Spectroscopic Techniques
Outline

1. Vibrational Spectroscopy (IR and Raman)
2. UV-vis spectroscopy
3. Nuclear Magnetic Resonance (NMR)
4. Electron Spin Resonance (ESR)
5. X-ray spectroscopy
6. Electron spectroscopy
7. Mössbauer spectroscopy
8. Mass spectroscopy
9. Thermal analysis
Electromagnetic Radiation

Spectroscopic techniques all work on the principle of that, under certain conditions, *materials absorb or emit energy*

\[ \nu \lambda = c \]

Quantized energy: photon

\[ E = h\nu \]

\[ \Delta E = h\nu = hc/\lambda \]

X-axis: Frequency or wavelength
Different spectroscopic techniques operate over different, limited frequency ranges within this broad spectrum, depending on the processes and magnitudes of the energy changes.

<table>
<thead>
<tr>
<th>molecular effect</th>
<th>approx energy of $\Delta E$ (kJ mol$^{-1}$)</th>
<th>region</th>
</tr>
</thead>
<tbody>
<tr>
<td>nuclear spin transitions</td>
<td>$10^{-2}$</td>
<td>radio waves (NMR)</td>
</tr>
<tr>
<td>electron spin transitions</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>rotational excitation</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>vibrational excitation</td>
<td>10$^{-6}$</td>
<td>infrared</td>
</tr>
<tr>
<td>electronic excitation</td>
<td>10$^{-4}$</td>
<td>far infrared</td>
</tr>
<tr>
<td>ionization</td>
<td>10$^{6}$</td>
<td>microwaves</td>
</tr>
<tr>
<td>nuclear excitation</td>
<td>10$^{8}$</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>γ-rays</td>
<td>10$^{-12}$</td>
<td>far UV</td>
</tr>
<tr>
<td>X-rays</td>
<td>10$^{-10}$</td>
<td>visible</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>wavelength $\lambda$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^1$</td>
</tr>
<tr>
<td>$10^0$</td>
</tr>
<tr>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>$10^{-4}$</td>
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<tr>
<td>$10^{-5}$</td>
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<tr>
<td>$10^{-6}$</td>
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<tr>
<td>$10^{-7}$</td>
</tr>
<tr>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>$10^{-12}$</td>
</tr>
</tbody>
</table>
Visible and Ultraviolet Spectroscopy

- Transitions in the *electronic energy levels* of the bonds of a molecule and results in excitation of electrons from *ground* state to *excited* state
- Energy changes: $10^4$ to $10^5$ cm$^{-1}$ or 100 to 1000 kJ mol$^{-1}$

Four types of transitions:

i) Within the same atom e.g. d-d or f-f transition

ii) To adjacent atom (charge transfer)

iii) To a delocalized energy band, conduction band (photoconductivity)

iv) Promotion of an electron from valence band to conduction band (bandgap in semiconductors)
Beer-Lambert Law

\[
\log(I_0/I) = \varepsilon cl
\]

\[
\varepsilon = A/cl
\]

\(\varepsilon\): extinction coefficient
\(c\): concentration
\(l\): path length
\(I_0\): incident radiation
\(I\): transmitted radiation
\(A\): absorbance

\(\varepsilon\) value determines transition is \textit{allowed} or \textit{forbidden}.
Recording and Interpreting UV-vis Spectra

- Determine the coordination environment of transition metal ions
- Detection of conjugation and elucidation of its nature

![Diagram of UV-vis spectrometer](image)

### Aniline (in water)

- $E_2$-band: $\pi \rightarrow \pi^*$ transition
- $B$-band: $\pi \rightarrow \pi^*$ transition

- $\varepsilon_{\text{max}}$ and $\lambda_{\text{max}}$

#### Electronic Transitions

1. $\sigma \rightarrow \sigma^*$
2. $n \rightarrow \sigma^*$
3. $\pi \rightarrow \pi^*$
4. $n \rightarrow \pi^*$

