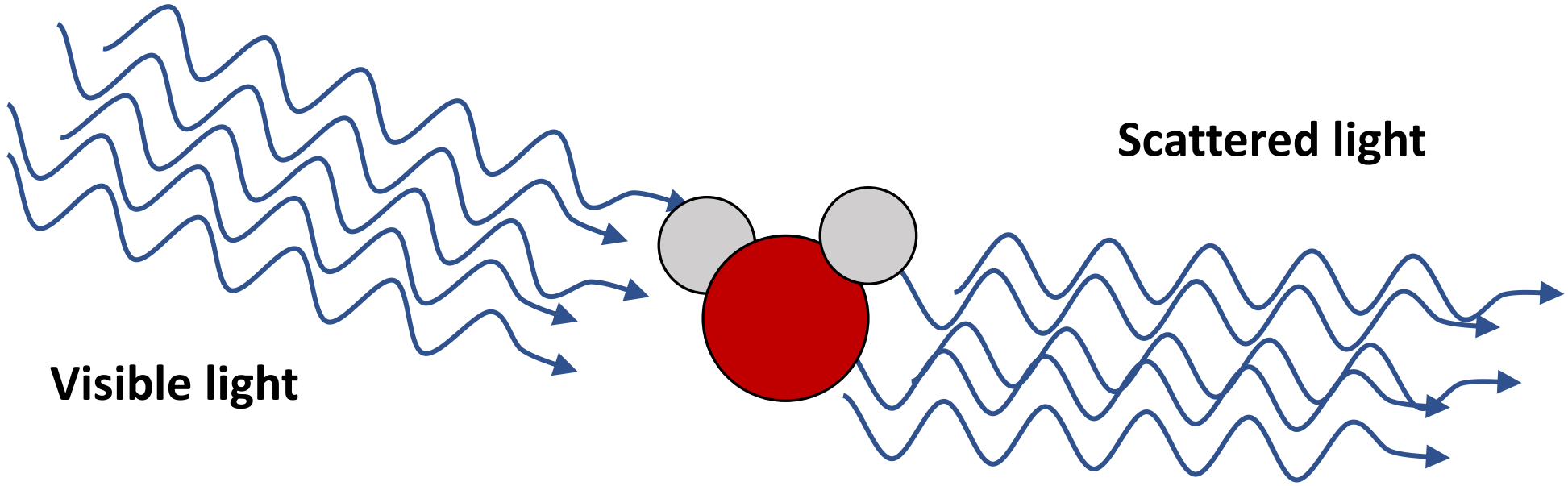
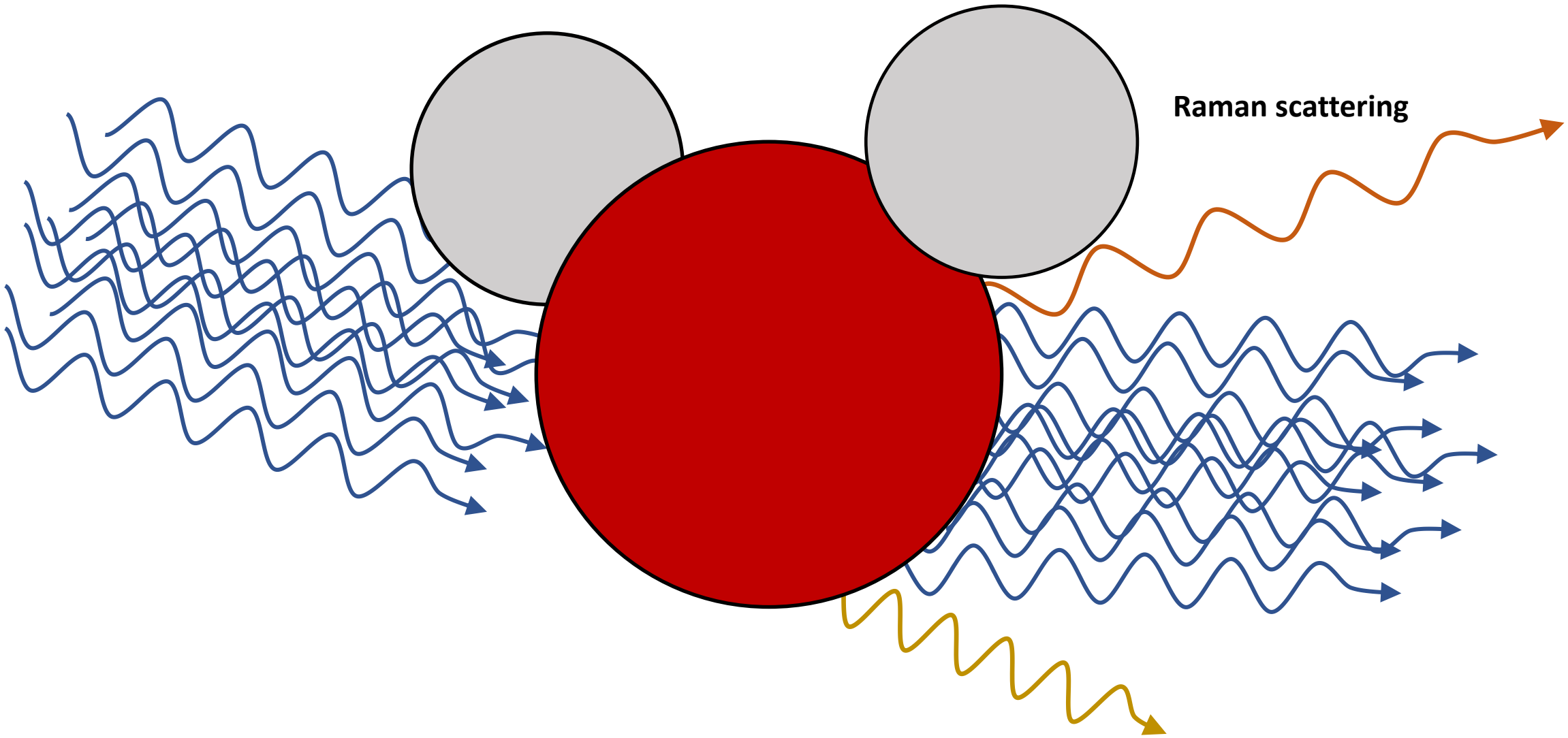
Materials design & selection for Circular Economy

