

RAMAN SPECTROSCOPY

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INTRODUCTION

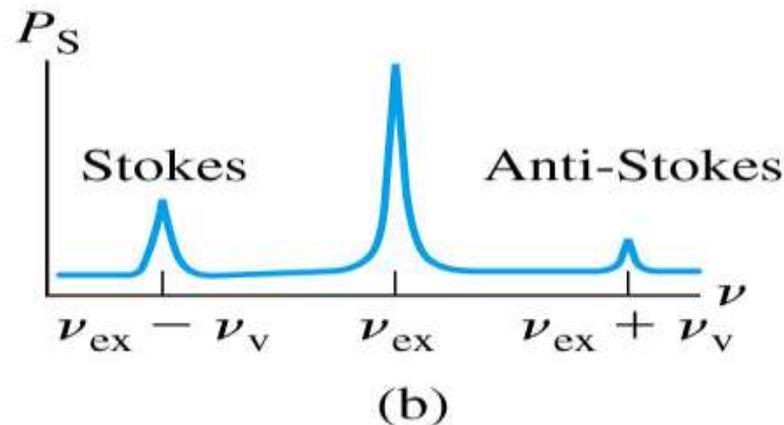
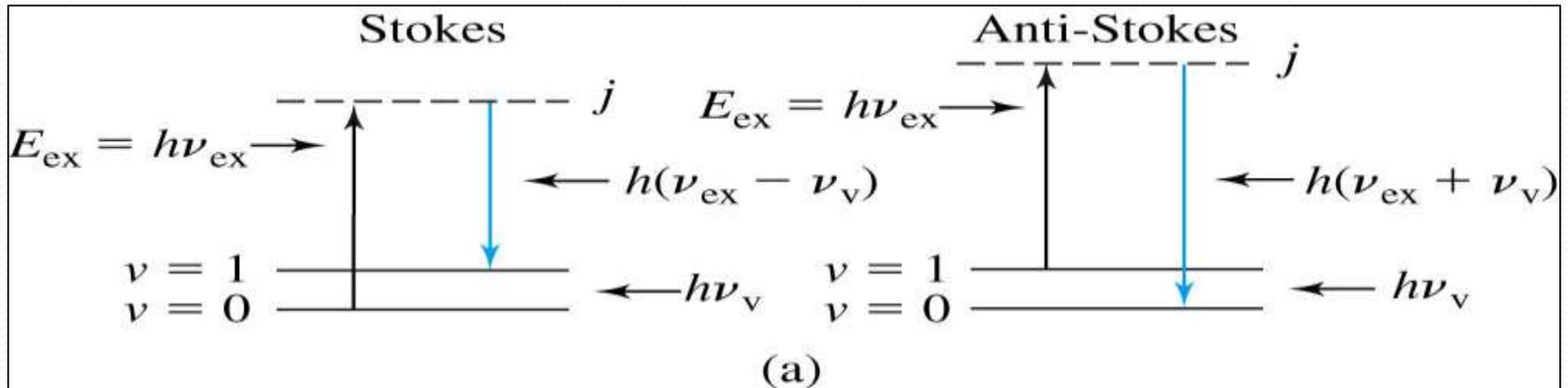
- Raman spectroscopy was discovered by C. V. Raman in 1928
- It is a spectroscopic technique used to observe vibration , rotational, and other low-frequency modes in a system.
- Raman spectroscopy is commonly used in chemistry to provide a fingerprint by which molecules can be identified.
- When the radiation pass through the transparent medium the species present scatter a fraction of the beam in all direction
- Raman scattering result from the same type of the quantities vibration changed associated with IR spectra
- The difference in wavelength in between the incident and scattered visible radiation correspond to wave length in mid IR region

PRINCIPLE

- When monochromatic radiation is incident upon a sample then this light will interact with the sample in some fashion. It may be reflected, absorbed or scattered in some manner. It is the scattering of the radiation that occurs which gives information about molecular structure
- Raman is based on scattering. The sample is irradiated with a coherent source, typically a laser. Most of the radiation is elastically scattered (called the Rayleigh scatter).
- A small portion is inelastically scattered (Raman scatter, composed of Stokes and anti-Stokes portions). This latter portion is what we are particularly interested in because it contains the information in which we are interested.

