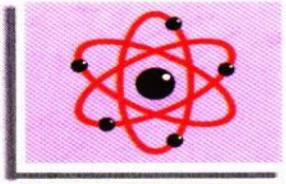
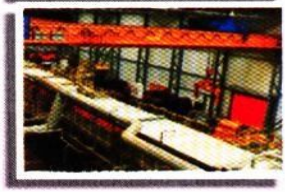




"THE QUESTION OF THE ELECTRON: ITS ORIGIN & IMPACT ON CHEMICAL PROCESSES"

27th Inaugural Lecture

of the Federal University of Technology, Owerri (FUTO), Imo State.

Delivered On

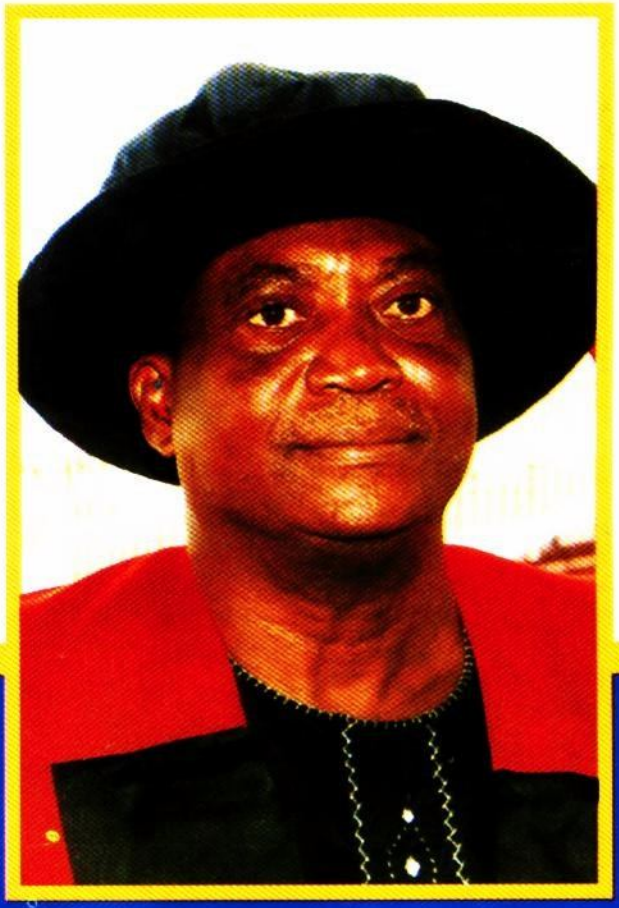
Thursday, March 10, 2016

By

PROF. ATU AUSAJI AYUK.

D.Sc., CChem., FICCON, MIPAN, FCSN
(Professor of Quantum and Theoretical Chemistry)
Dept. of Chemistry, Federal University Of Technology, Owerri.

INAUGURAL LECTURER



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Wer ueber Quantenmechanik nachdenken kann ohne wirr im kopf zu warden, hat sie nicht wirklich verstanden.[1]

Whoever reflects on or studies Quantum Mechanics and does not get confused, has not really understood the subject matter.[1]
Niels Bohr 1885 - 1962

PREAMBLE:

I give thanks to Almighty GOD to be privileged to give a second public lecture[2], this one being an inaugural.
The first lecture was delivered in the 500-capacity lecture theater, precisely on the 3rd of June, 2011 during the late Professor Celestine O E Onwuliri's tenure **as the fifth substantive** Vice Chancellor of the Federal Univversity of Technology, Owerri. May his gentle soul be in perfect harmony with the entire Universe. Suffice it to say that though Professor COE Onwuliri was a VC appointed from outside FUTO he was beloved and was a man of the people; like our in-house, sitting Professor of infrastructural development, Professor Chigozie Cyril Asia baka.Mr. Vice Chancellor, Sir, we need not remind you that we are all your children and equal treatment of staffs must be meted to all alike. I must thank you for having produced the largest number of Professors in one Senate meeting, equal to none in any Nigerian University. The promotion and arrears of promotion of our non-academic staff should not be forgotten before you leave office as VC in June this year. Inaugural lectures are meant for Professors. I am therefore taking this opportunity to fulfill all righteousness in a field that may not be palatable to the general public. I shall, as required of every Professor, make it simple to the understanding of a layman.

INTRODUCTION:

It is not as if I am unaware of the new trend of thoughts in the sciences[3] which tries to classify what I choose to call electrons as radicals but

that science started from **somewhere** and I will also start from that **somewhere**.

Science simply is accumulated knowledge based on observations. This knowledge can be tested, verified, properly organized and classified. We observe these phenomena or facts in nature or in our laboratories. The observation put in form of a general statement is what we call a 'law'. Exceptions or deviations from the law usually exist. A perfect example can be taken from the Gas laws. In Boyle's law for instance, we say that $PV = nRT$. This law does not hold good at high pressures and very low temperatures. One will note here that there are three constants in this mathematical expression. 'V' which is a given volume is constant; 'n' is the number of moles in the given volume is also a constant and 'R' is the gas constant. Usually we see explanations of experimental facts by putting forward a reasonable GUESS which we call a HYPOTHESIS. If a hypothesis is found correct, it becomes a THEORY. This now leads us to the Atomic Theory put forward by John J. Dalton[4] which has undergone a series of modifications and in some cases discarded totally. It is based on this theory that we develop our premise ***in search of the electron.*** Just as some laws have no satisfactory explanation and some theories are even discarded as the search goes on, here modern search probes explores into the areas of the unknown.

In the era before Christ or Mohammed (four hundred years after Christ), science was not divided but was practiced as natural observations. Before John J. Dalton's hypothesis in 1808 which later metamorphosed into a theory, observations of the nature of the atom were already formulated and even debated upon by the then observers or scientists in black Africa, China, Egypt[5,6] and India[7,8]. Other natural observations were also known to have taken place by American Indians in South America. Knowledge as at then could be divided into Astrology, Biology and Pharmacy.

Astrology is involved in the study of the universe and observations of

the movement of the earth and other planetary systems as is the case in the records of the University of Timbuktu[9]. Biology as at then involved the study of the plants and animals observed. Pharmacy on the other hand involved the study of how the sick could be cured with the help of plants and other animals observed around them. It is from the Prowers of the black Africans in using and producing new materials especially from plants that the Egyptians came up with the expression alchemist. The origin of the word is though Greek, *khemia* (the art of transforming, usually metals) but the idea was purely Egyptian.

In the beginning of the 17th Century no defensible ideas about the structure of matter could be put forward. To understand the basic concept of matter one has to fall back on the historical development of the atom which in chemistry began with Dalton. The question that occupied the minds of the medieval thinkers or philosophers was: what is matter made of? Ancient philosophers like Democritus[10] thought of matter as consisting of an infinite number of indivisible atoms that filled the universe. Democritus further thought that these atoms that filled the universe had different sizes, shapes and weights. Democritus could not prove his case and ancient philosophers discarded his ideas which could not even be backed by experiments. Aristotle[11] around the same period indeed believed that matter was continuous and definitely divisible. He had thought that matter was made up of the then known elements: air, earth, fire and water. The ancient philosophers tended to believe him because the facts were self-explanatory. Around the early nineteenth century an English schoolmaster of Quaker decent, published experimentally backed arguments in favour of the existence of atoms. The theory that gave rise to the ideas about the structure of matter came from John Dalton who put forward a postulate that everything (matter) consisted of indivisible particles called atoms. The word atom is of Greek origin and means indivisible. He further postulated that atoms of a given element are ***alike*** in ***mass*** and **different** from those of other elements. He also maintained that *atoms combine in small whole number ratios*

to form compounds.

