Part I : Introductory concepts

Topics

- Why spectroscopy?
- Introduction to electromagnetic radiation
- Interaction of radiation with matter
- What are spectra?
- Beer-Lambert law

Part II : Electronic Spectroscopy

Topics

- Born-Oppenheimer approximation
- The potential energy curve
- Franck-Condon principle
- Types of electronic transitions for a diatomic molecule
- Vibronic structure and spectra
- Fluorescence and phosphorescence

Advanced Topics

- Rates of absorption, emission and stimulated emission (Einstein coefficients) (will be added later)
- Interaction of dipole moments with electromagnetic field (will be added later)

Topic 1

Why spectroscopy?

- Analytical, organic and inorganic chemistry laboratories all over the world use spectroscopy to

  1. identify new compounds
  2. identify intermediates and
  3. predict reaction mechanisms

- Physical chemistry laboratories obtain molecular structural parameters, molecular geometries, molecular properties such as

  1. energy levels and transition frequencies,
  2. electric dipole moments, quadrupole moments, polarizability etc. and
  3. moments of inertia, nuclear magnetic moments, fine structure constants etc

- Atomic spectroscopy is the experimental technique based on which much of quantum mechanics evolved.

- Molecular spectroscopy permits us to study chemical reaction dynamics at the most fundamental level.

Topic 2

Introduction to electromagnetic radiation

- Electromagnetic radiation consists of oscillating waves of electric and magnetic fields.

- The directions of the oscillations of the electric and magnetic fields are perpendicular to each other.

- The direction of propagation of the radiation is perpendicular to the directions of oscillations.

If we assume electric field oscillating in the $\hat{x}$ direction as

$$\vec{E}(z,t) = E_0 \cos(kz - \omega t + \delta)\hat{x}$$

and magnetic field oscillating in the $\hat{y}$ direction as

$$\vec{B}(z,t) = \frac{1}{c} B_0 \cos(kz - \omega t + \delta)\hat{y}$$

then, the electromagnetic radiation propagates in the $\hat{z}$ direction,

ω - is the oscillating frequency,

k - is the wave vector $= \dfrac{2\pi}{\lambda}$ where λ is the wavelength of the radiation, δ is phase shift, E_0, B_0 the intensities of electric and magnetic fields and c is the speed of light.

Click the play button to view the animation.

■
Units and definitions

1. **Wavelength** : Distance beween two adjacent crests or troughs of a wave, λ dimension of length, L

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2. **Frequency** : Number of waves that pass a given point in unit time interval, υ, dimension of t^{-1}

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3. **Wave Number**: Number of waves in a unit length $\bar{v} = \dfrac{1}{\lambda}$, dimension of L^{-1}

Click the play button to view the animation.

4. **c**: Speed of light in vacuum $c = v\lambda$ or $v = c\bar{v}$

■Einstein's description of electromagnetic radiation consists of photons, of frequency(v) and energy (E=hv) where h is Planck's constant. Energy is also given by

$$E = h\left(\frac{c}{\lambda}\right) = hc\bar{v}$$

Topic 3

Interaction of radiation with matter:

- Electromagnetic radiation interacts with matter in many possible ways

- Magnetic field interacts with magnetic properties of matter.

- Electric field interacts with rotating/oscillating electric dipole moments present in molecules

- Interaction of radiation with matter is over approximately fifteen orders of magnitude in energy scale.

- The different regions of electromagnetic radiation are given in the table below: Energy of radiation (photon) decreases from top to bottom

Type of Radiation	Frequency (S^{-1})	Wavelength (nm)	Wave Number cm^{-1}
Cosmic	$>10^{20}$	$<10^{-1}$	$>10^{10}$
gamma rays	10^{20} to 10^{18}	10^{-3} to 10^{-1}	10^{10} to 10^{8}
X-rays	10^{18} to 10^{16}	10^{-1} to 10	10^{8} to 10^{6}
Ultraviolet (UV)	10^{16} to 10^{14}	10 to 3×10^{2}	10^{6} to 10^{4}
Visible	8×10^{14} to 3×10^{14}	3×10^{2} to 8×10^{2}	3×10^{4} to 10^{4}

Infrared (IR)	10^{14} to 10^{12}	8×10^2 to 3×10^5	10^4 to 30
Microwave	10^{12} to 10^8	10^5 to 10^9	30 to 10^{-2}
Radiowave	$<3\times10^8$	$>10^9$	$<10^{-2}$

- UV, Visible and IR regions: (Wave number, cm^{-1})

| Far UV	10^6 to 50,000
Near UV	50,000 to 26,000
Visible	26,000 to 13,000
Near IR	13,000 to 3,000
Mid IR	3,000 to 300
Far IR	300 to 30

