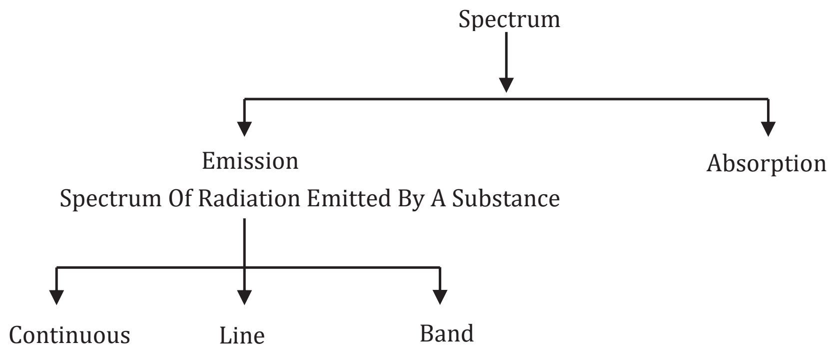
ATOMIC SPECTRA

Spectrum

A spectrum refers to the distinctive wavelengths of electromagnetic radiation (or a segment thereof) emitted or absorbed by the atoms or molecules of a substance.



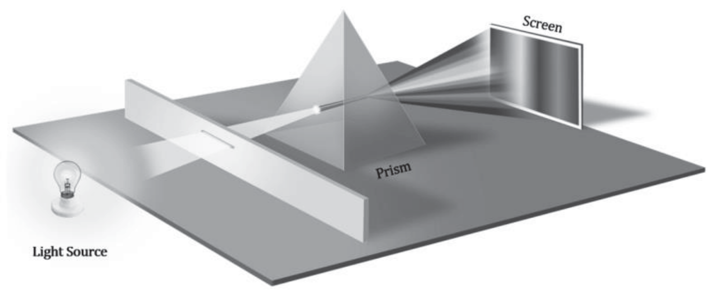
Each atom or molecule possesses a distinct spectrum, characterized by a unique set of wavelengths that it emits or absorbs.

Classification Of Spectrum

Continuous Spectrum

An emission spectrum comprises a continuous range of wavelengths, lacking any gaps or interruptions.

In general, solids and liquids produce continuous spectra when emitting light.

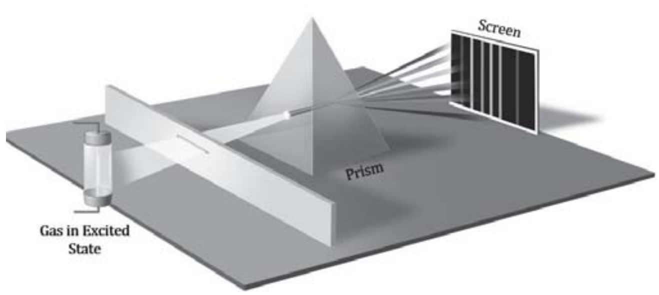


Line Spectrum

A structured arrangement of lines at specific wavelengths, interspersed with dark intervals.

Atoms of an element emit a line spectrum.

Every element possesses a distinct line spectrum, enabling its use in identifying unknown elements.



Band Spectrum

It comprises several bright bands, each representing groups of wavelengths of light.

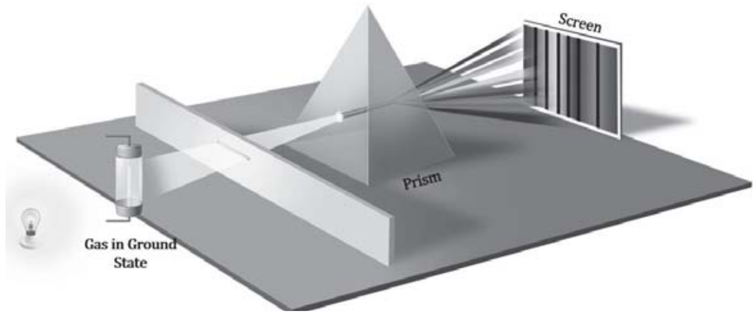
Molecular gases emit a band spectrum.

Ex. $-$ O_2, N_2, CO_2, NH_3

Band spectrum

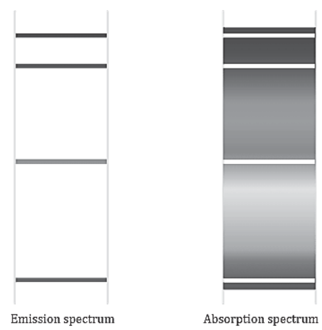
Absorption Spectrum

In an absorption spectrum, segments of a continuous spectrum (light containing all wavelengths) are absent due to absorption by the medium through which the light traversed.
The absent wavelengths manifest as dark lines or gaps.