The definition of the atom had taken a new dimension from John J. Dalton's concept. An atom now became the smallest part of an element that can take part in a chemical reaction. The atomic theory can be considered as the mother of modern chemistry. We cannot talk about atomic theory without first of all referring to what brought about the Dalton's atomic theory. Before then, it is important to note the theory came about through philosophy. It was through the divided opinions of the ancient Greek philosophers; some thinking that matter is made up of air, earth, fire and water others maintaining that matter is composed of small indivisible particles that retain the properties of the matter.

We have no doubt today that matter consists of atoms and ***our present day understanding of the nature of atoms and molecules is based on our knowledge of the quantum mechanical theory. Classical mechanics, the then known theory had failed to explain the behavior of microscopic matter so the development of quantum theory provided adequate description of the atomic and molecular models.***

The next thought is the discussion of Dalton's ideas step by step. Matter is made up of minute indivisible and indestructible particles called atoms ***though matter is made up of indivisible and indestructible particles, we cannot see atoms even with the most sophisticated microscope.*** We are then to depend on indirect methods to establish this fact. This can be done by inferences from experiments. Matter as we know has been defined as anything that has weight and occupies space. Although Dalton made us know that atoms are basic units of matter, we can also deduce this fact from the generalized chemical laws as can be seen in the laws of multiple proportions, constant composition.

That matter is made up of atoms is what is called the atomic theory

and the ideas, which make up the Dalton's Atomic Theory, are: *Each of the various types of matter is made up of minute indivisible, indestructible particles called atoms and that atoms can neither be created nor destroyed in a chemical reaction.*
Atoms of a given type of matter are alike in mass (weight) and other properties, but are different from those of other types of matter.
That in any chemical reaction between matter "A" and "B" the atoms of A combine with the atoms of B in small whole number ratios e.g. Atom A combines with B to form AB or two atoms of A combine with one atom of B to form A$_2$B.

The work of Michael Faraday on electrolysis[17] within the same period also established the connection between matter and electricity. He brought about this connection in his two laws called Faraday's laws of electrolysis.

1. *The mass of a given material deposited at the electrode is proportional to the quantity of electric charge that passes through the cell.*
2. *A given quantity of electricity produces masses of material that are proportional to the equivalent masses of the substances.*

This second law indicates that electricity is composed of a different kind of particle and GJ Stoney in 1874 named these particles *electrons*. One of nature's fundamental particles was discovered by the Irish physicist George Johnstone Stoney (1862 - 1911). GJ Stoney was born on 15-02-1826 and he at first introduced the term 'electrine' as the fundamental unit of electricity in 1874.[17,18] In 18971 he proposed the term 'electron' to describe the fundamental unit of charge and the contributions to research in this area led to the discovery of the particle in 1897 by Joseph John Thomson[19,20].

Apart from discovering the electron, Stoney was a great champion of the metric system and he therefore invented a standard unit of electricity. Initially he called this unit an "electrine" which was later

changed to an "electron" which he presented to the British Association for the Advancement of Science at its 1874 annual meeting. When in 1897, JJ Thomson discovered the cathode rays as beams of negatively charged particles which he called 'corpuscles' he did not realize that corpuscles were nothing else but electrons. GJ Stoney at 26 was made Professor at Queens College Galway against a better qualified John Tyndall, thanks to Lord Rosse's (William Pearson's) influence for whom he had worked. Stoney was a socialist and fought for the education of women which resulted in the first woman medical doctor being produced in Ireland.

Dalton over two thousand years later retained the idea that the atom was ultimately an indivisible particle. The electrical experiments of the 18th and 19th century beginning with Benjamin Franklin, had assumed that the current flowed from the concentration of arbitrarily named positive to that named negative.

The physicist William Crookes had showed that in actual fact, the assumption was wrong and the flow was from negative to positive. In 1876 the German physicist Eigen Goldstein named the flow "cathode rays"
A similar theory of electrical atomicity was advanced by Helmholtz in his Faraday lecture in 1881 and about ten years earlier Stoney had introduced the word " electron" for the fundamental unit. The term later came to be used for the "corpuscles" by Joseph John Thomson.

In 1897 J.J. Thomson discovered free electrons in a low - pressure gas between two electrodes. As was mentioned earlier Thomson called these particles **'corpuscles'** but later changed, to name them **'electrons'**. The glow from the tube were caused by rays coming from the cathode or negatively charged electrode. These rays were therefore called the cathode rays.

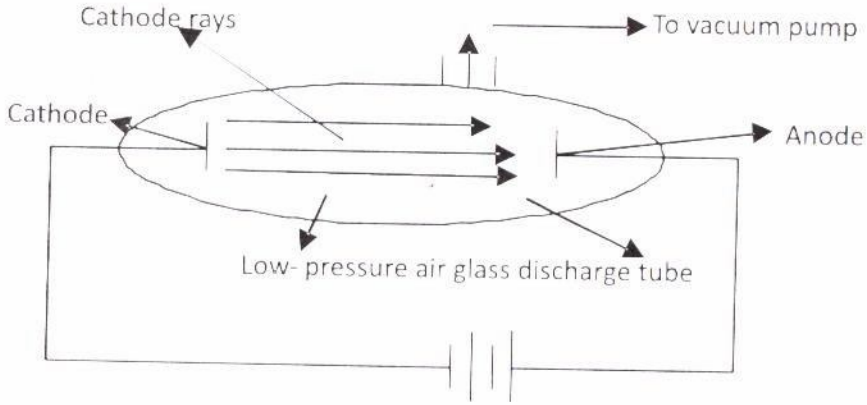


Fig 1.1: Diagram showing Cathode ray tube

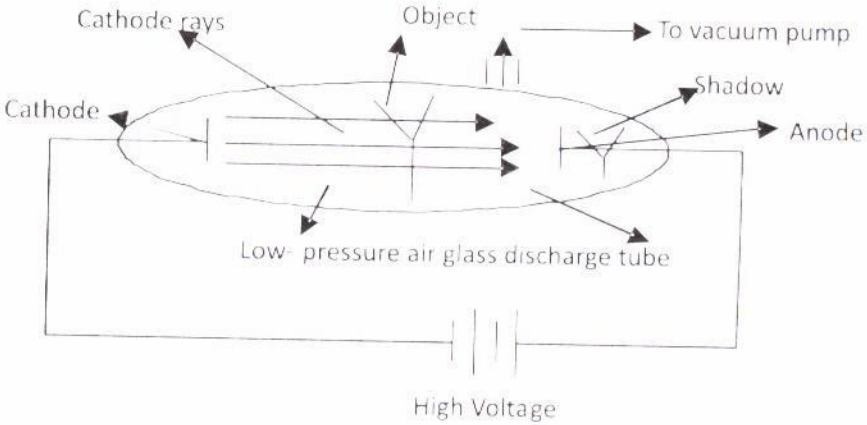


Fig 1.2: Diagram showing the effect of an object in the path of cathode ray tube

The determination of the charge/mass ratio of the electron was conceived from the fact that the electron is deflected by magnetic field. This fact is demonstrated by the figure below:

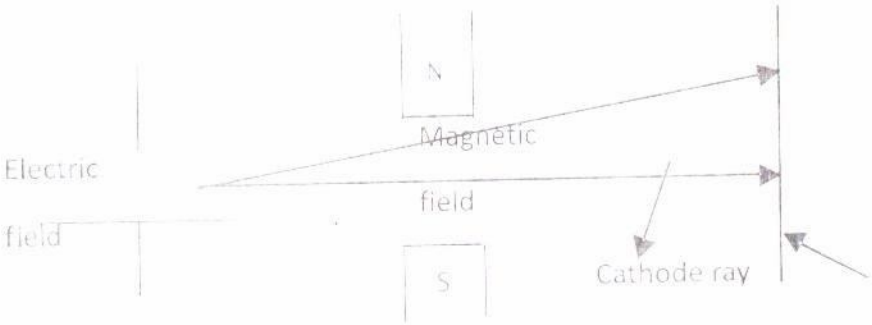


Fig 1.3: Diagram showing deflection of cathode ray by magnet field

Joseph John Thomson determined the charge to mass ratio based on the fact that the cathode rays are deflected when a magnetic field is placed in the path of the rays. When the field is removed the rays come back to their original path. The diagram above shows the method used in the determination of the charge to mass ratio.