The spectrum
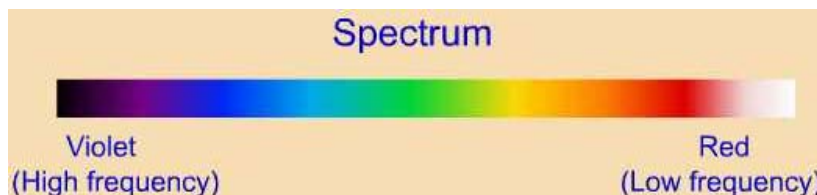
- In each of the region, the molecular properties which are probed by the radiation are different. The table below gives the list of properties studied using different types of radiation

| Types of Radiation	Properties expected
Radio-frequency	Nuclear magnetic dipole moment. magnetic dipole interaction, spin-spin coupling, Electric quadupole moments, etc
Microwave region	Molecular moments of inertia, rotation constants, equilibrium structure, molecular electric dipole moment, electronic magnetic dipole moment, etc.
Infrared region	Force constants, bond strengths, polarizability etc.
UV-Visible region	Electric dipole moments, dissociation energies, luminescence (fluorescence, phosphorescence)
X-ray region	Core electron energies, surface properties and characterization
gamma ray region	Chemical shift or isomer shift, nuclear quadrupole moment, etc.

Topic 4

What are spectra?

- The nuclear magnetic resonance spectrum (H^1-NMR) of benzene
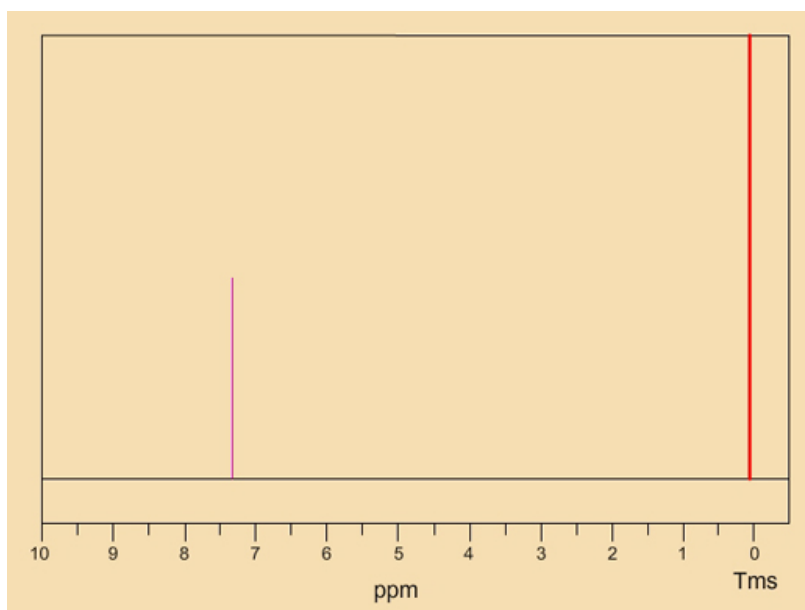
■ The infrared spectrum of benzene
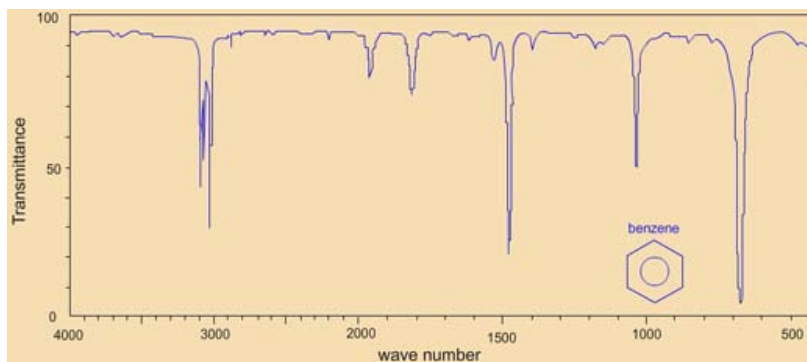
■ The UV – Visible spectrum of benzene (Reference Source: NIST Chemistry Web book)) (http://webbokk.nist.gov/chemistry)
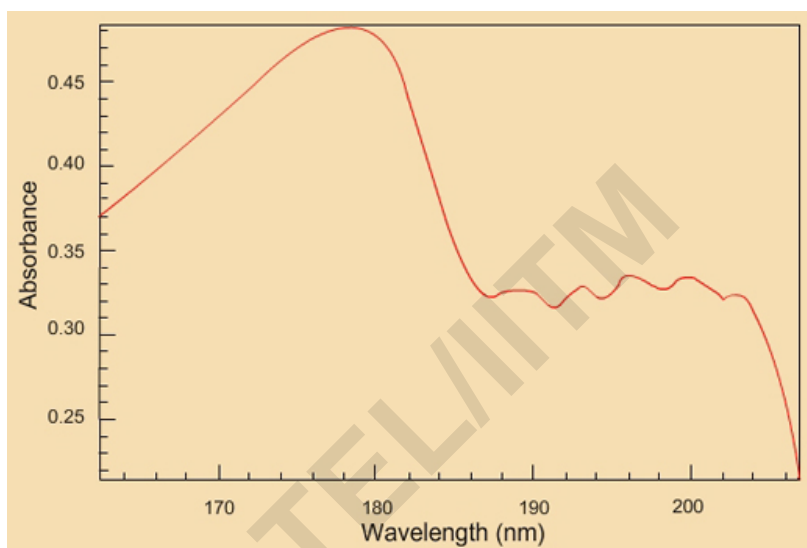
■ Spectrum is obtained when the intensity of radiation absorbed/ emitted is plotted as a function of the frequency or wavelength.

