

The Atom Model and Review of Quantum theory of Hydrogen atom

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The Atom and historical Model

- Ancient Greece has two school of thought about the atom
 - Atomic theory conveying particular nature of matter
 - Continuous theory of matter
- The later took over because of the kind of person behind the theory (Aristotle)

Old description of the atom

- John Dalton's Model of Atom
- -tiny, indivisible, indestructible particle like billiard balls.
- Model was silent about the internal structure of the atom
- J. J. Thompson's Model(Plumb and pubdding)
 - Sphere full of an electrically positive substance with embedded electrons

Old description of the atom

- Ernest Rutherford's Model
 - Alpha particle scattering
 - empty space with a tiny positively charged nucleus, contains the entire mass of the atom
 - negative electrons orbit like planets
- According Maxwell's Electromagnetic theory
 - charged particle in circular motion radiates energy
 - electron in atoms should continuously loose energy and spiral into the nucleus

- This does not not happens in nature
- Rutherford's is much-improved picture of the atoms but could not explain stability of atom
- From classical physics, emitted energy by an electron as its spirals down to the nucleus should have all frequencies (continuous spectrum)

Classical Model of the one-Electron atoms

- We shall consider a simple model for the atom, where an electron moves about the nucleus in an assumed circular orbit.
- we also assume the nucleus to have a positive charge of $q_N = Z\epsilon$
- This allows our model to describe the hydrogen atom and hydrogenic system is mechanically stable because the Coulomb potential ($U=-kZe^2/r$) provides the centripetal force

$$F = \frac{kZe^2}{r^2} = \frac{mv^2}{r}$$

- The hydrogen atom consists of a single electron, bound to its nucleus (single proton) by the attractive Coulomb force. The potential energy function $U(r)$ for this system is :

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r},$$

e= magnitude of the charge of the electron and the proton

r = the distance between electron and the proton

Constant

- It has spherical symmetry, so that the potential energy depends on only one variable- the separation ' r ' between the electron and the central proton.

The potential energy is negative for all values of r .
This is because we have (arbitrarily) chosen our zero of potential to correspond to $r = \infty$.

THE BOHR ATOM

1913: Extension of Rutherford model, with three new assumptions

1. Electrons only go in **circular** orbits due to attraction of nucleus
2. When the electron changes its configuration, energy is $E = hf = h\omega$ emitted in the form of a **single photon** of energy
3. The electrons *must* have angular momentum that is an **integer multiple of** $\frac{h}{m_e}$

$$\frac{m_e}{r} \left(\frac{n\hbar}{m_e r} \right)^2 = \frac{k e^2}{r^2}$$

$$\frac{n^2 \hbar^2}{m_e r^3} = \frac{k e^2}{r^2}$$

Electrostatic
Attraction:

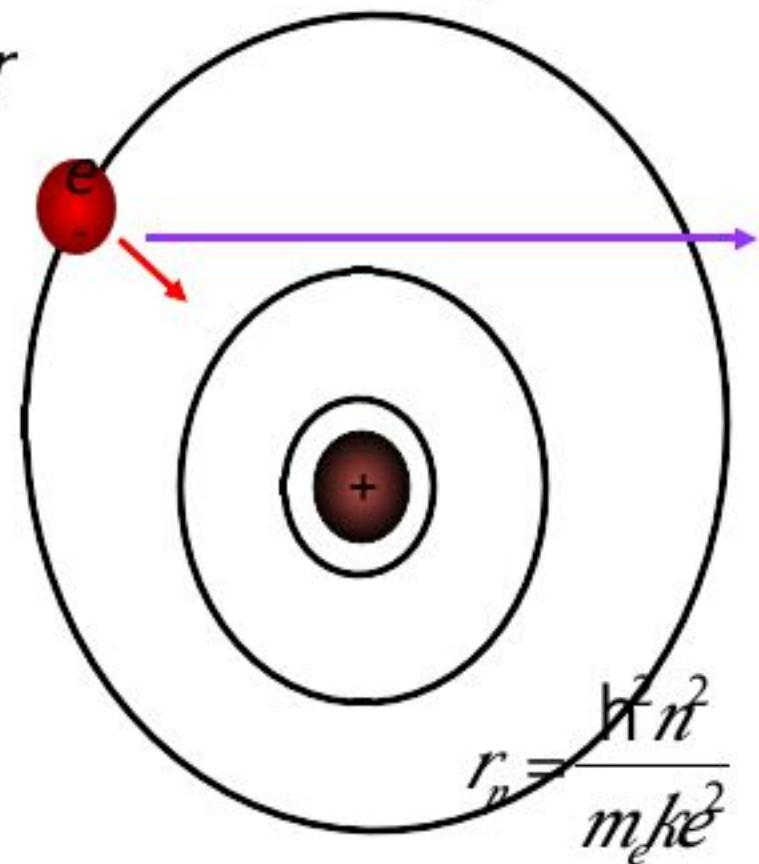
$$F = \frac{k e^2}{r^2}$$

$$\text{Centripetal Force: } F = \frac{m_e v^2}{r}$$

$$L = n\hbar = m_e v r$$

$$v = \frac{n\hbar}{m_e r}$$

qms



The Bohr Atom (Cont'd)

$$v = \frac{\hbar}{m_e r}$$

$$r_n = \frac{\hbar^2 n^2}{m_e k e^2}$$

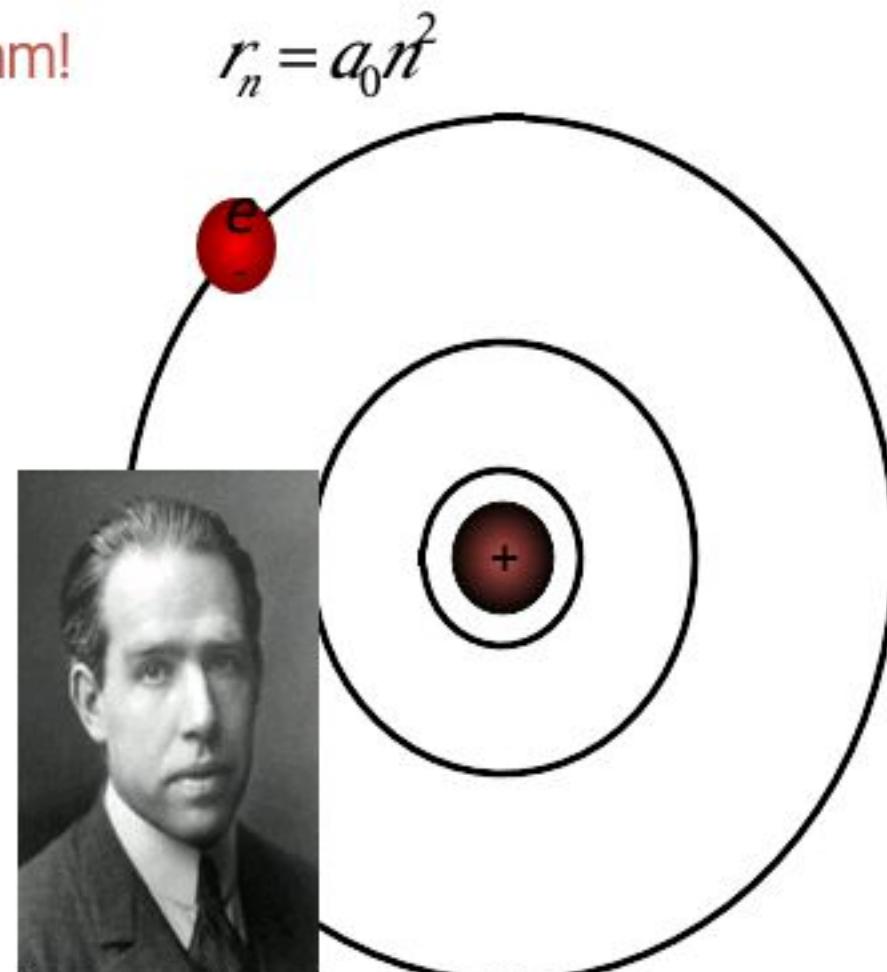
Define:
Bohr Radius

$$a_0 \equiv \frac{\hbar^2}{m_e k e^2} = 0.05297 \text{ nm}$$

- Diameter of H-atom for $n = 1$ is 0.106 nm!

$$v = \frac{\hbar}{m_e} \left(\frac{m_e k e^2}{\hbar^2 n^2} \right) = \frac{k e^2}{\hbar n}$$

But wait, there's more!



The Bohr Atom (Cont'd)

$$\nu = \frac{ke^2}{\hbar n} \quad r_n = \frac{\hbar^2 n^2}{m k e^2}$$

Energy has two components:

- Kinetic energy:
- Potential energy*

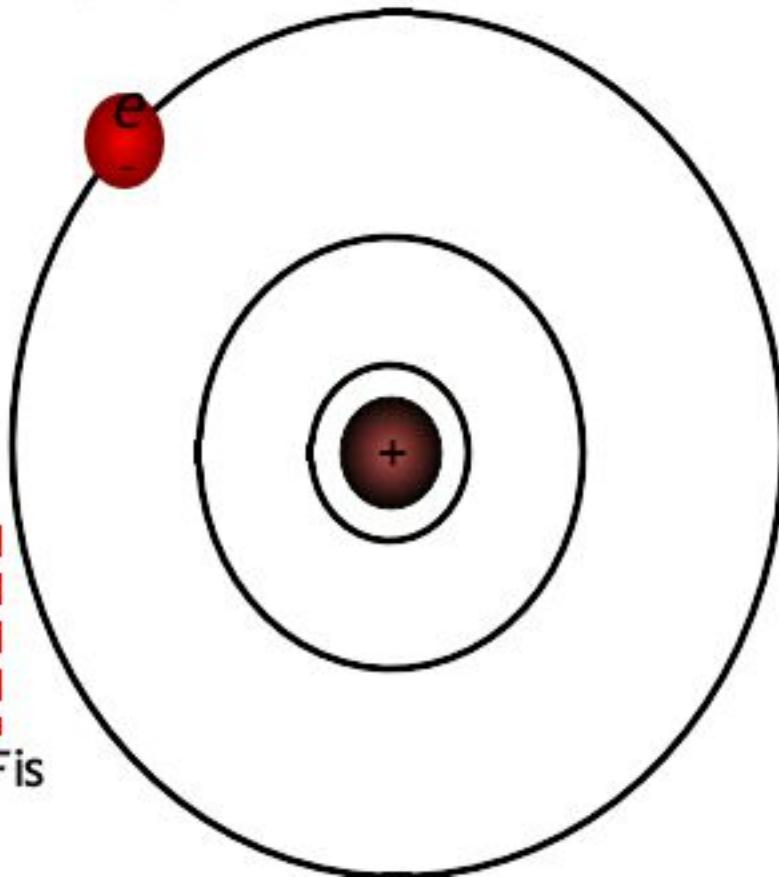
$$E_{\text{kin}} = \frac{1}{2} m \nu^2 = \frac{1}{2} m_e \left(\frac{ke^2}{\hbar n} \right)^2 = \frac{m k^2 e^4}{2 \hbar^2 n^2}$$

$$\begin{aligned} E_{\text{pot}} &= \int F dr = \int \frac{ke^2}{r^2} dr = -\frac{ke^2}{r} \\ &= -ke^2 \left(\frac{m k e^2}{\hbar^2 n^2} \right) = -\frac{m k^2 e^4}{\hbar^2 n^2} \end{aligned}$$

$$E = E_{\text{kin}} + E_{\text{pot}}$$

$$E = -\frac{m k^2 e^4}{2 \hbar^2 n^2} = -\frac{a^2 m_e c^2}{2 n^2} = -\frac{13.6 \text{ eV}}{n^2}$$

* Note: the sign of this equation assumes the force F is attractive.



Question:

Photon energy. Calculate the energy of a photon of blue light, $\lambda = 450 \text{ nm}$ in air (or vacuum).

Solution:

The photon has energy $E = hf$

Since $f = c/\lambda$, we have

$$E = hf = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.0 \times 10^8 \text{ m/s})}{(4.5 \times 10^{-7} \text{ m})} = 4.4 \times 10^{-19} \text{ J},$$

or $(4.4 \times 10^{-19} \text{ J}) / (1.60 \times 10^{-19} \text{ J/eV}) = 2.8 \text{ eV.}$

Energetics

Generally, the permitted energy state of the hydrogen atom of atomic number z and principal quantum number n is given by

$$E_n = -\frac{m_e e^4 z^2}{8\epsilon_0^2 h^2 n^2} \quad \text{J}$$

$$= -\frac{m_e e^3 z^2}{8\epsilon_0^2 h^2 n^2} \quad \text{eV}$$

For the hydrogen atom $z = 1$, the ionization potential E_i is given by

$$E_i = E_{\infty} - E_1 = -eV_i \text{ [J]} = E_1 \text{ [J]}$$

$$E_i = -V_i \text{ [eV]} = E_1 \text{ [eV]}$$

$$E_i = \frac{m_e e^4 z^2}{8 \varepsilon_0^2 h^2} \left[\frac{1}{1^2} - \frac{1}{\infty^2} \right] = \frac{m_e e^4 z^2}{8 \varepsilon_0^2 h^2} \quad [\text{J}]$$

$$= \frac{m_e e^3 z^2}{8 \varepsilon_0^2 h^2} \quad [\text{eV}]$$

$$-V_i = \frac{m_e e^3 z^2}{8\epsilon_0^2 h^2} \quad [\text{eV}]$$

$$V_i = -\frac{m_e e^3 z^2}{8\epsilon_0^2 h^2} \quad [\text{eV}]$$

For the hydrogen atom

$$E_1 = -\frac{m_e e^3 z^2}{8\epsilon_0^2 h^2} \quad [\text{eV}] \quad \text{and}$$

$$E_n = -\frac{m_e e^3 z^2}{8\epsilon_0^2 h^2 n^2} \quad [\text{eV}]$$

$$\Rightarrow E_n = \frac{E_1 z^2}{n^2} \quad [\text{eV}]$$

with

$$E_1 = -V_i \quad [\text{eV}]$$

$$E_n = -\frac{V_i z^2}{n^2} \quad [\text{eV}]$$

$$E_n = -\frac{13.6}{n^2} \quad [\text{eV}]$$

Holds for all hydrogenic atoms

For singly ionised Helium atom ($z = 2$),

$$E_n = \frac{-13.6 \times 4}{n^2} \text{ [eV]} = -\frac{54.4}{n^2} \text{ [eV]}$$

This is a lot of energy required.

