Scattering is a general physical process where some forms of radiation, such as light, sound, or moving particles, are forced to deviate from a straight trajectory by one or more localized non-uniformities in the medium through which they pass.
• Major forms of elastic light scattering (involving negligible energy transfer) are **Rayleigh scattering** and **Mie scattering**.

  ⇒ Rayleigh scattering (small particle compared to $\lambda$ of light)
  ⇒ Mie scattering (spherical particles about the same size as $\lambda$ of light)

  ⇒ **Tyndall scattering** is similar to Mie scattering: without the restriction to spherical geometry of the particles. Particularly applicable to colloidal mixtures and suspensions.

• Inelastic scattering includes **Brillouin scattering**, **Raman scattering**, inelastic X-ray scattering and Compton scattering.

  ⇒ Compton scattering is an inelastic scattering of a photon by a free charged particle, usually an electron.
FIGURE 6-18(a) As incident radiation of frequency $\nu_{ex}$ impinges on the sample, molecules of the sample are excited from one of their ground vibrational states to a higher so-called virtual state, indicated by the dashed level in (b).
FIGURE 6-18(b) When the molecule relaxes, it may return to the first vibrational as indicated and emit a photon of energy $E = h(\nu_{ex} - \nu_v)$ where $\nu_v$ is the frequency of the vibrational transition. Alternatively, if the molecule is in the first excited vibrational state, it may absorb a quantum of the incident radiation, be excited to the virtual state, and relax back to the ground vibrational state. This process produces an emitted photon of energy $E = h(\nu_{ex} + \nu_v)$. In both cases, the emitted radiation differs in frequency from the incident radiation by the vibrational frequency of the molecule $\nu_v$. 

$E_{ex} = h\nu_{ex}$

Stokes

$E_{ex} = h\nu_{ex}$

Anti-Stokes

First excited vibrational

Ground vibrational

$b$
FIGURE 6-18(c) The spectrum resulting from the inelastically scattered radiation shows three peaks: one at $v_{\text{ex}} - v_{v}$ (Stokes), a second intense peak at $v_{\text{ex}}$ for radiation that is scattered without a frequency change, and a third (anti-Stokes) at $v_{\text{ex}} + v_{v}$. The intensities of the Stokes and anti-Stokes peaks give quantitative information, and the positions of the peaks give qualitative information about the sample molecule.
Raman spectroscopy is based on the Raman effect first reported by the Indian physicist C. V. Raman in 1928. The recipient of the Nobel Prize for Physics in 1930.

C. V. Raman discovered that the visible wavelength of a small fraction of the radiation scattered by certain atoms or molecules differs from that of the incident beam and furthermore that the shifts in wavelength depend upon the chemical structure of the molecules responsible for the scattering.

Striking similarities between Raman and IR spectra, however, enough differences remain between the kinds of groups that are IR active and Raman active to make the techniques complementary rather than competitive.

Raman spectroscopy was not widely used until lasers became available in 1960s.
• An important advantage of Raman spectra over infrared lies in **water** being a quite useful solvent (no interference).

**THEORY OF RAMAN SPECTROSCOPY**

• Raman spectra are acquired by irradiating a sample with a powerful laser source of **visible or near-infrared** monochromatic radiation.

⇒ During irradiation, the spectrum of the scattered radiation is measured at some angle (often 90°) with a suitable spectrometer.

• At the very most, the intensities of Raman lines are **0.001 %** of the intensity of the source

⇒ It may be **more difficult to detect and measure Raman bands** than IR vibrational infrared spectra.

• The excitation wavelength is well away from an absorption band, excitation can be considered to involve a **virtual state** of energy level j.
When light is scattered from the surface of a sample, the scattered light is found to contain mainly wavelengths that were incident on the sample (Raleigh scattering) but also at different wavelengths at very low intensities (few parts per million or less) that represent an interaction of the incident light with the material.
FIGURE 18-2  Raman spectrum of CCl$_4$, excited by laser radiation of $\lambda_{\text{ex}} = 488$ nm ($v_{\text{ex}} = 20,492$ cm$^{-1}$). The number above the Raman lines is the Raman shift, $\Delta v = v_{\text{ex}} \pm v_v$, in cm$^{-1}$. Stokes-shifted lines are often given positive values rather than negative values as shown.
• It is important to appreciate that the magnitude of Raman shifts is independent of the wavelength of excitation.

