Electronic Spectroscopy

Qn-1: Which of the following molecules will show a pure rotational spectrum?

H_2, HCl, CO, CH_3Cl, H_2O (liquid), NH_3, NH_4Cl (s)

Qn-2: Which of the following molecules will show a vibrational spectrum?

H_2, HCl, CO, CH_3Cl, H_2O, NH_3, NH_4Cl, CO_2

Electronic Spectroscopy

 It involves the promotion of electron from the ground state to the higher energy state by absorption of radiation in the UV-visible region

 Also known as UV-visible spectroscopy

 Energies in the range of 200-800 nm are sufficient to excite the electron to a higher electronic energy level

According to Born-Oppenheimer approximation, the total energy of a molecule in the ground state is given by,

$$E'' = E''_{el} + E''_{vib} + E''_{rot}$$

The excited state energy E' is given by,

$$E' = E'_{el} + E'_{vib} + E'_{rot}$$

The **energy change** for **an electronic transition** is given by,

$$\Delta E = E' - E''$$
$$= (E'_{el} + E'_{vib} + E'_{rot}) - (E''_{el} + E''_{vib} + E''_{rot})$$
$$= (E'_{el} - E''_{el}) + (E'_{vib} - E''_{vib}) + (E'_{rot} - E''_{rot})$$
$$= \Delta E_{el} + \Delta E_{vib} + \Delta E_{rot}$$

The order of magnitude of these energy changes are:

$$\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot}$$

The frequency for the electronic transition is given by the Bohr frequency condition:

$$\tilde{v} = \Delta E / hc$$
$$= (\Delta E_{el} + \Delta E_{vib} + \Delta E_{rot} / hc) \text{ cm}^{-1}$$
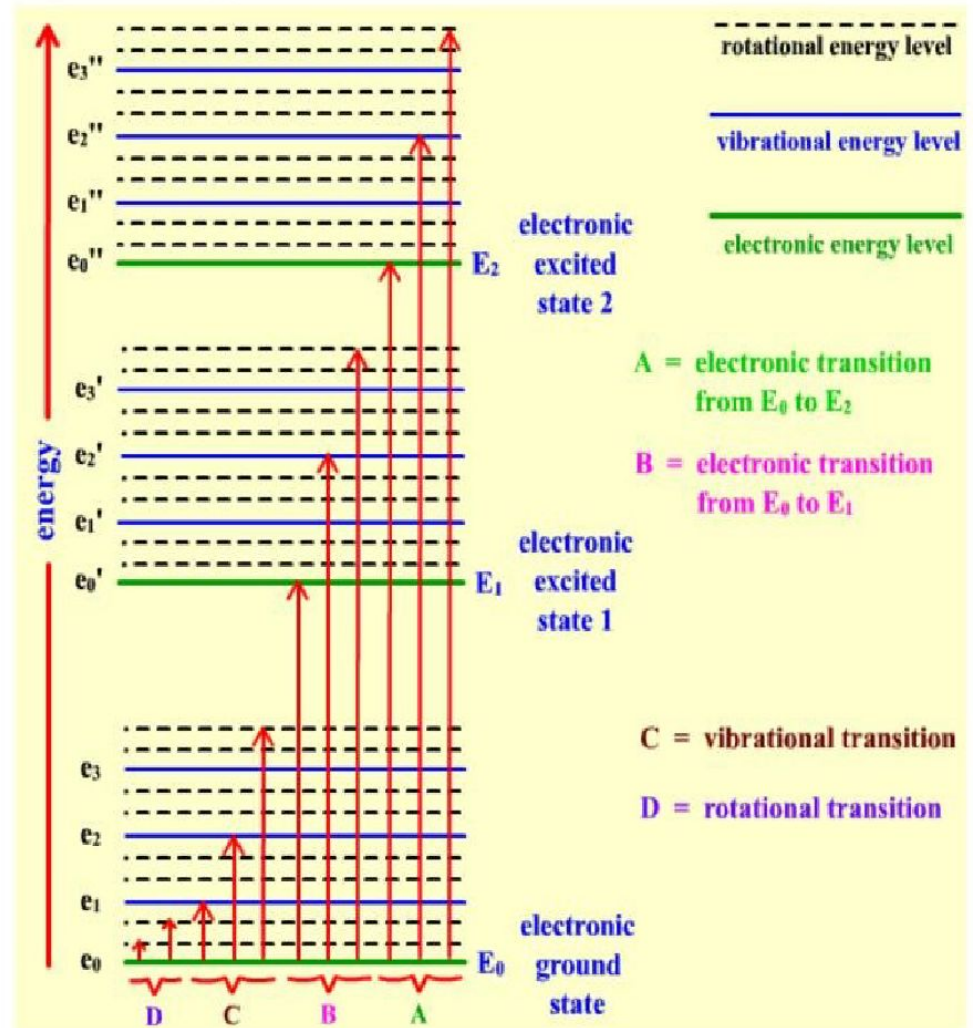
An electronic transition will be accompanied by simultaneous vibrational and rotational changes

$\Delta E = hc\bar{\upsilon} = \Delta E_{el} + \Delta E_{rot} + \Delta E_{vib}$

or, $\bar{\upsilon} = \Delta E /hc$
$= (\Delta E_{el} + \Delta E_{rot} + \Delta E_{vib}) /hc \ cm^{-1}$

Origin of Electronic Spectra

- - - - rotational energy level

──── vibrational energy level

──── electronic energy level

A = electronic transition from E_0 to E_2

B = electronic transition from E_0 to E_1

C = vibrational transition

D = rotational transition

Vibrational-Electronic spectra: The Franck-Condon Principle

Each electronic level has its characteristic potential energy diagram, which can be represented by a Morse curve

