Photons

Overview

- In this lecture you will learn,
- Quantum nature of light
- Energy levels in atoms and molecules
- Absorption of photons
- Keywords: Photons, energy levels, absorption of light

Photons

- Certain phenomena, such as, the blackbody emission spectrum and the photoelectric effect could not be explained using the classical EM approach. The solution came in the postulate that the energy of the wave can not be continuous but discrete values related to the frequency of oscillation.

- A photon is a single quantum, i.e. the smallest possible value, of EM energy. The energy of a photon is related its frequency, ν, by, $E = h\nu$

Photons

- If we consider a light radiation with energy E per second, we say that the number of photons impinging on the detector per second is n where $E = nh\nu$

- In addition photons also carry momentum p given by $p = h/\lambda$. This momentum is useful in applications where light can be used to manipulate the motion of small objects, e.g. optical tweezers

Quantum Picture of Matter

- The idea of photon and quantization led to the development of quantum theory, where the central equation is Schrodinger's wave equation, given by

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + (V - E)\Psi = 0$$

where h is the planck's constant,
m is the mass of the particle in potential field given by V and E is the energy of the particle, Ψ is called the wavefunction which is related to the probability of finding the particle in a given region of space.

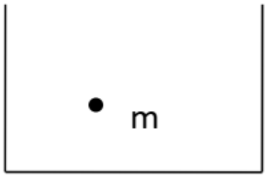
Quantum Picture of Matter

- As one can verify, this equation has the same form as the spatial part of the EM wave equation we saw in previous lectures. The interesting thing here is that mass, which is a particle attribute, and Ψ, which is a wave attribute, comes together in the same equation.

- After solving the equation for a given V, one obtains several 'modes' or 'states' for the wavefunction, each of which have distinct energies giving rise to the picture of energy levels in atoms.

Particle in a Box

- The simplest system that describes many of the quantum ideas is a particle in a box. Consider a particle of mass m, in a potential well as shown in the diagram. The potential is 0 inside and ∞ outside the box. When one solves the Schrodinger equation for this case with the boundary condition that the wave function goes to 0 at the boundaries of the well, one sees that any ψ_n of the form, $\psi_n(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$ is a solution



Particle in an infinite potential well

Particle in a Box

- The wavefunction in the previous slide leads to a quantized energy of the particle given by $E_n = n^2 \frac{h^2}{8ml^2}$

- This means that the particle can be in any of the n states with some probability. The lowest state with n = 1 has the lowest energy and higher states have increasing energies. The energy difference between successive levels increases with n. This simple model provides an intuitive understanding of devices such as quantum dots to be seen later.

Energy Levels in Atoms

- Electrons confined in an atom behave like particles in a box and their states are also quantized into various energy levels. Unlike the particle in a box which is characterized by a single quantum number, an electron is characterized by 4 quantum numbers, namely, principal, azimuthal, magnetic and spin quantum numbers, denoted by n, l, m and s.
- A state with a given combination of n,l,m is called an orbital. The allowed values for l and m depend on n. The allowed values of l is from 0 to n – 1. For a given l number, the m values can range from –l to +l. For each n,l,m combination two spins, +1/2 and -1/2 are allowed. The value of n and l determine the shape of the atomic orbital. For instance n = 1, l = 0, called the 1s orbital is spherically symmetric, while n = 2, l = 1 called the 2p oribtal is like a dumbbell.

Electronic Energy Levels in Atoms

- Electrons get filled in the atomic orbitals in the increasing order of energy, i.e. the lower energy levels get filled first. Pauli's exclusion principle states that two electrons can not have same quantum state. Therefore a given combination of n,l,m defining one orbital can only have two electrons with opposite spins.

Energy Levels in Molecules

- Molecules are complex entities where it is impossible to find straightforward analytical solutions to the Schrodinger equation. To address this complexity, Born and Oppenheimer approximated the energy states by partitioning the problem into energy states of the fast moving electrons and slow moving nuclei. These lead to the notion of electronic energy levels and vibrational energy levels due to the relative motion of the nuclei making up the molecule. There is also a rotational motion related to the relative angular displacements of nuclei.

- Electronic energy level separations are the largest in energy, covering a wavelength range from ultraviolet (UV) to infrared (IR). As we saw earlier, energies can be converted to frequency and consequently wavelength using the relation $E = h\nu = hc/\lambda$. Vibrational energy levels are separated by smaller energy values in IR spectral region while rotational energies are even smaller, in the microwave region. As well will see later probing the vibrational energy levels of molecules are specific to the chemical bonds present in the molecule.

Molecular Electronic Energy Levels

- The idea of a molecular orbital is used to describe electronic energy. A molecular orbital is a linear superposition of atomic orbitals. We have already seen that atomic orbitals arise due a situation similar to the particle in a box. When two atoms come together, their atomic orbitals can interact to produce a chemical bond. This interaction is described by a linear combination of the atomic orbitals involved and therefore this model is called LCAO (Linear Combination of Atomic Orbitals). Orbitals need to have similarly energy levels to interact strongly.