- Antibonding $\sigma$ orbital
- Antibonding $\pi$ orbital
- Bonding $\pi$ orbital
- Non-bonding $n$ orbital
Vibrational Spectroscopy

Atoms in solids vibrate at frequencies of $10^{12}$ to $10^{14}$ Hz

Hooke’s Law:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$\nu$: vibrational frequency
$\mu$: reduced mass
$m$: atomic mass
$k$: force constant

Identify the functional groups!
Fundamental Vibrational Modes

**XY₂ compounds:**

- **STRETCHING MODES**
  - symmetric
  - antisymmetric

- **BENDING MODES**
  - scissoring
  - rocking
  - twisting
  - wagging

Linear molecule: *3N-5* normal modes of vibration
Non-linear molecule: *3N-6* normal modes of vibration

- Fundamental frequencies
- Overtone bands (multiples of fundamental vibrations)
Infrared Spectroscopy

- Frequency of the incident radiation is varied and the quantity of radiation *absorbed or transmitted* by the sample is obtained
- 4000 - 400 cm\(^{-1}\) (2.5 – 25 \(\mu\)m)

Solid:  
- finely ground powder mixed with one or two drops of nujol
- solid mixed with dry KBr powder to make a pressed disc
Infrared Spectra

- Identification
- Structural information
- Estimation of sample purity
- Calculation of force constant
- Monitor the progress of reaction
- Study of hydrogen bonding

Selection rule for IR active transition:

Vibrations involve a change of dipole moment!
Sir C.V. Raman:

“When a beam of strong radiation of a definite frequency is passed through a transparent substance, the radiation scattered at right angles has not only the original frequency (*Rayleigh Scattering*) but also some other frequencies, which are generally lower (*Stokes line*) and occasionally higher (*anti-Stokes line*) than that of the incident radiation”

Raman active: involve a *change of polarizability*
Origin of Raman Scattering

Quantum theory: \[ E_p + \frac{1}{2}mv_i^2 + h\nu_i = E_q + \frac{1}{2}mv_s^2 + h\nu_s \]
\[ E_p + h\nu_i = E_q + h\nu_s \]
\[ \nu_s = \nu_i + (E_p - E_q)/h \]

Rayleigh scattering: \( E_p = E_q \); Stokes lines: \( E_p < E_q \); anti-Stokes lines: \( E_p > E_q \)

Number of molecules in the particular state \( E_p \): \[ N_p = CNg_p e^{-E_p/kT} \]
Raman Scattering

Raman frequency shift:

\[ \Delta \nu = \nu_i - \nu_s \]

The frequency difference is constant and characteristic of the substance exposed to radiation and is completely *independent of the incident radiation*

- Raman lines are symmetrically displaced about the parent line
- Intensity of Stokes lines > anti-Stokes lines
- Raman shifts represent the frequencies of absorption bands of substance
- Identical with absorption frequencies obtained from IR spectrum
- Complementary to IR spectroscopy (symmetrical bonds are Raman active)
## Raman vs. IR

<table>
<thead>
<tr>
<th><strong>Raman spectra</strong></th>
<th><strong>IR spectra</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Originate from scattering of radiation</td>
<td>Originate from absorption of radiation</td>
</tr>
<tr>
<td>Change in molecular polarizability</td>
<td>Change in dipole moment</td>
</tr>
<tr>
<td>Weak in intensity</td>
<td>Strong in intensity</td>
</tr>
<tr>
<td>Water can be used as solvent</td>
<td>Water lead to strong absorption and attack the holder</td>
</tr>
<tr>
<td>Optical system: Glass, quartz</td>
<td>Optical system: NaCl, KBr</td>
</tr>
<tr>
<td>Record by using a beam of monochromatic radiation</td>
<td>Record by using a beam of radiation having a large number of frequencies</td>
</tr>
<tr>
<td>Homonuclear diatomic molecules are Raman active</td>
<td>Homonuclear diatomic molecules are IR inactive</td>
</tr>
</tbody>
</table>
Surface Enhanced Raman Spectroscopy (SERS)