When radiation from a light source traverses through a gas in its ground state and undergoes dispersion by a prism, we observe the absorption spectra of the gas displayed on the screen.
It's noteworthy that the wavelengths emitted by the gas in its excited state are the same wavelengths absorbed by it in its ground state.

The emission and absorption spectra complement each other.
The wavelengths emitted and absorbed by a specimen are identical.
The fusion of "Emission spectra" and "Absorption spectra" results in a "Continuous spectrum".



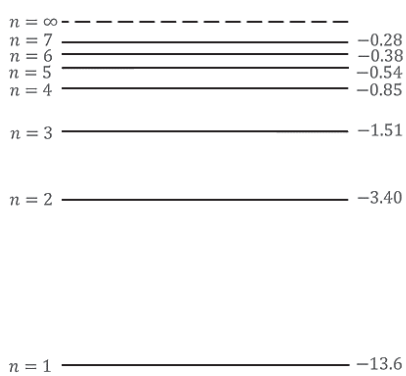
Ground And Excited States Of Hydrogen Atom.

$$E = -13.6 \times \frac{Z^2}{n^2} eV$$

Energy of Hydrogen atom ($Z = 1$) in different states

$$n = 1; E = -13.6eV$$

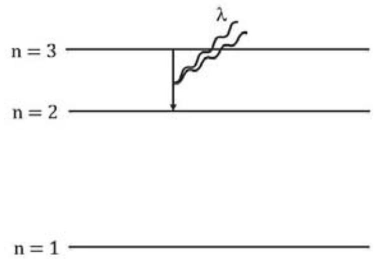
$$n = 2;\ E = \frac{-13.6}{4} = -3.4eV$$

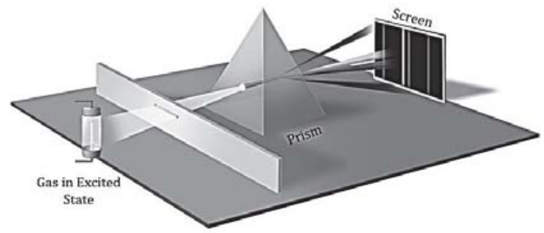


The lowest energy level is referred to as the ground state, while higher energy levels are known as excited states.
An atom, in this instance, Hydrogen, can only occupy these distinct states.

Hydrogen Spectra By Bohr's Model

When a gas is heated, electrons in the ground state transition to higher energy states, or excited states, by absorbing heat energy. However, electrons in the excited state are unstable and return to lower energy levels, emitting radiation. The energy of these emitted radiations equals the difference between the energies of the two transition states.





Line Emission Spectra Of Hydrogen Atom

The hydrogen atom can solely occupy discrete energy states, leading to corresponding discrete transitions. Consequently, only specific wavelengths are possible, resulting in discrete lines observed in the emission spectra of hydrogen.

$$E_i - E_f = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E_i - E_f}$$

Wavelength Of Radiation.

$$E = -13.6 \times \frac{Z^2}{n^2} eV$$

Suppose the transition occurs from the mth orbit to the nth orbit, with m being greater than n.

Energy of the m^{th} orbit is given by,

$$E_m = -13.6 \frac{z^2}{m^2} eV$$

Energy of the n^{th} orbit is given by,

$$E_n = -13.6 \frac{z^2}{n^2} eV$$

Therefore, the difference in the energy of these transition states is

$$\Delta E = E_m - E_n = 13.6Z^2[\frac{1}{n^2} - \frac{1}{m^2}]eV$$

Equating the value of ΔE with $\frac{hc}{\lambda}$, we can find the wavelength (λ) of the emitted radiation.

Rydberg's Formula

If the transition is happening from m^{th} orbit to the n^{th} orbit and $m > n$, we get:

$$\Delta E = E_m - E_n = 13.6Z^2[\frac{1}{n^2} - \frac{1}{m^2}]eV$$

Equating the value of ΔE with $\frac{hc}{\lambda}$, we get:

$$\Delta E = 13.6Z^2[\frac{1}{n^2} - \frac{1}{m^2}]eV = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = \frac{13.6eV}{hc} z^2[\frac{1}{n^2} - \frac{1}{m^2}]$$

Where R = Rydgerg constant $= \frac{13.6eV}{hc}$

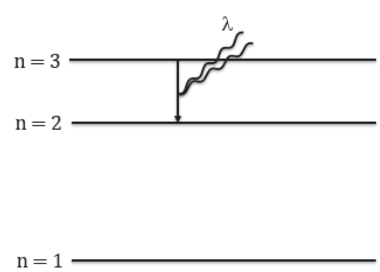
$$\frac{1}{\lambda} = Rz^2[\frac{1}{n^2} - \frac{1}{m^2}]$$

1 rydberg of energy $= Rhc = 13.6eV$

$$\frac{1}{\lambda} = RZ^2(\frac{1}{n^2} - \frac{1}{m^2})m^{-1}$$

$$R = 1.0973 \times 10^7 m^{-1}$$ (Rydberg constant)

Ex. Calculate the wavelength of radiation emitted when He^+ makes a transition from the state n = 3 to the state n = 2.



