University of Babylon
College of Science
Department of Chemistry
Course No. Chsc 424

Undergraduate Studies
Physical chemistry
Fourth year - Semester 2
Credit Hour: 3 hrs.
Scholar units: three units

Lectures of Molecular Spectroscopy
Second Semester, Scholar year 2024-2025
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Lecture No. 1: General Introduction of Molecular Spectroscopy

1-Introudction.

Q/ Explain the mean features of molecular spectroscopy.

- Spectroscopy is the measurement of radiation intensity as a function of wavelength and is often to describe experimental spectroscopic methods.
- The devices of spectral measurement:
  are spectrometers, spectrophotometers, spectrographs or spectral analyzers.
- Spectroscopic studies were central to the development of quantum mechanics and their theories for explanation of chemical structure through spectra.
- Spectroscopy is depend on chemistry because atoms and molecules have unique spectra. These spectra can used to detect, identify and quantify information about the atoms and molecules.

Classification methods// Give general classification method of spectroscopy

Spectroscopy is included various implementations and techniques that's can be classify in several ways:-

1-Type of radiative Energy

The type of radiative energy involved in the interaction distinguishes the types of spectroscopy. In many applications, the spectrum is determined by measuring changes in the intensity or frequency of this energy. The types of radiative energy studied include:

- Electromagnetic radiation was the first source of energy used for spectroscopic studies. Techniques that employ electromagnetic radiation are typically classified by the wavelength region of the spectrum and include microwave, infrared, ultraviolet-visible, Magnetic resonance, and x-ray.
- Particles, because of their de Broglie waves, can also be a source of radiative energy. Both electron and neutron spectroscopy are commonly used. For a particle, its kinetic energy determines its wavelength.

2-Nature of interaction:-

The types of spectroscopy also can be distinguish by the nature of the interaction between the energy and the material. These interactions include:

- Absorption spectroscopy:

  Absorption occurs when the material absorbs energy from the radiative source. Absorption is often determined by measuring the fraction of energy transmitted through the material, with absorption decreasing the transmitted portion.

- Emission spectroscopy:

  Emission indicates that the material releases radiative energy. A material's blackbody spectrum is a spontaneous emission spectrum determined by its temperature. This feature can be measure in the infrared by instruments such as the atmospheric emitted radiance interferometer.

Emission also induced by other sources of energy such as flames or sparks or electromagnetic radiation in the case of fluorescence.

- Elastic scattering and reflection spectroscopy determine how incident radiation is reflect or scattered by a material. Crystallography employs the scattering of high-energy radiation, such as x-rays and electrons, to examine the arrangement of atoms in proteins and solid crystals.
- Inelastic scattering phenomena involve an exchange of energy between the radiation and the matter that shifts the wavelength of the scattered radiation. These include Raman and Compton scattering.
- Coherent or resonance spectroscopy are techniques where the radiative energy couples two quantum states of the material in a coherent interaction that is sustain by the radiating field. The coherence can disrupted by other interactions, such as particle collisions and energy transfer, and so often require high intensity radiation to be sustain. Nuclear magnetic resonance (NMR) spectroscopy is a widely used resonance method, and ultrafast laser spectroscopy is possible in the infrared and visible spectral regions.

3-Type of material:-

Spectroscopic studies are design so that the radiant energy interacts with specific types of matter.

- Atoms

Atomic spectroscopy was the first application of spectroscopy developed. Atomic absorption spectroscopy and atomic emission spectroscopy involve visible and ultraviolet light. These absorptions and emissions, often referred to as atomic spectral lines, are due to electronic transitions of outer shell electrons as they rise and fall from one electron orbit to another. Atoms also have distinct x-ray spectra that are attributable to the excitation of inner shell electrons to excited states.

Modern implementations of atomic spectroscopy for studying visible and ultraviolet transitions include flame emission spectroscopy, inductively coupled plasma atomic emission spectroscopy, glow discharge spectroscopy, microwave induced plasma spectroscopy, and spark or arc emission spectroscopy. Techniques for studying x-ray spectra include X-ray spectroscopy and X-ray fluorescence.