SERS is a Raman spectroscopic technique that provides *greatly enhanced Raman signal* from Raman active analyte molecules that have been adsorbed onto certain *metal nanoparticles*

- Enhancement: $10^4 - 10^6$, up to $10^{14}$
- *Electromagnetic* enhancement and *chemical* enhancement

\[
\mu = \alpha E 
\]

induced dipole moment \rightarrow electromagnetic field

↑ polarizability

1. The formation of a charge-transfer complex between the surface and analyte molecule \rightarrow resonance enhancement
Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering

Shuming Nie* and Steven R. Emory

Optical detection and spectroscopy of single molecules and single nanoparticles have been achieved at room temperature with the use of surface-enhanced Raman scattering. Individual silver colloidal nanoparticles were screened from a large heterogeneous population for special size-dependent properties and were then used to amplify the spectroscopic signatures of adsorbed molecules. For single rhodamine 6G molecules adsorbed on the selected nanoparticles, the intrinsic Raman enhancement factors were on the order of $10^{14}$ to $10^{15}$, much larger than the ensemble-averaged values derived from conventional measurements. This enormous enhancement leads to vibrational Raman signals that are more intense and more stable than single-molecule fluorescence.

- Silver colloidal nanoparticles
- Enhancement factor $\sim 10^{14}$ to $10^{15}$
- More intense and stable than single-molecule fluorescence
- Molecular information
- No photobleaching

S. Nie and S. R. Emory, *Science* **275** 1102 (1997)
Coherent Anti-Stokes Raman Spectroscopy (CARS)

- Non-linear optical process (three wave mixing)
- Stronger signal (~$10^5$) than spontaneous Raman response
- Blue shift

Biomedical imaging:
- Intrinsic vibrational contrast
- Strong signal
- Enable 3D imaging
- Higher frequency than fluorescence
- Little scattering and absorption of the near-infrared excitation beams (deep penetration and reduced photodamage)

Prof. Sunney Xie (Harvard University)
Nuclear Magnetic Resonance Spectroscopy (NMR)

Absorption spectroscopy: radio-frequency region 3 MHz to 30000 MHz
Transition between magnetic energy levels of the nuclei
Atomic nuclei possess *spin* (angular momentum, with *half integer spin* number)

<table>
<thead>
<tr>
<th>Mass number</th>
<th>Atomic number</th>
<th>Spin number</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odd</td>
<td>Odd or even</td>
<td>$\frac{1}{2}$</td>
<td>$^{1}H$, $^{13}C$, $^{15}N$, $^{19}F$, $^{31}P$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\frac{3}{2}$</td>
<td>$^{11}B$, $^{35}Cl$, $^{37}Cl$, $^{79}Br$, $^{81}Br$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\frac{5}{2}$</td>
<td>$^{127}I$, $^{17}O$</td>
</tr>
<tr>
<td>Even</td>
<td>Even</td>
<td>0</td>
<td>$^{12}C$, $^{16}O$, $^{32}S$, $^{34}S$</td>
</tr>
<tr>
<td>Even</td>
<td>Odd</td>
<td>1</td>
<td>$^{14}N$, $^{2}H$ (or D)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>$^{10}B$</td>
</tr>
</tbody>
</table>
Spinning nuclei behave like a tiny bar magnet with a magnetic moment $\mu$

\[ \nu = \frac{\gamma H_0}{2\pi} \]

\[ \gamma = \frac{2\pi\mu}{hI} \]

\[ h\nu = \Delta E = \frac{\mu H_0}{I} = 2\mu H_0 \]
**Theory of NMR**

The precessional frequency of spinning nucleus is exactly equal to the frequency of EM radiation necessary to induce a transition from one nuclear spin state to another.

\[
\omega_0 = \gamma H_0
\]
\[
\omega_0 = 2\pi \nu
\]
\[
2\pi \nu = \gamma H_0
\]

\[\frac{N_\alpha}{N_\beta} = e^{\Delta E/RT}\]