Sol. Method I:

Energy of the m^{th} orbit: $E_m = -13.6 \frac{z^2}{m^2} eV$

Energy of the n^{th} orbit: $E_n = -13.6 \frac{z^2}{n^2} eV$

If the transition is happening from mth orbit to the nth orbit and $m > n$, then, m = 3 and n = 2.

Therefore,

$$E_3 = -13.6\frac{Z^2}{3^2} = -1.51Z^2 eV$$

$$E_2 = -13.6\frac{Z^2}{2^2} = -3.4Z^2 eV$$

Therefore, the difference in the energy is,.

$$\Delta E = E_3 - E_2 = [-1.51 - (-3.4)]Z^2 eV = 1.89Z^2 eV$$

For Helium atom, $Z = 2$. Thus, the difference in the energy becomes,

$$\Delta E = E_3 - E_2 = 1.89 \times 2^2 = 1.89 \times 4eV$$

Therefore, the wavelength of emitted radiation is given by,

$$\lambda = \frac{1240eVnm}{1.89 \times 4eV} = 164.02nm \approx 164nm$$

Method II:

From Rydberg's formula, we know,.

$$\frac{1}{\lambda} = RZ^2(\frac{1}{n^2} - \frac{1}{m^2})m^{-1}$$

The above formula holds true if the transition is happening from mth orbit to the nth orbit and m > n. Thus, m = 3 and n = 2.

Substituting the value of m and n in the Rydberg's formula, we get,

$$\frac{1}{\lambda} = 1.097 \times 10^7 \times 2^2[\frac{1}{2^2 - 3^2}]$$

$$\frac{1}{\lambda} = 1.097 \times 10^7 \times 4[\frac{5}{4 \times 9}]$$

$$\lambda = \frac{9}{5 \times 1.097 \times 10^7} m \approx 164nm$$

$$\lambda \approx 164 \text{ nm}$$

Ex. **(a)** Find the wavelength of the radiation required to excite the electron in Li^{++} from the first to the third Bohr orbit.

(b) How many spectral lines are observed in the emission spectrum of the above excited system?

Sol. **(a)** Energy required for Hydrogen atom to make a transition from the first to the third Bohr orbit is given by,

$$\Delta E = 13.6 - 1.5$$
$$= 12.1eV$$

It is important to note that:

Energy of transition for any Hydrogen like atom having atomic number Z = (Energy of transition for Hydrogen atom) $\times Z^2$

Now, Li^{++} is Hydrogen like atom and it has Z = 3. Thus, energy required for Li^{++} to make a transition from the first to the third Bohr orbit is given by.

$$(\Delta E)_{Li} = 12.1 \times 3^2 = 12.1 \times 9eV$$

For excitation of electron, the energy of radiation required should be equal to the energy of transition. Thus,

$$\frac{hc}{\lambda} = 12.1 \times 9eV$$

$$\lambda = \frac{1240eV-n\,m}{12.1 \times 9eV} \approx 11.4 \text{ nm}$$

(b) A transition always requires only 2 states. If total n number of states are available for transition of an electron, then, the number of ways in which 2 states can be chosen out of n states is $= n_{C_2}$

This gives the number of spectral lines in emission/absorption spectra.

Here, $n = 3$

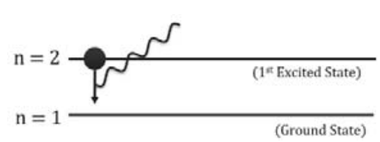
Therefore, $3C_2 = 3 \Rightarrow$ so, no. of spectral lines $= 3$

Ex. The energy needed to detach the electron of a hydrogen like ion in ground state is 4 rydberg.

(a) What is the wavelength of the radiation emitted when the electrons jump from the first excited state to ground state?

(b) What is the radius of the first orbit for this atom?

Sol. **(a)** The electron is said to be detached from the atom when it jumps to the $n = \infty$ orbit upon getting energy.