Thomson's experiment did not stop at the discovery of the electron from the cathode rays. He also determined the ratio of charge to mass e/m for the cathode rays, which were known by him to be deflected in both electric and magnetic fields.

2.0 MODELS OF THE ATOMS: RUTHERFORD AND BOHR MODELS. THE NATURAL PARTICLES OF THE ATOM

Thomson in 1906 then proposed the first model of the atom as shown in the diagram below:

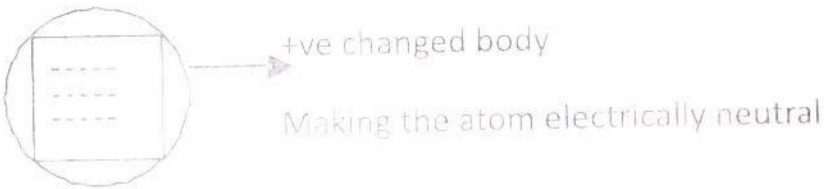


Fig 2.1: Thomson's model of the atom

This model did not survive long. At this time, experiments were being carried out to determine the properties and behaviour of - particles. Geiger, Marsden and Rutherford[21] carried out experiments in which - particles were bombarded against gold foil. Most of the particles passed through the foil undisturbed. A few of them were deflected and even scattered back to the source. The atom was then conceived to have a concentration of its mass centrally located called the nucleus and possessing a positive charge.
Surrounding the nucleus was the electron revolving around it.

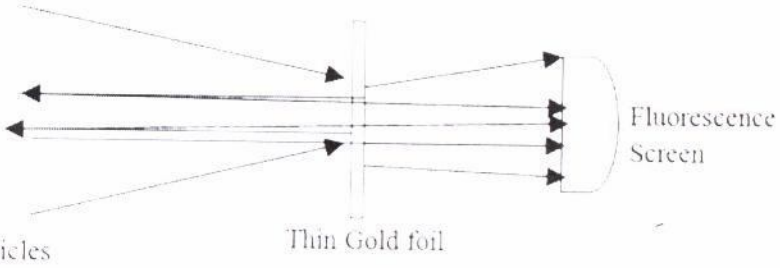


Fig2.2: Rutherford's Gold-foil experiment

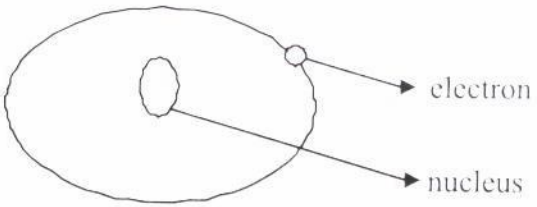


Fig 2.3: Diagram of Rutherford's concept of the atom

Unlike Thomsom, Rutherford's[21] gold foil experiment showed that the electrons reside outside the nucleus of the atoms. At this time classical mechanism could not find explanation for the stability of such a system.

Rutherford's (a student of J.J Thomson) concept of the atom was the true origin of the structure of an atom. He concluded that an atom consisted of a positively charged nucleus around which electrons revolved as in our planetary system. The atomic model was a great success in the study and research of the structure of the atom but had its drawbacks.

Before this time much was already known of electrodynamics. The electrostatic forces of attraction and repulsion of like and unlike charges respectively were well known.

A positively charged nucleus with electrons revolving around it could provoke consequences. One of such a consequence is: If the force of attraction between oppositely charged particles were not equal as a result of the energy lost during revolution, the electron could fly out of the atom. The other consequence being that for equally charged particles with one revolving around the other and thereby loosing energy as result of the accelerated charge particle, the positive charge which maintains its energy could attract the lower energy negative charge and the electron would collapse into the nucleus.

These were the drawbacks in Rutherford's atomic model, which could not explain why revolving electrons did not lose energy and also was not attracted to the nucleus in accordance with the established facts of electrodynamics.

At this time Planck and Einstein had developed theories to explain the results of the attraction of radiation and matter. They were both Germans and theoretical physicist. On the other hand Rutherford and Thomson were British and experimental physicist.

In 1900 Max Planck analyzed radiation from a blackbody (radiation emitted by a hot glowing object) from which it is considered to be of continuous energy.

Earlier investigations had already found that the strength of the emitted radiation varied with the wavelength in a manner that the wave theory could not explain.

Planck then proposed that this radiant energy of the oscillators was not continuous and that harmonic oscillators could absorb or radiate energy in a manner characteristic of waves but rather in small packets or

bundles that he latter called *QUANTA*. He stated that the energy is directly proportional to the frequency.

$E \propto \upsilon$ or $E = h\upsilon$

where h is Planck's constant. In his assumption Planck has also introduced unaware another phenomenon, that of the dual nature of electrons. This is sometimes referred to as the Corpuscular and the wave nature of matter first introduced by Isaac Newton[22]. Quantum mechanics is thus a unification of two theories: electromagnetic waves exhibiting particle character and the classical physical particles exhibiting wave character. The wave-particle duality can fall under any of the four natural forces, viz.:

Electromagnetic force
Weak nuclear or covalent forces
Strong nuclear or ionic forces and
Gravitational forces.

Evidence to prove this is given by Compton Effect and Maxwell's wave theory.

Neils Bohr[23] a young Dane who at one time Rutherford's research student brought together the two thoughts of physics to advance a completely new concept which accounted for the stability of the nucleus-electron system of the atom.

Bohr's atomic model (exemplified by the H-atom was based on the following postulates:

Electrons circle around the nucleus of an atom in definite shell or allowed stationary states.

An electron does not radiate energy in its shell. When it absorbs or gives off energy, the energy required, for the electron to leave from one shell to the other is equal to the energy difference between the two shells.

$$\Delta E = E_f - E_i$$

where E_f is final energy and E_i is initial energy.

The allowed stationary states are those in which the properties of the electron have unique values of the angular momentum of the electron revolving round the nucleus of the atom which must be an integral multiple of

nh, where 'n' can take values from 1 to ∞ and h is Planck's constant.

From Bohr's third postulate of quantized - angular momentum we have that

$$\text{Angular Momentum} = I\omega = nh$$

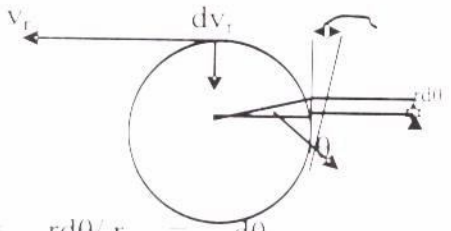
To calculate the radius of the allowed stationary states or shells predicted by Bohr's postulate, the principles of classical mechanics and electrodynamics are employed. For classical mechanics, Newton's Second Law of Motion $F_c = ma$ is employed. For Electrodynamics, Coulomb's force between the positively charged nucleus and the negatively charged electron is used.