Franck-Condon principle states that:
An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition

This is true, because the electrons move so much faster than the nuclei that during the electronic transition the nuclei do not change their position

Hence an electronic transition may be represented by a vertical line on a plot of potential energy versus the internuclear distance
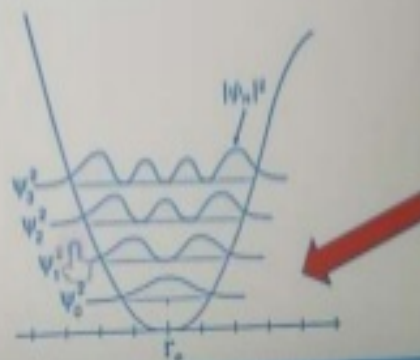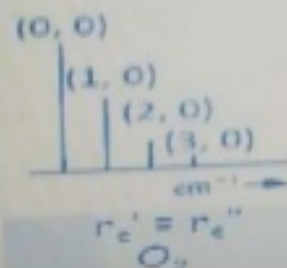
Explanation using Morse Diagrams

Case 1 : <u>The upper electronic state having the same equilibrium internuclear distance as the lower.</u>
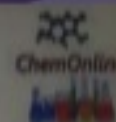
The transition occurs vertically on this diagram

The strongest spectral line will be the (0,0).

The most probable transition

$U' = 0$

$U'' = 0$

Energy

(0, 0)

(1, 0)

(2, 0)

(3, 0)

$cm^{-1} \longrightarrow$

$r_e' = r_e''$

O_2

$|\psi_v|^2$

r_e

The probability distribution for a diatomic molecule according to quantum theory. The nuclei are most likely to be found at distances apart given by the maxima of the curve for each vibrational state.

Case 2 : <u>The upper state internuclear distance a little less than that in the lower state.</u>
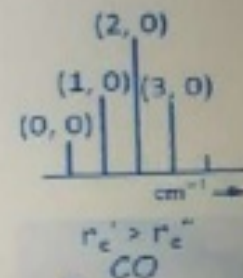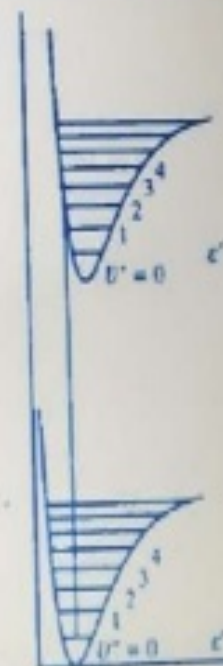
Case 3 : <u>The upper state internuclear distance a little greater than that in the lower state.</u>
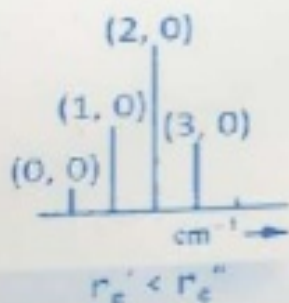
The most probable transition is from $v''=0$ to $v'=2$

$r_e' < r_e''$

$r_e' > r_e''$
CO

Origin of Electronic Spectra

In the ground state electrons are paired

❖ If transition of electron from ground state to excited state takes place in such a way that spins of electrons are paired, it is known as **excited singlet state.**
❖ If electrons have parallel spins, it is known as **excited triplet state.**

Ground Singlet State   Excited Singlet State   Excited Triplet State
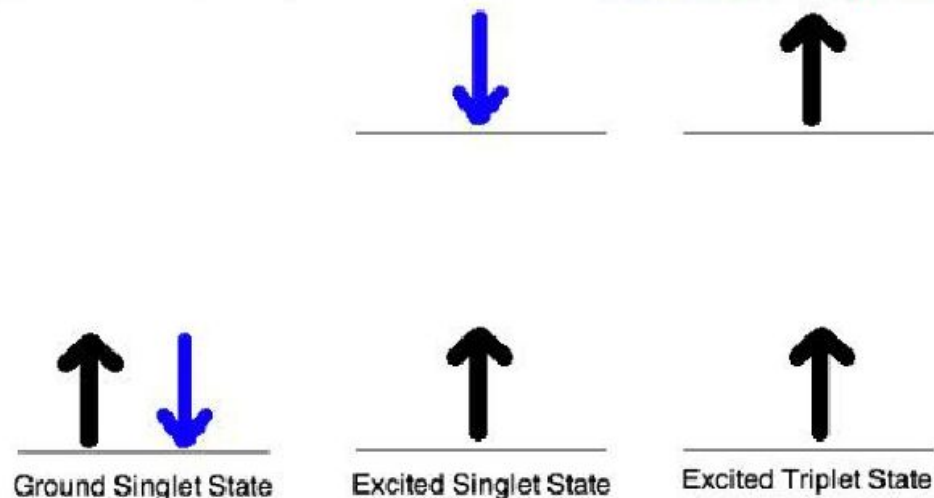
❖ Excitation of uv light results in excitation of electron from singlet ground state to singlet excited state
❖ Transition from singlet ground state to excited triplet state is **forbidden** due to symmetry consideration

The valence electrons are the only ones whose energies permit them to be excited by near UV/visible radiation.