■ All spectra consist of three features, lines, intensities and line widths

■ **Lines**: Transitions which correspond to absorption of electromagnetic radiation at specific frequencies and not all frequencies. This is explained as due to the presence of discrete energy levels in molecules and transitions are due to jumps between discrete levels.The study of this is through quantum mechanics)

Click the play button to view the animation.

■ **Intensities**: The different intensities/ heights of lines/ areas under a given narrow peak do not all have the same intensities. This is explained as due to the

distribution of molecules over various energies, so that at any given temperature, more molecules are likely to be in one energy state or other. They are not equally populated. The study of this aspect requires knowledge of quantum and statistical mechanics.

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- **Line widths**: The lines are not infinitely sharp but have a certain width. The widths of different lines are different, and are not all the same. This is due to the fact that all energy levels are not sharply defined, due to continuous transfer of energies between molecules through collision, motion etc. The study of this phenomenon is among the most difficult areas in chemistry and physics and requires expertise in several areas such as classical and quantum mechanics, statistical mechanics, molecular reaction dynamics, scattering theory etc.

Click the play button to view the animation.

- Every spectrum contains these three features. Every branch of spectroscopy addresses these three characteristics in the determination of molecular structure and dynamics of molecules. Thus the complete understanding of a spectrum requires a wide range of topics to be studied. Spectroscopy is a fundamental subject.

Advanced topics for quantitative description of broadness/line widths will be included in this site later.

Topic 5

Beer-Lambert Law

- It is a quantitative relation between amount of light absorbed and the concentration of the species.

- It is used for detection of small concentration of various chemical species which absorb in the visible region of electromagnetic radiation.

- It is a standard analytical tool employed in the chemistry laboratory.

- Radiation falls on a sample contained in a standard cell, used for measurement. It is a rectangular cell, with transparent walls, and has a length l ; contains a solution with concentration of C moles per litre of the species.

- Consider a small thickness dx in the cell at a length x. The relation may be stated by noting the following:

  I′ – intensity of light falling at x

  I'-dI' intensity of light emerging out of x+dx. (dI is the amount of light absorbed)

- Beer- Lambert's law states that:

$-dI' \propto I'$

$-dI' \propto dx$

$-dI' \propto C$

where

dx = length or width of the region

C = Concentration

- or $-dI = \varepsilon IC\ dx$

ε is the proportionality constant. If I_O is the intensity of light falling on the cell at (x=0), and I is the intensity of light transmitted by the cell (at x = l). Then,

$$or\ -\int \frac{dI'}{I'} = \int_0^1 \varepsilon\ C\ dx$$

$$i.e.\ \ln \frac{I_0}{I} = \varepsilon\ cl$$

$$or\ 2.303 \log \frac{I_0}{I} = \varepsilon\ Cl$$

$$\log \frac{I_0}{I} = \frac{\varepsilon}{2.303} Cl = \varepsilon' Cl$$

Topic 1

Born-Oppenheimer Approximation

- The transitions of an electron in a hydrogen atom from a level with principal quantum n_1 to another level with quantum number n_2 are well known. These are Lyman series (n_1 = 1, to any n_2>1), Balmer series (n_1=2 to n_2>2), Paschen series (n_1=3 to n_2>3), Brackett series (n_1=4 to n_2>4), Pfund series (n_1=5 to n_2>5) etc.

- Molecular electronic energy levels cannot be formulated in such a simple manner as in the case of atoms such as hydrogen, helium etc. The reasons are that molecular motion is much more complex with rotational, vibrational motion of atoms being a part of the overall dynamics of molecule.

- The solution of the molecular Schrödinger equation is complex due to the kinetic energies of all nuclei, all electrons and potential energies between electron and nuclei. Analytic expressions like 1s, 2s, 2p orbital functions of hydrogen cannot be obtained, and approximations are necessary.

- The approximations are,

1. The overall wave function ψ, which is the solution of the molecular Schrödinger equation $H\psi = E\psi$ can be written as the product of a nuclear wave function ψ_N and an electronic wave function ψ_e .