Module 3: Molecules and materials chemico-physical characterisation

Academic year 2026/2027

Lecturer: **Paolo Dolcet**


Scattered light
Visible light

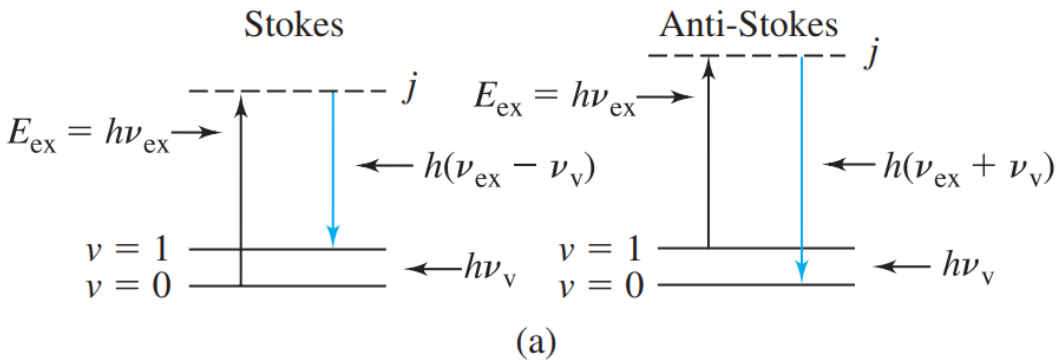

Raman scattering

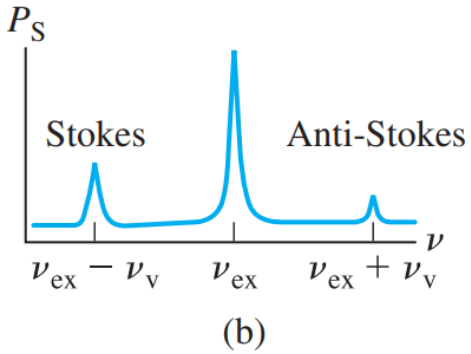
The Raman effect

- Discovered in 1921 by C. V. Raman (Nobel prize in 1931)
- Small fraction of the scattered radiation has different frequency
- Raman intensity very low
  - Incident beam: 1
  - Elastic scattering (Rayleigh): 10^{-3}
  - Raman scattering: 10^{-6} - 10^{-10}
- Raman spectrometer became spread with the availability of intense laser sources