⇒ For CCl$_4$: regardless of whether excitation was carried out with an argon-ion laser (488 nm) or a helium-neon laser (632.8 nm).

• Fluorescence may interfere seriously with the Raman signals.

• Raman and fluorescence spectra arise from fundamentally different processes.
Partial energy-level diagrams for a fluorescent organic molecule.

- Nonradiative relaxation: The light emitted is at the same frequency as the light absorbed.

**FIGURE 6-24**

- Resonance fluo.

© 2007 Thomson Higher Education

Ch6 An Introduction to Spectrometric Methods
Mechanism of Raman and Rayleigh Scattering

FIGURE 18-3
Origins of Rayleigh and Raman Scattering.

When the Raman process initiates from the excited vibrational level, relaxation to the ground state is possible, producing scatter of higher energy (shorter wavelength) than that of the laser light.
• The relative populations of the two upper energy states are such that **Stokes emission is much favored over anti-Stokes.**

• **Rayleigh scattering** has a considerably higher probability of occurring than Raman because the most probable event is the energy transfer to molecules in the ground state and reemission by the return of these molecules to the ground state.

• The ratio of anti-Stokes to Stokes intensities will increase with **temperature** because a larger fraction of the molecules will be in the first vibrationally excited state under these circumstances.

• If the bonds were IR active, the energy of its absorption would also be ΔE.

  \[ \Rightarrow \text{Raman frequency shift and IR absorption frequency are identical.} \]
Infrared absorption requires change in dipole moment or charge distribution associated with it.

Raman scattering involves a momentary distortion of the electrons distributed around a bond in a molecule, followed by relaxation and reemission of the radiation as the bond returns to its normal state.

IR vs Raman: mechanism

- IR radiation does not have enough energy to induce electronic transitions. ⇒ vibrational and rotational states.
• Phonons in general are divided into two categories: acoustic and optical.

Vibrations in a crystal with two atoms per unit cell with masses $M_1$, $M_2$ connected by force constant $C$ between adjacent planes.

**Equations of motion:**

**Unit cell $s$**

$$M_1 \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s)$$

$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s)$$

We look for solutions of the traveling waveform, but with different amplitudes $u$ and $v$ on alternating planes

$$u_s = u \exp(is\kappa)\exp(-i\omega t)$$

$$v_s = v \exp(is\kappa)\exp(-i\omega t)$$
acoustic phonons vs optical phonons

- Solids with more than one type of atom: either with different masses or bonding strengths in the smallest unit cell, exhibit two types of phonons (vibrations).

\[ \omega_{\pm}^2 = K \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \pm K \sqrt{\left( \frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4 \sin^2(ka/2)}{m_1m_2}} \]

\( k \): the wave-vector of the vibration related to its wavelength by \( k=2\pi/\lambda \).

- The connection between frequency and wave-vector, \( \omega=\omega(k) \), is known as a dispersion relation.
  \( \Rightarrow + \): optical mode: two adjacent different atoms move against each other
  \( \Rightarrow - \): acoustic mode: two adjacent different atoms move together.
Lattice vibrations: Acoustic vs optical vibrations

- If the displacement is in the direction of propagation, then in some areas the atoms will be closer, in others farther apart, as in a sound wave in air.
- This occurs if the lattice is made of atoms of different charge or mass. They are called optical because in ionic crystals, such as sodium chloride, they are excited easily by infrared radiation.
• *Raman* scattering: The interaction of the incident light with *optical phonons*.
• *Brillouin* scattering: while the interaction with *acoustic phonons*.
• Optical phonons have higher energies than acoustic phonons giving larger photon energy shifts, but even for *Raman scattering the energy shift is small*.  
  ⇒ For example, the exciting photon energy is several eV (Ar laser light with $\lambda = 488$ nm has an energy of $h\nu = 2.54$ eV), while the optical phonon energy in Si is about 0.067 eV
• Since the intensity of Raman scattered light is very weak (about 1 in 108 parts), *Raman spectroscopy is only practical when an intense monochromatic light source like a laser is used.*
Raman scattering vs. Brillouin scattering