2. The electronic wave function is a function of all electronic and nuclear coordinates ($\vec{r_1}, \vec{r_2}, \vec{r_3}, \ldots \ldots \vec{r_n}$, n electrons and $\vec{R_1}, \vec{R_2}, \vec{R_3}, \ldots \ldots \vec{R_N}$, N nuclei)

3. The nuclear wave function is a function of nuclear coordinates ($\vec{R_1}, \vec{R_2}, \vec{R_3}, \ldots \ldots \vec{R_N}$) only. Denote ψ_N and ψ_e as $\psi_N\left(\left\{\vec{R_N}\right\}\right)$ and $\psi_e\left(\left\{\vec{r_n}\right\}, \left\{\vec{R_N}\right\}\right)$ for

simplicity. Let us write this as $\psi_n\left(\vec{R_N}\right)$ and

$$\psi_e\left(\vec{r_n}, \vec{R_N}\right)$$

4. Split the overall Hamiltonian into two sets of terms:-
One containing electronic kinetic energies, electron-electron repulsive potential energies and the electron-nucleus attractive potential energies,

another containing nuclear kinetic energies and nuclear-nuclear potential energies.

- The next part of Born-Oppenheimer approximation is to separate the above equation into two equations, one for the nuclear motion and the other for the electronic motion. Follow the next few lines of algebra carefully.

$$\widehat{H} = \widehat{H}_e + H_N$$

$$\psi = \psi_e\left(\vec{r}_n, \vec{R}_N\right)\psi_N\left(\vec{R}_N\right)$$

$$\widehat{H}\,\psi = E\psi$$

$$\left(\widehat{H}_e + \widehat{H}_N\right)\psi_e\left(\vec{r}_n, \vec{R}_N\right)\psi_N\left(\vec{R}_N\right)$$

$$\widehat{H}_e\psi_e\left(\vec{r}_n, \vec{R}_N\right)\psi_N\left(\vec{R}_N\right) + \widehat{H}_N\psi_e\left(\vec{r}_n, \vec{R}_N\right)\psi_N\left(\vec{R}_N\right)$$

$$= E\psi_e\left(\vec{r}_n, \vec{R}_N\right)\psi_N\left(\vec{R}_N\right)$$

- Symbolically,

$$\widehat{H}_N\psi_e\left(\vec{r}_n, \vec{R}_N\right)\psi_N\left(\vec{R}_N\right)$$

$$= \psi_e\left(\vec{r}_n, \vec{R}_N\right)\widehat{H}_N\psi_N(\vec{R}_N) + \psi_N\left(\vec{R}_N\right)\widehat{H}_N\psi_e\left(\vec{r}_n, \vec{R}_N\right) + \left\{\widehat{H}'_e\,\psi_e\left(\vec{r}_n, \vec{R}_N\right)\right\}\left\{H'_N\,\psi_e\left(\vec{r}_n, \vec{R}_N\right)\right\}$$

- The second term on the right hand side above consists of all second order derivatives of electronic wave functions with respect to nuclear coordinates. The third term with the primes on the Hamiltonian corresponds to first order derivatives in the Hamiltonian of electronic and nuclear coordinates. (Because the nuclear Hamiltonian $\widehat{H}_N$ contains second derivatives, $\dfrac{\partial^2}{\partial R_N^2}$.) This splitting is the same as we do in calculus for a simple two function product whose second derivatives with respect to the variable is calculated as below:

$$\frac{\partial}{\partial x}\big[u(x)v(x)\big] = \frac{\partial u}{\partial x}v(x) + u(x)\frac{\partial v}{\partial x}$$

$$\frac{\partial^2}{\partial x^2}\big[u(x)v(x)\big] = \frac{\partial}{\partial x}\left[\frac{\partial u}{\partial x}v(x) + u(x)\frac{\partial v}{\partial x}\right]$$

$$= \frac{\partial^2 u}{\partial x^2}v(x) + 2\frac{\partial u}{\partial x}\frac{\partial v}{\partial x} + u(x)\frac{\partial^2 v}{\partial x^2}$$

- The second and the third terms in the Hamiltonian acting on the product of the wave functions are neglected in comparison to the first term $\widehat{H}_N\psi_N(r_n, R_N)$ to give

$$\widehat{H}_N\psi_e(\vec{r}_n, \vec{R}_N)\psi_N(\vec{R}_N)$$

$$\approx \psi_e(\vec{r}_n, \vec{R}_N)\,\widehat{H}_N\,\psi_N(\vec{R}_N)$$

- Thus, the overall Schrödinger equation is written as

$$\left(\widehat{H}_e + \widehat{H}_N\right)\psi_e(r_n, R_N)\psi_N(R_N)$$

$$\approx \psi_N(R_N)\widehat{H}_e\psi_e(r_n, R_N) + \psi_e(r_n, R_N)\widehat{H}_N(r_n, R_N)$$

$$= E\psi_e(r_n, R_N)\psi_N(R_N)$$

- An electronic Schrodinger equation is written for each and every set of $\left\{\vec{R}_N\right\}$ as

$$\widehat{H}_e\psi_e\left(\vec{r}_n, \vec{R}_N\right) = E_e\left(\vec{R}_N\right)\psi_e\left(\vec{r}_n, \vec{R}_N\right)$$

- The energy $E_e(\vec{R}_N)$ is a function of $\{\vec{R}_N\}$, but not $\{\vec{r}_n\}$, the electronic coordinates, because in solving this differential equation in $\{\vec{r}_n\}$, the energy obtained is independent of the coordinates $\{\vec{r}_n\}$.