The incident wavelength does not match any absorption of the sample

The Raman effect





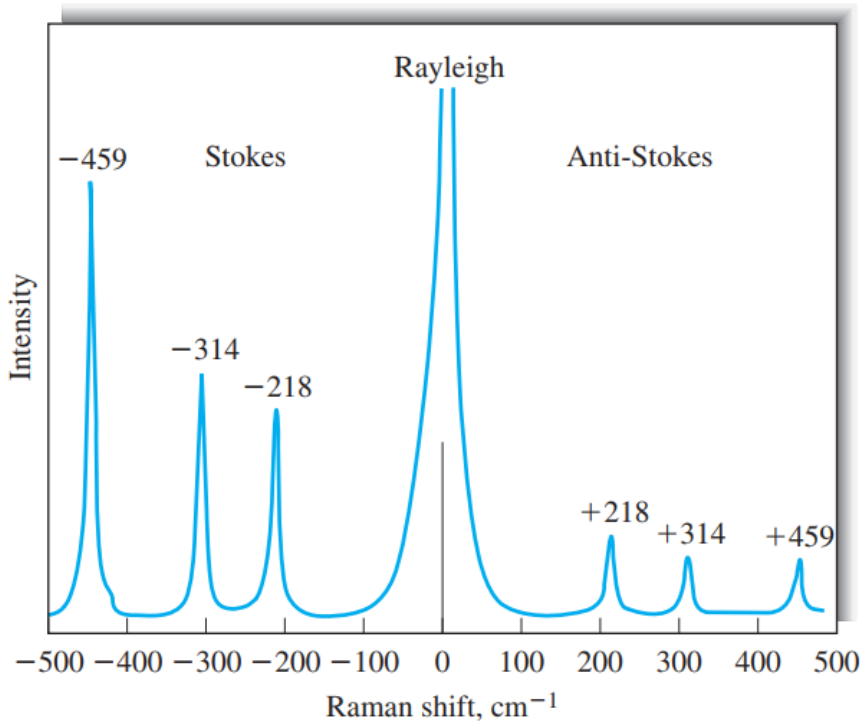
- Typical Raman experiment:

$$\lambda_{exc} \neq \lambda_{abs\ sample}$$

- Fluorescence is minimized
- Raman process involves excitation to a **virtual state**
- Depending on the vibrational states involved, different transitions:
  - **Stokes**:
    - v = **0** → virtual → v = **1**
    - $E_{emit.photon} = h(\nu_{exc} - \nu_v)$
  - **Anti-Stokes**:
    - v = **1** → virtual → v = **0**
    - $E_{emit.photon} = h(\nu_{exc} + \nu_v)$

