscopy Applications

Raman spectroscopy is used in industry for a variety of applications, including:

- Crystallization Processes

- Polymorphism Identification
- Polymerization Reactions
- Hydrogenation Reactions
- Chemical Synthesis
- Biocatalysis and Enzymatic Catalysis
- Flow Chemistry
- Bioprocess Monitoring
- Synthesis Reactions
- Quality by Design



Raman or FTIR Spectroscopy

A Comparison

Although Raman and FTIR Spectroscopy give complimentary information and are often interchangeable, there are some practical differences that influence which one will be optimal for a given experiment. Most molecular symmetry will allow for both Raman and IR activity. One special case is if the molecule contains a center of inversion. In a molecule that contains a center of inversion, Raman bands and IR bands are mutually exclusive, i.e. the bond will either be Raman active or it will be IR active but it will not be both. One general rule is that functional groups that have large changes in dipoles are strong in the IR, whereas functional groups that have weak dipole changes or have a high degree of symmetry will be better seen in Raman spectra.

Choose Raman Spectroscopy when:

- Investigating carbon bonds in aliphatic and aromatic rings are of primary interest
- Bonds that are difficult to see in FTIR (i.e., O-O, S-H, C=S, N=N, C=C etc.)
- Examination of particles in solution is important, e.g. polymorphism
- Lower frequency modes are important (e.g. Inorganic-Oxides)
- Reactions in aqueous media are investigated
- Reactions in which observation through a reaction window is easier and safer (e.g. high pressure catalytic reactions, polymerizations)
- Investigating lower frequency lattice modes is of interest
- Investigation of reaction initiation, endpoint, and product stability of biphasic and colloidal reactions

Choose FTIR Spectroscopy when:

- Studying liquid-phase reactions
- Reactions in which reactants, reagents, solvents and reaction species fluoresce
- Bonds with strong dipole changes are important (e.g. C=O, O-H, N=O)
- Reactions in which reagents and reactants are at low concentration
- Reactions in which solvent bands are strong in Raman and can swamp key species signal
- Reactions in which intermediates that form are IR active



Advantages of Inline Raman Spectroscopy

Raman Spectroscopy offers numerous advantages. Since Raman instruments use lasers in the visible region, flexible silica fiber optic cables can be used to excite the sample and collect the scattered radiation, and these cables can be quite long if necessary. Since visible light is used, glass or quartz can be used to hold samples. In the study of chemical reactions, this means that the Raman probe can be inserted into a reaction or can collect Raman spectra through a window, for example in an external reaction sample loop or flow cell. The latter approach eliminates the possibility of sample stream contamination. The ability to use quartz or Hi-grade Sapphire as a window material means that high pressure cells can be used to acquire Raman spectra of catalytic reactions. In the study of catalysts, operando spectroscopy using the Raman effect is

quite useful for studying in situ, real-time reactions on catalytic surfaces. Another advantage of Raman is that hydroxyl bonds are not particularly Raman active, making Raman spectroscopy in aqueous media straightforward. Raman spectroscopy is considered non-destructive, though some samples may be effected by the laser radiation. One consideration that needs to be made when choosing this technique is how fluorescent a particular sample may be. Raman scattering is a weak phenomena and fluorescence can swamp the signal making it difficult to collect quality data. This issue often can be alleviated by using a longer wavelength excitation source.

With respect to reaction analysis, Raman spectroscopy is sensitive to many functional groups but is exceptional when obtaining molecular backbone information, providing its own unique molecular fingerprint. Because Raman utilizes a bonds polarizability and has the potential to measure lower frequency, it is sensitive to crystal lattice vibrations giving the user polymorphic information that can be challenging to obtain by FTIR. This allows Raman to be used very effectively to study crystallization and other complex processes.

Raman Spectroscopy Instrumentation

A modern, compact Raman spectrometer consists of several basic components, including a laser that serves as the excitation source to induce the Raman scattering. Typically, solid state lasers are used in modern Raman instruments with popular wavelengths of 532 nm, 785 nm, 830 nm and 1064 nm. The shorter wavelength lasers have higher Raman scattering cross-sections so the resulting signal is greater, however the incidence of fluorescence also increases at shorter wavelength. For this reason, many Raman systems feature the 785 nm laser. The laser energy is transmitted to and collected from the sample by fiber optics cables. A notch or edge filter is used to eliminate Rayleigh and anti-Stokes scattering and the remaining Stokes scattered light is passed on to a dispersion element, typically a holographic grating. A CCD detector captures the light, resulting in the Raman spectrum. Since Raman scattering yields a

weak signal, it is most important that high-quality, optically well-matched components are used in the Raman spectrometer.