Try that of Li: Now!!

THE HYDROGEN SPECTRUM

The wavelengths of the hydrogen spectrum are given by the Rydberg formula

$$1/\lambda = R \left(\frac{1}{n^2} - \frac{1}{n_u^2} \right)$$

R is the Rydberg Constant

$$R = 1.0967758 \times 10^{-3} \text{ per } \text{\AA}^\circ$$

The Hydrogen Spectrum (Cont'd)

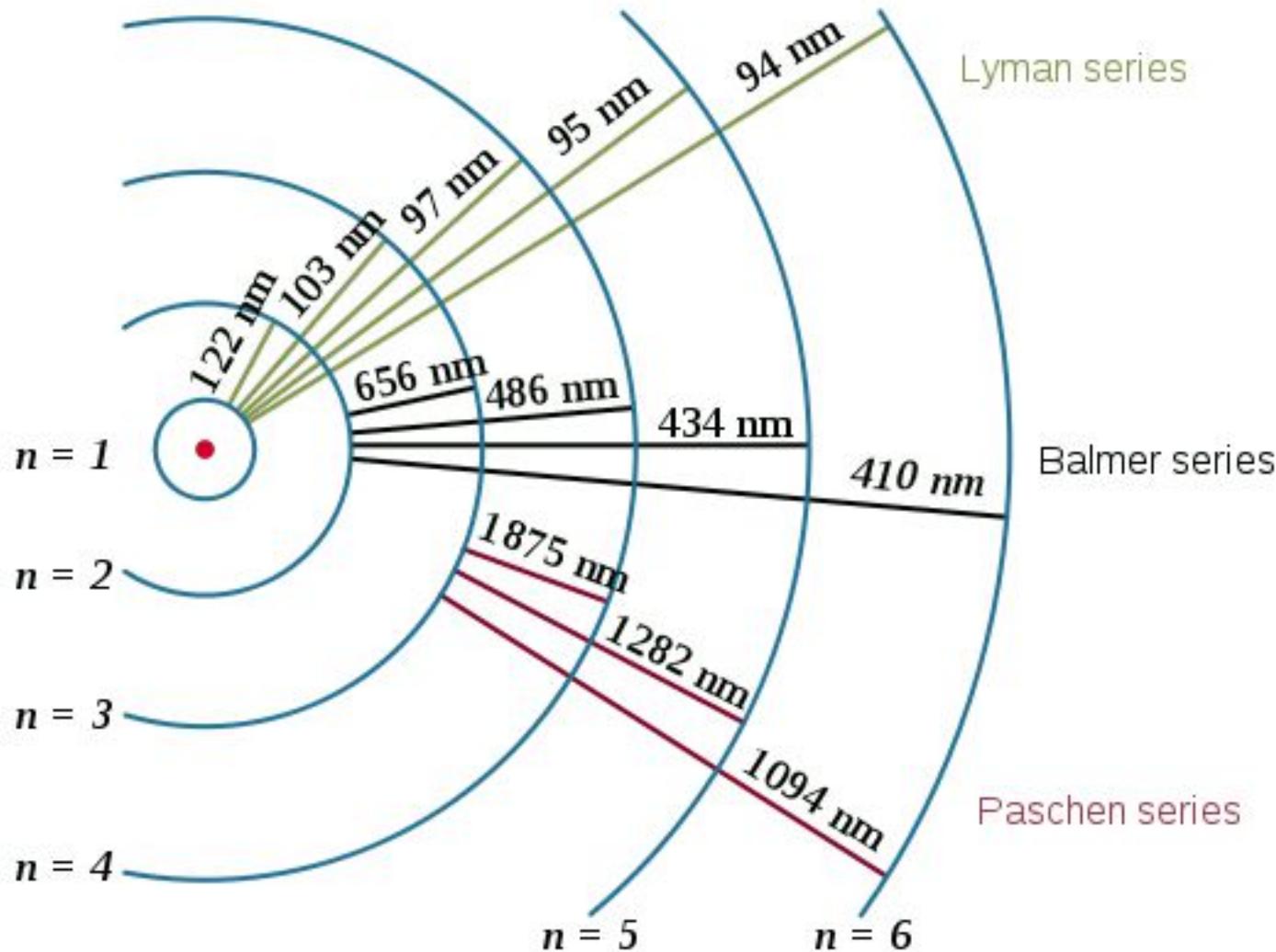
$n_l = 1$ and $n_u = 2, 3, 4 \dots$ gives the Lyman series
(ultraviolet region)

$n_l = 2$ and $n_u = 3, 4, 5 \dots$ gives the Balmer series
(optical region)

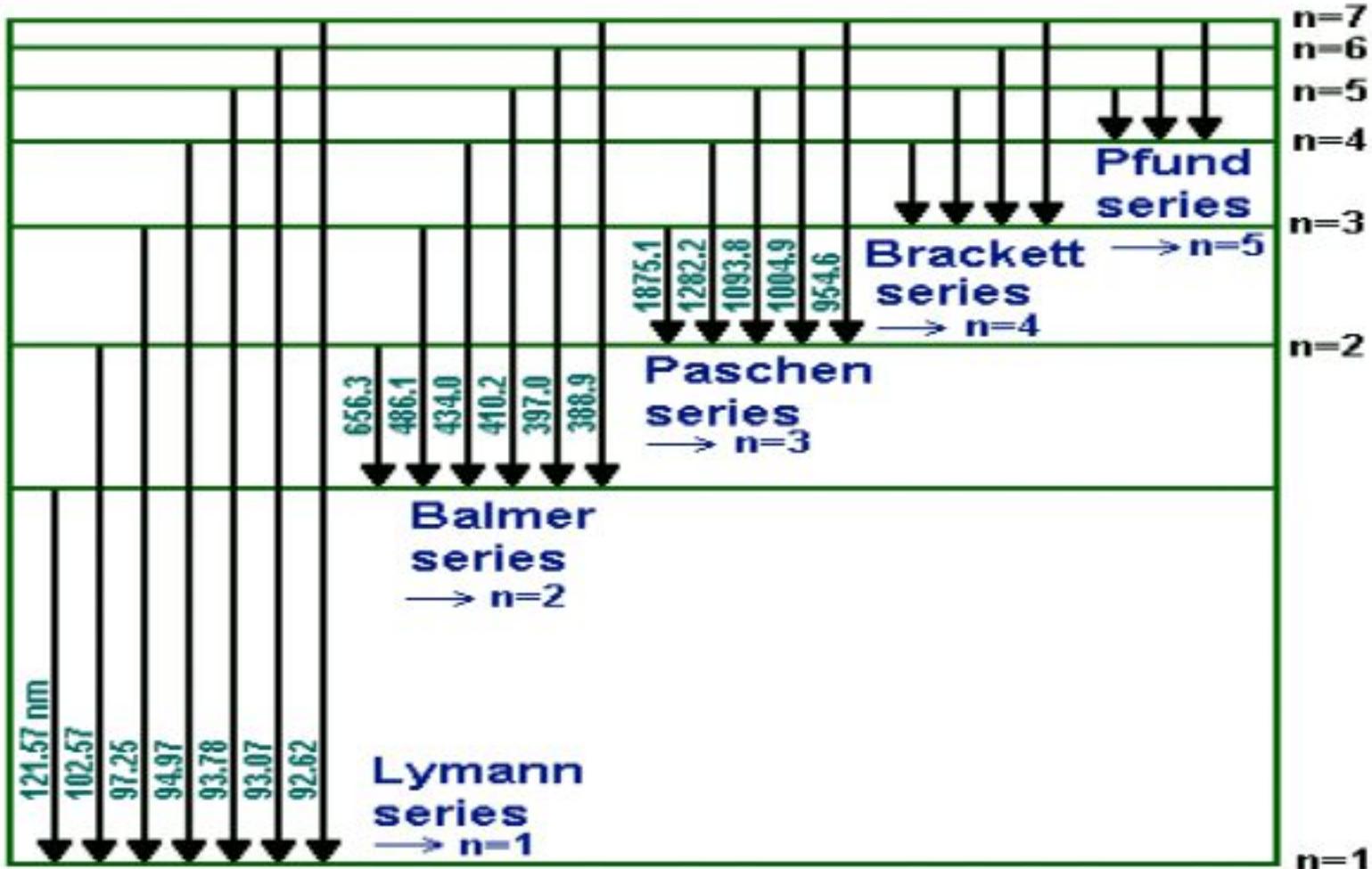
$n_l = 3$ and $n_u = 4, 5, 6 \dots$ gives the Paschen series
(infrared region)

$n_l = 4$ and $n_u = 5, 6, 7 \dots$ gives the Brakett series (far infrared region)

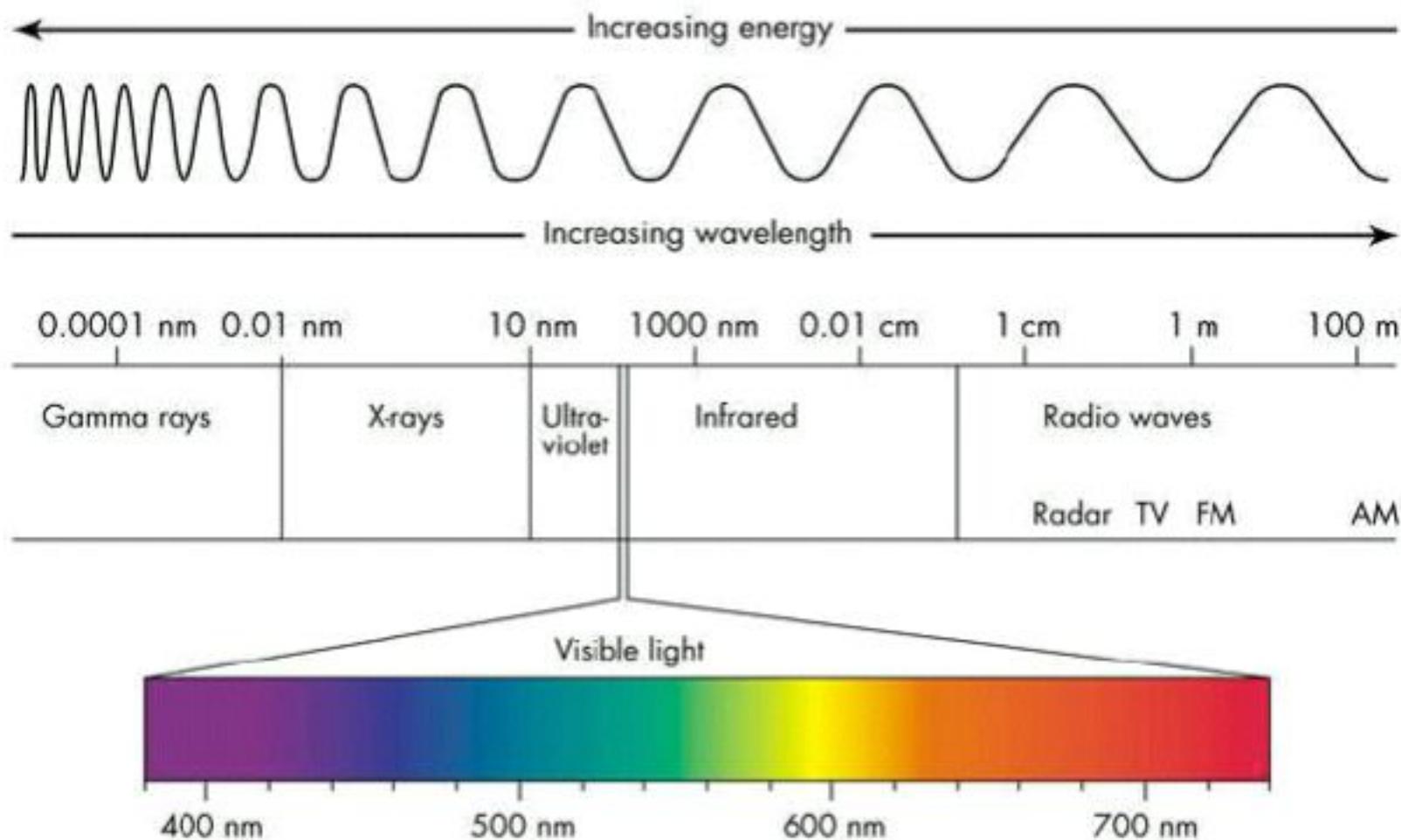
The Hydrogen Spectrum (Cont'd)



The Hydrogen Spectrum (Cont'd)



The Hydrogen Spectrum



The Electromagnetic Spectrum

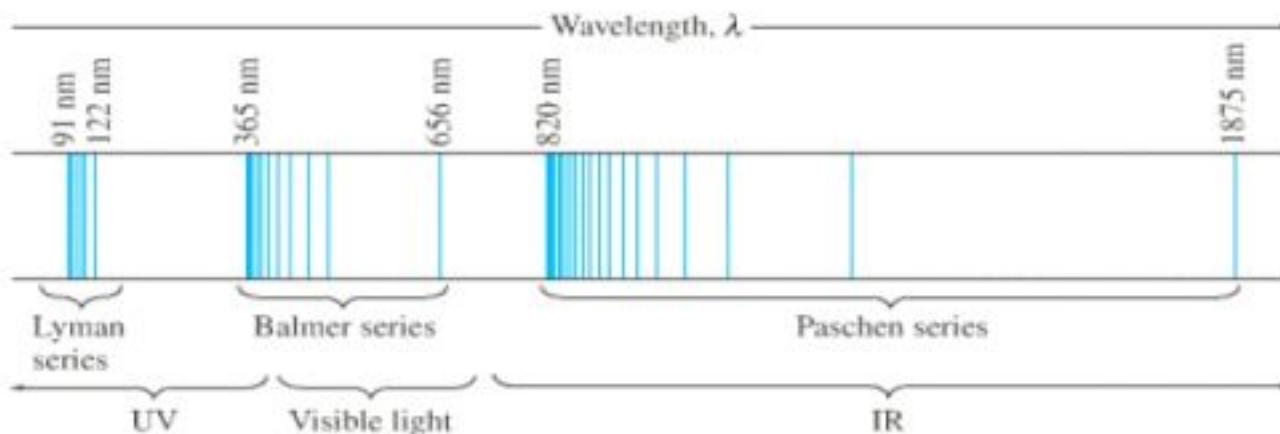
Question: **Wavelength of a Lyman line.** Use Fig. 27–27 to determine the wavelength of the first Lyman line, the transition from $n = 2$ to $n = 1$. In what region of the electromagnetic spectrum does this lie?