$\sigma*$ (anti-bonding)

$\pi*$ (anti-bonding)

n (non-bonding)
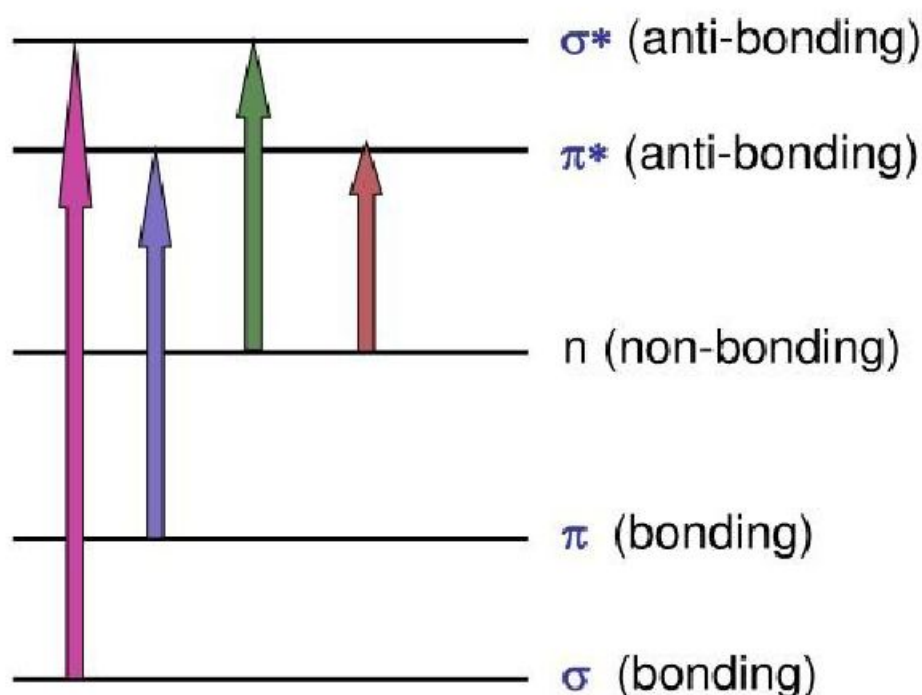
π (bonding)

σ (bonding)

Four types of transitions

$\sigma \rightarrow \sigma^*$

$\pi \rightarrow \pi^*$

$n \rightarrow \sigma^*$

$n \rightarrow \pi^*$

$\sigma \rightarrow \sigma^*$ transition in vacuum UV ($\lambda \sim 150$ nm)
$n \rightarrow \sigma^*$ saturated compounds with non-bonding electrons
$\lambda \sim 150$-250 nm
$\varepsilon \sim 100$-3000 (not strong)

$n \rightarrow \pi^*, \pi \rightarrow \pi^*$ requires unsaturated functional groups most commonly used, energy good range for UV/Vis
$\lambda \sim 200$ - 700 nm
$n \rightarrow \pi^*$: $\varepsilon \sim 10$-100
$\pi \rightarrow \pi^*$: $\varepsilon \sim 1000 - 10,000$

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Possible Electronic Transitions

- **σ-σ* transition**: this type of transition is possible in saturated hydocarbons (alkane) where only σ bonds are formed and no atom has non-bonding electrons

- **n-σ* transition**: compounds which contain non-bonding electrons exhibit this type of transition

- Organic compounds containing nitrogen, oxygen, sulphur or chlorine have non-bonding electrons

- **π-π* transition**: this type of transition takes place in unsaturated compounds containing double or triple bonds

- **n- π* transition**: this type of transition occurs in compounds containing non-bonding electrons on hetero atom

- The electron gets excited to π* antibonding orbital

Observed electronic transitions:

- Although the UV spectrum extends below 100 nm (high energy), oxygen in the atmosphere is not transparent below 200 nm

- Special equipment to study *vacuum* or *far UV* is required

- Routine organic UV spectra are typically collected from 200-700 nm

- This limits the transitions that can be observed:

$\sigma \longrightarrow \sigma^*$ alkanes	150 nm	
$\sigma \longrightarrow \pi^*$ carbonyls	170 nm	
$\pi \longrightarrow \pi^*$ unsaturated cmpds.	180 nm	**√ - if conjugated!**
$n \longrightarrow \sigma^*$ O, N, S, halogens	190 nm	
$n \longrightarrow \pi^*$ carbonyls	300 nm	**√**

Electronic spectra of transition metal ions

❖ Compounds of transition metal ions containing unpaired electrons are coloured and show their absorption spectra in the UV-Visible regions

❖ The characteristic features of these spectra are peaks of low intensity and in some cases peak of high intensity

❖ The weak peak arises from the promotion of electrons from one d-orbital to the other and are called d-d transitions.

❖ These d-d transitions are forbidden, because they take place between two energy levels with same azimuthal quantum number, l, i.e., $\Delta l = 0$

❖ In atomic spectra, the selection rule for the allowed transition is $\Delta l = \pm 1$. This is called **Laporte selection rule**

character.)