- The spectrum is measured with the laser line as a reference. Hence, the peaks are measured as the shift from the laser line.
- The peak positions are determined by the vibrational energies associated with the bonds in the molecule(s) of which the sample is composed. Because of this, the spectrum ends up looking very similar to an IR spectrum and is interpreted similarly.
- There is a footnote to this however, as the principle of mutual exclusion applies. That is, peaks that are emphasized in IR (polar bonds with high dipole moments) are de-emphasized somewhat in Raman.
- The bands that are emphasized in a Raman spectrum are those that are due to highly polarizable bonds such as those with π electrons.

- The emitted radiation is of three types:
 1. **Stokes** scattering
 2. **Anti-stokes** scattering
 3. **Rayleigh** scattering



INSTRUMENTATION

Sample cell



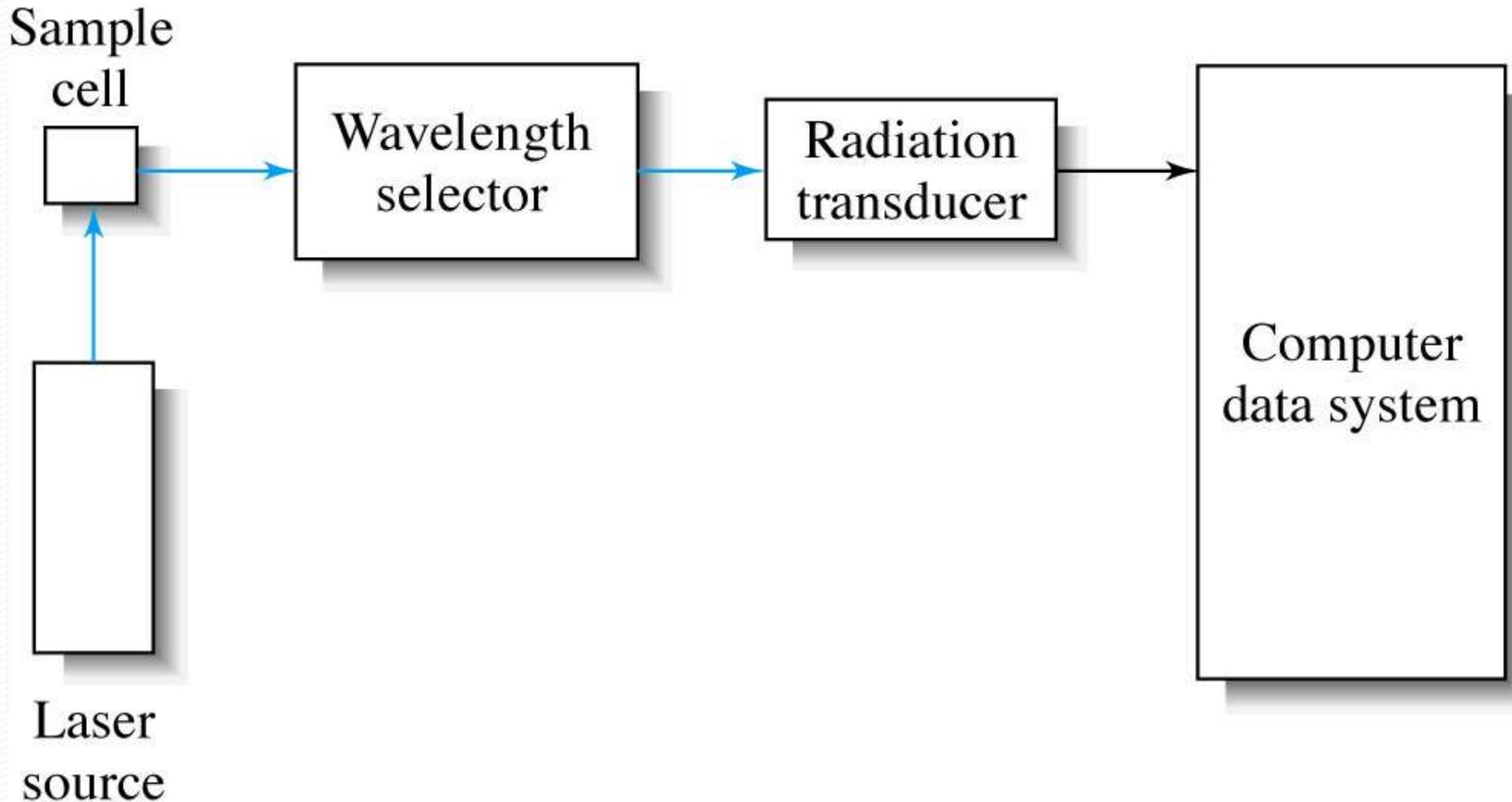
Wavelength selector

Radiation transducer

Computer data system



Laser source



INSTRUMENTATION

- Instrumentation for modern Raman spectroscopy consists of three components:
 - laser source
 - sample illumination system
 - suitable spectrometer.