Solution:

In this case, $hf = E_2 - E_1 = \{-3.4 \text{ eV} - (-13.6 \text{ eV})\} = 10.2 \text{ eV} = (10.2 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV}) = 1.63 \times 10^{-18} \text{ J}$. Since $\lambda = c/f$, we have

$$\lambda = \frac{c}{f} = \frac{hc}{E_2 - E_1} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{1.63 \times 10^{-18} \text{ J}} = 1.22 \times 10^{-7} \text{ m},$$

or 122 nm, which is in the UV region of the EM spectrum



Question :

Wavelength of a Balmer line. Determine the wavelength of light emitted when a hydrogen atom makes a transition from the $n = 6$ to the $n = 2$ energy level according to the Bohr model.

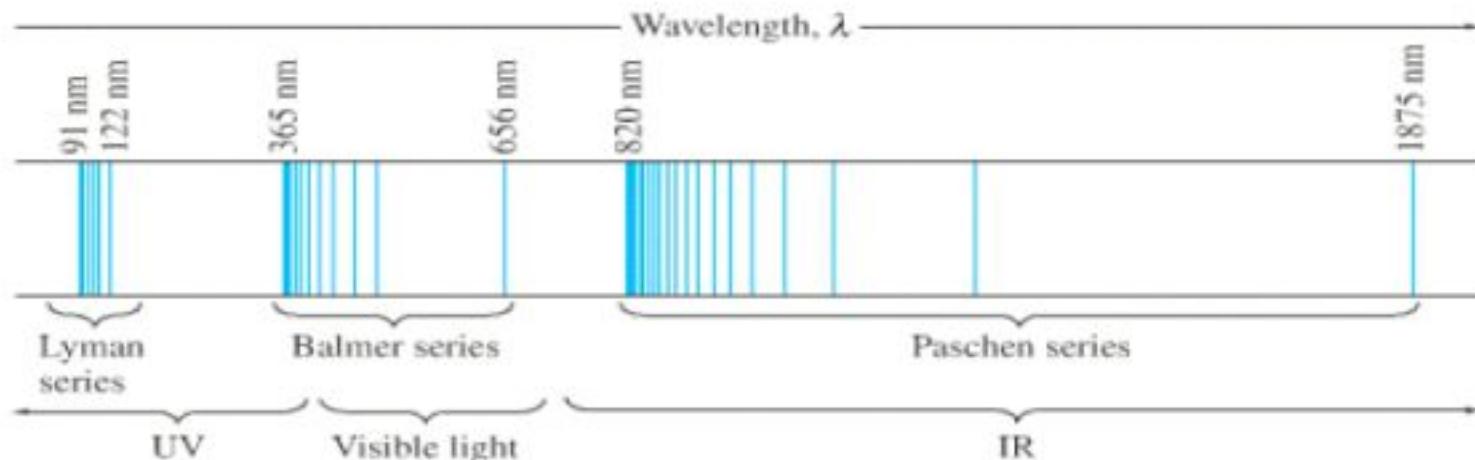
Solution:

$$\frac{1}{\lambda} = R \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$$

$$R = 1.097 \times 10^7 \text{ m}^{-1}.$$

$$\frac{1}{\lambda} = (1.097 \times 10^7 \text{ m}^{-1}) \left(\frac{1}{4} - \frac{1}{36} \right) = 2.44 \times 10^6 \text{ m}^{-1}.$$

$$\text{So } \lambda = 1/(2.44 \times 10^6 \text{ m}^{-1}) = 4.10 \times 10^{-7} \text{ m or } 410 \text{ nm.}$$



Quantum Mechanics Concepts

The Uncertainty Principle

Heisenberg (1924 - 25)

- In the period 1924-25 Heisenberg created theory of Quantum Mechanics.
- It overcame some of the problems with Bohr's theory.
- It was first developed using noncommuting algebra and then by matrices
- It was difficult to apply them practically.

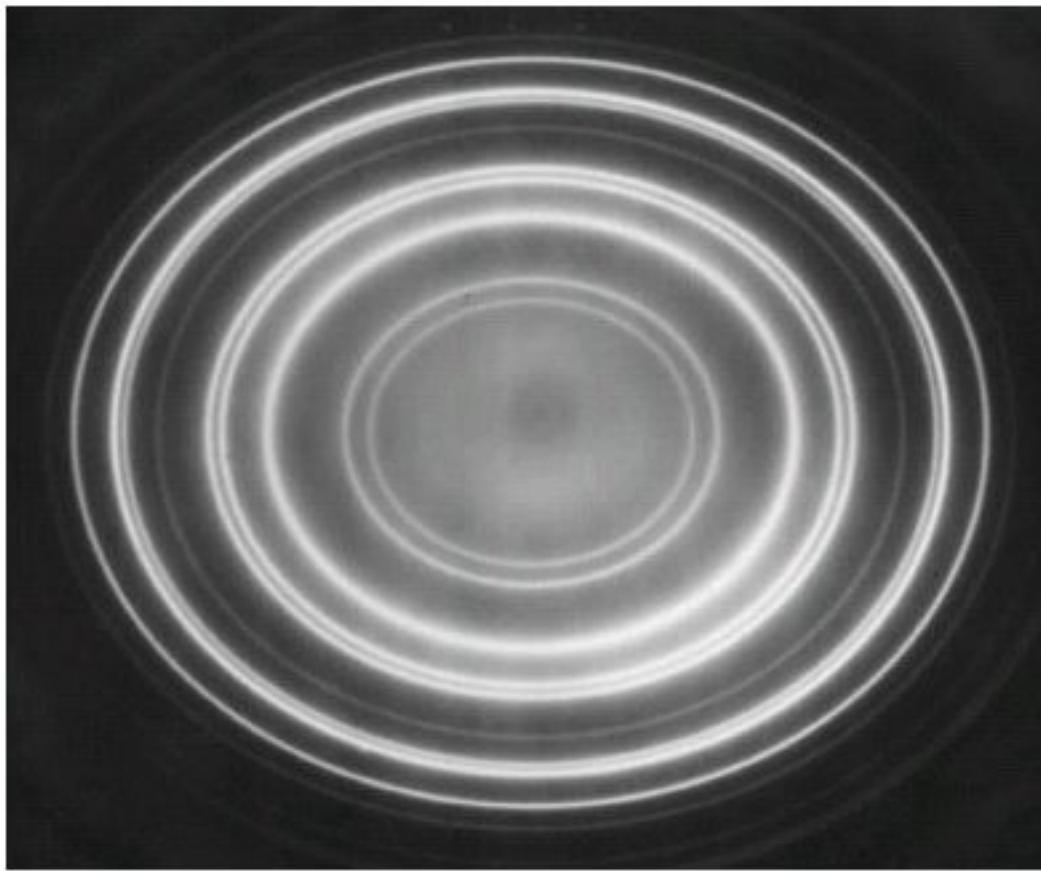
The Uncertainty Principle

- We start with the observation of an experiment showing *electron diffraction* (Davisson and Germer 1925).
- When a beam of electrons passes through a crystal a diffraction pattern similar to what is formed by an EM-wave is produced.

The Uncertainty Principle

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- When a beam of electrons passes through a crystal a diffraction pattern similar to what is formed by an EM-wave is produced.
- That is a series of maxima and minima.

The Uncertainty Principle



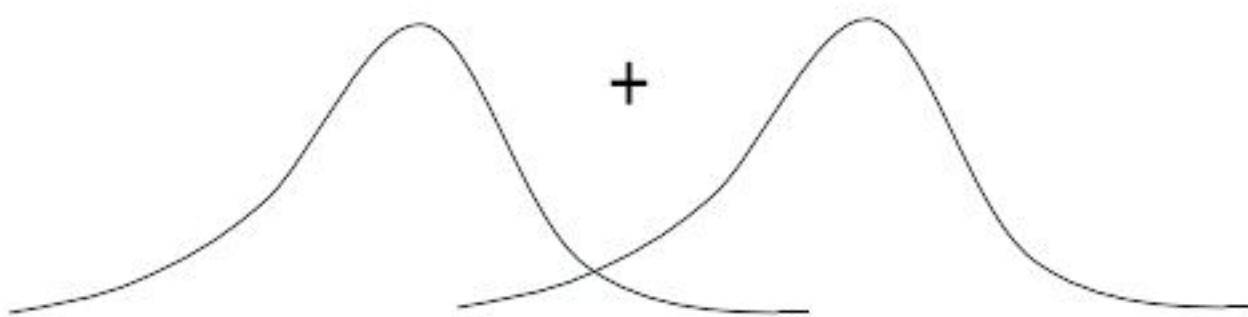
The Uncertainty Principle

- Consider the following thought experiment.
- Take the set up for Young's double slit experiment.

The Uncertainty Principle

- If we observe a beam of electrons through one slit with the other closed we get some intensity pattern.
- Similarly if we now open that slit and cover the other a similar pattern is observed.
- Classically, if both slits are open a pattern formed by a superposition should be the result.

The Uncertainty Principle



The Uncertainty Principle

- There is no such concept as the path of a particle.
- This forms the content of what is called the uncertainty principle.
- The fact that an electron has no definite path means it also has no characteristics (quantities defining the motion).
- Only when the electron interacts with a classical object can its characteristics be defined

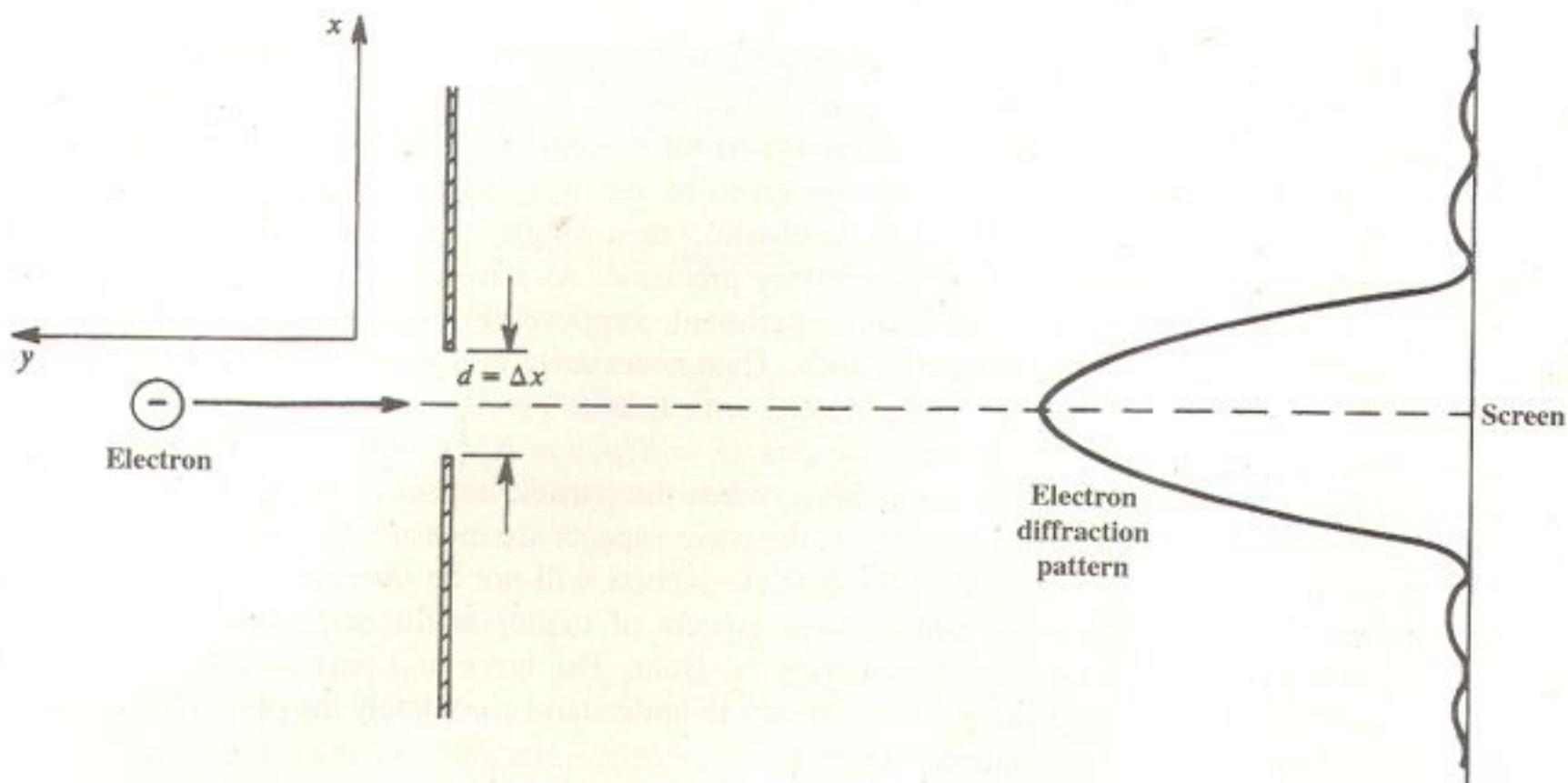
The Uncertainty Principle

- The interaction between a classical object and a quantum particle is called a measurement.
- The interaction between a classical object and a quantum particle is called a measurement.
- The classical object is called the apparatus.

The Uncertainty Principle

- The measuring process in QM always effects the subjected quantum particle.
- The more exact the measurement the greater the effect.
- Reducing the accuracy reduces the effect on the particle.
- It is impossible in principle to make the effect arbitrarily small.

Heisenberg Uncertainty Principle



- The x-position of the particle, upon (and before) entering the slit will have been determined up to an *uncertainty* Δx given by $\Delta x = d$.
- The smaller we make the slit width, the smaller is the uncertainty in the x-position of the body, and hence the more precisely is its location known.
- Because of the wave nature of matter the particle will be diffracted as it passes through the slit.
- Though it is not possible to predict where on the screen it will strike, as long as the body strikes the screen *somewhere* you know that it has gone through the slit. .
- The diffraction process, however, has an effect on the momentum of the particle. .

Heisenberg Uncertainty Principle

- The uncertainty principle may be stated as:
If a measurement of position is made with precision Δx and a simultaneously measurement of momentum is made with precision Δp , then the product of the uncertainties can not be smaller than the order of \hbar .

Heisenberg Uncertainty Principle:

$$\Delta p_x \Delta x \geq \frac{h}{2\pi}$$

$$\Delta E \Delta t \geq \frac{h}{2\pi}$$

Question:

Position uncertainty of electron. An electron moves in a straight line with a constant speed $v = 1.10 \times 10^6$ m/s which has been measured to a precision of 0.10%. What is the maximum precision with which its position could be simultaneously measured?