Raman scattering

• Inelastic scattering processes of light with vibrational properties of matter.
• Raman scattering photons are scattered by interaction with vibrational (optical phonons) and rotational transitions in single molecules.
• Raman spectroscopy is used to determine the chemical composition and molecular structure.
• Raman setup can be based on either interferometer or dispersive (grating) spectrometer.
• Raman scattering considers random and incoherent thermal fluctuations.
Brillouin scattering

• Brillouin scattering: inelastic scattering of light in a physical medium by thermally excited acoustical phonons or temp. gradient.

• The scattering of photons from low-frequency phonons.

• Brillouin scattering: consider the correlated, periodic fluctuations (acoustic phonons).

• Brillouin scattering measures acoustic phonon energies, remote water temp, etc..


• Brillouin scattering are detected with a high-contrast Fabry-Perot interferometer.
  ⇒ energy shifts are very small (< 100 cm\(^{-1}\)) and very weak (intensity)
**FIGURE 18-6** Block diagram of a Raman spectrometer. The laser radiation is directed into a sample cell. The Raman scattering is usually measured **at right angles (90°)** to avoid viewing the source radiation. A wavelength selector isolates the desired spectral region. The transducer converts the Raman signal into a proportional electrical signal that is processed by the computer data system.
FT-Raman Spectrometer

Thermo Scientific, Nicolet 6700 / NXR FT-Raman Module
1. Source

• Nearly always lasers used 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 advantage over the other sources.

<table>
<thead>
<tr>
<th>Laser Type</th>
<th>Wavelength, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon ion</td>
<td>488.0 or 514.5</td>
</tr>
<tr>
<td>Krypton ion</td>
<td>530.9 or 647.1</td>
</tr>
<tr>
<td>Helium-neon</td>
<td>632.8</td>
</tr>
<tr>
<td>Diode</td>
<td>785 or 830</td>
</tr>
<tr>
<td>Nd-YAG</td>
<td>1064</td>
</tr>
</tbody>
</table>

• For example, the same input power, Argon ion vs. He-Ne ⇒ Raman lines nearly three times in intensity for Argon ion.
• However, these short-\(\lambda\) sources can produce significant fluorescence and cause photodecomposition of the sample.

• Laser power is usually held below 5 mW to reduce sample heating and specimen decomposition.

2. Sample Illumination System

• Simpler than for infrared spectroscopy

• **Window glass** that is transparent to visible light absorbs infrared radiation by the vibration of its constituent atoms. ⇒ **not good for IR**

• **Raman spectra are recorded in the NIR or visible regions where glass is transparent.** This means that holders for Raman samples are readily available. In fact, many samples can be studied directly through their laboratory bottles.
• Because **glass** can be used for windows, lenses, and other optical components instead of the more fragile and atmospherically less stable crystalline **halides**.
  \(\Rightarrow\) **Good for Raman**

• **Glass, water and plastic packaging** have weak Raman spectra, making the technique even easier to use. Samples usually can be analyzed directly inside a glass bottle or plastic bag without having to open the package and risk contamination.

• In addition, the laser source is easily focused on a small sample area and the emitted radiation efficiently focused on a slit.
  \(\Rightarrow\) very small samples can be investigated.

**No sample preparation**

• Raman analysis: as received samples are ok, either is a solid, liquid, powder, slurry or gas.
• But to reach a reliable result, cleaning the sample is required.
A major advantage of sample handling in Raman spectroscopy compared with infrared arises because water is a weak Raman scatterer 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.

The impurities can be removed by filtering through a fine filter, which reduces background noise.