1) Source:

- The sources used in modern Raman spectrometry are nearly always lasers because their high intensity is necessary to produce Raman scattering of sufficient intensity to be measured with a reasonable signal-to-noise ratio.
- Because the intensity of Raman scattering varies as the fourth power of the frequency, argon and krypton ion sources that emit in the blue and green region of the spectrum have an advantage over the other sources.

Some Common Laser Sources for Raman Spectroscopy

| Laser Type | Wavelength, nm |
|-------------------|-----------------------|
| Argon ion | 488.0 or 514.5 |
| Krypton ion | 530.9 or 647.1 |
| Helium-neon | 632.8 |
| Diode | 785 or 830 |
| Nd-YAG | 1064 |

Source used now a days are laser because high intensity is necessary to produce Raman scattering

2. Sample Illumination System

- ❑ **Liquid Samples:** A major advantage of sample handling in Raman spectroscopy compared with infrared arises because water is a weak Raman scattered but a strong absorber of infrared radiation. Thus, aqueous solutions can be studied by Raman spectroscopy but not by infrared.
- This advantage is particularly important for biological and inorganic systems and in studies dealing with water pollution problems.
- ❑ **Solid Samples:** Raman spectra of solid samples are often acquired by filling a small cavity with the sample after it has been ground to a fine powder. Polymers can usually be examined directly with no sample pretreatment.
- ❑ **Gas samples:** Gas are normally contain in glass tubes, 1-2 cm in diameter and about 1mm thick. Gases can also be sealed in small capillary tubes

3. Raman Spectrometers

- Raman spectrometers were similar in design and used the same type of components as the classical ultraviolet/visible dispersing instruments.
- Most employed double grating systems to minimize the spurious radiation reaching the transducer. Photomultipliers served as transducers.
- Now Raman spectrometers being marketed are either Fourier transform instruments equipped with cooled germanium transducers or multichannel instruments based upon charge-coupled devices.