Fig. 31. The energy level diagram for $[Ni(H_2O)_6]^{2+}$

25,300

13,500

8,500

ENERGY cm^{-1}

Ground state
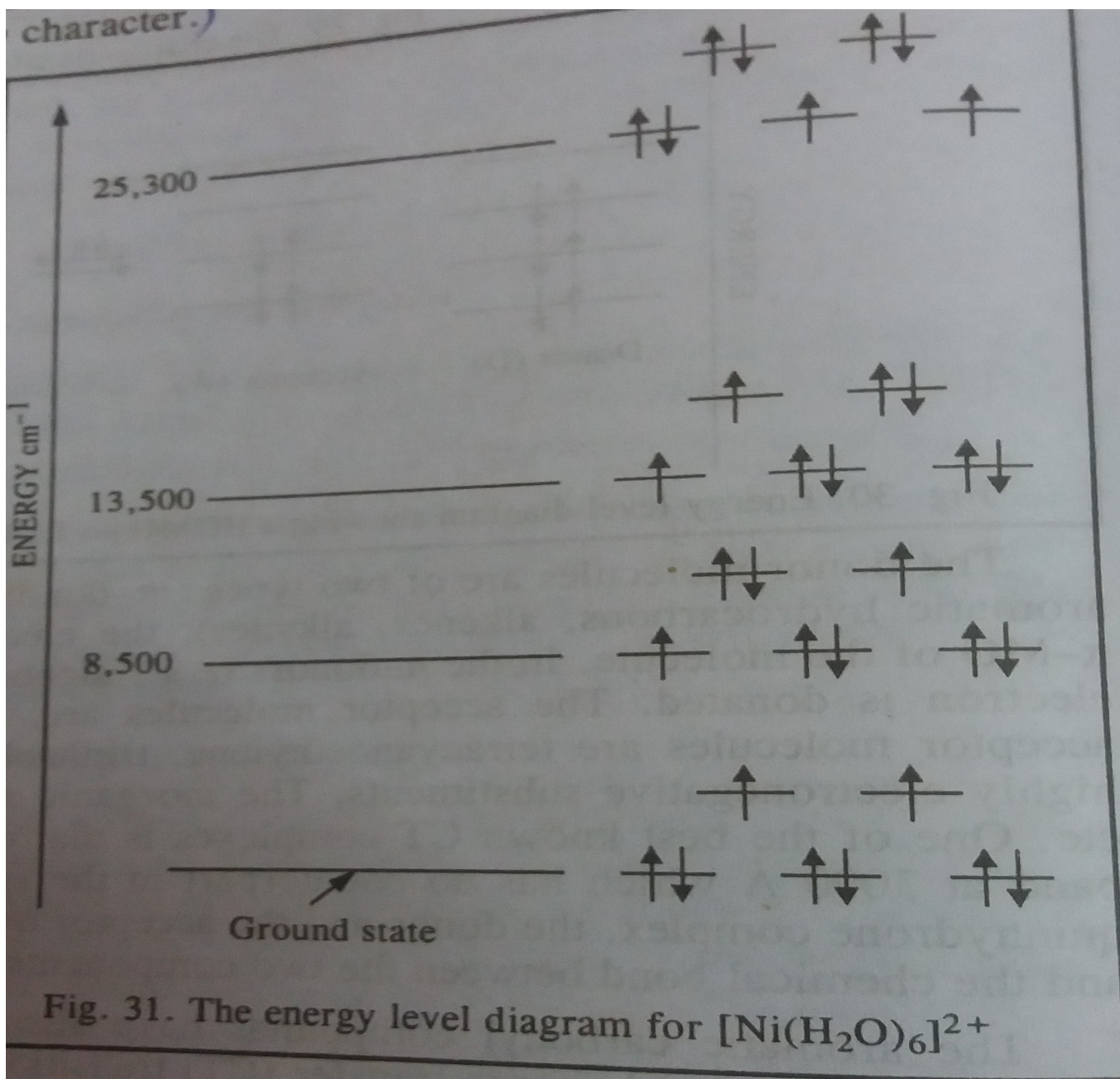
Electronic spectra of Hydrogen atom

Bohr's theory of Hydrogen atom:
Bohr introduced the concept of stationary or non-radiating orbits

Bohr's postulates:

1.   An atom consists of positively charged nucleus and the electrons revolve round the nucleus in certain permitted circular orbits of definite radii

2. The permitted orbits are those for which the angular momentum of An electron is an integral multiple of h/2π
The angular momentum L is given by,
L = mur =nh/2π, n=1,2, …

3. When electrons move in permitted orbits, they do not radiate energy. Such orbits are called stationary or non-radiating orbits

4. The energy is radiated when an electron jumps from higher to lower orbit and the energy is absorbed when it jumps from lower to higher orbit

The frequency of radiation emitted is given by
$$h\upsilon = \Delta E = E_f - E_i$$

This equation is known as **Bohr frequency condition.**

Spectrum of Hydrogen atom

The energy of electron in the **nth orbit** is given by,
$E_n = -1/(4\pi\epsilon_0)^2 (2\pi^2 Z^2 me^4/n^2 h^2)$; n= 1, 2, 3,……

According to Bohr, the spectrum arises when the electron in the initial higher orbit jumps to the final lower orbit so that the difference of energy associated with these orbits is emitted as photon of frequency υ

Thus, $h\upsilon = E_i - E_f = = -1/(4\pi\epsilon_0)^2 (2\pi^2 Z^2 me^4/n_i^2 h^2) - \{-1/(4\pi\epsilon_0)^2 (2\pi^2 Z^2 me^4/n_f^2 h^2)\}$

or $h\upsilon = 1/(4\pi\epsilon_0)^2 (2\pi^2 me^4/h^2) [(1/n_f^2) - (1/n_i^2)]$ (as Z=1 for H atom)

or $\upsilon = 1/(4\pi\epsilon_0)^2 (2\pi^2 me^4/h^3) [(1/n_f^2) - (1/n_i^2)]$
or $\bar{\upsilon} = 1/(4\pi\epsilon_0)^2 (2\pi^2 me^4/ch^3) [(1/n_f^2) - (1/n_i^2)]$
or $\bar{\upsilon} = R_H [(1/n_f^2) - (1/n_i^2)]$ where R_H is Rydberg constant

1. **Lyman series:** Transition of electron from higher orbit to lower energy state with $n_f = 1$

$$\bar{\upsilon} = R_H [1/1^2 - 1/n_i^2], \quad n_i = 2, 3, 4, \ldots.$$

2. **Balmer series:** The lower energy state is $n_f = 2$

$$\bar{\upsilon} = R_H [1/2^2 - 1/n_i^2], \quad n_i = 3, 4, \ldots.$$

3. **Paschen Series:** The lower energy state is $n_f = 3$
$$\bar{\upsilon} = R_H [1/3^2 - 1/n_i^2], \quad n_i = 4, 5, 6, \ldots.$$