Solution:

The momentum of the electron is

$$p = mv = (9.11 \times 10^{-31} \text{ kg}) \cdot (1.10 \times 10^6 \text{ m/s}) = 1.00 \times 10^{-24} \text{ kg} \cdot \text{m/s},$$

The uncertainty in the momentum is $\Delta p = 0.0010p$.

Hence, $\Delta p = 1.0 \times 10^{-27} \text{ kg} \cdot \text{m/s}$.

From the uncertainty principle, the best simultaneous position measurement will have an uncertainty of

$$\Delta x \approx \frac{\hbar}{\Delta p} = \frac{1.06 \times 10^{-34} \text{ J} \cdot \text{s}}{1.0 \times 10^{-27} \text{ kg} \cdot \text{m/s}} = 1.1 \times 10^{-7} \text{ m},$$

or 110 nm.

Question:

Position uncertainty of a baseball. What is the uncertainty in position, imposed by the uncertainty principle, on a 150-g baseball thrown at (93 ± 2) mph = (42 ± 1) m/s?

Solution:

The uncertainty in the speed is $\Delta v = 1$ m/s. We multiply Δv by m to get Δp and then use the uncertainty principle, solving for Δx .

The uncertainty in the momentum is

$$\Delta p = m \Delta v = (0.150 \text{ kg})(1 \text{ m/s}) = 0.15 \text{ kg} \cdot \text{m/s}.$$

Hence the uncertainty in a position measurement could be as small as

$$\Delta x = \frac{\hbar}{\Delta p} = \frac{1.06 \times 10^{-34} \text{ J} \cdot \text{s}}{0.15 \text{ kg} \cdot \text{m/s}} = 7 \times 10^{-34} \text{ m}.$$

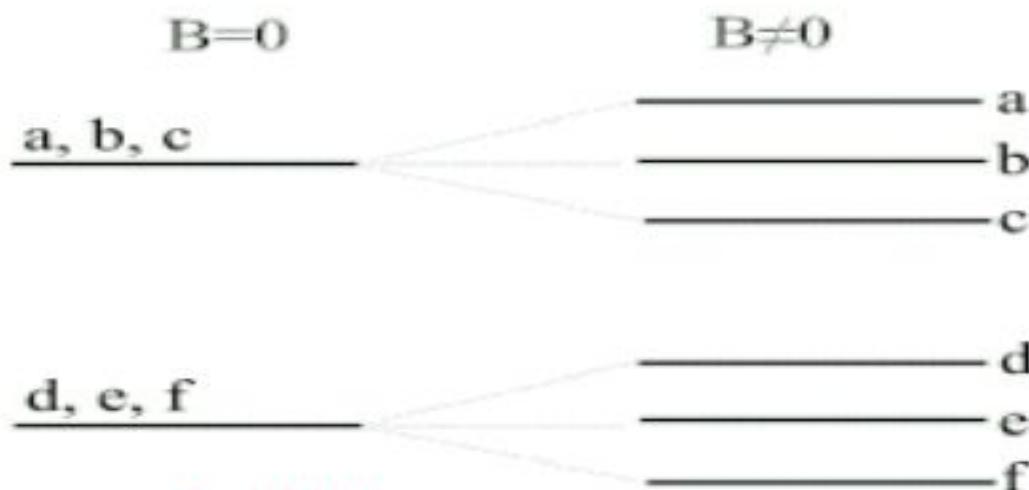
THE ZEEMAN EFFECT

The Zeeman effect is the splitting of a spectral line into several components in the presence of a static magnetic field.

The splitting is due to the interaction between the magnetic field and the magnetic dipole moment associated with the orbital angular momentum.

In most atoms, there exist several electronic configurations that have the same energy (degeneracy), so that transitions between different pairs of configurations correspond to a single spectral line.

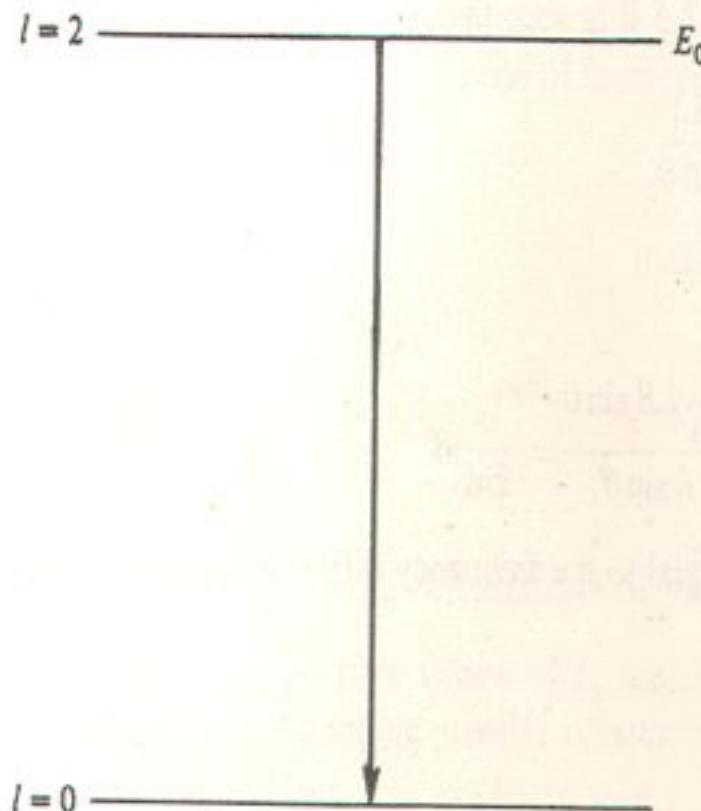
The presence of a magnetic field breaks the degeneracy, since it interacts in a different way with electrons with different quantum numbers. This modifies their energies. As a result, there are several configurations with the different energies, which give rise to several very close spectral lines.



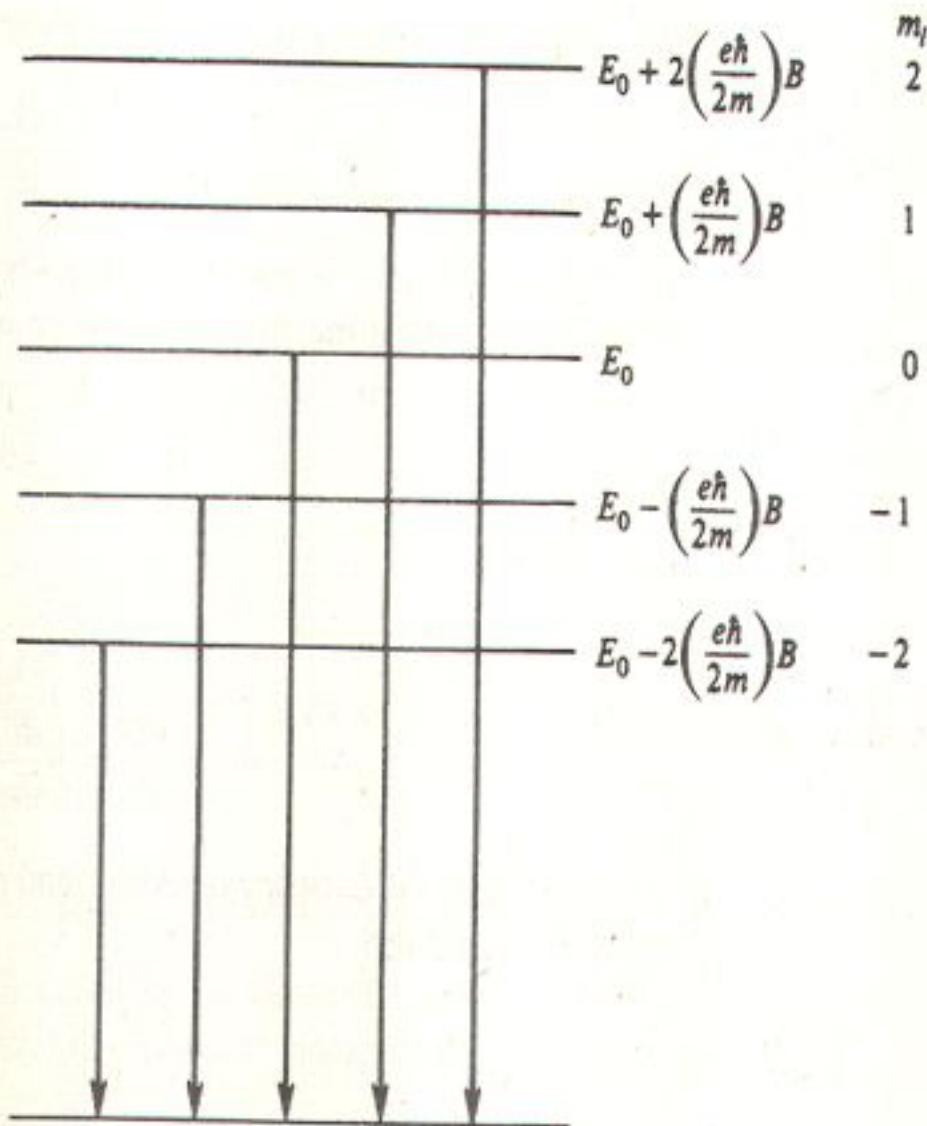
Without a magnetic field, configurations a, b and c have the same energy, as do d, e and f.

The presence of a magnetic field splits the energy levels. A line produced by a transition from a, b or c to d, e or f now will be several lines between different combinations of a, b, c and d, e, f.

Not all transitions will be possible, as regulated by the transition rules.



(a) Single transition without
an external magnetic field



(b) Five transitions with an
applied external magnetic field

Splitting of Spectra lines

Zeeman splitting is observed in two different cases:

1. when the summed spin (S) of the electrons of the atom is equal to zero, but the orbital angular momentum (L) is different than zero,
 $S=0, L \neq 0$
2. when the spin and the orbital angular momentum are different from zero and the external magnetic field is strong enough ,
 $L \neq 0, S \neq 0$

The Zeeman effect is very important in applications such as nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, magnetic resonance imaging (MRI) and Mössbauer spectroscopy and also used by astronomers to measure the magnetic field of the Sun and other stars.

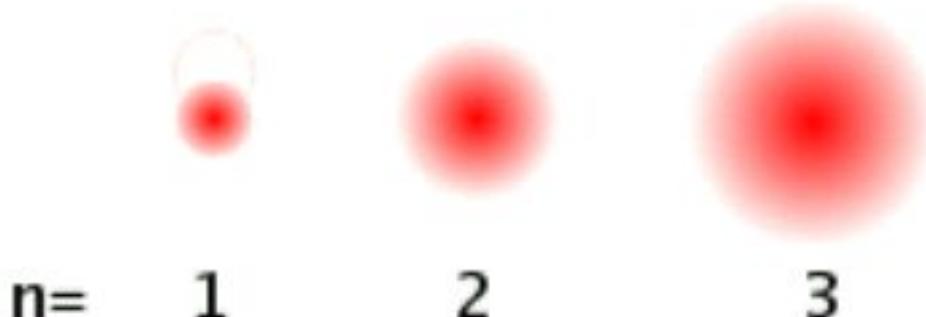
Electrons in an Atom

- Electrons under the influence of positive charges of atomic nuclei are confined to the neighbourhood of the atomic nuclei.
- The motion of these electrons has been treated as **waves**.
- Equations that describe the **wave motions** have been applied to represent the electrons.
- Solutions to the equations lead to wave functions.
- Confinement of electron in the neighbourhood of the atomic nuclei, these solutions are associated with some integers called **quantum numbers**.
- For the descriptions of electrons in an atom, we rely on quantum numbers and **wave functions**.
- Wave functions are used to describe the shape of the electron cloud e.g. in a chemical bonding.

The Quantum Numbers n, m, l

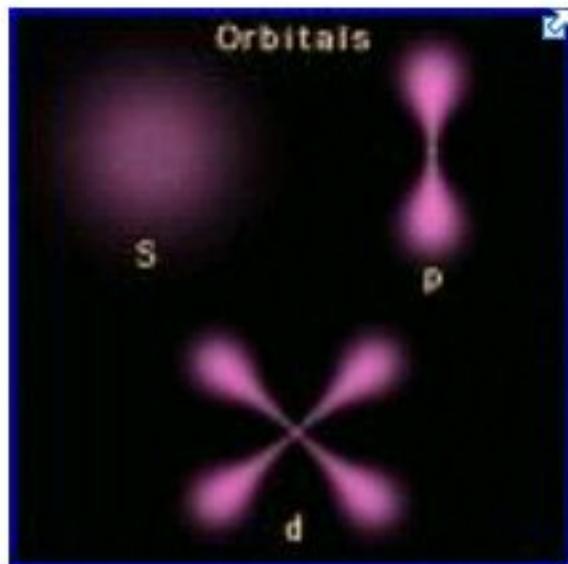
QN n

The principle quantum number *n* most affects the energy of the state of the electron. It gives the relative **size** and **energy** of atomic orbitals.



QN /

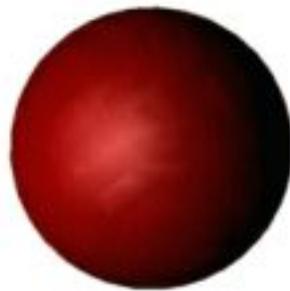
The angular momentum quantum number l is related to the directional property of the wave-function. It gives the **shape** of the orbitals.



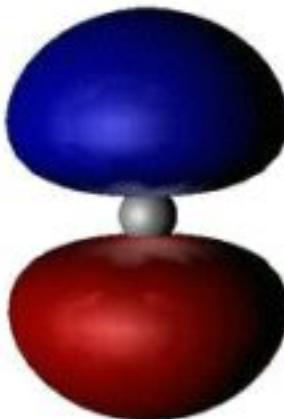
It ranges from 0 to $n-1$. For a spherical wave, $l=0$, the number of nodal planes is equal to l .