\(N_\alpha \& N_\beta\) : population of \(\alpha\) and \(\beta\) spin states

- Probability of observing absorption of energy is quite small
- Larger \(H_0\) and lower \(T\) lead to higher sensitivity
Shielding ➔ Chemical Shift

Circulating electron cloud:

- Shield or deshield applied field
- Resonance at different frequencies

Differences in the chemical environment modify the electron density and distribution about nuclei

Chemical shift:

\[
\delta (\text{ppm}) = \frac{\text{chemical shift (Hz)}}{\text{oscillator frequency (Hz)}} \times 10^6
\]

\[
\delta = \frac{v - v_{\text{ref}}}{v_{\text{ref}}}
\]

Reference compound: TMS
- Chemical shift: chemical environment
- Coupling: how nuclei interact with each other
- Intensity: number of nuclei
Solid State NMR

*Magic angle spinning* technique:

Sample is rotated at a high velocity at a critical angle of 54.74° to the applied magnetic field

$^{29}$Si NMR:
Electron Spin Resonance (ESR) Spectroscopy

It detects changes in *electron spin* configuration in substance containing one or more unpaired electrons.

Absorption spectroscopy, operate at microwave frequency $10^4 - 10^6$ MHz (~1.0 J mol$^{-1}$)

Stable paramagnetic substances: simple molecules (e.g. NO, O$_2$) and ions of transition metals and their complexes e.g. Fe$^{3+}$, [Fe(CN)$_6$]$^{3-}$

Unstable paramagnetic substances: free radicals
Theory of ESR

Absorption of energy occurs at:

\[ \Delta E = h\nu = g\beta_e H_0 \]

- \( H_0 \): applied magnetic field
- Bohr magneton:
  \[ \beta_e = \frac{eh}{4\pi mc} = 9.273 \times 10^{-24} \text{ JT}^{-1} \]
- \( g \) factor (\( g \)): depends on the particular ion, its oxidation state and coordination number

Determination of \( g \) values of free radicals:

Reference substance: \( g = 2.0036 \)

\[ g = g_{\text{ref}} \left[ 1 - \frac{\Delta H_0}{H} \right] \]
ESR Spectrum

First derivative of the absorption

Hyperfine structure:

*Hydrogen atom*

(a) Applied field  
(b)  

Effect of applied field and nuclear spins of proton
Associated with the unpaired electrons of the isotope, for example

Naturally occurring Cr is a mixture of $^{52}\text{Cr}$ (nucleus spin $I = 0$) and $^{53}\text{Cr}$ (nucleus spin $I = 3/2$)
NMR vs. ESR

**NMR spectroscopy**

1. Different energy states are produced due to the alignment of the **nuclear** magnetic moments relative to the applied magnetic field and a transition between these energy states occurs on the application of an appropriate frequency in the radio frequency region.

2. NMR absorption positions are expressed in terms of **chemical shifts**.

3. Nuclear spin-spin coupling causes the splitting of NMR signals.

**ESR Spectroscopy**

1. Different energy states are produced due to the alignment of the **electronic** magnetic moments relative to the applied magnetic field and a transition between these energy states occurs on the application of an appropriate frequency in the microwave region.

2. ESR absorption positions are expressed in terms of **g values**.

3. Coupling of the electronic spin with nuclear spins (hyperfine coupling) causes the splitting of ESR signals.
X-ray Spectroscopy

X-ray: Diffraction, Emission and Absorption

[Diagram showing the process of X-ray spectroscopy with nodes for XRD, ED, EM, EELS, ESCA (XPS, UPS), AEFS, EXAFS, and AUGER connected by arrows indicating diffraction, emission, and absorption processes.]
X-ray Emission

X-ray Fluorescence (XRF)

\[ \lambda^{-\frac{1}{2}} = C(Z - \sigma) \]

Peak positions vary slightly with local environment of atoms such as coordination numbers and bond distances.
Absorption Techniques

Electron may leave the atom with a net kinetic energy: \[ E = h\nu - E_0 \]
X-ray Absorption Near Edge Structure (XANES)