4. **Brackett series:** The lower energy state is $n_f = 4$
$$\bar{\upsilon} = R_H [1/4^2 - 1/n_i^2], \quad n_i = 5, 6, 7 \ldots.$$

5. **Pfund Series:** The lower energy state is $n_f = 5$
$$\bar{\upsilon} = R_H [1/5^2 - 1/n_i^2], \quad n_i = 6, 7, 8 \ldots.$$

Lymen Series (Ultra−violet Region)

First Line: $n_1 = 1, n_2 = 2$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = 82.26 \times 10^5 m^{-1}$$
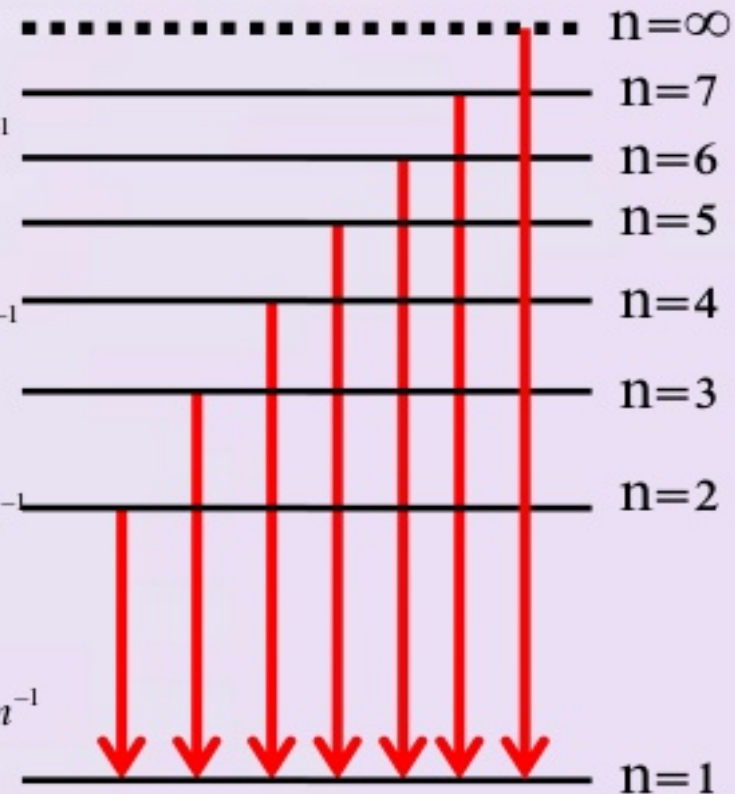
Second Line: $n_1 = 1, n_2 = 3$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{3^2} \right) = 97.60 \times 10^5 m^{-1}$$

Third Line: $n_1 = 1, n_2 = 4$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{4^2} \right) = 102.70 \times 10^5 m^{-1}$$

Limiting Line: $n_1 = 1, n_2 = \infty$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) = 1.09678 \times 10^7 m^{-1}$$

$n = \infty$
$n = 7$
$n = 6$
$n = 5$
$n = 4$
$n = 3$
$n = 2$
$n = 1$

Balmer Series
(Visible Region)

First Line $(H\alpha$ Line$)$: $n_1 = 2, n_2 = 3$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 15.234 \times 10^5 \, m^{-1}$$
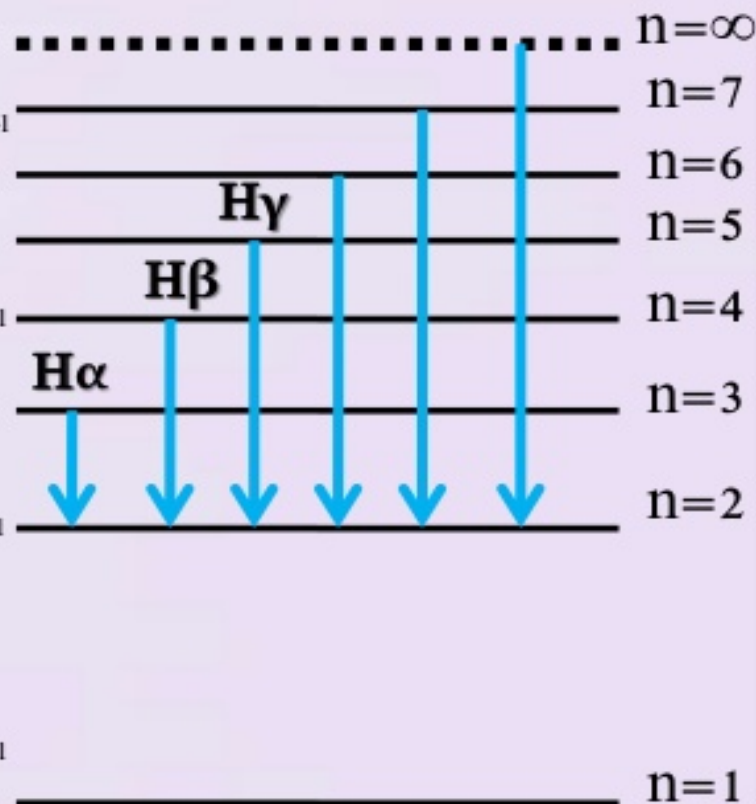
Second Line $(H\beta$ Line$)$: $n_1 = 2, n_2 = 4$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = 20.566 \times 10^5 \, m^{-1}$$