$F_C = - q^2/(4\pi \varepsilon_0 r^2)$

The two forces balance to give a neutral atom

Thus $F_N + Fc = 0 \ldots\ldots\ldots A$

$F_N = ma = mv^2/r$



$dv_t/ v = \underline{rd\theta/ r} = d\theta$

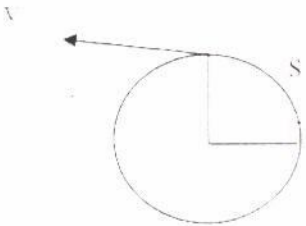
$dv_t/d\theta = v$

$\frac{dv_t}{d\theta} = v$

$dv_t/ d\theta = \lim_{\Delta\theta \to 0} \Delta v_t/ \Delta\theta = v$

$a_t = dv_t/dt = vd\theta/dt = v\omega = v^2/r$ where a_t is the centripetal acceleration.

Note that



$\omega = \theta/t$

θ in rad, ω in rad s^{-1}

v is instantaneous velocity of particle with its direction tangential to the circle at every instance,

$s = r\theta$ and $s = vt$

Therefore $r\theta = vt$ or $r\theta/t = v$

But $\theta/t = \omega$, it follows that $v = r\omega$ or $\omega = v/r$

$\therefore a_r$ (centripetal acceleration) $= v\omega = v.\ v/r = v^2/r$.

ω = angular velocity which is the rate of change of the angle θ

i.e. $\omega = d\theta/dt$

But $\omega = r/r \times v/r = r\,v/r^2$

where v is the velocity of the electron in circular path.

And momentum = m v

Angular momentum = m v r = m ωr^2

$\therefore$ Angular momentum = m $r^2 \omega$

Also I (moment of Inertia = m r^2)

$\therefore$ Angular momentum = I ω = n h

This is a quantum restriction introduced by Bohr, where n = 1, moment of inertia of the electron proton system is given by the last equation with $I = mr^2$ where m is the mass of the electron.

The columbic force is given by

$Fc = - q\ q / 4\pi\varepsilon_0 r^2$

$= - q^2 / 4\pi\varepsilon_0 r^2$

This is the coulomb's force of attraction between the nucleus and the electron. This negative sign shows that this is a force of attraction. Note that $4\pi\varepsilon_0$ is the permittivity constant with a value of $1.113 \times 10^{-10} C^2 N^{-1} m^{-2}$.

The charge of an electron, q is -1.6029×10^{-19} C, r is the distance between the charges, $\varepsilon_0 = 8.8542 \times 10^{-12} C^2 N^{-1} m^{-2}$ is a constant which depends on the system of units used to measure the force, charge, and distance.

Substituting F_N and F_C in equation (A) we have

$(mv^2)/r + (-q^2/4\pi\varepsilon r^2) = 0$ .....B

where $m^* = m_e$

Note the 3rd postulate states that $m\,v\,r = n\,h$
where $n = 1, 2, 3 \ldots\ldots\infty$

It follows that

$$\int_{\theta=0}^{2\pi} prd\theta = nh$$

That is $pr\Big|_0^{2\pi}$

$= pr2\pi - pr\,0$

$= 2\pi pr = 2\pi mvr = nh$ .....(C)

Note $p = m\,v$

Rearranging (B) we have $mv^2/r = q^2/4\pi\varepsilon_o r^2$... (D)

or $mv^2r^2/r = q^2/4\pi\varepsilon_0$

i.e $mv^2r.mr = q^2/4\pi\varepsilon_o.mr$

This is the same as

$m^2v^2r^2 = q^2 mr/4\pi\varepsilon_0$ ..... (E)

But from equation (C)

$2\pi mvr = nh$

or $mvr = nh/2\pi$

$\therefore m^2v^2r^2 = n^2h^2/4\pi^2$

Equation (E) therefore becomes $n^2h^2/4\pi^2 = q^2mr/4\pi\varepsilon_0$ which when rearranged takes the form

$$\frac{n^2h^2 4\pi\varepsilon_0}{4\pi^2} = q^2mr$$

$\hbar = h/2\pi$ or $\hbar^2 = h^2/4\pi^2$

or $n^2h^2 4\pi\varepsilon_0$

$r = n^2h^2 4\pi\varepsilon_0 / q^2m$

where n can take values of n = 1, 2, 3 .....∞

For $r_n = n^2h^2 4\pi\varepsilon_0 / q^2m$ ..... (F)

For n = 1

$r_1 = 1^2 h^2 4\pi\varepsilon_0/q^2m$

For n = 2

$r_2 = 2^2 h^2 4\pi\varepsilon_0/q^2m$

$= h^2 16\pi\varepsilon_0/q^2m$

For n = 3

$r_3 = 3^2 h^2 4\pi\varepsilon_0/q^2m$

$= h^2 36\pi\varepsilon_0/q^2m$

2.1 BEHAVIOUR OF THE ELECTRON and THE DUAL NATURE OF LIGHT

We have in the Dalton's Atomic Theory discovered that matter is made up of individual particles called atoms. Furthermore, we noticed that atoms are composed of subatomic particles, like protons, neutrons and electrons.
In chemistry, the most striking property of matter is the arrangement of its electrons in the different atoms. This fact gives you an understanding of the similarities and the periodic arrangement of atoms in a chart called the periodic table.

Electrons and the light we perceive which according to ***John Falk***[24] says that **'when light hits the eye we experience a sensation of sight and when it hits the skin a sensation of warmth'** have properties in common. Light as we know sometimes behaves as waves and sometimes as particles. So do electrons, as we shall later notice in the treatment of Planck – Einstein equation.
Evidence that light has wave properties is the existence of interference patterns