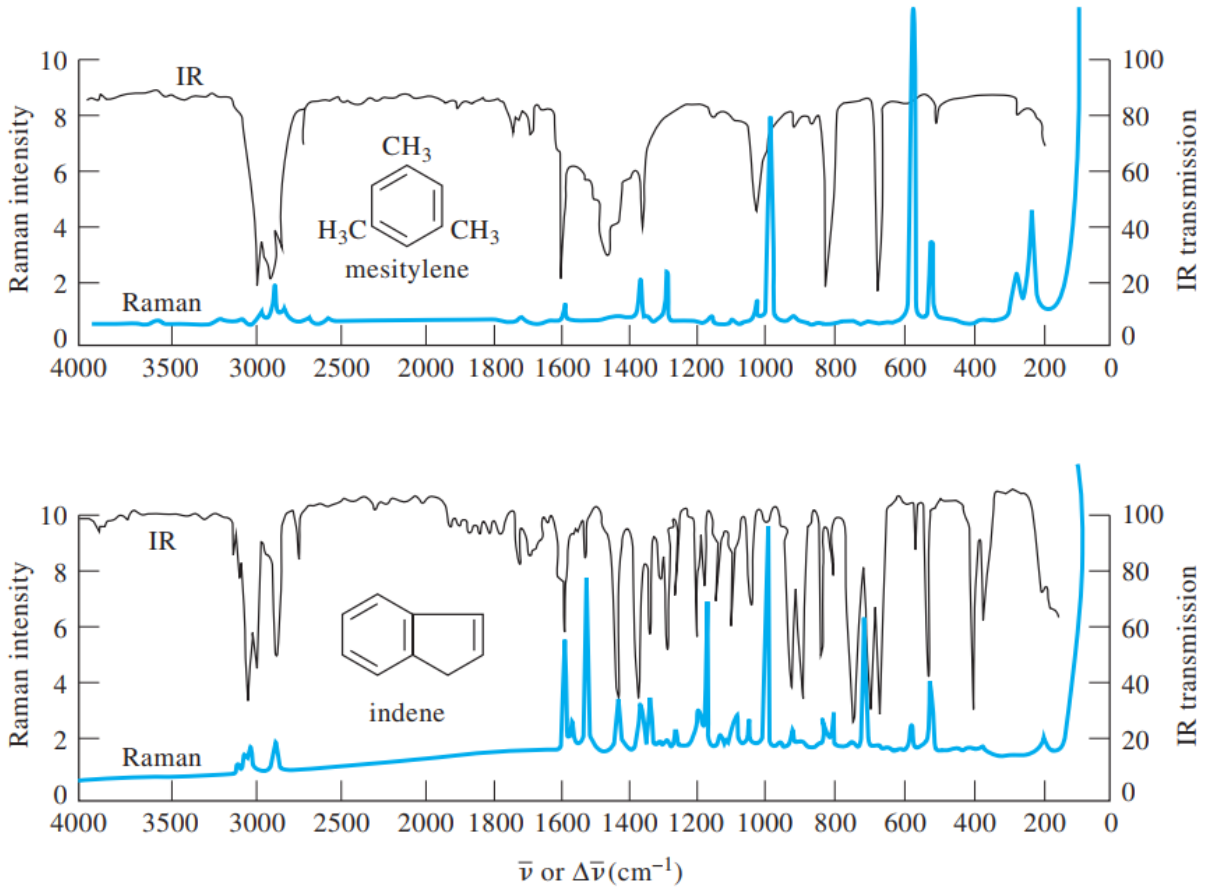
Stokes vs Anti-Stokes

- Population in vibrationally excited state (v = 1) < Pop. vibrational ground state (v = 0) (*at RT)
- Anti-Stokes signal intensity < Stokes signal intensity
- Stokes and anti-Stokes shifts are specular with respect to Rayleigh peak
- Raman shifts are **independent** of λ_{exc}
- Excitation process is not quantized
- Since the process involves vibrational levels, $\Delta E_{Raman} = \Delta E_{infrared}$

