拉曼光譜顯微鏡的原理簡介

112年AI-MAT暑期實習課程

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C. V. Raman

- Named after Indian scientist C. V. Raman.
- Observed the Raman effect in organic liquids in 1928 together with K.S. Krishnan, and independently by Grigory Landsberg and Leonid Mandelstam in inorganic crystals.



Raman Scattering

- Inelastic photon-phonon interactions in the sample
- formation of a very short-lived complex between the photon and molecule, commonly called the **virtual state** of the molecule.
- The oscillating electromagnetic field of a photon induces a polarization of the molecular electron cloud which changes the energy state of the molecule.



What is Raman Spectroscopy?

- An analytical technique where scattered light is used to measure vibrational energy modes of molecules.
- Only detects vibrations where the polarizability changes during the movement (Raman-active)
- Complementary with fourier-transform infrared spectroscopy (FTIR)



Figure 7: The symmetric stretching vibration of carbon dioxide (CO2) increases the size of the electron cloud. It is therefore Raman-active.

Raman Spectrum

- Provide both chemical and structural information, as well as the identification of substances through their characteristic Raman 'fingerprint'.
- The vibrations of certain distinct subunits of a molecule, called its functional groups, will appear in a Raman spectrum at characteristic Raman shifts.



Raman Shift

 Energy difference between the incident light and the scattered light, usually expressed in wavenumbers.

Raman shift
$$(cm^{-1}) = \left(\frac{1}{\lambda_{laser}(nm)} - \frac{1}{\lambda_{Raman}(nm)}\right) \times 10^7$$

Stokes & Anti-Stokes



Components in Micro-Raman Spectroscopy



Simple Raman Setup



Laser

Wavelength

- Excitation below bandgap can avoid photoluminescence
- \succ Raman scattering efficiency is proportional to λ^{-4}
- Resonance wavelength

Bandwidth

- Affects spectral resolution
- Crucial for low frequency Raman mode detection.

Power

Below damage threshold can avoid sample degradation

Raman spectrum of polystyrene



Raman spectrum of sulfur



Filter



Laser line filter

Reduces the laser bandwidth

Long-pass filter

Transmitting light above its cut-off wavelength

Dichroic mirror

- Selectively reflect and transmit light depends on its wavelength range
- Eliminates the laser wavelength from the total signal ND filter
- Attenuates the laser intensity





Typical long-pass filter transmission



30 20

Objective lens



- On sample laser intensity
- Spatial resolution (associate with laser wavelength)



Spectrometer

Slit width

➢Spectral resolution

Grating

Spectral resolution, measurement wavenumber range

i**R**550

iHR 32

CCD

Effective wavenumber range, spectral resolution



Focal Length

Detecto

Focusing mirror

Optical Fiber



Fiber core size

- Signal intensity
- Spectral & spatial resolution





Application

Chemistry

Identify molecules and study chemical bonding and intramolecular bonds

Solid-state physics

- Characterize materials
- Measure temperature
- > Indentify the crystallographic orientation

Biology and medicine

- > Identify active pharmaceutical ingredients
- Low-frequency phonons in proteins and DNA

The End

Thank you