Liquid Samples

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.

Dust particles need to be removed to avoid noise (Tyndall scattering).
Raman Spectrometers

Old
• 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 amount of stray and Rayleigh-scattered radiation reaching the transducer. ⇒ Photomultipliers served as transducers.

New
• Now Raman spectrometers being marketed are either Fourier transform instruments equipped with cooled germanium transducers or multichannel instruments based upon charge-coupled devices.
Old

Dispersive Raman Spectroscopy

Thermo Fisher Scientific

<table>
<thead>
<tr>
<th>Laser Type</th>
<th>Wavelength, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon ion</td>
<td>488.0 or 514.5</td>
</tr>
<tr>
<td>Krypton ion</td>
<td>530.9 or 647.1</td>
</tr>
<tr>
<td>Helium-neon</td>
<td>632.8</td>
</tr>
<tr>
<td>Diode</td>
<td>785 or 830</td>
</tr>
</tbody>
</table>
FIGURE 18-12 Optical diagram of an FT-Raman instrument. The laser radiation passes through the sample and then into the interferometer, consisting of the beamsplitter and the fixed and movable mirrors. The output of the interferometer is then extensively filtered to remove stray laser radiation and Rayleigh scattering. After passing through the filters, the radiation is focused onto a cooled Ge detector. To avoid saturating many transducers, 6 times higher than Stokes (1064 nm) is poor for aqueous.

Ch18 Raman Spectroscopy
In place of visible excitation lasers, an FT-Raman spectrometer uses a laser in the near infrared – usually at 1064 nm.
⇒ At this wavelength fluorescence is almost completely absent.

however because of the $1/\lambda^4$ relationship between Raman scattering intensity and wavelength, the Raman signal is weak.

In addition, silicon CCD detectors cannot be used in this region of the spectrum.

FT-Raman uses sensitive, single-element, near-infrared detectors such as indium gallium arsenide (InGaAs) or liquid nitrogen-cooled germanium (Ge) detectors.
APPLICATIONS OF RAMAN SPECTROSCOPY

Various properties can be characterized:

1. Compositions
2. Crystal structure
   ⇒ Different crystal orientations give slightly different Raman shifts.
   ⇒ Damage and structural imperfections induce scattering, allowing implant damage to be monitored.
   ⇒ The Stokes line shifts, broadens and becomes asymmetric for microcrystalline Si with grain sizes below 100 Å.
   ⇒ The lines become very broad for amorphous semiconductors, allowing a distinction to be made between single crystal, polycrystalline, and amorphous materials.
3. Stress and strain: the frequency is also shifted by stress and strain in thin film.
   ⇒ The strain in Si MOS technology introduced by SiGe and other approaches is eminently suitable for Raman characterization.
⇒ Both **compressive and tensile stress** can be determined with compressive stress giving an upward and tensile stress a downward shift from the unstressed 520 cm\(^{-1}\) \((1/\lambda \approx 0.067 \text{ eV})\) Si shift.

⇒ Example next slide.

- The relation between strain or stress and the Raman frequency is **rather complex**. **All non-zero strain tensor components** influence the position of the Raman peak.

- If **more complex strain** pictures are expected, such as for example at the edge of a film, or near a trench or LOCOS structure, the relation between \(\Delta \omega\) and the strain tensor components is more complicated.

Raman spectroscopy: about chips and stress by I. De Wolf IMEC, Belgium

- Since the light beam can be focused to a small diameter, one can measure stress in small areas.

- **Raman spectroscopy** is free from **charging effects**. ⇒ it is finding increased use in semiconductor characterization.
• SiGe has larger lattice constant than Si. Si grown on SiGe is under tensile stress leading to downward shift.

⇒ The higher the Ge content, the higher the stress and the larger the shift.
Can Raman be used to analyze crystallinity of a material?

- Raman scattering is sensitive to the degree of crystallinity in a sample.
- Typically a crystalline material yields a spectrum with very sharp, intense Raman peaks, whilst an amorphous material will show broader, less intense Raman peaks.