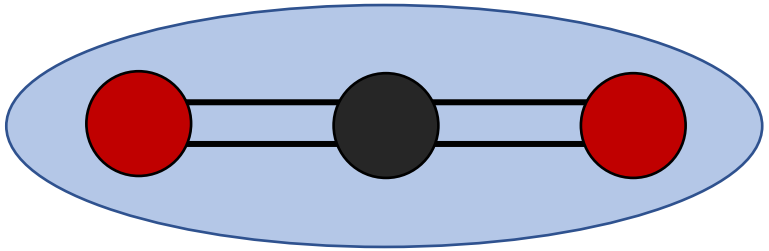


Raman spectrum of CCl_4

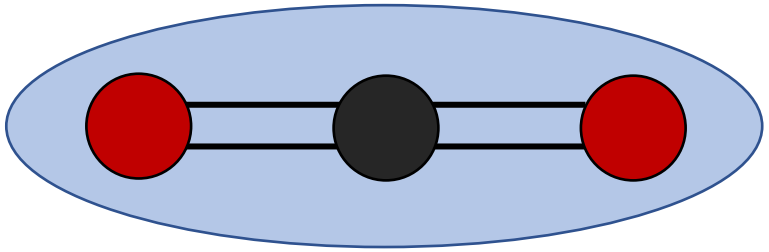
Raman vs infrared



Raman active modes



Raman **active**

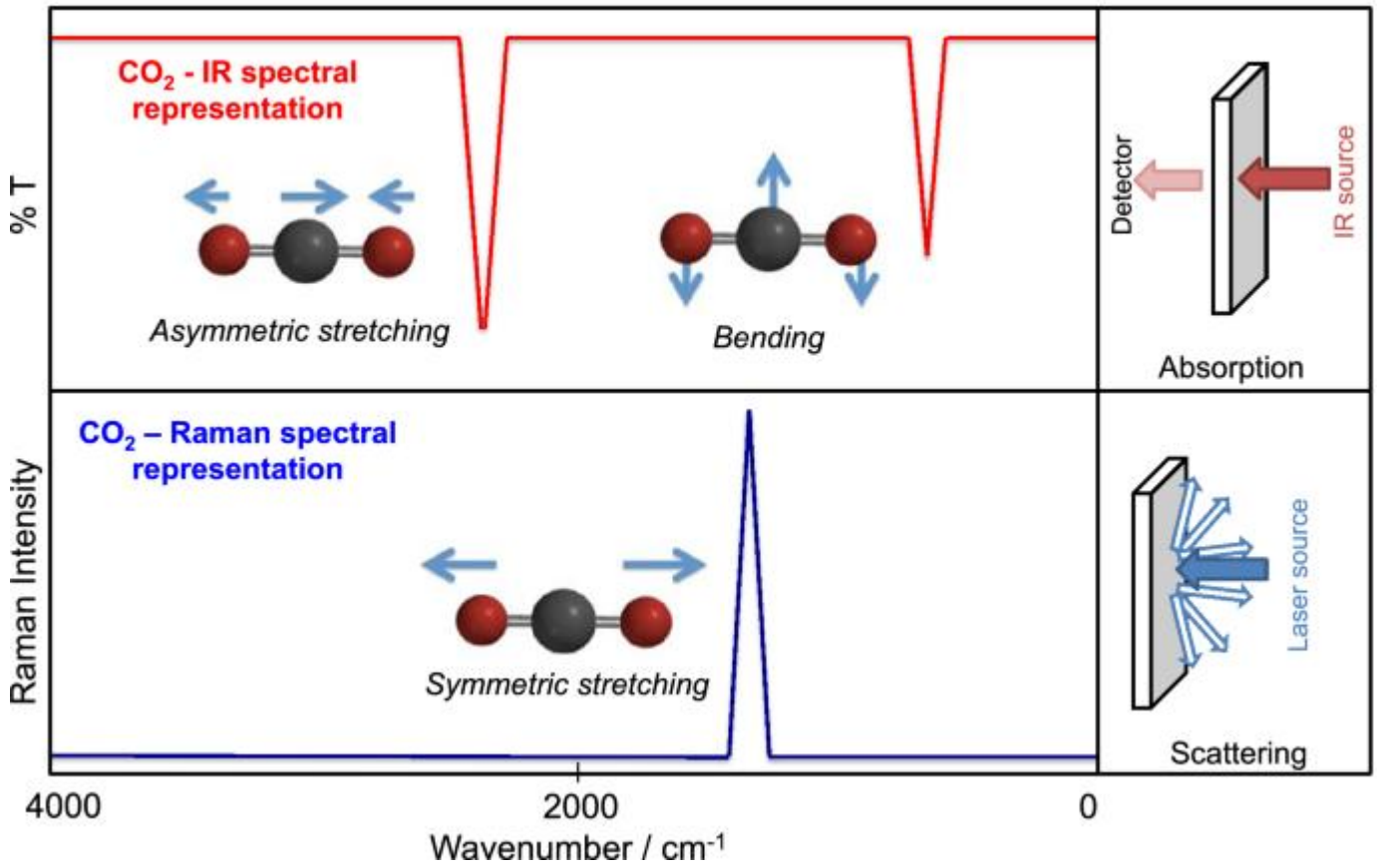


Raman **inactive**

- A vibration will give rise to a Raman signal **only if** a **net change in polarizability** occurs