- For every different set of $\{\vec{R}_N\}$, one must solve an electronic equation as above. Then,

$$\left(\widehat{H}_e + \widehat{H}_N\right)\psi_e\left(\vec{r}_n, \vec{R}_n\right)\psi_N\left(\vec{R}_N\right)$$

$$= E_e\psi_e\left(\vec{r}_n, \vec{R}_n\right)\psi_N\left(\vec{R}_N\right) + \widehat{H}_N\psi_e\left(\vec{r}_n, \vec{R}_n\right)\psi_N\left(\vec{R}_N\right)$$

$$\approx E_e\psi_e\left(\vec{r}_n, \vec{R}_n\right)\psi_N\left(\vec{R}_N\right) + \psi_e\left(\vec{r}_n, \vec{R}_n\right)\widehat{H}_N\psi_N\left(\vec{R}_N\right)$$

$$= E\psi_e\left(\vec{r}_n, \vec{R}_n\right)\psi_N\left(\vec{R}_N\right)$$

In the last equality, cancel the electronic wave function on both sides to obtain

$$\Rightarrow \widehat{H}_N\psi_N\left(\vec{R}_N\right) + E_e\left(\vec{R}_N\right)\psi_N\left(\vec{R}_N\right)$$

$$= E\psi_N\left(\vec{R}_N\right)$$

- Thus the solution of electronic energies $E_e \{\vec{R}_N\}$ acts as a potential energy background to the nuclear motion in addition to nuclear-nuclear repulsion

- There is an infinite number of solutions to the electron problem for each set of nuclear coordinates.

- There are many nuclear coordinates.

- Therefore there are many such infinite sets of energies. In the next page these are illustrated for a diatomic molecule with only one nuclear coordinate, namely the internuclear distance.

Topic 2

The potential energy curve

- Consider a diatomic molecule. There is only one nuclear coordinate of interest to us, namely the distance between the two nuclei, expressed in terms of all six nuclear coordinates (R_{1x}, R_{1y}, R_{1z} and R_{2x}, R_{2y}, R_{2z}) of nuclei 1 and 2

$$R = \sqrt{\left(R_{1x} - R_{2x}\right)^2 + \left(R_{1y} - R_{2y}\right)^2 + \left(R_{1z} - R_{2z}\right)^2}$$

When the electronic Schrodinger equation is solved for one R value for the internuclear distance, we get many (generally infinite number of) energies. Then we take another value of R and generate another set of many energies. We repeat this process for large enough numbers of R which can be plotted as follows: In the plot, all values of electronic energy obtained for a given internuclear distance appear vertically. The animation below this figure will illustrate this concept.
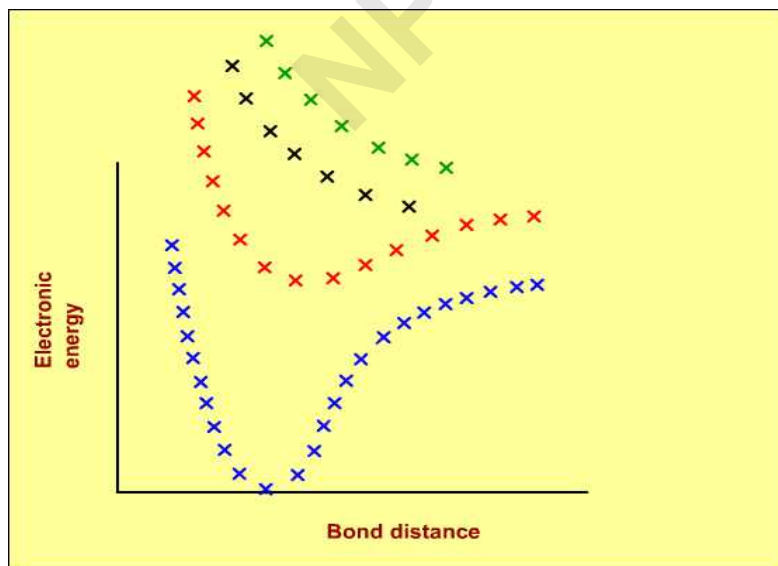
- Connect all the lowest points for each bond length. (blue points) to get the ground (lowest) electronic state potential energy curve

- Connect all the second lowest points for each bond length, to get the first excited electronic state potential energy curve. (red points)

- Connect the third lowest energy points for each bond length to get the second excited electronic state potential

energy curve etc. (black points)

- The electronic transitions are simple jumps (Bohr model for example) of electrons between different electronic states. They result is changes not only of electrons but also nuclei.

  Click the play button below to view the animation on the Born-Oppenheimer potential energy surface.

- This is quantum chemistry. (electronic structure of molecules)

- The solution of nuclear motion in the presence of $E_e(\overrightarrow{R_N})$, given by

$$\hat{H}_N \psi_N\left(\overrightarrow{R_N}\right) + E_e\left(\overrightarrow{R_N}\right)\psi_N\left(\overrightarrow{R_N}\right) = E\,\psi_N\left(\overrightarrow{R_N}\right)$$

- Is the object of molecular spectroscopy. The infinite solutions E obtained by solving the above equation are known as molecular energy levels. The infinite wave functions $\psi_N\left(\overrightarrow{R_N}\right)$ are known as nuclear eigen functions.