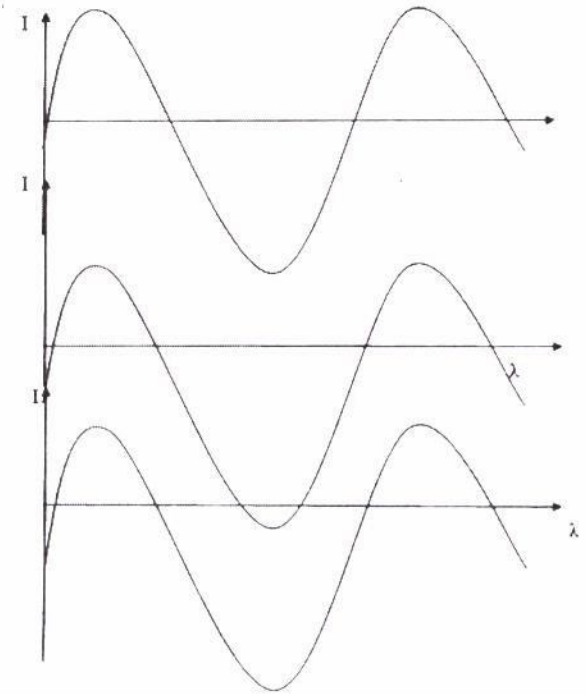


Fig 2.4: Wave patterns of light

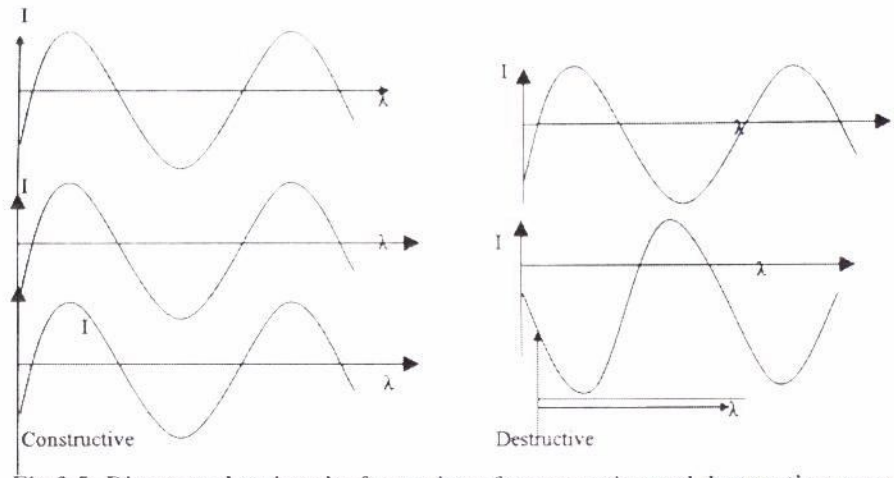


Fig 2.5: Diagram showing the formation of constructive and destructive waves

de Broglie capitalized on this wave-particle duality and derived a relationship by using Einstein's mass energy relationship : $E = mc^2$ and Planck's frequency relation: $E = hv$. So, we can rightly say that $mc^2 = hv$. But note that $v = c/\lambda$ and $p = mc$. It therefore follows that $mc^2 = pc = hc/\lambda$ or $p = h/\lambda$, where h (the Planck's constant) is a proportionality constant. Upfront, we should note here that like Newton's laws, the Schrödinger equation cannot be derived. A one-dimentional equation of a wave can be mathematically written from a standing wave as

$$\partial U/\partial x^2 = 1/v^2 \partial U/\partial t^2$$

This equation has been solved by method of separation of variables which implies that U (x, t) can be written as the product of a function x and a harmonic or sinusoidal function of time, t. So we can now write this this equation as

$$U(x, t) = \psi(x)\cos \omega t$$

where $\psi(t)$ is the spatial factor or amplitude of the wave. On substitution into the equation:

$$\partial U/\partial x^2 = 1/v^2 \partial U/\partial t^2 \text{ we have}$$

$$\partial^2\psi/\partial x^2 + \omega^2/v^2\psi(t) = 0 \ldots\ldots\ldots\ldots G$$

$$\text{It follows that } \partial^2\psi/\partial x^2 + 4\pi 2/\lambda 2\psi(x) = 0$$

$$\text{since } \omega = 2\pi v \text{ and } v\lambda = v.$$

And we know from classical mechanics that

since $\omega = 2\pi\nu$ and $\nu\lambda = v$.

And we know from classical mechanics that

total energy = kinetic energy + potential energy or
$E_t = E_k + E_p$

$E_k = p^2/2m$ from de Broglie's relation.
So we have $E_t = p^2/2m + V(x)$,
where V(x) is the potential energy.

Solving this equaeion for p we obtain

$$p = (2m[E_t - V(x)])^{1/2}$$

substituring this expression in de Broglte's formula $\lambda = h/p = h(2m[E_t - V(x)])^{1/2}$

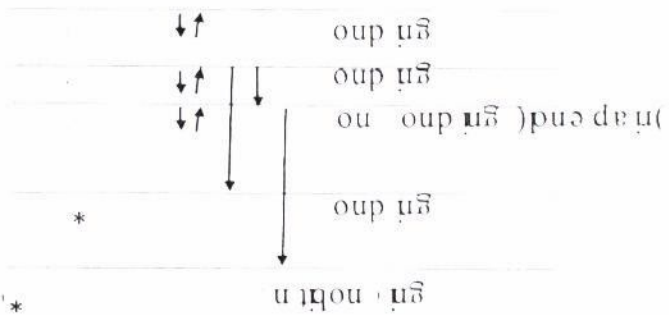
On substitution into equation G, we have

$$\partial^2\psi/\partial x^2 + 2m\,h^2\,[E_t - V(x)]\psi(x) = 0$$

This is a second order differential equation whose solution $\psi(x)$ describes a particle of mass 'm' moving in a potential field V(x). This equation is called the time-independent Schrödinger equation.

HOMO/LUMO Concept and the Basics of Electron Transfer:

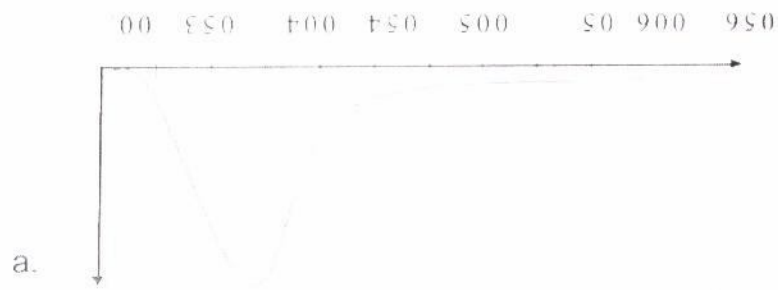
An electron is promoted from the HOMO (Highest Occupied Molecular Orbital) to the LUMO (Lowest Unoccupied Molecular Orbital). As conjugation increases, the HOMO-LUMO gap decreases and the position of the $\pi \rightarrow \pi^*$ absorption shifts to longer wavelength. The intesity of the resulting peak is a measure of the transition probability. These transitions consist of excitation of an electron from an occupied molecular orbital (HOMO) of a non-bonding p-orbital or a bonding π-orbital to the next higher energy orbital that is an anti-bonding (LUMO) π* or σ*-orbital as depicted in Fig. 2.6 below.



The band due to $\pi \rightarrow \pi^*$ transition in a compound with conjugated π-system is usually intense and it is freely called the K-band (from the German word konjugierte) in contrast to the $n \rightarrow \pi^*$ transition called the R-band.

Photoinduced electron transfer (ET) are important elementary reactions that occur in biochemical, photochemical and photophysical reactions.[26-28] The most widely known example of this reaction is photosynthesis. Electron transfer plays crucial roles in processes like solar energy conversion and storage[27, 29-33], information process and storage[26, 34], photocatalysis[29] and photopolymerization[26, 35] and other applications like photomedicine[26, 34].

Excited state electron transfer (ET) can be studied by molecules with donor (D)–acceptor (A) moieties joined together by a set of conjugated bonds. Donor – acceptor molecules when excited form highly polar intramolecular charge transfer (ICT) states. Molecules that possess this property are usually organic molecules which have both donor and acceptor moieties.[41] The earliest and most important of such a molecule is 4-Dimethylaminobenzonrile (DMABN) with the amino group being the electron donor and the cyano group being the electron acceptor. The fluorescence spectrum exists in polar solutions and the molecule has two Fluorescence Bands (dual fluorescence). This phenomenon was discovered by Lippert[42] in 1954 and in 1981under the supervision of Lippert, Ayuk[43] also made a contribution with another molecule, 1-Dimethylamino-4-cyanonaphthalene (DMACN). This molecule also dual fluoresces in polar solvents like its predecessor DMABN. The one band, the long wave length band is the charge transfer band which results from the short wave length band and this can be established from the temperature dependence of the spectrum.[43] These are emission bands which result from the structural change of the excited state. This excited state structural change can involve the rotational relaxation of the donor group, the dimethylamino group which twists to an orientation where the lone pair of electrons on the nitrogen atom is now transfered to the electron accepting group of the cyano moiety in the TICT process.[44,45]