- Homonuclear molecules **can** show Raman signal

Mutual exclusion principle



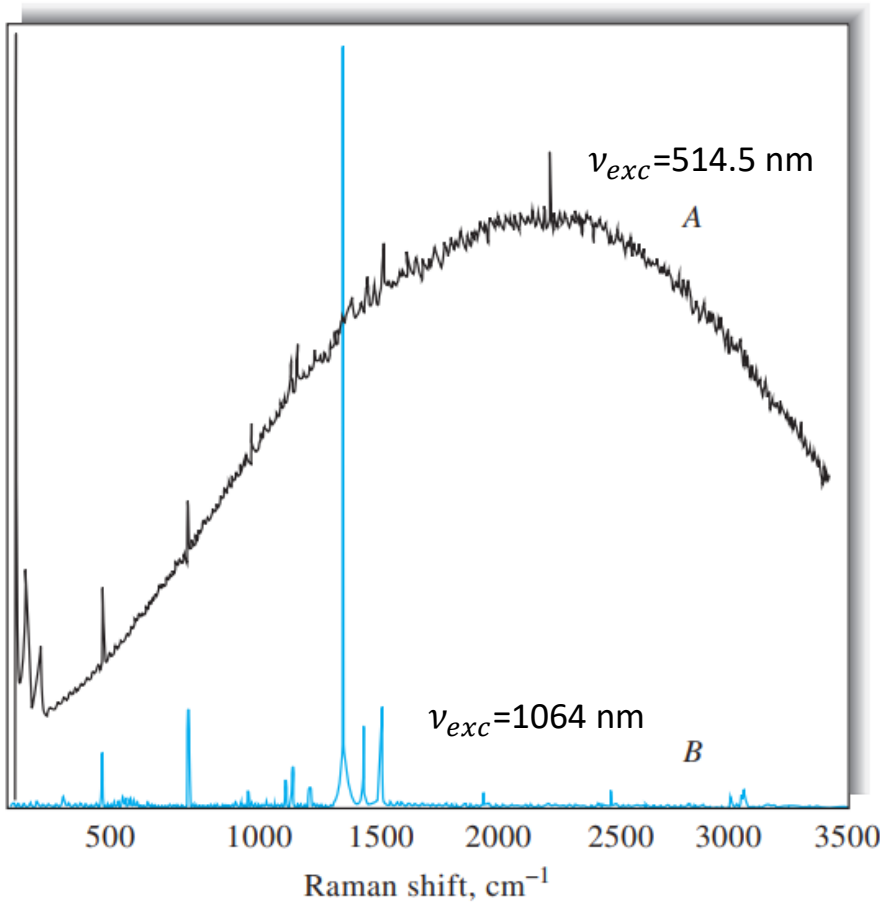
Mutual exclusion principle
For molecule with a **center of symmetry**, **no IR active** transitions are **in common with Raman active** transitions

Excitation sources

- Different excitation (laser) sources are available
- $I_{Raman} \propto \nu_{exc}^4$
- Beware of photodecomposition!

TABLE 18-1 Some Common Laser Sources for Raman Spectroscopy

Laser Type	Wavelength, nm
Argon ion	488.0 or 514.5
Krypton ion	413.1, 530.9, 647.1
Helium-neon	632.8
Diode	660–880
Nd-YAG	1064



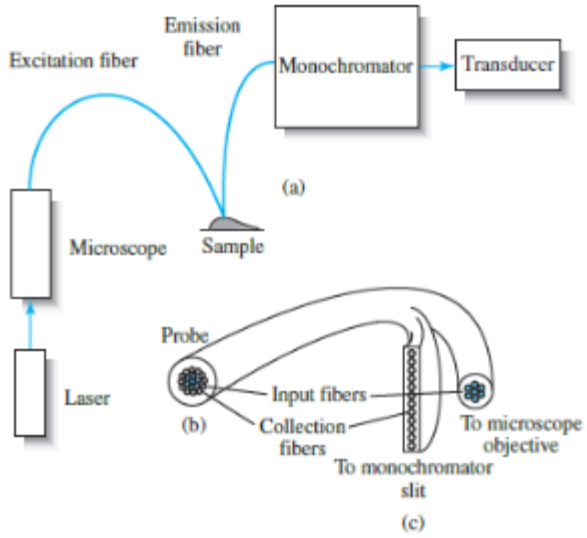
Typical instrument can provide multiple sources

Versatility of Raman spectroscopy

- Due to the use of Vis light as excitation, **fiber optics** can be used to transport the signal

- Raman **microprobe**: Raman coupled with an optical microscope → point illumination, mapping

- Mapping possible both in 2D and in depth





Complementarity of Raman to FTIR

- Raman can analyze aqueous solution
- Many inorganic compounds have signal in the 100 - 700 cm^{-1} → Raman accessible
- Raman often does not require sample preparation