Third Line $(H\gamma$ Line$)$: $n_1 = 2, n_2 = 5$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = 23.05 \times 10^5 \, m^{-1}$$

Limiting Line : $n_1 = 2, n_2 = \infty$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) = 27.421 \times 10^5 \, m^{-1}$$

n=∞

n=7

n=6

Hγ   n=5

Hβ   n=4

Hα   n=3

n=2

n=1

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Paschen Series
(Infra Red Region)

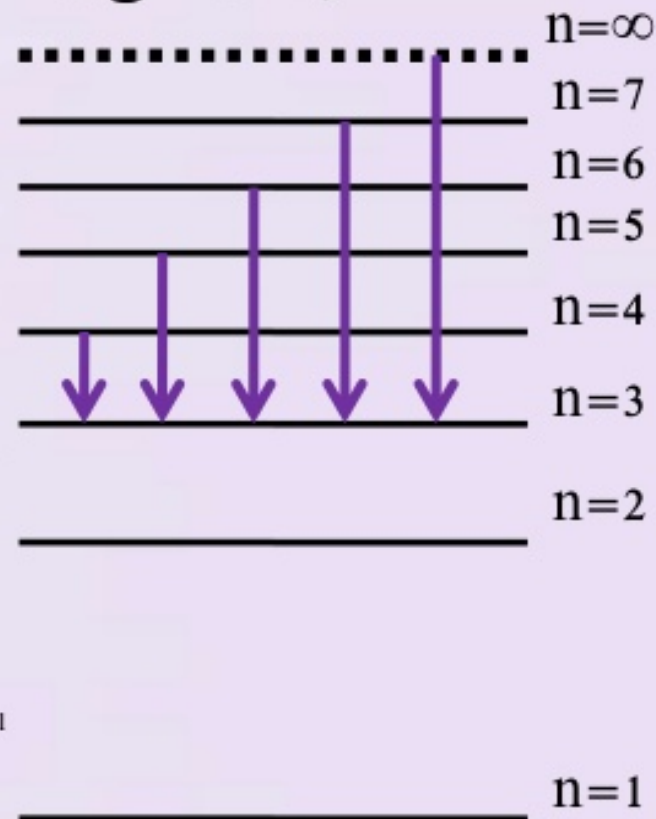First Line: $\qquad n_1 = 3, n_2 = 4$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{3^2} - \frac{1}{4^2} \right) = 5.3310 \times 10^5 \, m^{-1}$$

Second Line: $\qquad n_1 = 3, n_2 = 5$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{3^2} - \frac{1}{5^2} \right) = 7.99 \times 10^5 \, m^{-1}$$

Limiting Line: $\qquad n_1 = 3, n_2 = \infty$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{3^2} - \frac{1}{\infty^2} \right) = 12.187 \times 10^5 \, m^{-1}$$

n=∞

n=7

n=6

n=5

n=4

n=3

n=2

n=1

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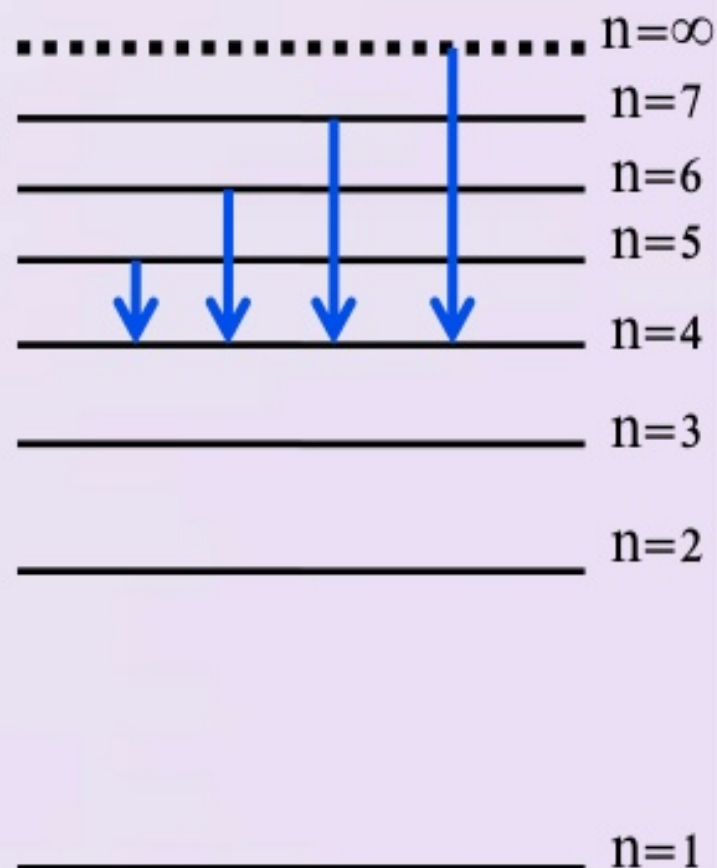
Brackett Series

First Line: $n_1 = 4, n_2 = 5$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{4^2} - \frac{1}{5^2} \right) = 2.45 \times 10^5 \, m^{-1}$$

SecondLine: $n_1 = 4, n_2 = 6$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{4^2} - \frac{1}{6^2} \right) = 3.808 \times 10^5 \, m^{-1}$$