Related to /are 4 orbitals. These are the *s*, *p*, *d* and *f* orbitals.
They are described briefly as follows:

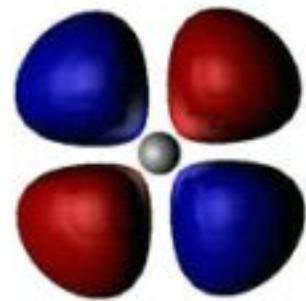
1. S orbital - 0 = "sphere"



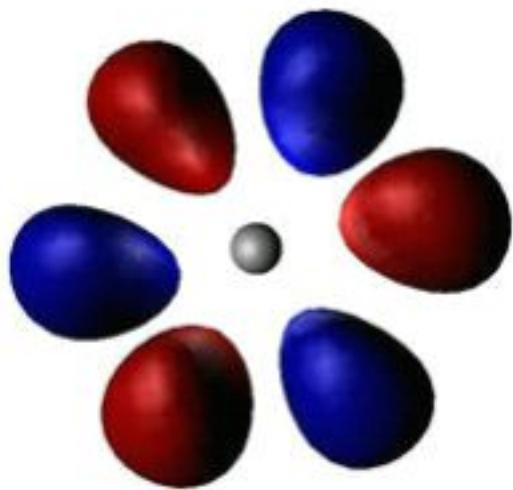
2. P orbital - 1= "polar"



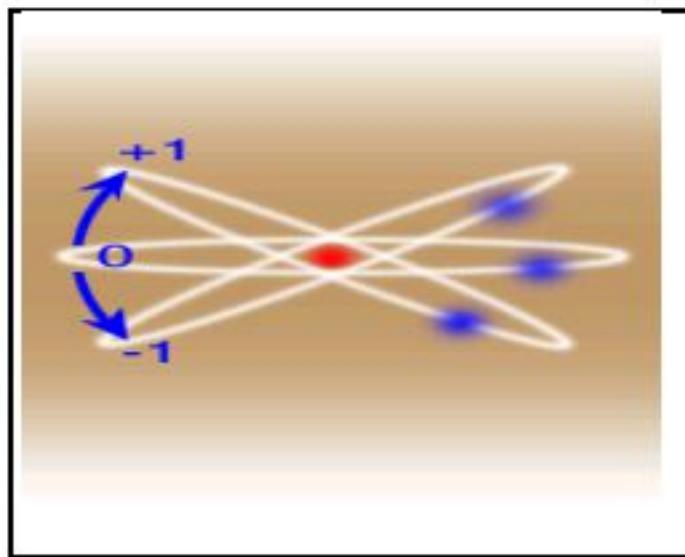
3. D orbital - 2 = "dual polar"



4. F orbital - 3 = "irregular"



The angular momentum ℓ is further quantized by the quantum number m_ℓ based on the orientation of the orbital angular momentum. Since the orientation is related to ℓ , m_ℓ has values ranging from $-\ell$ to ℓ i.e. $-\ell$ - $(\ell-1)$, ... 0, ..., $\ell-1$, and ℓ .



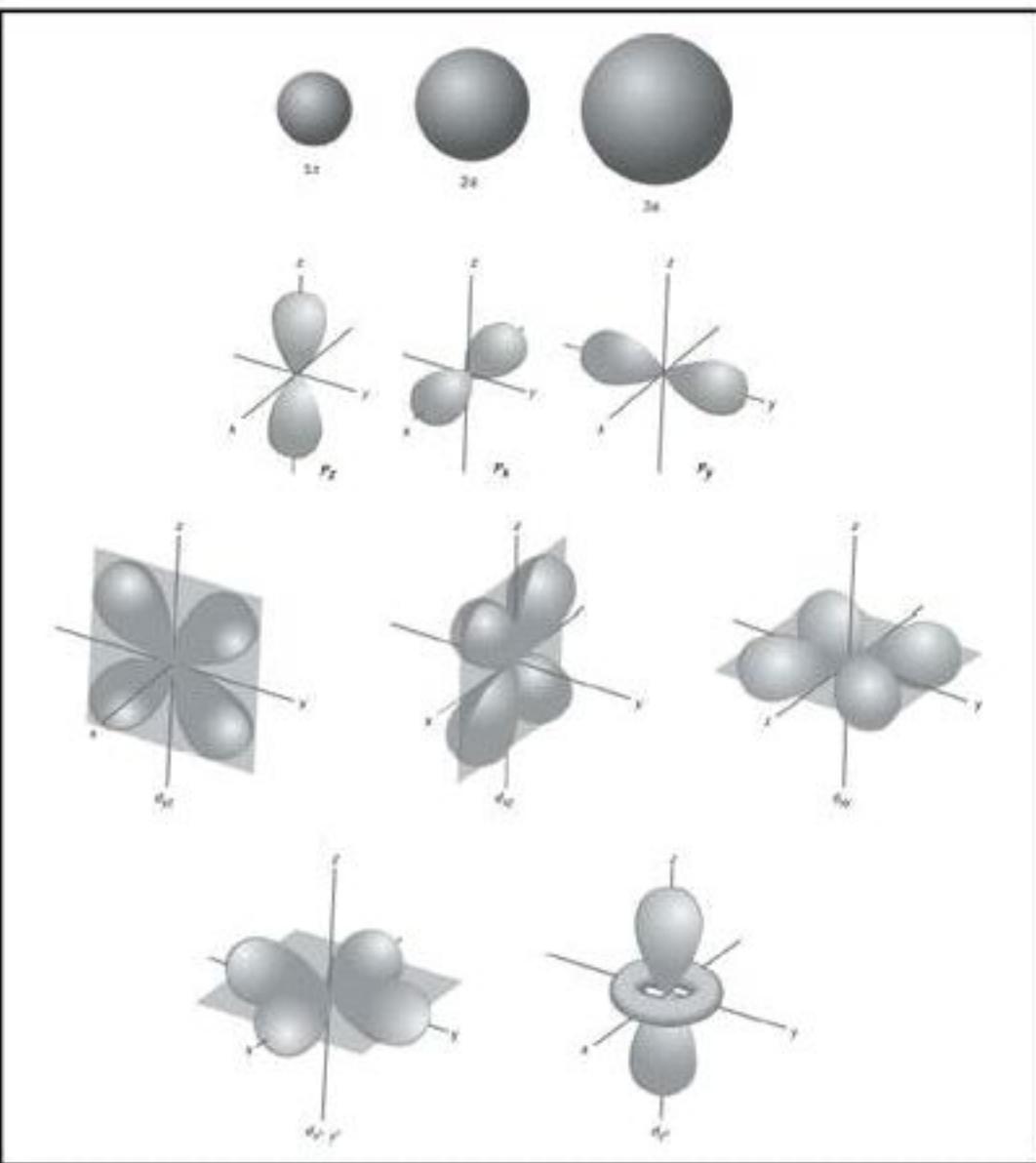
Rules for n,m, l

The three quantum numbers n, l, m follow the rules:

1. For the principal quantum number n (1,2,3 ...),
 - i. the azimuthal quantum number $l = 0, 1, 2, \dots, n-1$
 - ii. the magnetic quantum number $m_l = -l, -(l-1), \dots, (l-1), l$
2. Rules are algorithms, by which we generate possible quantum numbers. The lowest value of n is 1 (NOT zero). For $n = 1$, the only possible value for quantum number l is 0, and $m_l = 0$. Each set of quantum numbers is called a **state**. Thus, for $n = 1$, there is only one state (1,0,0). The states are represented by symbols, and special symbols have been used to represent the quantum number l as follows:
 - i. $l = 0, 1, 2, 3, 4, \dots$
 - ii. symbol = s, p, d, f, g, ...
 - iii. Using symbols, the valid quantum states can be listed in the following manner:

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f 5g
6s 6p 6d 6f 6g 7h
7s 7p 7d 7f 7g 7h 8i

- iv. $l = 0 \rightarrow$ s, $l = 1 \rightarrow$ p and $l = 2 \rightarrow$ d orbitals
- v. There are $2l+1$ values of m_l , and thus $2l + 1$ allowed orientations or quantum states of the nucleus. All have the same energy in the absence of a magnetic field.



For hydrogen-like atoms, that are atoms or ions with one electron, the energy level is solely determined by the principle quantum number n . and the energy levels of the sub-shells np and nd etc. are the same as the ns .

Question :

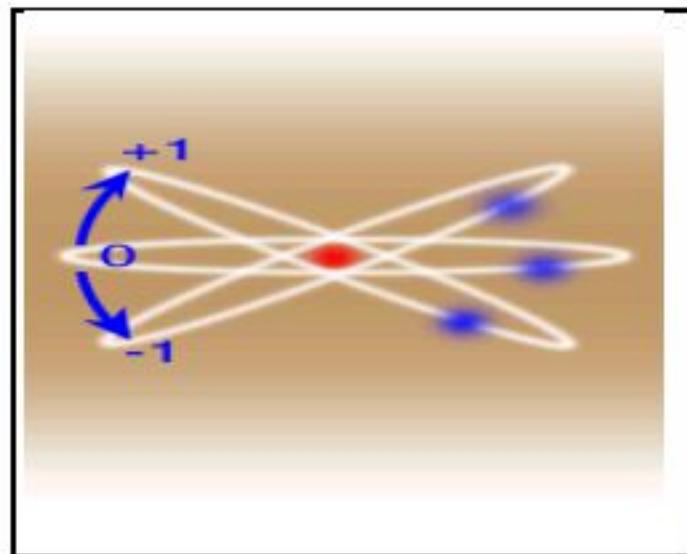
How many distinct (n, l, m_l) states of the hydrogen atom with $n = 3$ are there? Find the energy of these states.

Solution:

When $n = 3$, l can be 0, 1, or 2. When $l = 0$, m_l can be only 0 (1 state). When $l = 1$, m_l can be $-1, 0$, or 1 (3 states). When $l = 2$, m_l can be $-2, -1, 0, 1$, or 2 (5 states). The total number of (n, l, m_l) states with $n = 3$ is therefore $1 + 3 + 5 = 9$.

The energies of these states are all the same because the energy depends only on n .

$$E_3 = \frac{-13.60 \text{ eV}}{3^2} = -1.51 \text{ eV}$$



CHEMICAL BONDING

Ionic Bonding

The ionic bonding is formed if **an electron** is transferred from the less electronegative element to the more electronegative.

The ions of this elements differ by one electronic charge and are thus attracted to one another.

Some ions may gain or lose more than one electron.

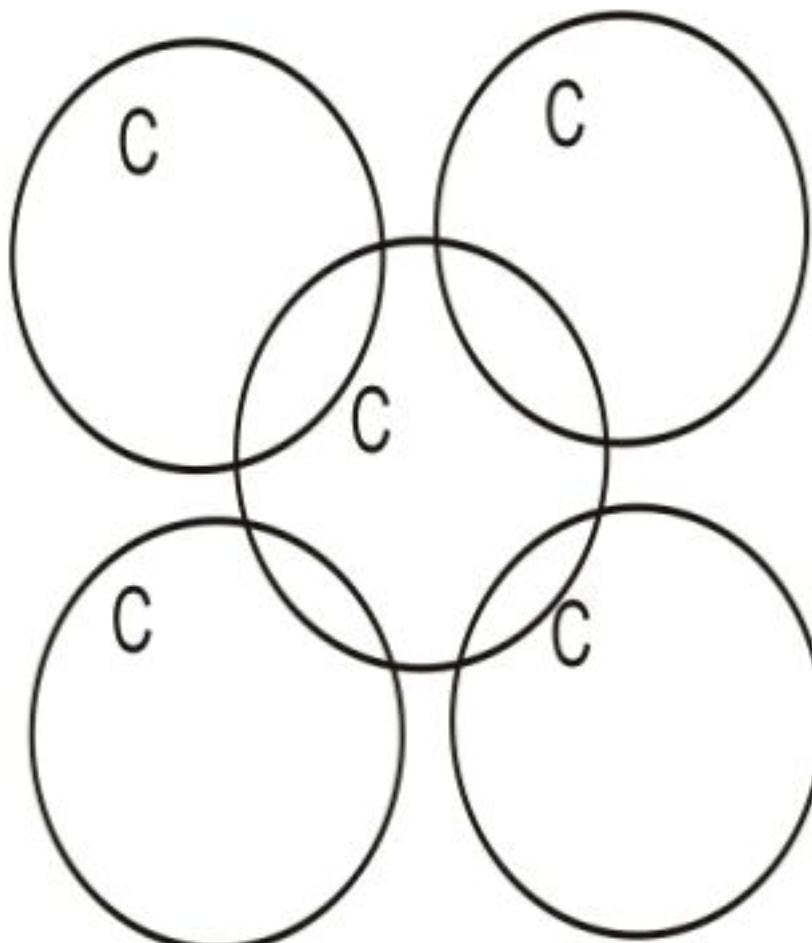
Eg: Bonding in NaCl

Covalent Bonding

Covalent materials are formed from bonding electron sharing between two or more atoms.

Eg: Carbon atoms form covalent bond with other carbon atoms, because each carbon atoms has four outer electrons which can be share with other four carbon atoms

Materials such as Diamond and polyethylene are covalent material.