It is given that the energy needed to detach the electron of a hydrogen like ion in ground state is 4 rydberg. Let the atomic number of the hydrogen like ion is Z.
Thus, the energy required to detach the electron from the ion is,

$$13.6\text{eV} \times Z^2 = 4 \text{ rydberg } = 4 \times 13.6\text{eV}$$
$$Z = 2$$

Energy difference when the electron of the ion jumps from first excited state (n = 2) to ground state (n = 1) is: $\Delta E = 10.2\text{eV} \times 2^2 = 10.2 \times 4\text{eV}$

Therefore, the wavelength of corresponding emitted radiation is:

$$\lambda = \frac{1240\text{eV}-\text{nm}}{10{\cdot}2 \times 4\text{eV}} \approx 30.4\text{nm}$$

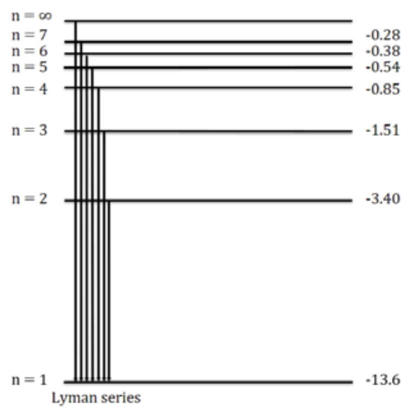
(b) Radius of the first orbit (n = 1) for this atom (Z = 2):

$$r = 53\text{pm}\frac{n^2}{2} = \frac{53\text{pm}}{2}$$
$$r \approx 26.5\text{pm}$$

Spectral Series Of Hydrogen Atom

Lyman Series

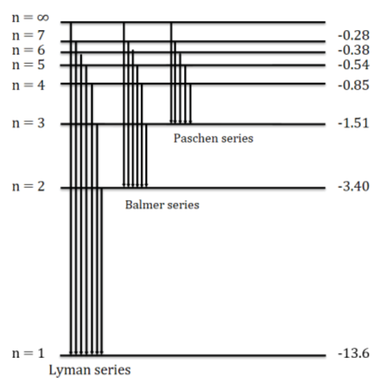
Initial state	Final state	Wavelength formula	λ_{min}	λ_{max}	Spectral region
$n_i = 2,3,4,.$	$n_f = 1$	$\frac{1}{\lambda} = R(\frac{1}{1^2} - \frac{1}{n_i^2})$	911Å	1216Å	UV Region



The series limit is defined as the shortest wavelength within the series.
Corresponding to the transition from $n = \infty$ to $n = 1$, we get the shortest wavelength

Balmer Series

Initial state	Final state	Wavelength formula	λ_{min}	λ_{max}	Spectral region
$n_i = 3,4,5.$	$n_f = 2$	$\frac{1}{\lambda} = R(\frac{1}{2^2} - \frac{1}{n_i^2})$	3646Å	6563Å	Visible Region

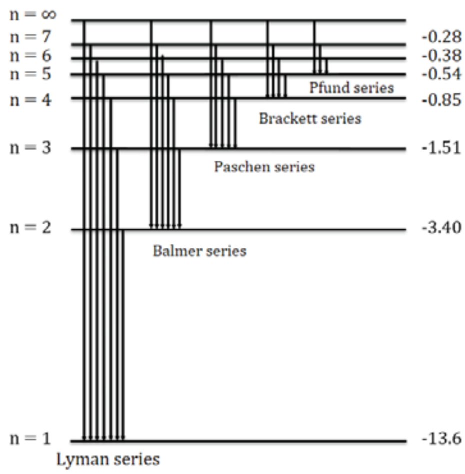


Paschen Series

Initial state	Final state	Wavelength formula	λ_{min}	λ_{max}	Spectral region
$n_i = 4,5,6.$	$n_f = 3$	$\frac{1}{\lambda} = R(\frac{1}{3^2} - \frac{1}{n_i^2})$	8204Å	18753Å	IR Region

Brackett Series

Initial state	Final state	Wavelength formula	λ_{min}	λ_{max}	Spectral region
$n_i = 5,6,7.$	$n_f = 4$	$\frac{1}{\lambda} = R(\frac{1}{4^2} - \frac{1}{n_i^2})$	14585Å	40515Å	IR Region



Pfund Series

Initial state	Final state	Wavelength formula	λ_{min}	λ_{max}	Spectral region
$n_i = 6,7,8.$	$n_f = 5$	$\frac{1}{\lambda} = R(\frac{1}{5^2} - \frac{1}{n_i^2})$	22790Å	74583Å	Far IR Region

Humphreys Series

For this series, $n_f = 6$ and $n_i = 7,8,9, \ldots$