Raman spectra of zirconium silicate ($\text{ZrSiO}_4$), showing typical amorphous (blue) and crystalline (red) spectra.

Figure 1: Raman spectra of silicon samples ranging from pure crystalline to one containing predominantly amorphous silicon. The spectra show the sharp band at 521 cm$^{-1}$ from crystalline silicon and the much broader band centered at approximately 480 cm$^{-1}$ from the amorphous silicon. Spectra were collected on a DXR Raman microscope using a 532 nm excitation laser.
• Silicon-silicon bonds are **symmetrical** and result in strong Raman scattering. Crystalline silicon has highly **uniform bond angles and bond lengths** and exists in **a limited number of states**. This results in sharp Raman peaks with a characteristic strong band at 521 cm⁻¹.

• Amorphous silicon is **less orderly** in its arrangement with a wider array of bond angles, bond energies and bond lengths in addition to dangling bonds. The **distribution of possible states** leads to a broad Raman band centered at 480 cm⁻¹ that is readily distinguishable from that of crystalline silicon.

• These very distinct spectra make it possible to use a simple Beer’s law calculation based on the ratio of the peak heights at 521 cm⁻¹ and 480 cm⁻¹ to estimate **the relative amounts of the two forms**.
• An unstrained grain \( (d_0) \): the diffraction line from these planes (a).

• If the grain is given a uniform tensile strain \( (\text{their spacing } d > d_0) \):
  the corresponding diffraction line shifts to lower angles (b)

• The grain is bent and the strain is nonuniform:
  \( \Rightarrow \) on the top (tension) side: the plane spacing \( > d_0 \)
  \( \Rightarrow \) on the bottom (compression) side: \( < d_0 \)
  \( \Rightarrow \) somewhere in between it equals \( d_0 \)
  \( \Rightarrow \) this grain to be composed of a number of small regions in each of
  which the plane spacing is substantially constant but different from
  the spacing in adjoining regions. These regions cause the various
  sharp diffraction lines indicated on the right of (c) by the dotted
  curves. The sum of these sharp lines, each slightly displaced from
  the other, is the broadened diffraction line shown by the full curve.
**Fig. 9-2.** Effect of lattice strain on Debye-line width and position.
1. 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 (fingerprint). These vibrations are frequently Raman active and peaks with Δν values in this range are readily observed.