Electronic Energy Levels in Molecules

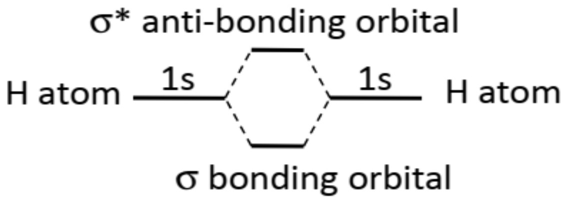
- The wavefunction of the molecular orbital (MO) can be written in terms of atomic orbitals AO_1, AO_2 as,

$$\psi_{MO} = c_1\psi_{AO1} \pm c_2\psi_{AO2}$$

- The + sign corresponds to a situation similar to constructive interference and it produces a molecular orbital called the bonding orbital which has an energy lower than the energies of the atomic orbitals. The – sign corresponds to an anti-bonding molecular orbital with a higher energy than the atomic orbitals.

Molecular Orbitals

- The diagram below shows the formation of molecular orbitals in the case of H2 molecule. The 1s orbitals of each hydrogen atom interact to produce s bonding orbital and s* anti-bonding orbital. There are two electrons in total which are filled in the same manner as atomic orbitals, i.e. in the increasing order of energies, first filling one electron in each and then pairing with an electron with opposite spin. Going by this procedure, we see that the two electrons from each hydrogen atom will occupy the bonding orbital.
- It is also possible for s orbital to interact with other orbitals such as p. σ molecular bonding orbitals are formed when the resulting molecular wavefunction is symmetric about the internuclear axis. If it is not, the resulting orbitals are called π orbitals or π bonds



Molecular Bonds

- In the case of covalent bonds, the bonding molecular orbital has a well defined minimum energy state with respect to the interatomic separation and orientation. This gives rise to the detailed molecular structure for complex covalent molecules.
- In certain cases the electrons are not equally shared, the resulting wavefunction may be asymmetrically shifted towards one of the atoms, e.g. F in HF. In this case we get an ionic bond due to the imbalance in charge distribution where the molecular attraction is predominantly electrostatic in nature.
- In the case of metals the electrons are shared between several nuclei leading to a sea of 'free electrons' which are responsible for the high electrical conductivity and high optical reflectivity (in the visible region) of metals.

Vibrational Energy Levels

- As we saw atoms are held together in a molecule by various bonds. However, they are still free to move about as in a spring mass system. For a given molecule the relative motion of atoms can be described by an effective mass and an effective spring constant and potential V in the form of $\frac{1}{2} kx^2$. Putting this V in Schrodinger's equation and solving for energy levels, we see that vibrational energy levels are also quantized with $E_n = (n + \frac{1}{2})h\nu$. There are many modes of vibrations, for e.g. a diatomic molecule can have stretching vibrations, a triatomic molecule can have stretching along various directions and so on.

Vibrational Energy Levels

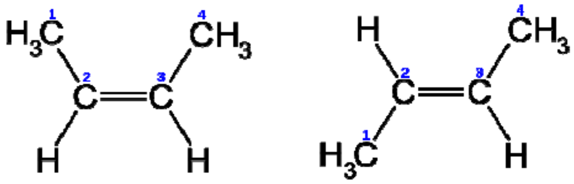
- The vibrational energy level spacing is in the IR region of the spectrum. The vibrational modes are coupled leading to distinct frequency spectra for different molecules. As we will see in later sections vibrational spectroscopy is a powerful tool in the identification of chemical groups present in a sample.

Intermolecular Effects

- Molecules interact with one another by various mechanisms. In the simplest case there can be electrostatic interaction between molecules that are charged (ionized) in solution.
- There can be van der Waals interaction between molecules which is due to temporal asymmetries in the electron cloud densities occurring even for neutral molecules. These are weak, short range interactions.
- There can be hydrogen bonding which is the result of electrostatic bonding between a electrodeficient H atom (e.g H bonded to an electronegative atom like F) to another electrorich atom.
- There can be other interactions such as hydrophobic interactions where non-polar groups in molecules adhere to each other.
- These interactions are responsible for a wide variety of processes that occur in biological systems.

Geometric and Optical Isomers

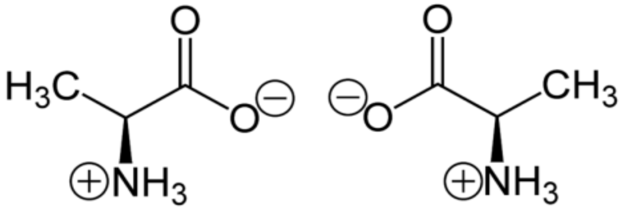
- Isomerism is a phenomena exhibited by some molecules. Consider a molecule as shown in the diagram below. The double bond does not allow the rotation of atoms around its axis. Therefore the two forms of the molecular structure shown below are distinct. One form can not be transformed to the other. These forms are called geometric isomers.



- The H and the CH3 groups of one form can not interchange their positions due to the double bond resulting in two distinct structures for the same molecule which co-exist.

Chiral Molecules

- There are classes of molecules which display handedness, i.e. the mirror image of one can not be super imposed on the other. These are called chiral molecules. An example of a chiral molecule is shown below.



- Chiral molecules are said to be 'optically active' because they rotate the plane of polarization of linearly polarized incident light. The amount of polarization rotation is a measure of the chirality of the molecule. Some chiral molecules show a difference in absorption of light for right circular and left circular polarized light. This phenomena is called circular dichroism (CD) which is another tool to characterize chiral molecules.