DIFFERENCE

RAMAN

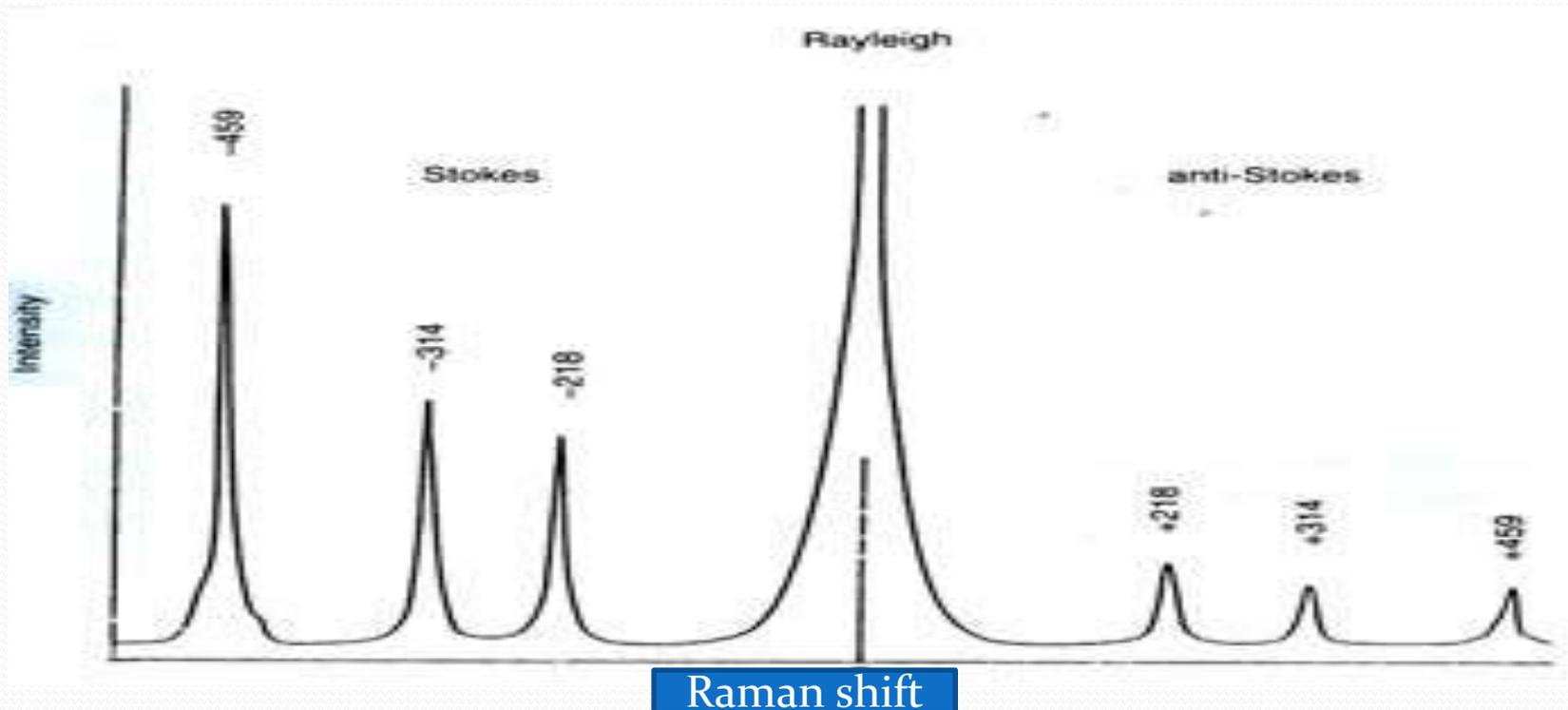
- It is due to the scattering of light by the vibrating molecules.
- The vibration is Raman active if it causes a change in polarisability.
- The molecule need not possess a permanent dipole moment.
- Water can be used as a solvent.
- Sample preparation is not very elaborate, it can be in any state.
- Gives an indication of covalent character in the molecule.
- Cost of instrumentation is very high

INFRA RED

- It is the result of absorption of light by vibrating molecules.
- Vibration is IR active if there is change in dipole moment.
- The vibration concerned should have a change in dipole moment due to that vibration.
- Water cannot be used due to its intense absorption of IR.
- Sample preparation is elaborate
Gaseous samples can rarely be used.
- Gives an indication of ionic character in the molecule.
- Comparatively inexpensive.

Raman spectrum

- Typical Raman spectrum
- Plot of signal intensity vs Raman shift
- (Raman shift, in cm^{-1} = energy of photon in - energy of photon out)