- Raman studies are potentially useful sources of information concerning the composition, structure, and stability of coordination compounds.
FIG. 1. The Raman spectrum of HfO$_2$, monoclinic (baddeleyite) phase at ambient pressure (bottom) and the high-pressure orthorhombic I ($Pbcm$) phase at 5.7 GPa recorded with the Spex Raman Double Monochromater.
<table>
<thead>
<tr>
<th>Raman frequency (cm$^{-1}$)</th>
<th>Mode assignment</th>
<th>$d\omega/dP$ (cm$^{-1}$/GPa)</th>
<th>$\gamma$</th>
<th>Raman frequency (4.3 GPa) (cm$^{-1}$)</th>
<th>$d\omega/dP$ (cm$^{-1}$/GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>113 s</td>
<td>$A_g$</td>
<td>6</td>
<td>10.6</td>
<td>117 m</td>
<td>1</td>
</tr>
<tr>
<td>133 s</td>
<td>$A_g + B_g$</td>
<td>1.8</td>
<td>2.7</td>
<td>135 w</td>
<td>0.5</td>
</tr>
<tr>
<td>148 s</td>
<td>$A_g$</td>
<td>1.6</td>
<td>2.2</td>
<td>143 w</td>
<td>1</td>
</tr>
<tr>
<td>164 m</td>
<td>$B_g$</td>
<td>1.5</td>
<td>1.8</td>
<td>164 m</td>
<td>1</td>
</tr>
<tr>
<td>242 m</td>
<td>$B_g$</td>
<td>0.5</td>
<td>0.4</td>
<td>174 m</td>
<td>0.2</td>
</tr>
<tr>
<td>257 s</td>
<td>$A_g$</td>
<td>1</td>
<td>0.8</td>
<td>198 vs</td>
<td>0.2</td>
</tr>
<tr>
<td>324 m</td>
<td>$A_g$</td>
<td>5</td>
<td>3.0</td>
<td>221 w</td>
<td>1</td>
</tr>
<tr>
<td>337 m</td>
<td>$B_g$</td>
<td>2.5</td>
<td>1.5</td>
<td>319 w</td>
<td>1</td>
</tr>
<tr>
<td>383 s</td>
<td>$A_g$</td>
<td>3.5</td>
<td>1.8</td>
<td>333 w</td>
<td>4</td>
</tr>
<tr>
<td>399 s</td>
<td>$B_g$</td>
<td>3.5</td>
<td>1.8</td>
<td>352 w</td>
<td>4</td>
</tr>
<tr>
<td>496 vs</td>
<td>$A_g$</td>
<td>$-1$</td>
<td>$-0.4$</td>
<td>383 vs</td>
<td>2.5</td>
</tr>
<tr>
<td>520 m</td>
<td>$B_g$</td>
<td>$-1$</td>
<td>$-0.4$</td>
<td>435 m</td>
<td>3.5</td>
</tr>
<tr>
<td>551 w</td>
<td>$B_g$</td>
<td>4</td>
<td>1.5</td>
<td>464 m</td>
<td>3.5</td>
</tr>
<tr>
<td>577 m</td>
<td>$A_g$</td>
<td>3.5</td>
<td>1.2</td>
<td>477 m</td>
<td>1.5</td>
</tr>
<tr>
<td>640 m</td>
<td>$B_g$</td>
<td>5</td>
<td>1.5</td>
<td>519 m</td>
<td>2.5</td>
</tr>
<tr>
<td>671 m</td>
<td>$A_g$</td>
<td>3</td>
<td>0.9</td>
<td>587 s</td>
<td>3.5</td>
</tr>
<tr>
<td>733* vw</td>
<td></td>
<td></td>
<td></td>
<td>597 s</td>
<td>4</td>
</tr>
</tbody>
</table>

TABLE I. Observed Raman frequencies in the baddeleyite and in the high-pressure orthorhombic I phase and their pressure dependencies. $\gamma = K_0 \times 1/\omega (d\omega/dP)$; the Gruneisen parameter $\gamma$ was calculated using $K_0$ approximated to 200 GPa (see discussions). s,m,vs,w,vw indicate the intensity of the Raman peak.
REPRESENTATIONS OF SYMMETRY POINT GROUPS

1) Mulliken labels

A means symmetric with respect to the highest order axis $C_n$;
B - antisymmetric

One- (A, B), two- (E), three- (T), four (G), five (H) dimensional representation

Symmetric ('') or antisymmetric ('') with respect to $\sigma_h$

Presence (g) or absence (u) of a center of inversion

$A'_{1g}$

Symmetric (1) or antisymmetric (2) behavior with respect to a second symmetry element ($C_2$ or $\sigma_v$)

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>$C_2$</th>
<th>$\sigma_{xz}$</th>
<th>$\sigma_{yz}$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>z</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$R_z$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$x$, $R_y$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$y$, $R_x$</td>
</tr>
</tbody>
</table>

www2.chem.umd.edu/groups/vedernikov/Lecture2009-10-02.pdf
$C_n$: rotations of $360°/n$.

$n$ is the **foldness** of the rotation axis

$\sigma_h$ (horizontal): horizontal plane perpendicular to principal axis.

$\sigma_v$ (vertical): vertical plane parallel to principal axis.
2. Raman Spectra of Organic Species (next slide)

- 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.

3. 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.
A major limitation in Raman spectroscopy is the interference caused by fluorescence, either of impurities or the sample itself.

The fluorescent background problem is eliminated by combining Raman spectroscopy with FTIR, dramatically demonstrated with the spectra in Fig. 9.32.
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.
• The intensity is directly **proportional to concentration**. Typically a calibration procedure will be used.