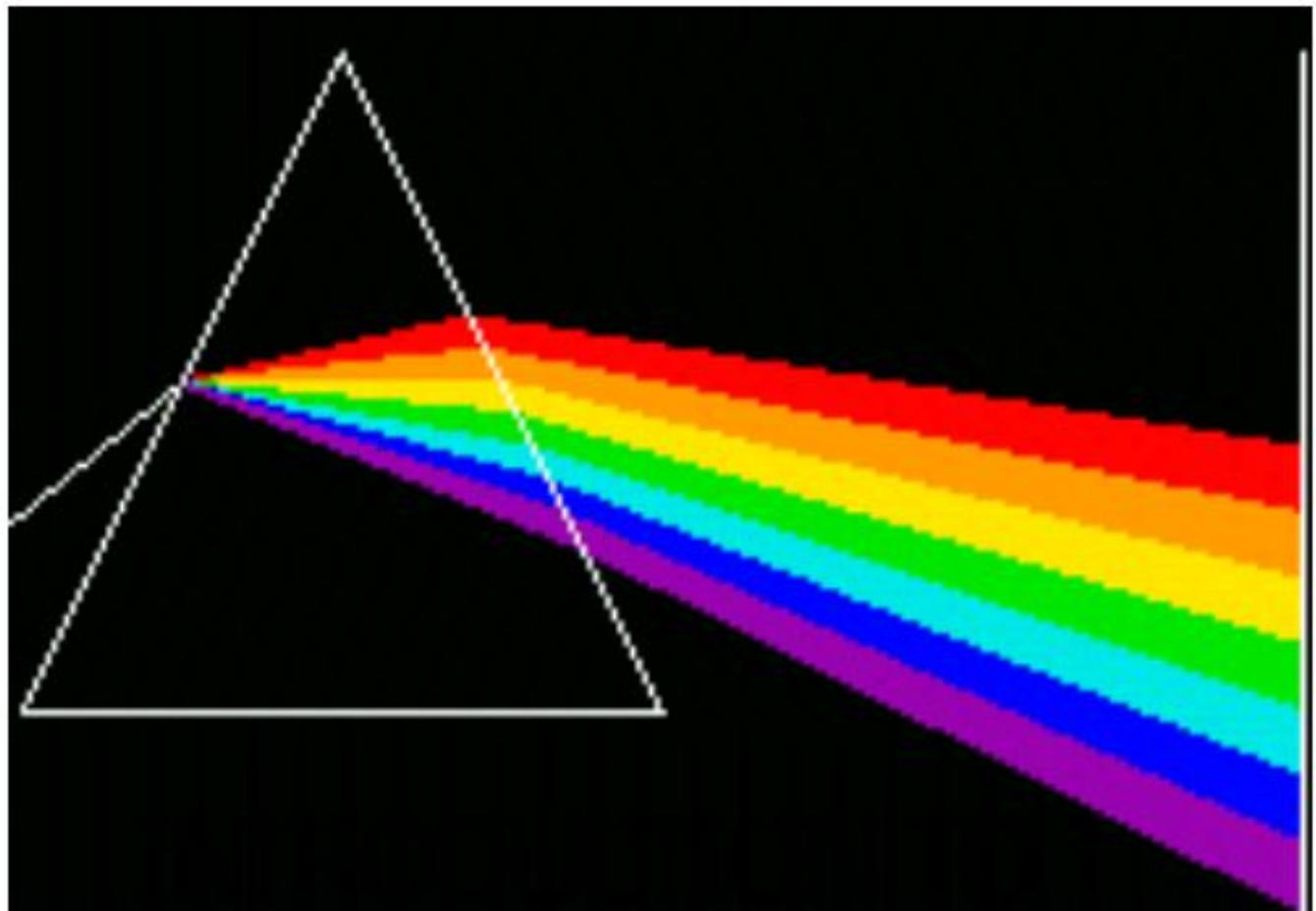


Van der Waal's Bond

Any two separated molecules will be attracted to one another by a **weak electrostatic force** called the Van der Waal's force.

This weak force arises from the interaction of the instantaneous electric dipole moments of the molecules. Two polar molecules with permanent electric dipole moments, eg. water molecules bond due to Van der Waal force.

At any instant **more electrons may appear on one side of the molecule than the other and the center of the negative charge distribution is slightly displaced (distorted) from the positive charge on the nucleus.** This give room for attraction of the electric dipoles with a weak force called the Van der Waal's force



SPECTROSCOPY

SPECTROSCOPY

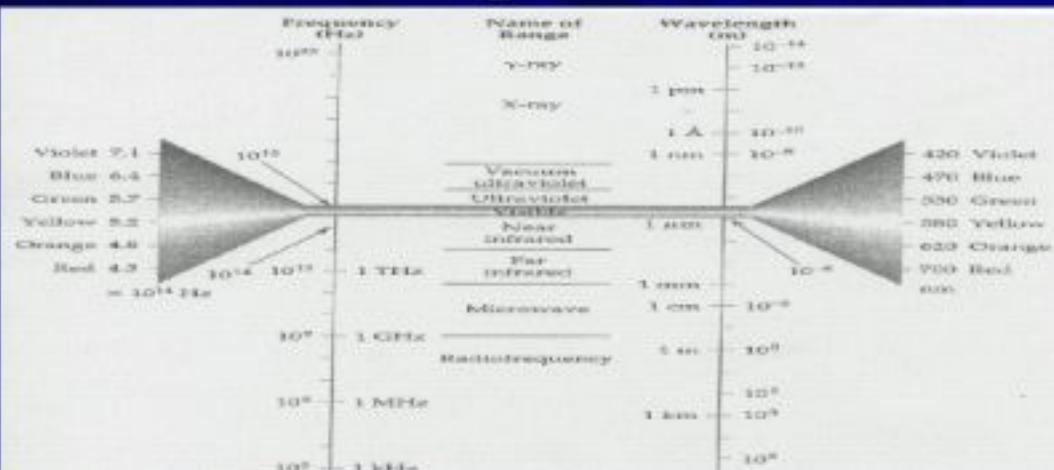
What is It?

Spectroscopy is the study of how 'species' (i.e., atoms, molecules, solutions) interact with electromagnetic radiation.

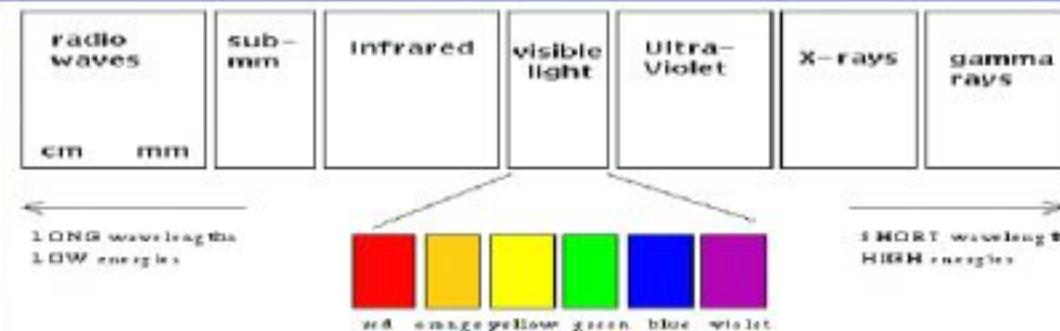
Exactly how the radiation interacts with matter is directly dependent on the energy of the radiation

The electromagnetic radiation absorbed, emitted or scattered by the molecule is analyzed.

Electromagnetic Radiation



Radiation Spectrum



Spectroscopy

A photograph of a prism at the bottom of a dark frame. Light enters from the left and is dispersed into a spectrum of colors (red, orange, yellow, green, blue, purple) exiting through the prism on the right.

The higher energy ultraviolet and visible wavelengths affect the energy levels of the outer electrons.

Infrared radiation is absorbed by matter resulting in rotation and/or vibration of molecules.

Radio waves are used in nuclear magnetic Resonance and affect the spin of nuclei in a magnetic field.

Particle Nature of Radiation

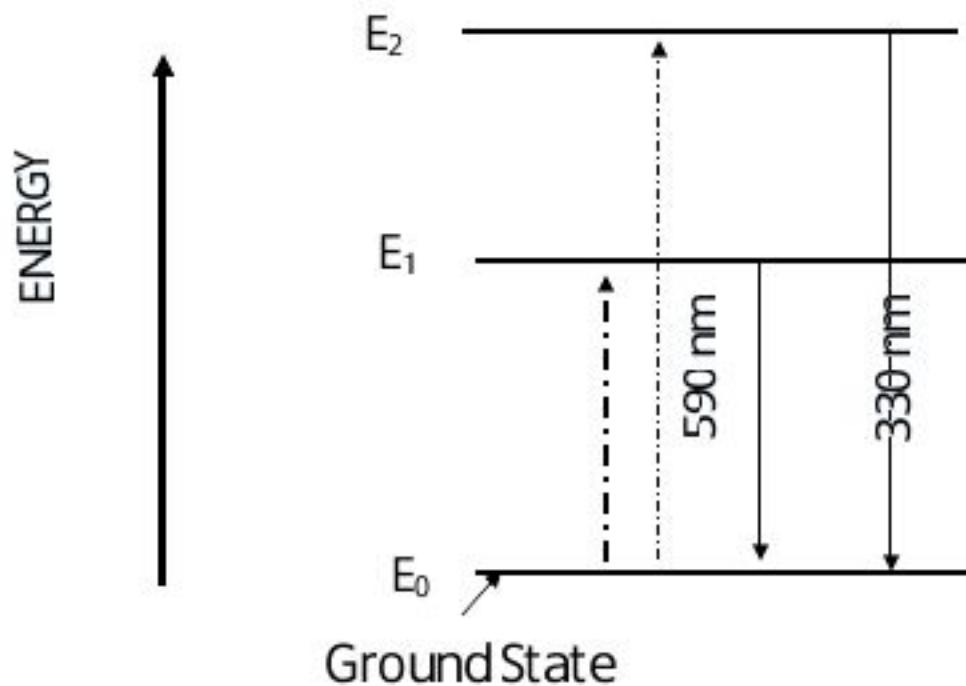
Electromagnetic radiation is also described as having the properties of particles.

Molecules exist in a certain number of possible states corresponding to definite amounts of energy.

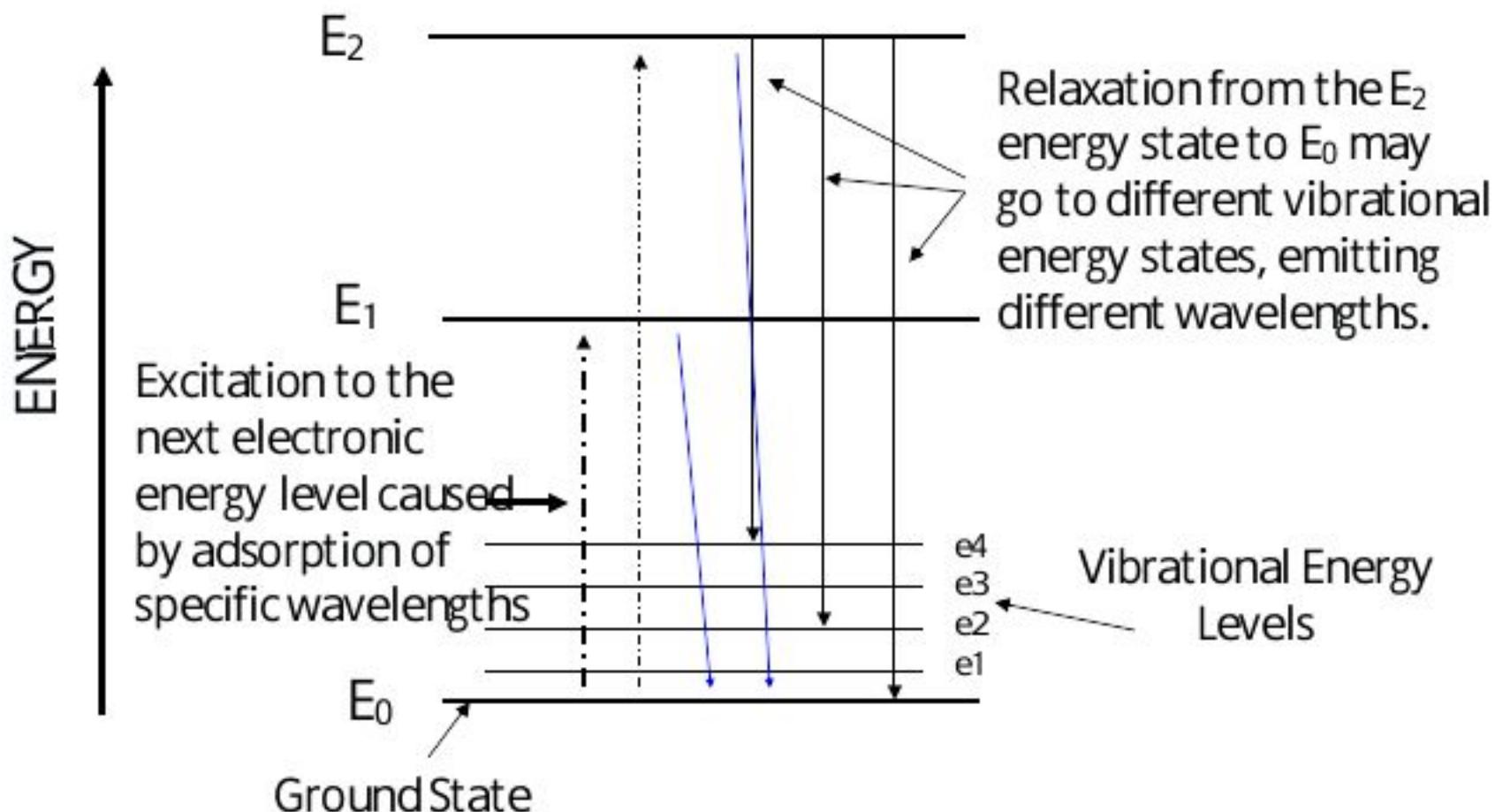
Molecules can absorb energy and change to a higher energy level called the excited state.

The amount of energy absorbed in this transition is exactly equal to the energy difference between the states.

Energy Level Diagram for an Atom of Sodium



Energy Level Diagram for a Simple Molecule



UV/Vis Spectroscopy

Visible (380-780 nanometers)

Ultraviolet (UV) (10 – 380 nanometers).

Below about 200 nm, air absorbs the UV light
and instruments must be operated under a vacuum

How many μm is 780 nanometers?

What is the corresponding wave number?

Wavelengths Absorbed by Functional Groups

Chromophore	Example	Excitation	λ_{\max} , nm	ϵ	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$	290	15	hexane
		$\pi \rightarrow \pi^*$	180	10,000	hexane
N=O	Nitromethane	$n \rightarrow \pi^*$	275	17	ethanol
		$\pi \rightarrow \pi^*$	200	5,000	ethanol
C-X X=Br X=I	Methyl bromide	$n \rightarrow \sigma^*$	205	200	hexane
	Methyl iodide	$n \rightarrow \sigma^*$	255	360	hexane

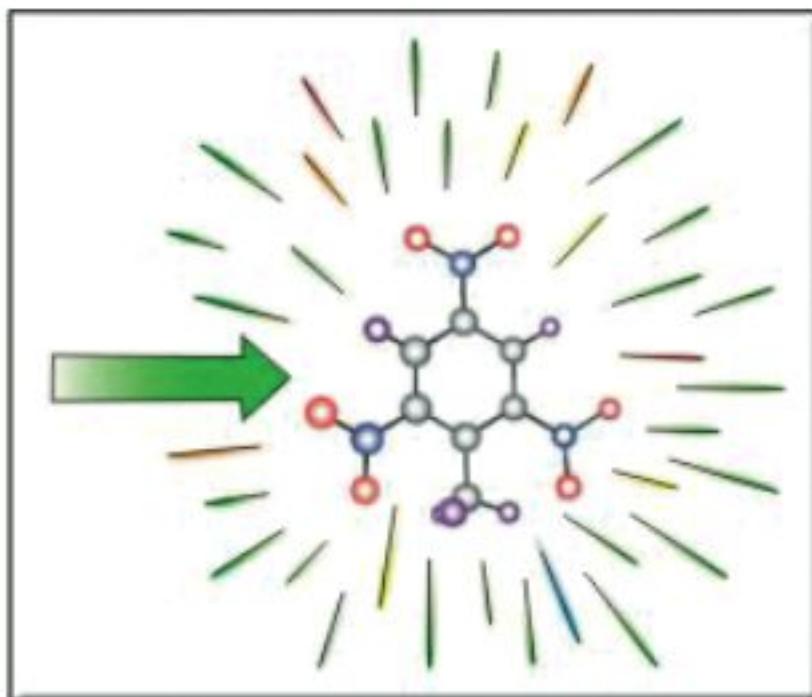
Again, demonstrates the moieties contributing to absorbance from 200-800 nm, because pi electron functions and atoms having no bonding valence shell electron pairs.