FTIR

VERSUS

RAMAN SPECTROSCOPY

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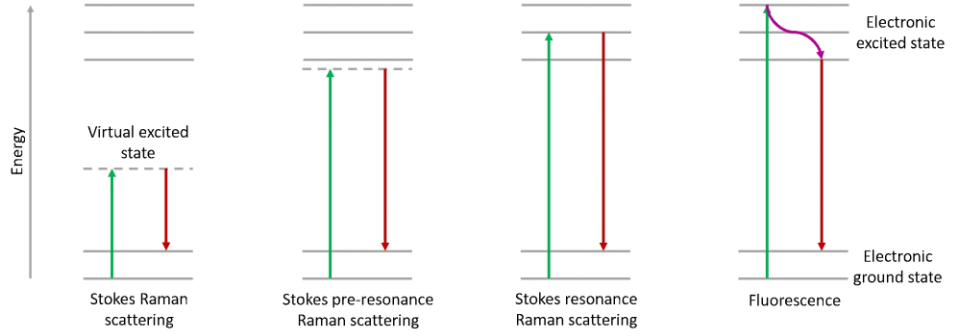
FTIR	RAMAN SPECTROSCOPY
FTIR (Fourier Transform Infrared Spectroscopy) is an analytical technique used to identify and characterize molecular structures in materials by measuring the absorption of infrared radiation	Raman spectroscopy is an analytical technique utilized to identify and analyze molecular structures in materials by measuring the scattering of monochromatic light
Measures the absorption of infrared radiation by a sample	Measures the scattering of monochromatic light by a sample
Transitions occur due to changes in molecular dipole moments, leading to selection rules based on dipole moment changes	Transitions occur due to changes in polarizability of the molecule, leading to different selection rules compared to FTIR
Requires the sample to be in direct contact with a suitable IR-transparent material, such as a salt plate or a thin film	Can analyze samples in various states, including solids, liquids and gases, without the need for special sample preparation techniques

Resonance Raman and Surface enhanced Raman spectroscopies

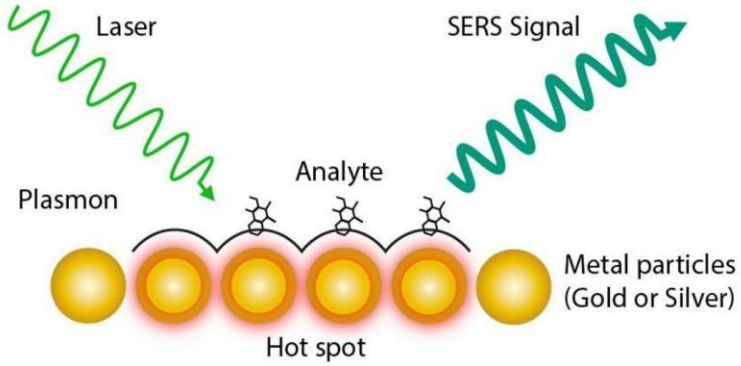
- Standard Raman process: transition to virtual levels
- **Resonance Raman**: transition to virtual levels close to/equal to electronic transitions
- With RR, **scattering intensity increases** by a factor $10^2 – 10^6$