Disadvantage
• Despite these advantages, Raman spectroscopy has not yet been exploited widely for quantitative analysis.
• This lack of use has been due largely to the rather **high cost of Raman spectrometers** relative to that of absorption instrumentation.
Resonance Raman Spectroscopy

• Resonance Raman scattering refers to a phenomenon in which Raman line intensities are greatly enhanced by excitation with wavelengths that closely approach that of an electronic absorption peak of an analyte.

⇒ so that vibrational modes associated with the excited electronic state are greatly enhanced.

• Under this circumstance, the magnitudes of Raman peaks associated with the most symmetric vibrations are enhanced by a factor of $10^2$ to $10^6$.

• As a consequence, resonance Raman spectra have been obtained at analyte concentrations as low as $10^{-8}$ M.
By excitation with wavelengths that closely approach that of an electronic absorption peak of an analyte.

Figure 18-13 Energy diagram for (a) resonance Raman scattering and (b) fluorescence emission. Radiationless relaxation is shown as wavy arrows. In the resonance Raman case, the excited electron immediately relaxes into a vibrational level of the ground electronic state giving up a Stokes photon $\nu_s$. In fluorescence, relaxation to the lowest vibrational level of the excited electronic state occurs prior to emission. Resonance Raman scattering is nearly instantaneous, and the spectral bands are very narrow. Fluorescence emission usually takes place on the nanosecond time scale. Fluorescence spectra are usually broad because of the many vibrational states.
Raman Spectroscopy: Absorption, Scattering, and Fluorescence

Excitation Energy, $\sigma$ (cm$^{-1}$)

- 2nd Electronic Excited State
- 1st Electronic Excited State

Stokes, Anti-Stokes

- IR
- Raman
- Resonance Raman

$\sigma$, $\sigma_{\text{emit}}$, $\sigma_{\text{emit}} - \sigma$, $\Delta \sigma$

• Fig. 18-13 differs from the energy diagram for normal Raman scattering in that the electron is promoted into an excited electronic state followed by an immediate relaxation to a vibrational level of the electronic ground state.

• The time scales for the two phenomena are also quite different:
  ⇒ Raman relaxation: less than $10^{-14}$ s.
  ⇒ Fluorescence emission: $10^{-10}$ s.

• The most important application of resonance Raman spectroscopy has been to the study of biological molecules under physiologically significant conditions; that is, in the presence of water and at low to moderate concentration levels.

• As an example, the technique has been used to determine the oxidation state and spin of iron atoms in Hemoglobin: iron-containing oxygen-transport metalloprotein in the red blood cells of all vertebrates.
Surface-Enhanced Raman Spectroscopy (SERS)

- Surface-enhanced Raman scattering (SERS): to amplify weak Raman signals.
- Surface enhanced Raman spectroscopy involves obtaining Raman spectra in the usual way on samples that are adsorbed on the surface of colloidal metal particles (usually silver, gold, or copper) or on roughened surfaces of pieces of these metals.
- The Raman lines of the adsorbed molecule are often enhanced by a factor of $10^3$ to $10^6$. 
There are two primary mechanisms of enhancement described:

1. electromagnetic enhancement (EME): dominant. 
   ⇒ dependent on the presence of the metal surface’s roughness features.

- The electromagnetic theory: the excitation of localized surface plasmons

- When the incident light strikes the surface, localized surface plasmons (the collective oscillation of electrons stimulated by incident light) are excited.

- The field enhancement is greatest when the plasmon frequency is in resonance with the radiation.

- Roughened surfaces or arrangements of nanoparticles are typically employed in SERS.

2. chemical enhancement (CE): involving changes to the adsorbate electronic states due to chemisorption of the analyte.

- When surface enhancement is combined with the resonance enhancement technique, the net increase in signal intensity is roughly the product of the intensity produced by each of the techniques. 
  ⇒ Consequently, detection limits in the $10^{-9}$ to $10^{-12}$ M range have been observed.