  The overall wave functions which are products of nuclear and electronic wavefunctions are known as molecular eigenfunctions.

- Electronic Spectroscopy links quantum chemistry or electronic structure with molecular spectroscopy.

Topic 3

Franck-Condon principle (only vertical transitions)

- An electronic transition is so fast compared to the nuclear motion that during an electronic transition the vibrating molecule does not change its inter-nuclear distance.

- All transitions are assumed to be drawn by vertical lines and not slanted lines as in the figure below.

- The electronic potential energy of a diatomic molecule with bond length as the nuclear coordinate is depicted below. The molecule is assumed to be stable both in the ground and excited electronic state

Franck - Condon Principle (only vertical transitions)
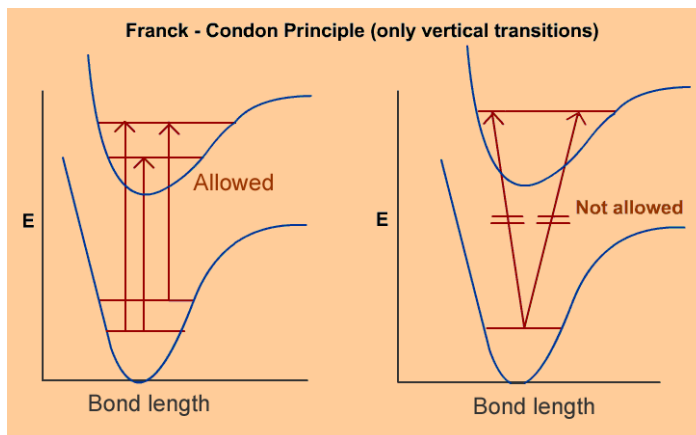
- The left hand figure illustrates Franck-Condon principle. The transitions are vertical from one state to another state

- The right hand figure shows that the bond length of the diatomic molecule in the excited state is not the same as that of the ground state. Such transitions are not possible (not allowed)

- The general reason for this is that the inter-nuclear distance changes due to vibration or rotation of the molecule (centrifugal distortion) which are very slow compared to the time taken for an electronic transition.

  You must know that the Franck-Condon principle is generally valid and is quite important in calculating energies and intensities of transitions in electronic spectroscopy. Exceptions to the rule are also known.

Topic 4

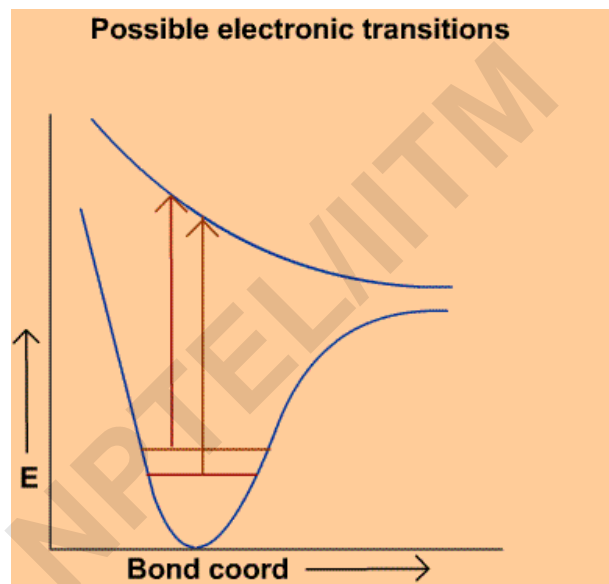### Types of electronic transitions for a diatomic molecule

- Several possible cases arise for Franck-Condon transitions which do or do not lead to any dissociation of diatomic molecule.

  1. The equilibrium bond distance is approximately the same in both the ground as well as the first excited electronic state. (The potential energy minima are the same for both curves)
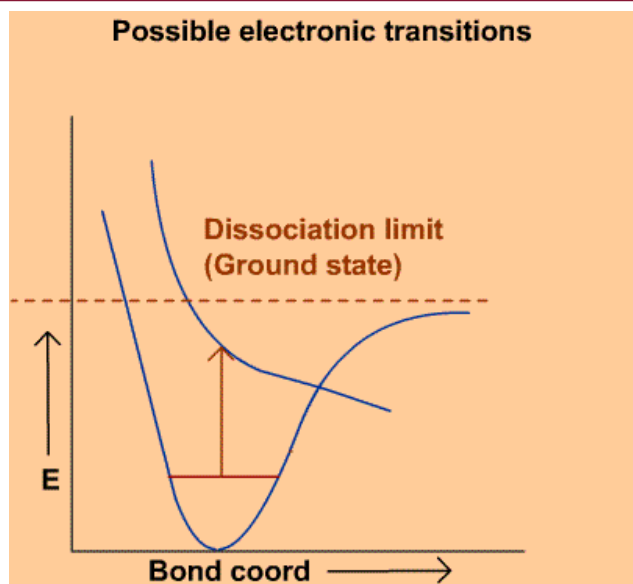