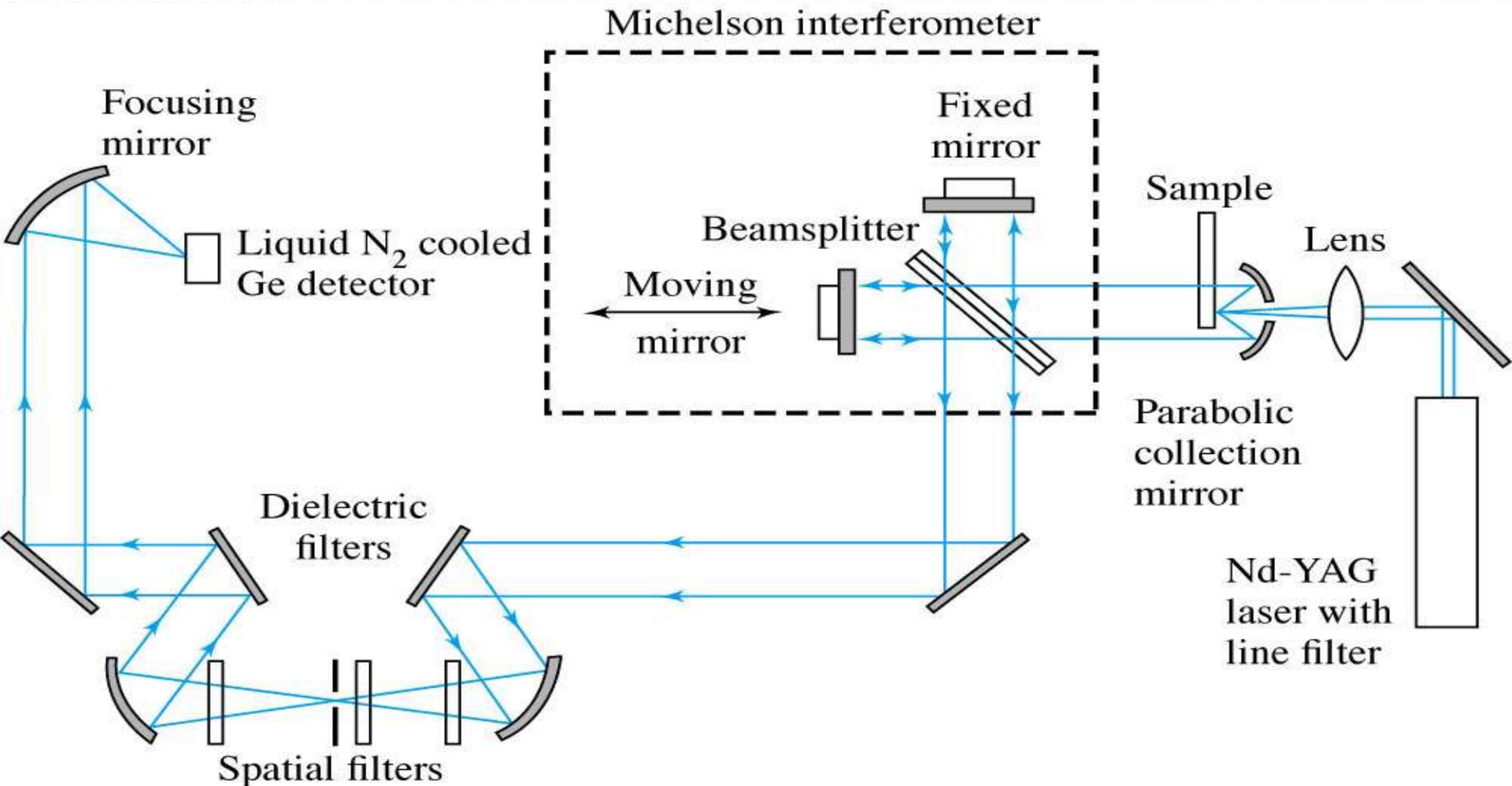
Different types of Raman Spectroscopy

- Resonance Raman spectroscopy (RRS)
- Surface-enhanced Raman spectroscopy (SERS)
- Micro-Raman spectroscopy
- Nonlinear Raman spectroscopic techniques

Fourier transform Raman spectroscopy

- The Raman instrument can be on the same bench as the FTIR.
- Often, a YAG:Nd³⁺ laser (1064 nm) is used to excite the sample, so that the excitation energy is lower than the absorption band energies of organic systems.
- Fluorescence is then minimized.
- Instruments may be combined with a microscope, or optical fibre, so that scanning over a few (microns)² of surface area, and Raman mapping is easily performed.

Fourier transform Raman spectroscopy



APPLICATION

Raman Spectra of Inorganic Species

- The Raman technique is often superior to infrared for spectroscopy investigating inorganic systems because aqueous solutions can be employed.
- In addition, the vibrational energies of metal-ligand bonds are generally in the range of 100 to 700 cm^{-1} , a region of the infrared that is experimentally difficult to study.
- These vibrations are frequently Raman active, however, and peaks with $\Delta\nu$ values in this range are readily observed.
- Raman studies are potentially useful sources of information concerning the composition, structure, and stability of coordination compounds.

APPLICATION

(cont.)

- **Raman Spectra of Organic Species**

Raman spectra are similar to infrared spectra in that they have regions that are useful for functional group detection and fingerprint regions that permit the identification of specific compounds.

Raman spectra yield more information about certain types of organic compounds than do their infrared counterparts.

- **Quantitative applications**

Raman spectra tend to be less cluttered with peaks than infrared spectra. As a consequence, peak overlap in mixtures is less likely, and quantitative measurements are simpler. In addition, Raman sampling devices are not subject to attack by moisture, and small amounts of water in a sample do not interfere.



- **Biological Applications of Raman Spectroscopy**

Raman spectroscopy has been applied widely for the study of biological systems.

The advantages of this technique include the small sample requirement, the minimal sensitivity toward interference by water, the spectral detail, and the conformational and environmental sensitivity.



thank you