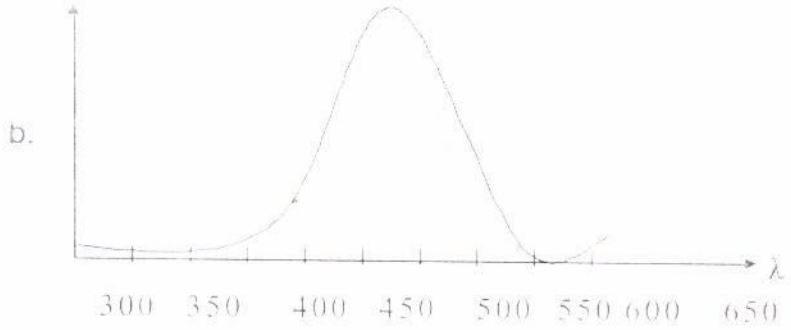
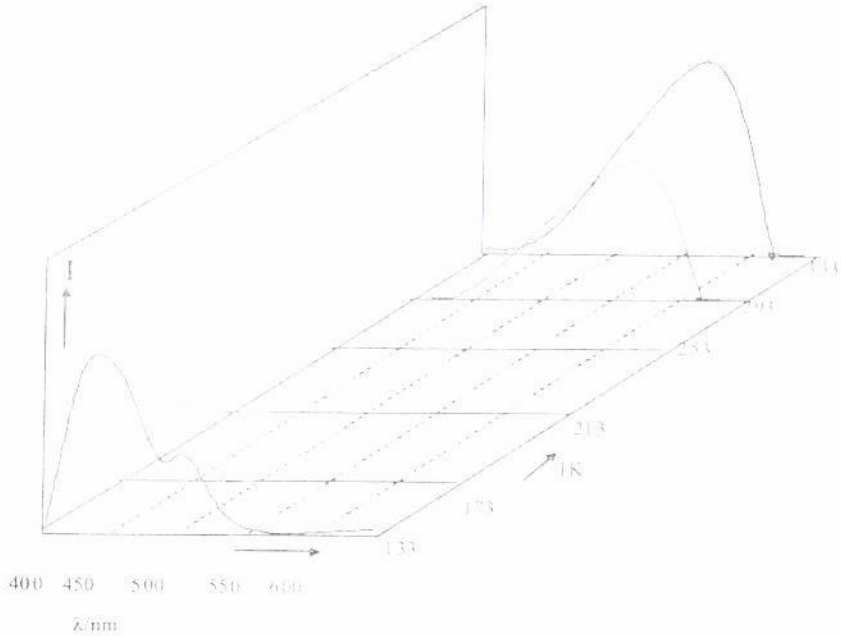


Fig. 2.7: a. Short wavelength band b. long wavelength band



F.g. 2.8: Temperature Dependence Of A Dual Fluorescing Molecule

D-A molecules upon excitation form TICT states as can be seen by solvent dependent dual fluorescence. This phenomenon was shown in the work of Lippert[38] et al. and Ayuk[54]. Two fluorescence bands are emitted from the local fluorescence band which is the substrate and the product of the electron transfer reaction which is the TICT state. It should have been my concern to illustrate elaborately the nature of the geometrical distortion of the excited state which gives rise to the ICT or IET state and the role of the environment in the excited-state electron transfer configurational changes of the dimethylamino chromospheres is induced by the solent to provoke or initiate a charge transfer or electron transfer in the excited molecule in what is explained in Platt's[30] nomenclature.

These configurational changes resulting from the chromophores of the donor and acceptor groups can form solute-solvent clusters which should not be confused with exiplex formation. This is so, because the operational concentrations are very low or the solutions are very dilute that exciplex formation is highly unlikely. The use of molecular clusters is advantageous because the content and size of their model systems can be controlled and varied. The electronic properties of the aromatic chromophores of the donor-acceptor moieties of dual fluorescence compounds are strongly dependent on the nature of the substituents and the surroundings. They should never be confused with exiplexes as their concentrations of less than 10^{-6} M are in a range where one cannot talk in terms of exiplex formation in photochemistry or photophysics.

Dual fluorescence is strongly environmental, polarity and temperature dependent. In non-polar solvents only one fluorescence band is observed. This band originates from the ^1L_a excited state using Platt's convention based on the symmetry classification of B or L_b state and the charge transfer state designated as A or L_a state. In polar solvents a mobile environment, a second red-shifted fluorescence band, still using Platt's nomenclature, the ^1L_a excited state band appears (see [Fig. 2.9] of the dipole moment in the ground and excited

states). This band is more polar than the ^1L_b excited state band and it is therefore stabilized in the polar solution. The ^1L_a state being stabilized and red-shifted, it therefore becomes lower in energy than the ^1L_b state and it is therefore the lowest singlet state.

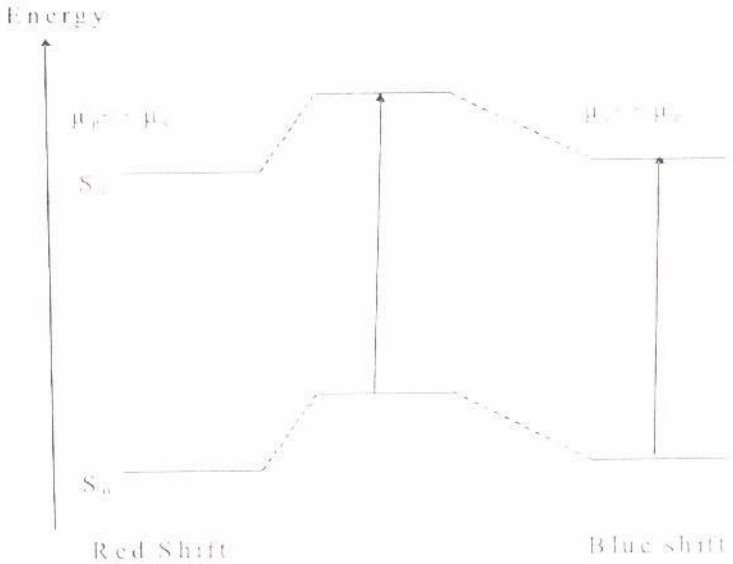


Fig. 2.9: Dipolemoment in excited state, μ_e and in ground state, μ_g

According to Kasha fluorescence spectrum is dominated by emission band from the lowest excited singlet state[49]. But because the ^1L_a band is solvated and relaxed, it is lower in energy than the ^1L_b band. The lowest excited singlet state is therefore the ^1L_a band and this band is called ***"ANOMOLOUS"*** fluorescence band and this band is obviously an exception from Kasha's rule.

The lowest excited singlet state according to Platt's nomenclature are the ^1L_a and ^1L_b states. The states can be seen to occur from two low-lying $\pi\pi^*$ (^1L_a) and $\pi\pi^*$ (^1L_b) states. Dual fluorescence depends on both the environment of the molecule and the temperature. In nonpolar solvents and even at very low temperatures only the ^1L_b state (the short wave-length fluorescence band) is observed. In polar solvents, depending on the viscosity of the solvent, a second fluorescence band appears the long wave-length fluorescence band especially at very low temperatures. This band has been assigned the ^1L_a state. It is more polar than the ^1L_b state. It is also strongly stabilized in polar media, or more viscous polar solvents. Hence, its existence in less polar solvents like propylene glycol. Normally, according to Kasha[40] in Kasha's rule which states that the fluorescence spectrum is mainly from a single emission band from the lowest excited singlet state. It is only appropriate to introduce the mechanism of the excited state process of the ^1La and ^1L_b conformers. It was Grabowski and coworkers[41-43] and Rettig[7] who have tried to give an explanation to the existence of the excited state conformers. They were of the opinion that in the excited state the specie as a result of rotational relaxation of the dimethylamino group facilitated by dielectric polarization of the solvent, a twisted intramolecular charge transfer band, the ^1L_a state was created. This model assumes that the π-electron system of the donor-acceptor group lie almost perpendicular to the frame of the aromatic ring resulting in the charge separation of the moieties.