Possible electronic transitions
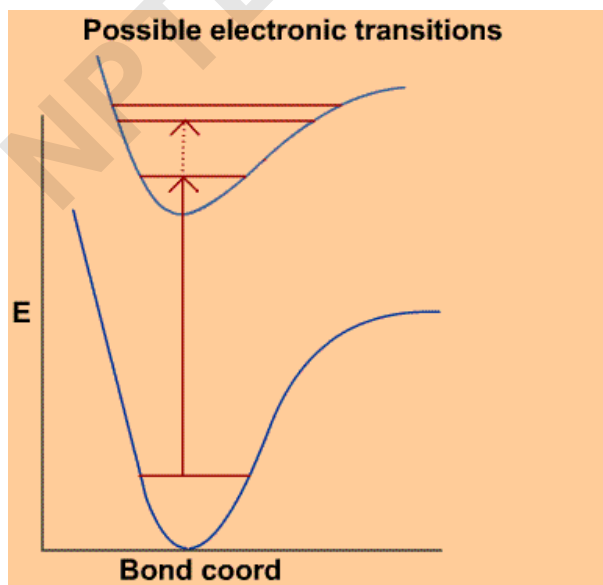
2. The minimum in the energy of the first excited state corresponds to a slightly more stretched bond, than that of the ground state.

Possible electronic transitions
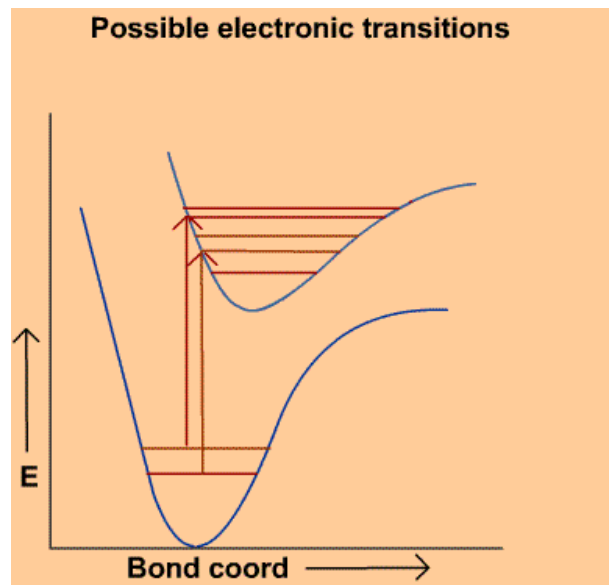
3. The first excited state does not have any minimum in the energy so that the molecule dissociates when it is electronically excited.

Possible electronic transitions

4. The potential energy curves for the ground and excited electronic state cross each other below the dissociation region of the ground state. (Such a phenomenon is called pre-dissociation)

Possible electronic transitions

- Three types of electronic transitions are common:
  1. d-d (bonding d orbital to bonding d orbital) transitions
  2. Pi-Pi* $\left(\pi - \pi^{\bullet}\right)$ (bonding pi orbital to antibonding pi orbital) transitions and
  3. n - $\pi^{\bullet}$ (non-bonding orbital to antibonding pi porbital) transitions

- d-d transitions are important in coordination chemistry. (transition metal complexes).

- The d -orbitals of transition metal complexes are not five -fold degenerate, but split into at least two different energy levels. They are often not completely filled, leading to the possibility of electrons in the lower d-orbital being excited by visible light to higher d-orbitals. This explains why many transition metal complexes are highly colored.

- $\left(\pi - \pi^{\bullet}\right)$ and n - $\pi^{\bullet}$ are usually transitions of an electron from a bonding (π) or a non bonding (n) orbital to an antibonding orbital. $\pi^{\bullet}$ eg. absorption in C=O bonds is a transition from non-bonding oxygen orbital to an antibonding orbital of C=O molecule.
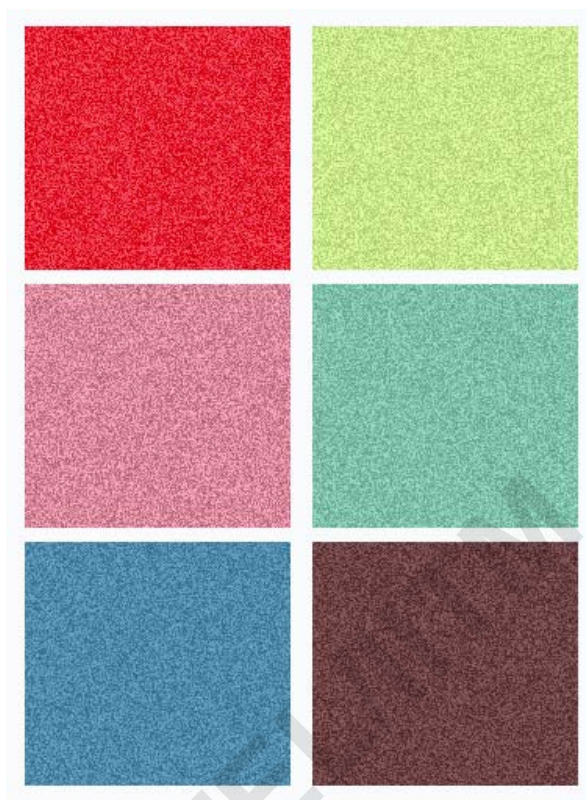
Fluorescence:

When a species is excited by an electromagnetic radiation, the radiation might be absorbed or emitted back at the same or different frequency compared to the incident radiation.