Limiting Line: $n_1 = 4, n_2 = \infty$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{4^2} - \frac{1}{\infty^2} \right) = 6.855 \times 10^5 \, m^{-1}$$

n=∞
n=7
n=6
n=5
n=4
n=3
n=2
n=1

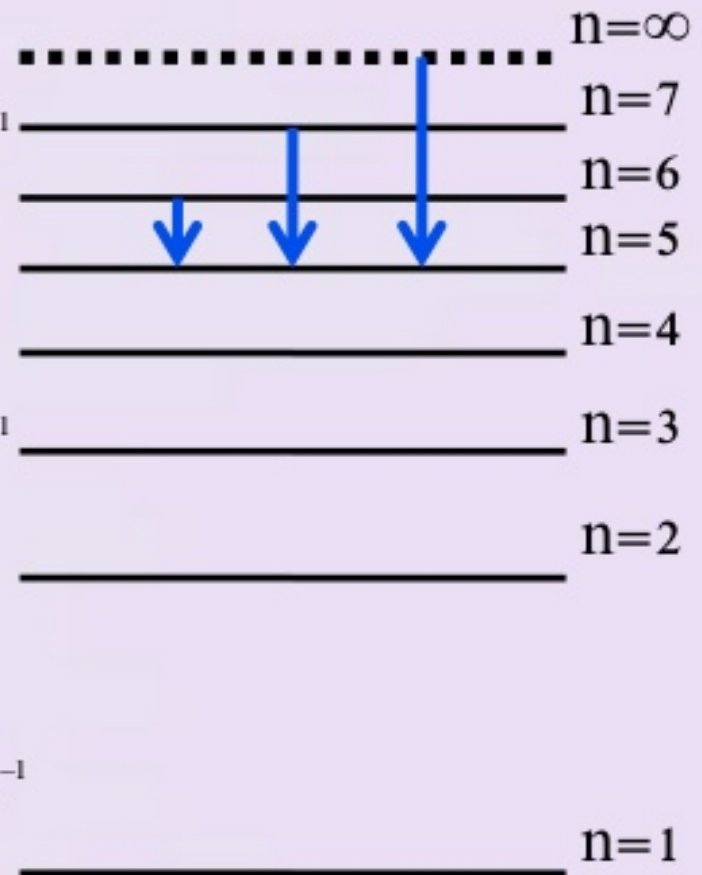# Pfund Series

First Line: $n_1 = 5, n_2 = 6$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{5^2} - \frac{1}{6^2} \right) = 1.340 \times 10^5 \, m^{-1}$$
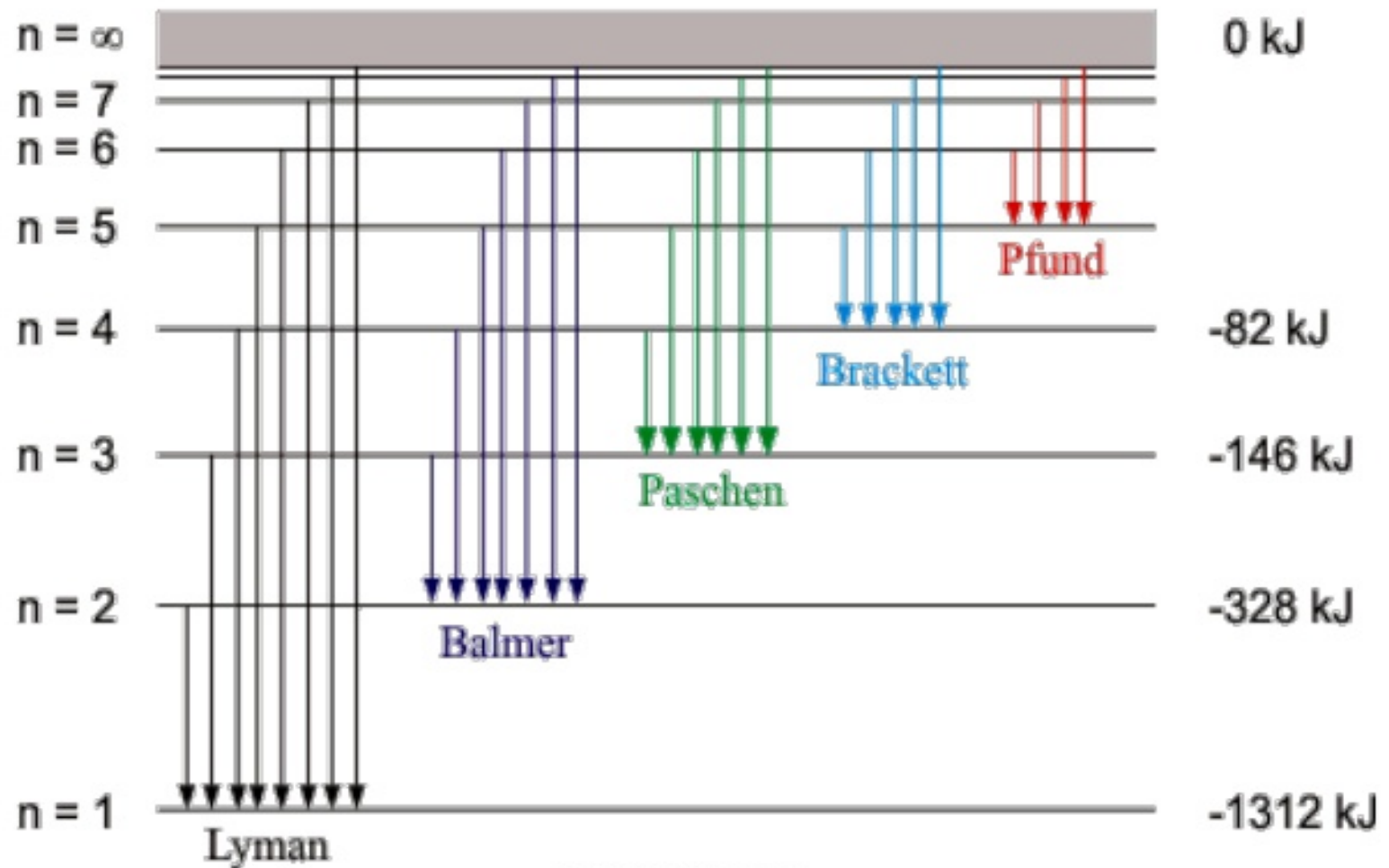
Second Line: $n_1 = 5, n_2 = 7$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{5^2} - \frac{1}{7^2} \right) = 2.148 \times 10^5 \, m^{-1}$$