- Molecules

The combination of atoms into molecules leads to the creation of unique types of energetic states and therefore unique spectra of the transitions between these states. Molecular spectra can obtained due to electron spin states (electron paramagnetic resonance), molecular rotations, molecular vibration, and electronic states. Rotations are collective motions of the atomic nuclei and typically lead to spectra in the microwave and millimeter-wave spectral regions. Rotational spectroscopy and microwave spectroscopy are synonymous. Vibrations are relative motions of the atomic nuclei and are study by both infrared and Raman spectroscopy. Electronic excitations are study using visible and ultraviolet spectroscopy as well as fluorescence spectroscopy.

- Crystals and extended materials

The combination of atoms or molecules into crystals or other extended forms leads to the creation of additional energetic states. These states are numerous and therefore have a high density of states. This high density often makes the spectra weaker and less distinct, i.e., broader.

Pure crystals, though, can have distinct spectral transitions, and the crystal arrangement has an effect on the observed molecular spectra. The regular lattice structure of crystals also scatters x-rays, electrons or neutrons allowing for crystallographic studies.

- Nuclei

Nuclei have distinct energy states that are widely separated and lead to gamma ray spectra. Distinct nuclear spin states can have their energy separated by a magnetic field, and this allows for nuclear magnetic resonance spectroscopy.

Electromagnetic radiation and Characteristics of wave

- Frequency, v - number of oscillations per unit time, unit: *hertz* (Hz) - cycle per second.
- Velocity, c - the speed of propagation, for E. M. R $c=2.9979 \times 10^{8}$ m. s^{-1} (in vacuum).
- Wavelength, l - the distance between adjacent crests of the wave (units of length l).
- Wave number, v', - the number of waves per unit distance $v'=l^{-1}$.
- The energy carried by an EMR or a photon is directly proportional to the frequency, i.e.

  where h is Planck's constant $h=6.626\times10^{-34}$ J×s

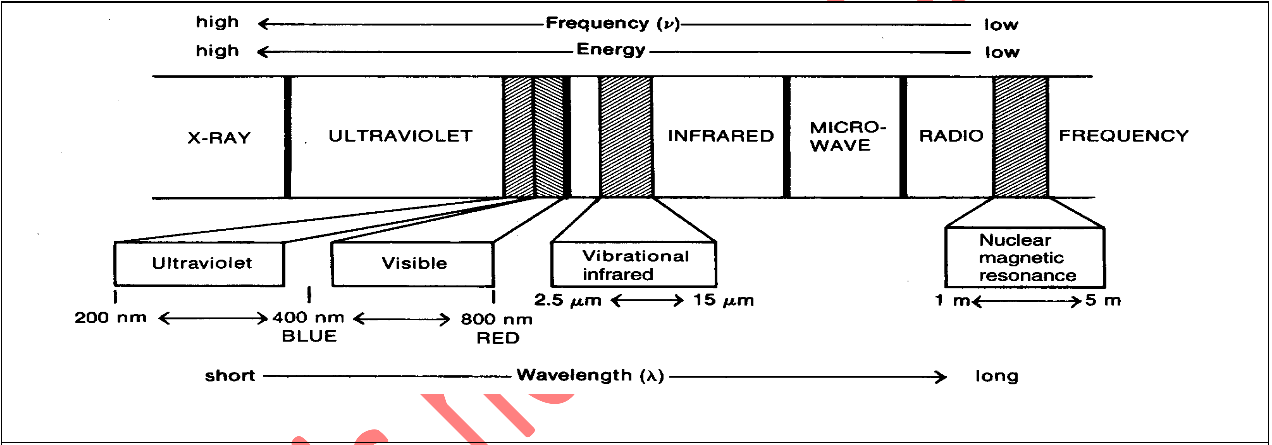
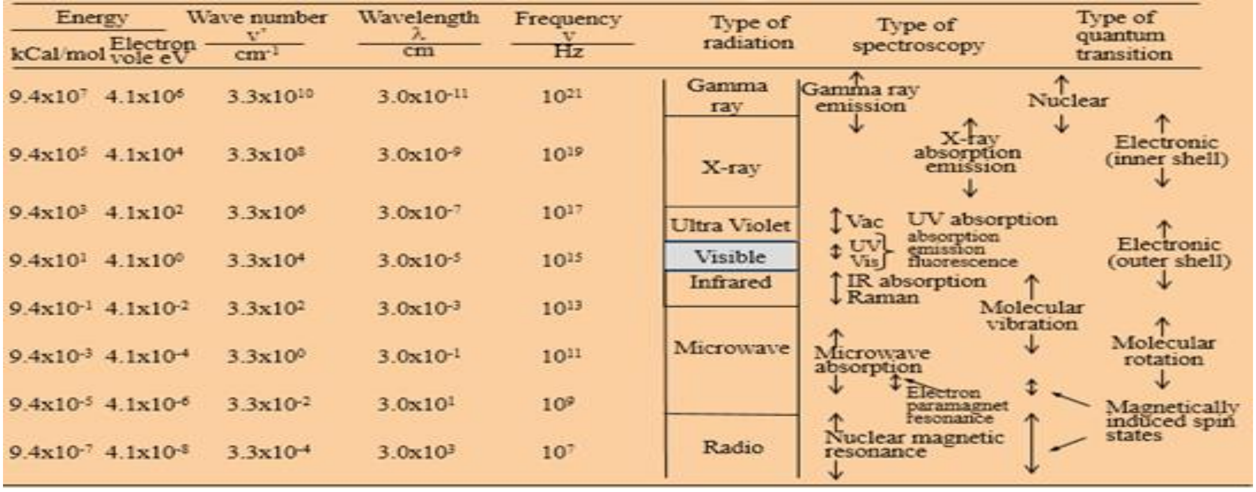