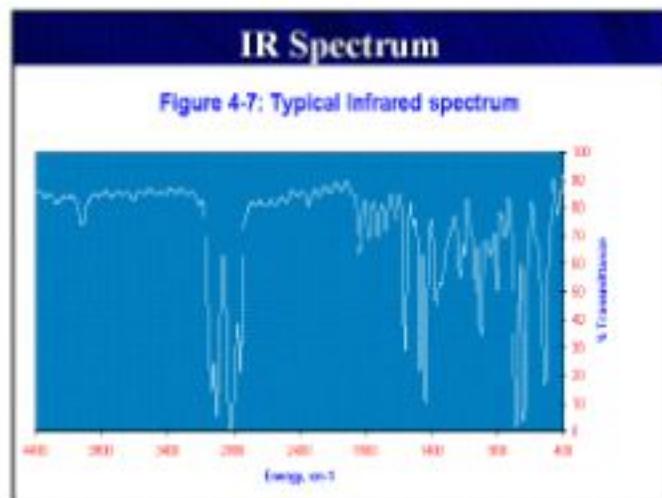
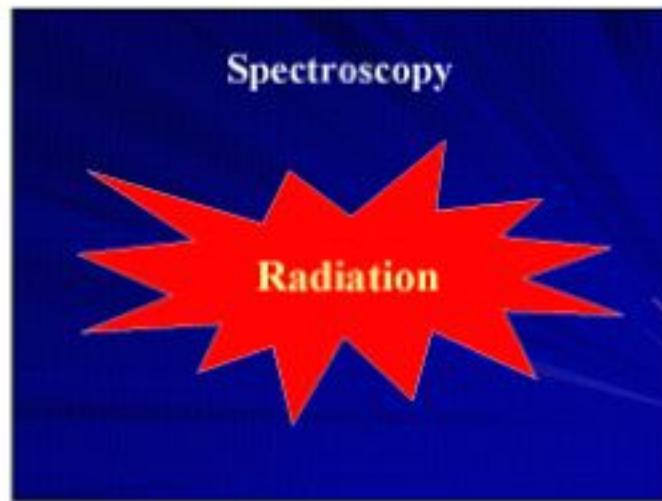
Other Concepts Important to UV/Vis Spectroscopy

- UV/Visible spectra can be used to some extent for compound identification, however, many compounds have similar spectra.
- Solvents can cause a shift in the absorbed wavelengths. Therefore, the same solvent must be used when comparing absorbance spectra for identification purposes.
- Many inorganic species also absorb energy in the UV/Vis region of the spectrum.

What Exactly Is Being Measured?

When Light hits a sample, it becomes excited, and forced to vibrate and move. These vibrations are measured and analysed.





Scattering

- The two main categories of scattering are *Rayleigh and Raman scattering*
- Rayleigh scattering refers to the case when the quantum states n , L , and J (total angular momentum) are the same for the initial and final states of the scattering process
- Raman scattering when any of the quantum states is different.

Raman Spectroscopy

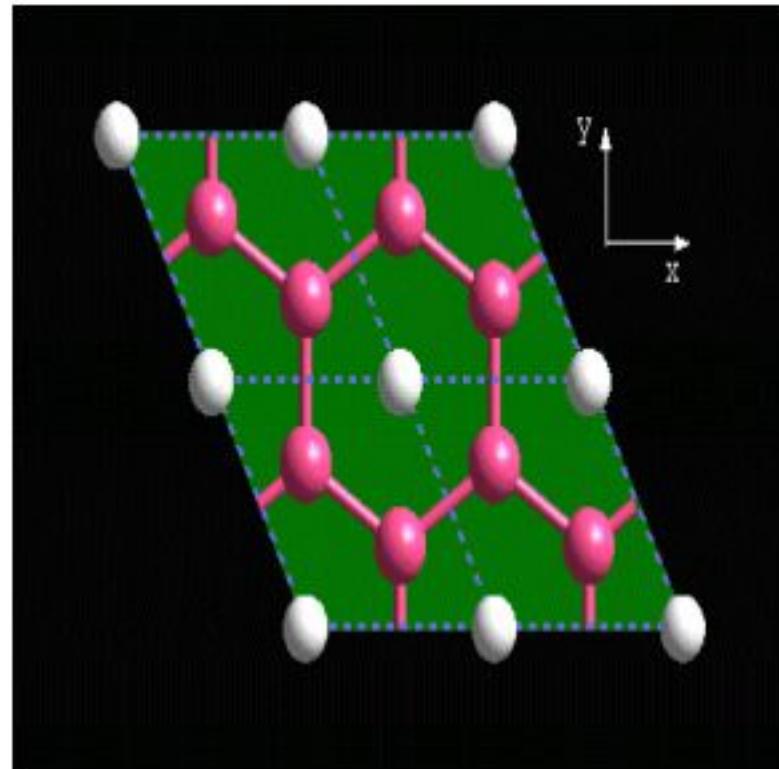
- When radiation passes through a transparent medium, the species present scatter a fraction of the beam in all directions.
- In 1928, the Indian physicist C. V. Raman discovered that the visible wavelength of a small fraction of the radiation scattered by certain molecules differs from that of the incident beam and furthermore that the shifts in wavelength depend upon the chemical structure of the molecules responsible for the scattering.

Raman Spectroscopy

Raman spectroscopy is the measure of the wavelength and intensity of inelastically scattered light.

By varying the frequency of the radiation, a spectrum can be produced, showing the intensity of the exiting radiation for each frequency.

This shows which frequencies of radiation have been absorbed by a molecule to raise it to higher energy states.



Raman Spectroscopy

- The theory of Raman scattering shows that the phenomenon results from the same type of quantized vibrational changes that are associated with infrared absorption. Thus, the difference in wavelength between the incident and scattered visible radiation corresponds to wavelengths in the mid-infrared region.
- The Raman scattering spectrum and infrared absorption spectrum for a given species often resemble one another quite closely.

Raman Spectroscopy

- An important advantage of Raman spectra over infrared lies in the fact that water does not cause interference; indeed, Raman spectra can be obtained from aqueous solutions.
- In addition, glass or quartz cells can be employed, thus avoiding the inconvenience of working with sodium chloride or other atmospherically unstable window materials.

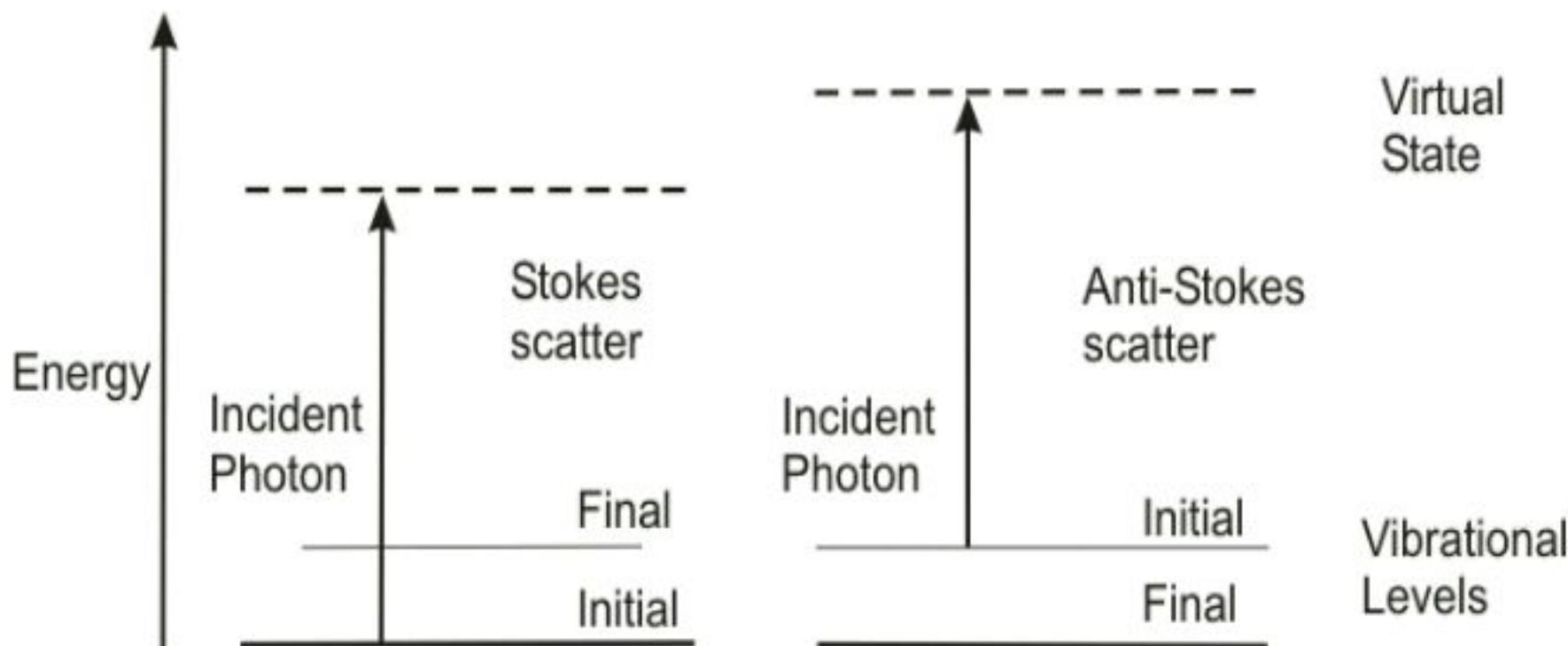
THEORY OF RAMAN SPECTROSCOPY

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 deg) with a suitable spectrometer. At the very most, the intensities of Raman lines are 0.001 % of the intensity of the source; as a consequence, their detection and measurement are somewhat more difficult than are infrared spectra.

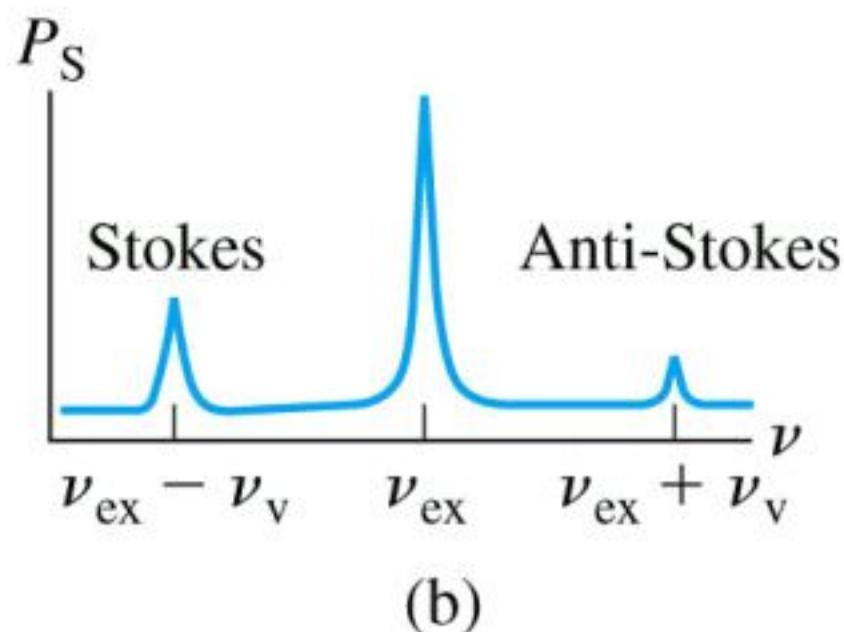
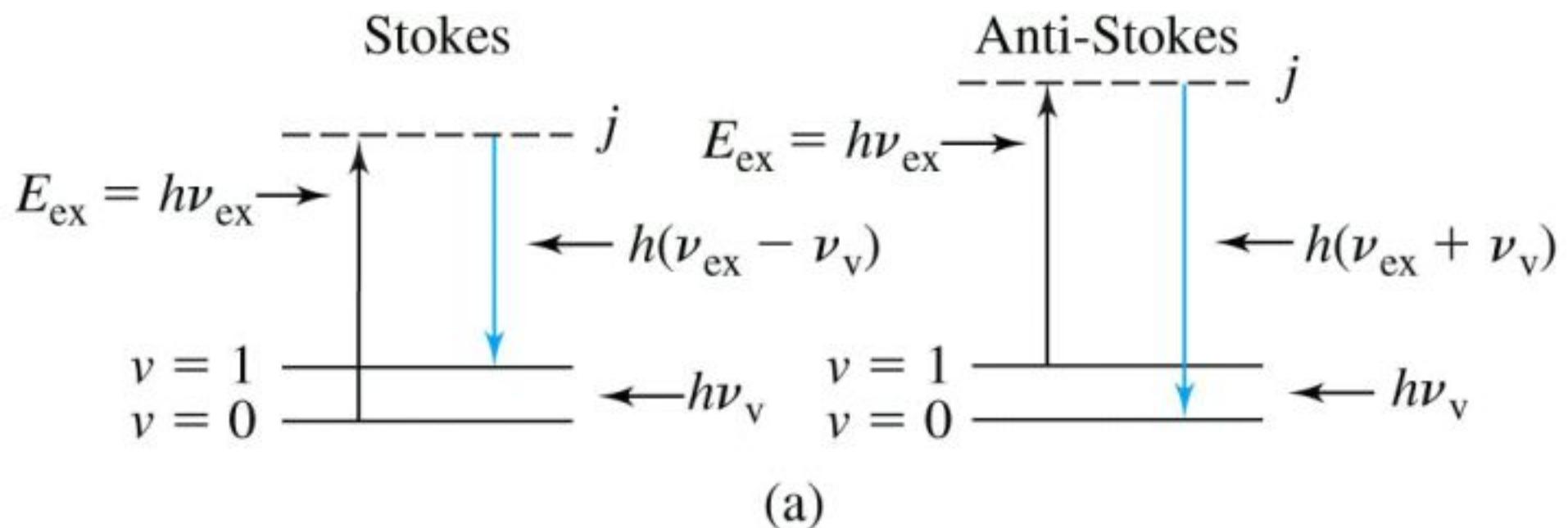
Excitation of Raman Spectra