- If radiation is emitted spontaneously immediately, the phenomenon is called fluorescence, and the molecule is said to fluoresce.

click the play button to view the animation

The radiation is emitted with a delay and persists for quite sometime, it is called phosphorescence.

- Fluorescent colour of natural dyes are examples. Light in the uv region is absorbed, some energy is lost in the vibrational mode and collisional process. The light emitted is usually of a lower frequency than the incident light. A few samples are given here.

- The potential energy curve for a typical fluorescence process is seen below. A fluorescing molecule gets excited from a lower electronic to an upper electronic state, and quite often reemits light through the sequence of jumps between vibrational states.
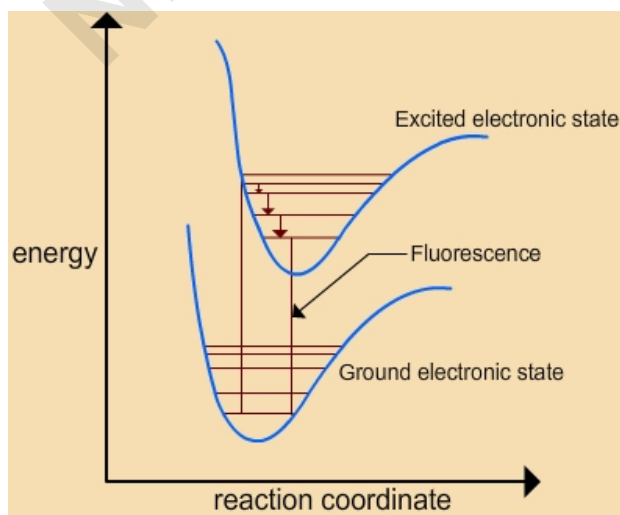
Phosphorescence:

If a molecule is excited from the ground electronic state to an excited electronic state and if it relaxes by emitting light energy after a considerable delay, it is often associated with phosphorescence. The delay in the emission of radiation is due to the fact that the electronic states undergo transition which are forbidden in general. The emission eventually occurs due to the spin-orbit coupling phenomenon by which the electronic spin angular momentum and the orbital angular momentum interact. The emission is usually from a triplet state to a singlet state (spin states for a pair of spins). Examples of phosphorescing materials are those present in displays-TV, watch, LCD etc as well as the light green colour that persists for a few seconds after shining ZnS with light and then placing it is the dark. Understanding of this phenomenon is through angular momentum coupling in electrons.

Topic 5

Vibronic structure and spectra

- Electronic spectra are possible for all molecules, homonuclear, heteronuclear etc.

- Spectra contain a coarse vibrational structure and a fine rotational structure.

- Neglecting the rotational structure and assuming a Morse oscillator model for vibrational motion, the energy of an vibrational- electronic (vibronic) state is

  $E = E_{electronic} + E_{vibrational}$
  $E = E_{electronic} + (n+1/2)h\,v_e - (n+1/2)^2 h\,v_e x_e$

  n = 0,1,2,3,….etc
  v_e = is vibrational frequency
  x_e = is anharmanicity, or a measure of deviation from a harmonic model,
  h = Planck's constant
  For morse oscillator energy levels, please read the lecture on vibrational spectoscopy.

- The transition frequency for a vibronic transition (E n to E" n") is

  $$\upsilon = \frac{\Delta E}{h}$$

  $$= \frac{\Delta E_{electronic}}{h} + \left\{ \left(n'+\frac{1}{2}\right)\upsilon'_e - \left(n'+\frac{1}{2}\right)\upsilon'_e x'_e - \left(n''+\frac{1}{2}\right)\upsilon''_e - \left(n''+\frac{1}{2}\right)\upsilon''_e x''_e \right\}$$

- The electronic transitions are assumed to be from vibrational level n" to n" both of which are modeled after Morse oscillator

- v'_e and v''_e are harmonic frequencies of the upper and lower vibrational states: x_e' and x_e'' are the respective anharmonicity constants

- $\triangle E_{electronic}$ is the transition energy between ground and excited electronic states (with n'= n"=0)

- All vibrational-electronic (vibronic) transitions are allowed, namely,

  $E'-E'' = \pm 1, \pm 2, \pm 3,……..$
  n '- n" = $\pm 1, \pm 2, \pm 3,……..$

  End of lecture 1 in spectroscopy module.