Figure 1- Diagram of spectroscopic region classification.

Table 1. Spectral properties, applications and interaction of electromagnetic radiation.



Energy		Wave number	Wavelength	Frequency	Type of radiation	Type of spectroscopy	Type of quantum transition
kCal/mol	Electron vole eV	v' cm^{-1}	λ cm	v Hz			
$9.4\text{x}10^{7}$	$4.1\text{x}10^{6}$	$3.3\text{x}10^{10}$	$3.0\text{x}10^{-11}$	10^{21}	Gamma ray	↑ Gamma ray emission ↓	↑ Nuclear ↓
$9.4\text{x}10^{5}$	$4.1\text{x}10^{4}$	$3.3\text{x}10^{8}$	$3.0\text{x}10^{-9}$	10^{19}	X-ray	↑ X-ray absorption emission ↓	↑ Electronic (inner shell) ↓
$9.4\text{x}10^{3}$	$4.1\text{x}10^{2}$	$3.3\text{x}10^{6}$	$3.0\text{x}10^{-7}$	10^{17}	Ultra Violet	↕ Vac UV absorption	
$9.4\text{x}10^{1}$	$4.1\text{x}10^{0}$	$3.3\text{x}10^{4}$	$3.0\text{x}10^{-5}$	10^{15}	Visible	↕ UV Vis } absorption emission fluorescence	↑ Electronic (outer shell) ↓
$9.4\text{x}10^{-1}$	$4.1\text{x}10^{-2}$	$3.3\text{x}10^{2}$	$3.0\text{x}10^{-3}$	10^{13}	Infrared	↕ IR absorption Raman	↑ Molecular vibration ↓
$9.4\text{x}10^{-3}$	$4.1\text{x}10^{-4}$	$3.3\text{x}10^{0}$	$3.0\text{x}10^{-1}$	10^{11}	Microwave	↑ Microwave absorption ↓	↑ Molecular rotation ↓
$9.4\text{x}10^{-5}$	$4.1\text{x}10^{-6}$	$3.3\text{x}10^{-2}$	$3.0\text{x}10^{1}$	10^{9}		↕ Electron paramagnet resonance	↕ Magnetically induced spin states
$9.4\text{x}10^{-7}$	$4.1\text{x}10^{-8}$	$3.3\text{x}10^{-4}$	$3.0\text{x}10^{3}$	10^{7}	Radio	↑ Nuclear magnetic resonance ↓	↕