Limiting Line: $n_1 = 5, n_2 = \infty$

$$\bar{\upsilon} = 1.09678 \times 10^7 \left(\frac{1}{5^2} - \frac{1}{\infty^2} \right) = 4.387 \times 10^5 \, m^{-1}$$

n=∞
n=7
n=6
n=5
n=4
n=3
n=2
n=1

n = ∞   0 kJ

n = 7

n = 6

n = 5   Pfund

n = 4   −82 kJ

Brackett

n = 3   −146 kJ

Paschen

n = 2   −328 kJ

Balmer

n = 1   −1312 kJ

Lyman

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Light absorption by solutions

The absorption of light by a solution in the visible and near ultraviolet regions is governed by Lambert-Beer law.

When a beam of monochromatic radiation of a suitable frequency Passes through a solution, it is absorbed by the solution

If I_0 is the intensity of incident beam and I_t is the intensity of transmitted beam, then the intensity of light absorbed, I_a is given as

$$I_a = I_0 - I_t$$

When a beam of monochromatic radiation is passed through a solution of an absorbing medium, the rate of decrease of intensity of radiation with thickness of the absorbing medium is directly proportional to the intensity of incident radiation as well as the concentration of the solution........
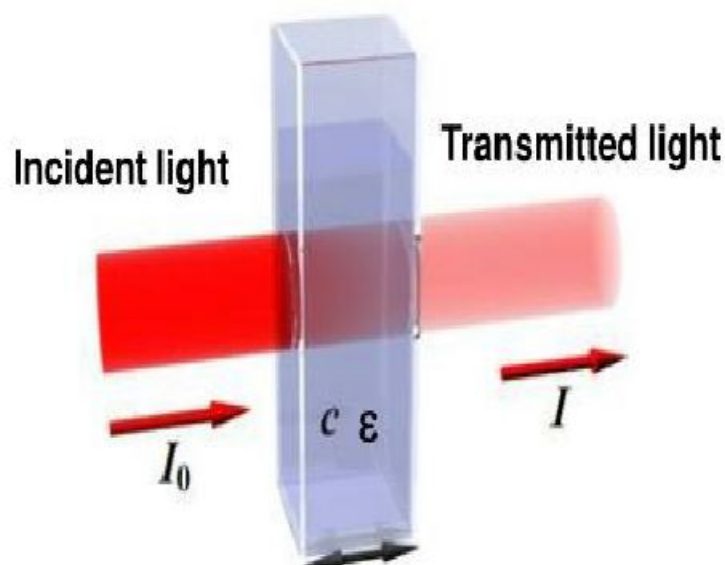
$$A = \varepsilon lc = \log I_0/I$$

Where A is absorbance

ε is the **molar absorbtivity** with units of $L\ mol^{-1}\ cm^{-1}$

l is the path length of the sample (typically in cm).

c is the concentration of the compound in solution, expressed in $mol\ L^{-1}$

Incident light

Transmitted light

$c\ \varepsilon$

I_0

I

I_0 = intensity of the incident light

I = intensity of the transmitted light

I = width of the cuvette

A = log (Original intensity/ Intensity)

Ex-1: A monochromatic radiation is incident on a solution of 0.05 molar concentration of an absorbing substance. The intensity of the radiation is reduced to ¼ th of the initial value after passing through 10 cm length of the solution. Calculate the molar extinction coefficient of the substance?

Ans: Given, $I = I_0/4$, c= 0.05 mol dm^{-3}, l=10cm

According to Lambert-Beer's law,

$\log(I_0/I) = \epsilon$cl

or, $\log (I_0/ (I_0/4)) = \epsilon \times 0.05 \times 10$ mol dm^{-3} cm

or, log 4 = 0.5 ϵ mol dm^{-3} cm

or, 0.602 = 0.5 ϵ mol dm^{-3} cm

or, ϵ = (0.602/0.5) mol^{-1} dm^3 cm^{-1}

or, ϵ = 1.204 mol^{-1} dm^3 cm^{-1}

Ex-2: A substance when dissolved in water at 10^{-3} molar concentration absorbs 10 percent of an incident radiation in a path of 1 cm length. What should be the concentration of the solution in order to absorb 90 percent of the same radiation?

Ans: Given: $c_1 = 10^{-3}$ M

$I_1 = I_0 - 0.1I_0 = 0.9\ I_0$

2nd case: $I_2 = I_0 - 0.9I_0 = 0.1\ I_0,\ c_2 = ?$

According to Lambert-Beer's law,

$\log(I_0/I_1) = \epsilon c_1 l$

Or $\log(1/0.9) = 10^{-3}\ \epsilon l$ ………..(1)

Similarly, $\log(I_0/I_2) = \epsilon c_2 l$

$\log(10) = \epsilon c_2 l$ ……………….. (2)

From Eqs. 1 and 2, we have

$\log(1/0.9)/\log(10) = 10^{-3}/c_2$

Or, $c_2 = 10^{-3}/\log(1/0.9) = 0.0218$ mol dm^{-3}