Fine structures on the an absorption edge

The peak positions depend on details of oxidation state, site symmetry, surrounding ligands and the nature of bonding
Extended X-ray Absorption Fine Structure (EXAFS)

In-situ electron diffraction event

Coordination number and bond distance

Equally suitable for non-crystalline and crystalline materials

Local environment of each element may be determined
Electron Spectroscopics

Measure the *kinetic energy* of electrons that are emitted from matter as a consequence of bombarding it with ionizing radiation

\[ E = h\nu - E_b \]

Ionization potential (characteristic)

(X-ray or UV)

![Diagram showing the process of electron spectroscopy](image)
ESCA and Auger Process

Atom A \xrightarrow{\text{radiation}} A^{++} + e^-

XPS or UPS: $A^{++} \rightarrow A^+ + h\nu$

Auger Process: $A^{++} \rightarrow A^{++} + e^-$
(Auger electron)

Vacuum

\[ \bullet \bullet \ bullet L \]
ionization

\[ \bullet \bullet \ K \]
X-ray Photoelectron Spectroscopy (XPS)

Study surface properties (ionized electron energy $<< 1$ keV)
2 to 5 nm from the surface
Electron binding energy $E_b$: charge and oxidation state
Mössbauer Spectroscopy

$\gamma$-ray spectroscopy, highly monochromatic beam

Change in population of energy levels *inside the nuclei*, $^{57}\text{Fe}_{29}^*$ or $^{119}\text{Sn}_{50}^*$

$\gamma$-ray energy is varied by making use of Doppler effect

![Diagram of Mössbauer Spectroscopy]

- Source
- Sample
- Detector

![Absorption Spectrum]

$\gamma$-ray absorption spectrum
Mössbauer Spectroscopy

Emitter and sample are identical: resonant absorption peak

Emitter and sample are not identical: absorption peak shift

- Quadrupole splitting
- Magnetic hyperfine
- Zeeman splitting
Mass Spectrometry

• Determine the mass/charge ratio (m/z) in the vapor phase
• Exact molecular masses
• Structure of the molecule

\[
\frac{1}{2} mv^2 = eV
\]
\[
Hev = \frac{mv^2}{r}
\]
\[
m/e = \frac{H^2r^2}{2V}
\]
Instrumentation of Mass Spectrometer

**Single focusing MS**
- Magnetic analyzer
- Collector slit
- Detector
- Ions are deflected according to $m/z$

**Double focusing MS**
- Increased resolution is possible with second analyzer
- Narrow slit

**Quadrupole MS**
- Quadropole rods
- Ion source
- Detector
- Ions are deflected by $V_f + V_d$
- Only ions with a specific $m/z$ will reach the detector for a given level of applied $V_f$ and $V_d$

**Time-of-Flight MS**
- Ionization chamber
- Acceleration
- Field free region (time of flight measurement)
- Detector
Ionization Methods

1. Electron impact method (electron)

\[ M + e \rightarrow M^+ + 2e \]

2. Chemical ionization method (ions)

\[ \text{NH}_4^+ + \text{RH} \rightarrow \text{RH}_2^+ + \text{NH}_3 \]

3. Fast Atom Bombardment (atom)

4. Electrospray (for macromolecules such as proteins)
MS Spectrum

Molecular structure

Marcomolecules (proteins, peptides)

Peptide mass fingerprint
Thermal Analysis

- Measurement of certain physical and chemical properties as a function of temperature
- Enthalpy, heat capacity, mass and coefficient of thermal expansion

1. Thermogravimetry (TG)

Measures the changes in mass of a substance as a function of temperature or time
Thermal Analysis

2. Differential Thermal Analysis (DTA) & Differential Scanning Calorimetry (DSC)

Temperature of a sample is *compared* with that of an inert reference materials during a programmed change of temperature.
Applications of Thermal Analysis

- Combination of TG and DTA analysis

Exothermic reaction: phase transition from meta-stable to more stable structure

- Reversible vs. irreversible reaction
- Hysteresis
Applications of Thermal Analysis

1. Determination of glass transition temperature

2. Decomposition process

3. Determination of phase diagram