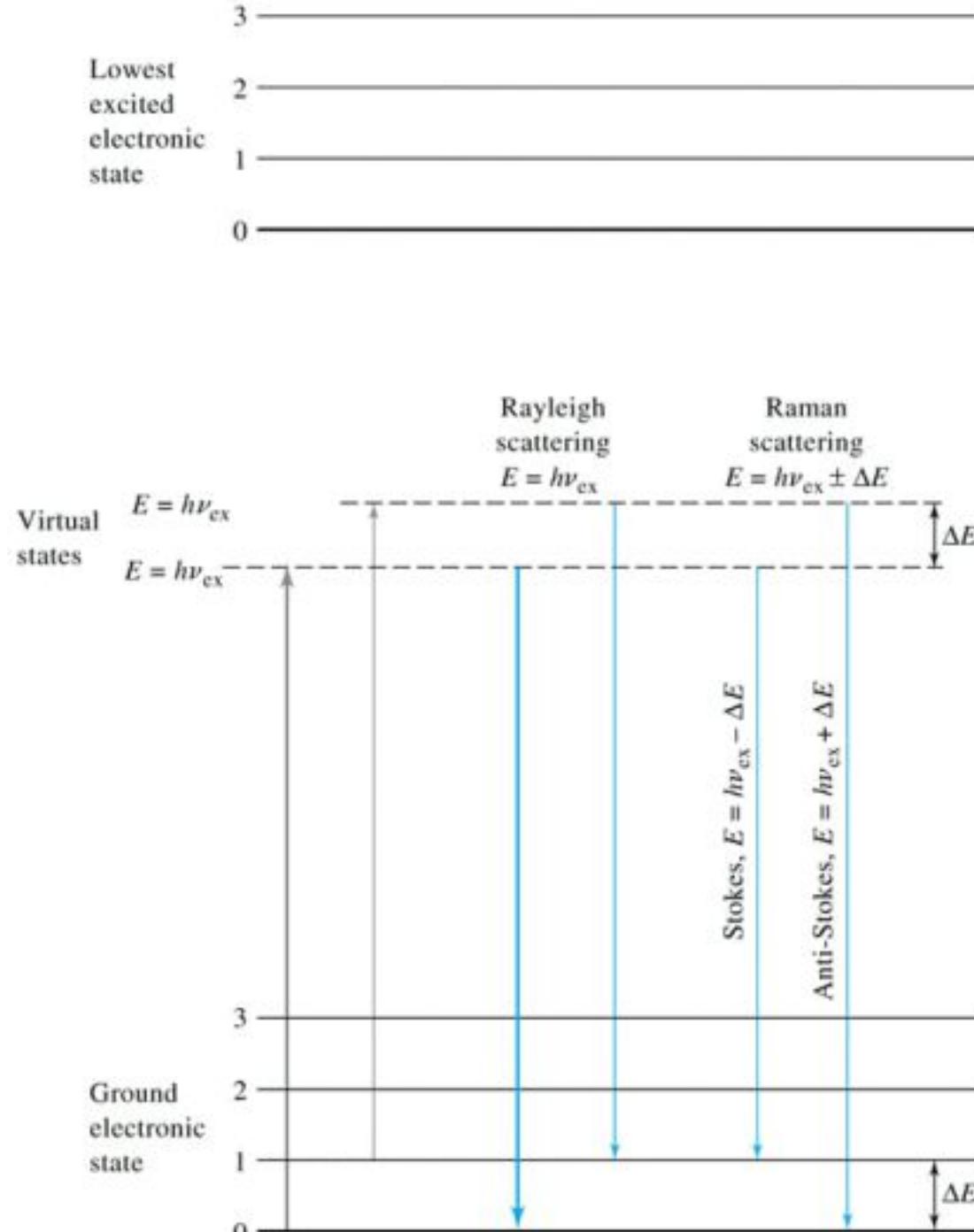
A Raman spectrum can be obtained by irradiating a sample of carbon tetrachloride (Fig 18-2) with an intense beam of an argon ion laser having a wavelength of 488.0 nm (20492 cm^{-1}). The emitted radiation is of three types:

1. Stokes scattering
2. Anti-stokes scattering
3. Rayleigh scattering



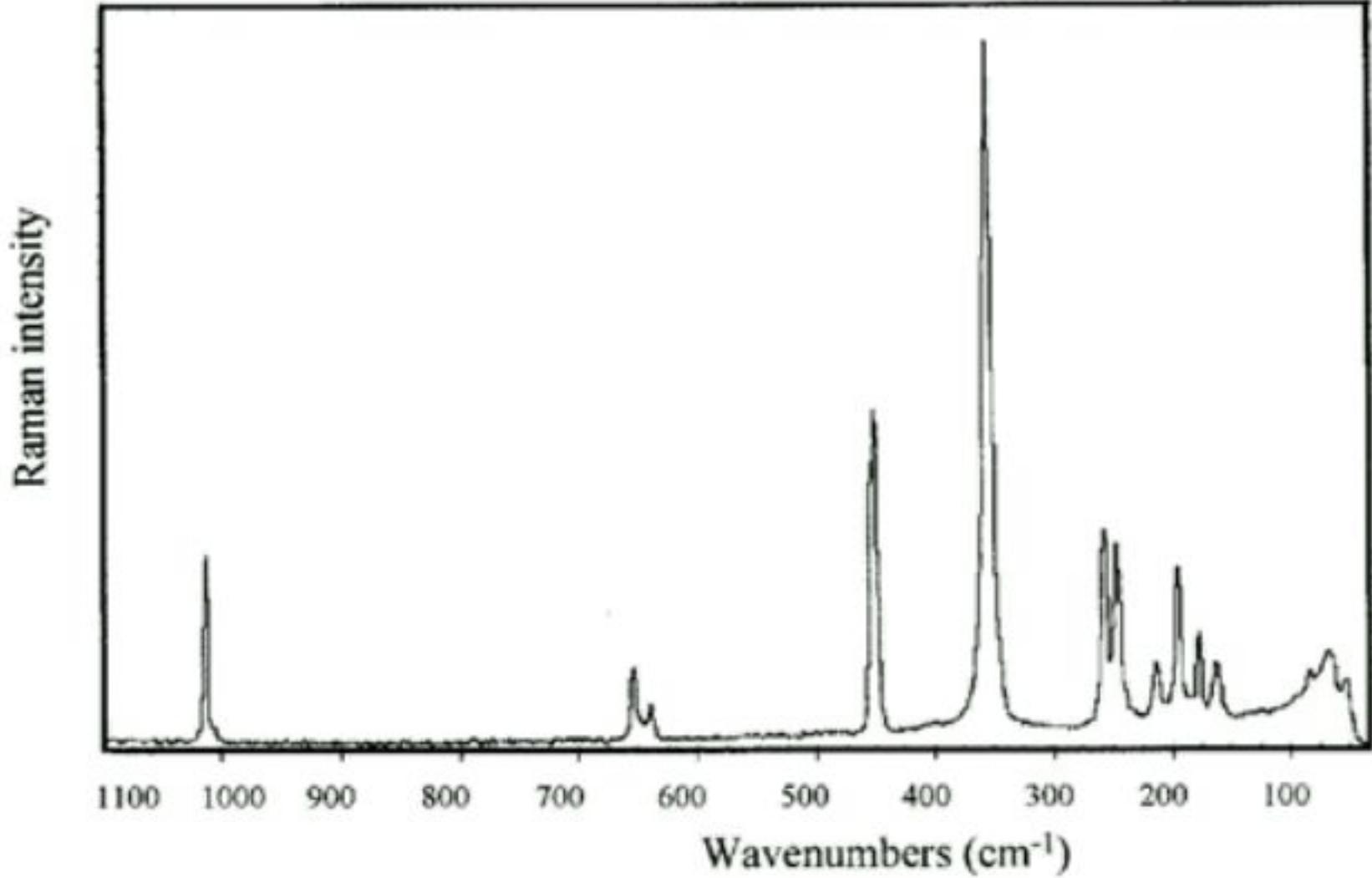
- (a) If the final vibrational state of the molecule is more energetic than the initial state, the emitted photon will be shifted to a lower frequency for the total energy of the system to remain balanced.
- (b) If the final vibrational state is less energetic than the initial state, then the emitted photon will be shifted to a higher frequency, and this is designated as an *anti-Stokes shift*.

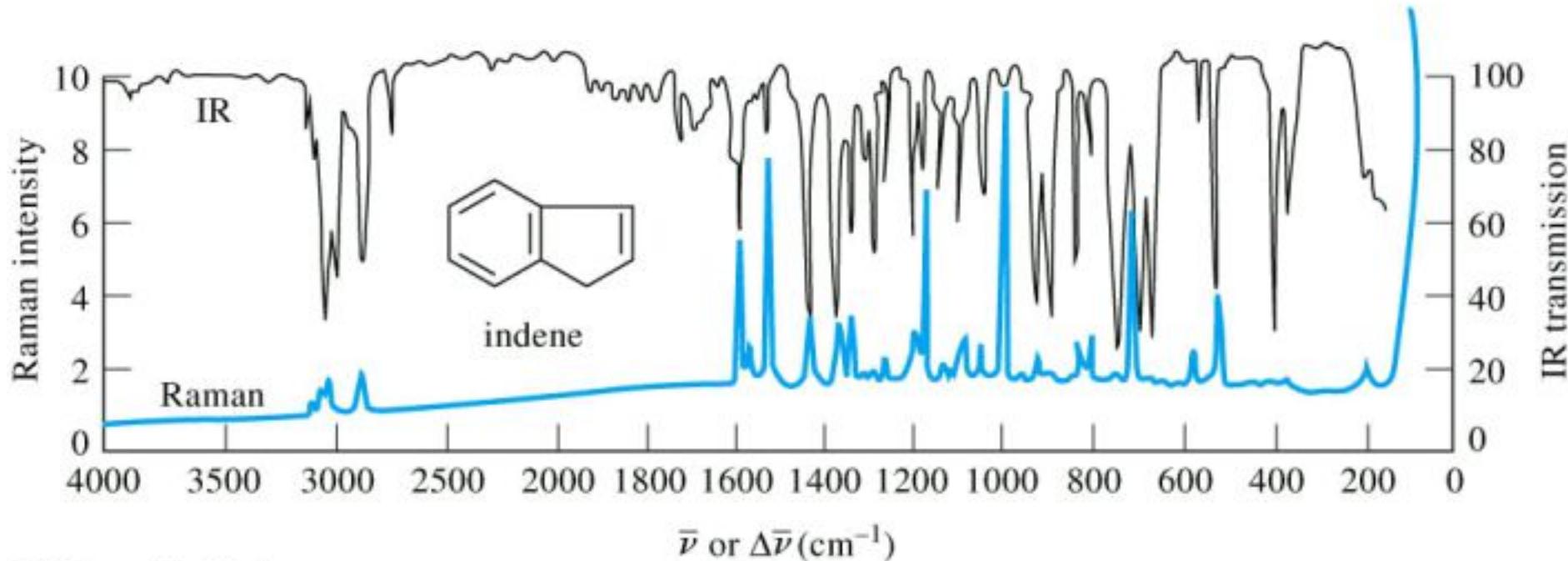
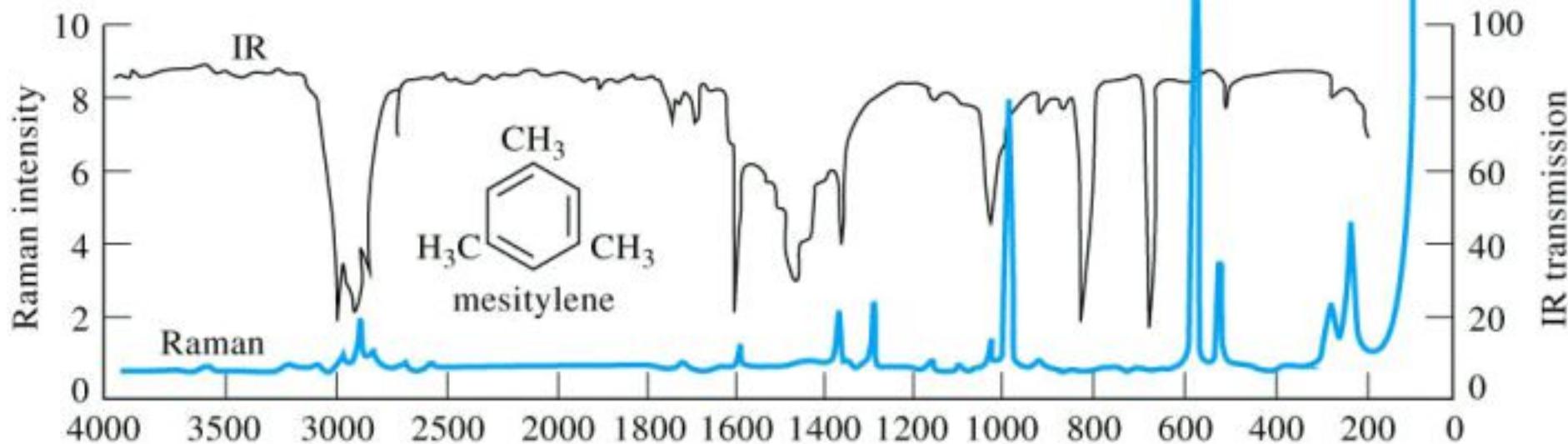




Raman Spectroscopy

- Raman spectroscopy is the measurement of the wavelength and intensity of inelastically scattered light.
- Raman spectroscopy is a two photon process.
- The Raman scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations.
- The mechanism of Raman scattering is different from that of infrared absorption, and Raman and IR spectra provide complementary information.





Surface enhanced Raman scattering, SERS

- In the vicinity of a rough metal surface the Raman cross section can drastically be enhanced, by a factor of up to 10^6 . This allows very sensitive measurements of adsorbates on surfaces.
- Good substrates for SERS are gold, silver and copper.
- Two mechanisms are responsible for the enhancement:
- (1) Enhancement of the local electromagnetic field at the surface of a metal. When the wavelength of the incident electromagnetic field is close to the plasma wavelength of the metal electrons can be excited into an extended surface electronic state (surface plasmon resonance). This leads to exceptionally large local fields.
- (2) The formation of charge transfer complexes between adsorbate and surface (resonance enhancement).

End of Lecture