$$\text{Intensity} \propto \frac{1}{(\nu_e - \nu_{\text{laser}})^2}$$

- Fluorescence competes with RR

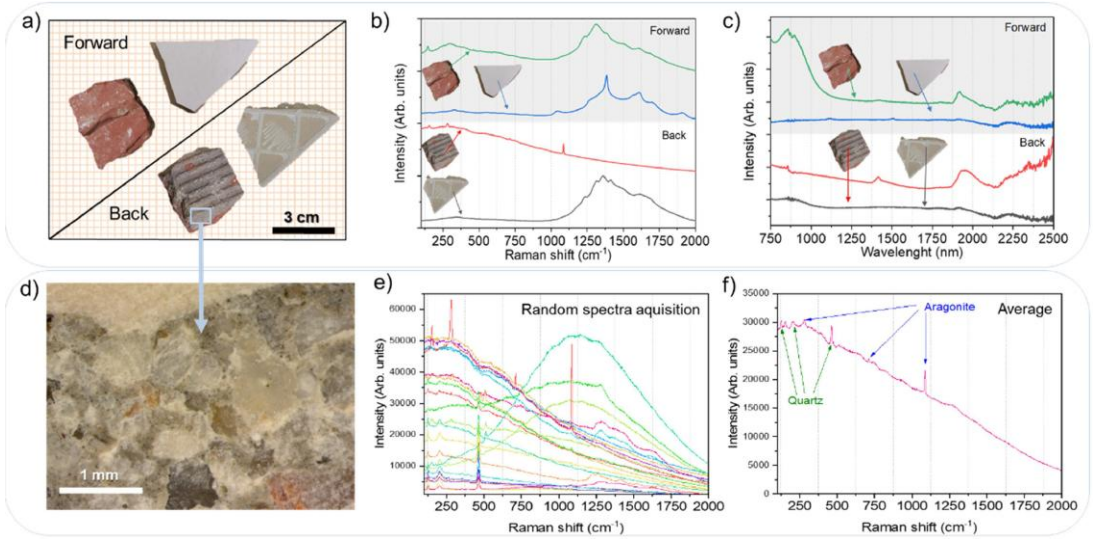


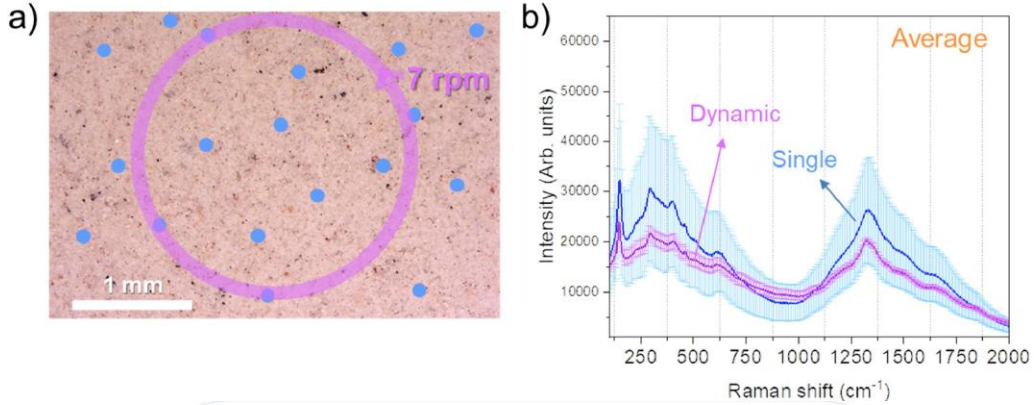
- **Surface enhance Raman spectroscopy** (SERS) is a highly sensitive technique to enhance Raman scattering of molecules (up to 10^{12})
- Core element: **interaction of target molecule** with **metallic nanoparticles** (Au or Ag)
- Upon irradiation, **surface plasmons of NPs resonate → enhancement of electric field** at the surface
- Adsorbed target molecule feels increased field → **increased Raman scattering**

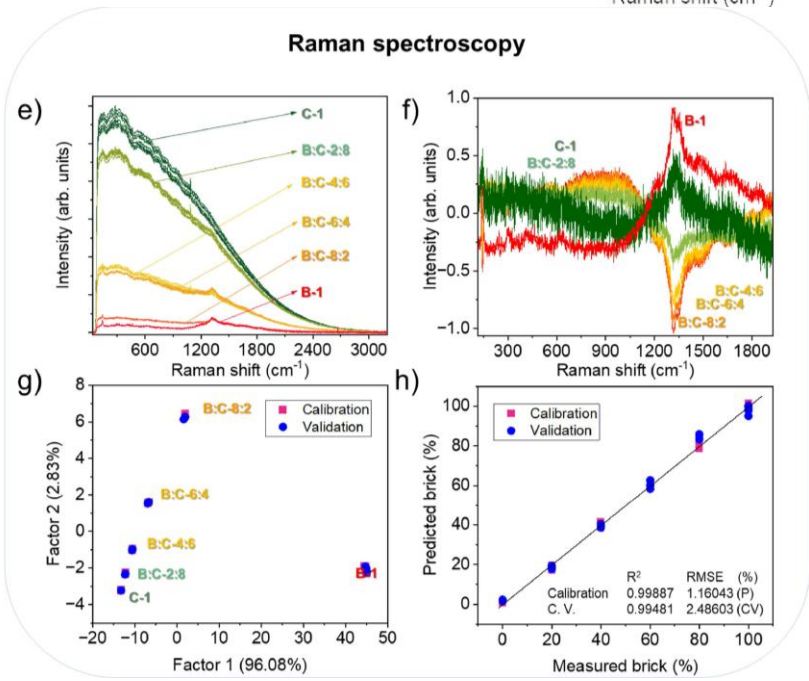


Recycling of construction and demolition wastes (CDW)

- CDW face low recycling rates due to reliable quantification methods
- Raman (and NIR) can be such methods







Resources, Conservation and Recycling, 199, **2023**, 107259