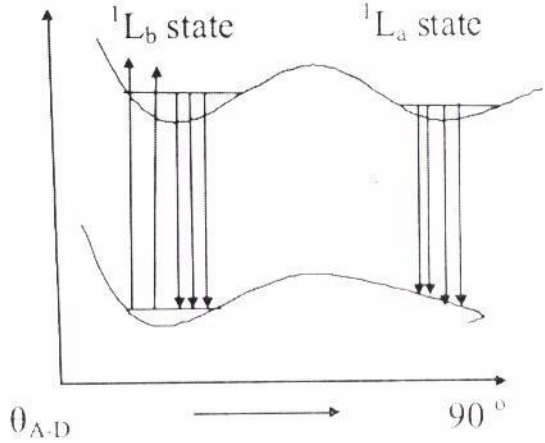
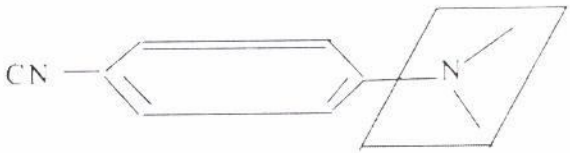


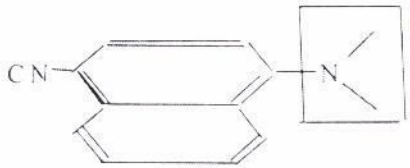
Fig. 2.10: Reaction coordinates of ground and lowest excited singlet state

Excited ^1L_b A-D moiety

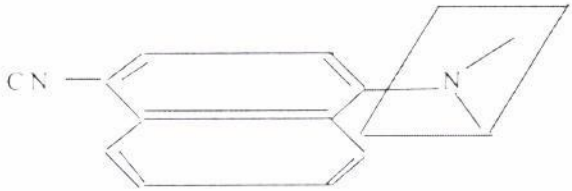


Excited ^1L_a state A^+ -D^- moiety

0Fig.2.11: Two conformations of the benzyl molecule



Excited ^1L_b A-D moiety



Excited ^1L_a state A^--D^+ moiety

Fig. 2.12: Two conformations of the naphthyl molecule

The intramolecular charge transfer moieties have large dipole moments resulting from the decoupling of the ^1L_a π-electronic state, which results in the full charge separation of the donor and acceptor moieties. This invariably gives rise to a large dipole moment and a low electronic transition dipole moment of the TICT fluorescence.

Clusters have been studied in the areas of physics and chemistry for the past forty (40) or more years[49,52]

In the 19th century its origin came from the research on colloids, aerosols and clouds. As far back as 1857 Michael Faraday gave a lecture on the exchange between photon and clusters titled "Experimental relation of (colloidal) gold to light"[50, 51]

Clusters are also important in the complex phenomena of photosynthesis, sight process or by the conversion of light to energy. The photo induced charge or energy transfer is important for Life on earth.[53] The light energy from the sun is absorbed by photoreceptors of living organisms and transported to the spots where the primary process of photosynthesis is carried out. The important molecule here

is the chlorophyll which acts as a charge separator in the primary reaction centre. Another important group of molecules are the carotenoids whose absorption spectra are complimentary to those of chlorophyll molecule. That which is responsible for sight is the molecule Rhodopsin which is composed of the protein Opsin and the molecule Retinal.

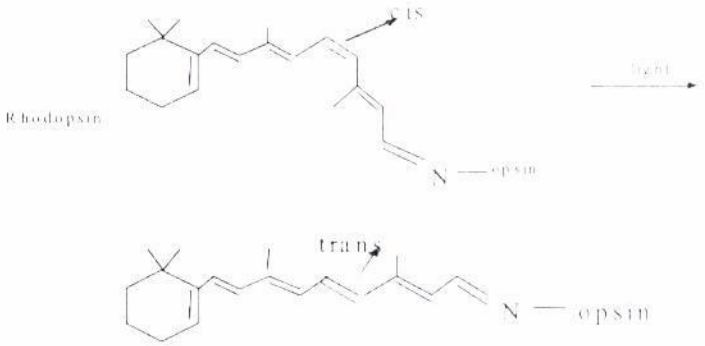
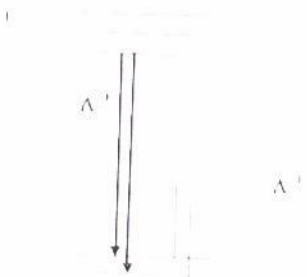


Fig. 2.13: Cis-Trans Isomerization of Rhodopsin

When visible light is absorbed, the molecule isomerizes from cis to trans. The structural change involves a rupture of the sight cells and consequently sight impression changes. The charge transfer on molecular level is also of importance for electrical transfer through organic materials. One would notice that electricity (or electron) has been created and stored. Molecules that possess this property are usually organic molecules which have both donor and acceptor moieties.[41] The supersonic jet studies of 4-dimethylaminobenzonitrile (DMABN)[29, 30] indicated that in the molecule the ^1L_a and ^1L_b states are strongly mixed in the lowest vibrational levels. It was therefore expected that the smaller number of solvent molecules are needed in the case of esters to induce the excited state electron transfer process.

LIF (Laser Induced Fluorescence) excitation spectrum represents the total number of photonsemitted by the molecule as a function of laser frequency that is used to excite the system.
The spectrum similar to the absorption spectrum contains information on the electronically excited state.



Before we go into the discussion of electron transfer in the molecular frames of benzene and naphthalene, I must first of all introduce the Hückel Molecular Orbitals (HMO) of these molecules. The basic frames of the molecular orbitals of benzene and naphthalene with their nodal planes are shown below:

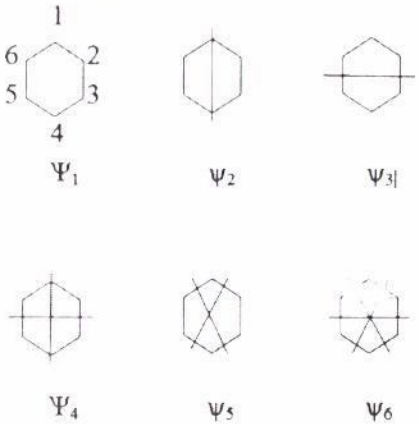


Fig. 2.15: Molecular orbitals and nodal planes of benzene

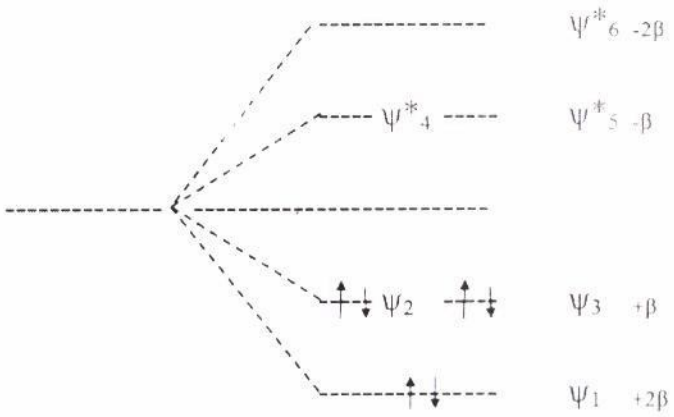


Fig. 2.16: Orbital Energies levels of Benzene π Molecular Orbitals

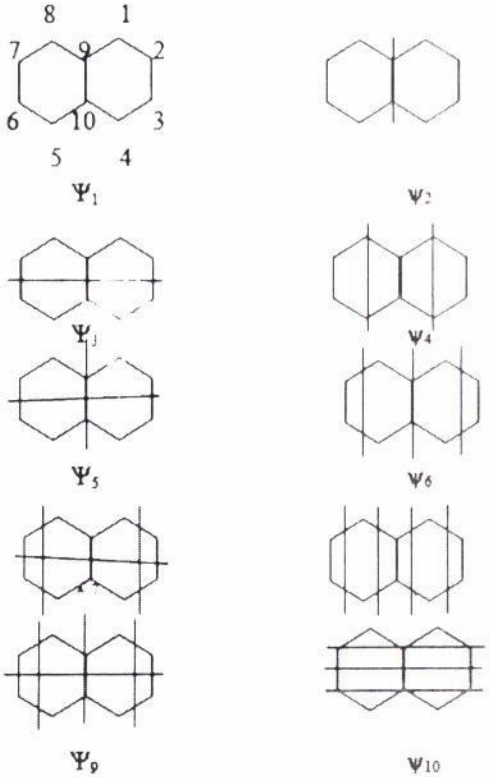


Fig. 2.17: Molecular orbitals and nodal planes of naphthalene

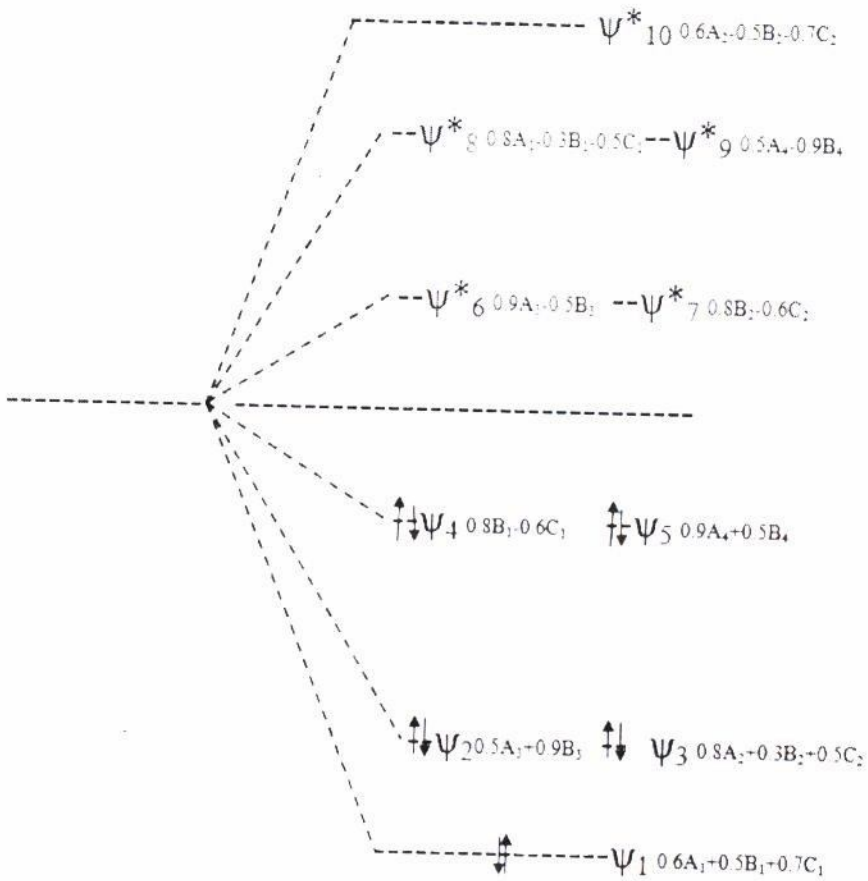
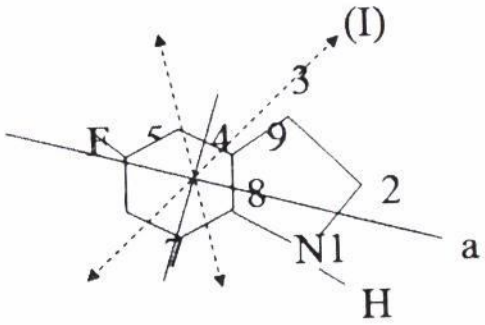


Fig. 2.18: Orbital Energies levels of Naphathalene π Molecular Orbitals

In the terminology of Michl's version of perimeter mode,[57, 58] pyridine is a soft chromophore, with ΔHOMO = ΔLUMO that is equal energy splitting between two highest occupied and two lowest unoccupied frontier π-orbitals. An extremely ***weak*** MCD signal is expected for such a case. Inspection of pyridine orbitals show that position 4 is classified as subdominant with regard to –E (electron donating)

substitution. This implies that ΔHOMO < ΔLUMO for weak substitution, which for strong substitution ΔHOMO becomes greater than ΔLUMO. Naturally, ΔHOMO ≈ ΔLUMO in intermediate regions. Position 3 is classified as dominant with regard to –E substitution. In this case, one expects ΔHOMO > ΔLUMO for both strong and weak -E substitution. The relative magnitude of ΔHOMO and ΔLUMO determines the sign of the terms of ^{1}L states.

The introduction of a cyano group, exerts a strong negative mesomeric (-M) effect and shifts the ^1L_a state below the ^1L_b state.[59] The lowest excited singlet states (called the ^1L_a and ^1L_b in the nomenclature of Platt[57]) might even change their energetic order, depending on the polarity of the local surroundings.



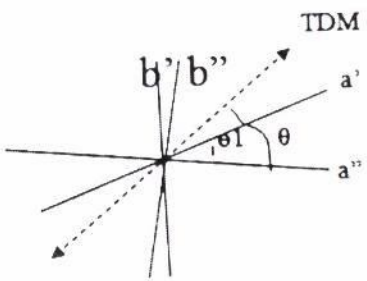


Fig. 2.19: Structures showing directions of transition dipole moments

3.0 Surface / Electro-Chemistry:

It is as a result of the interplay of electrons that we have phenomena such as I am going to display. Silver nitrate solution will be dissolved in ammonia. To this mixture we add formaldehyde and shake the mixture. Silver metal will be coated at the surface of the flask. Now the chemistry behind it:

$$AgNO_3 \xrightarrow{NH_3} Ag^+ + NO_3^-$$

$$Ag^+ + NO_3^- + H_2CO \xrightarrow{[H]} Ag + HCOOH$$

The Ag^+ is reduced to Ag and the formaldehyde oxidized to formic acid.

Two phenomena are responsible for surface reactions in chemistry. These are catalysis which involves building up surfaces and corrosion which involves breaking it down.

One cannot really talk of corrosion without mention of surface chemistry. This is because the surface of the material is involved in the corrosion process. Except for the metal gold, all metal surfaces in air are covered with their oxide films. In acidic solutions the oxide dissolves completely leaving the bare metal to the mercy of corrosion. In a near-neutral solution, the solubility of the metal oxide is slower and should the solution contain inhibiting ions (what in chemical kinetics is also called negative catalyst) the dissolution of

$$\underset{\text{An atom of metal in the surface}}{M} \longrightarrow \underset{\text{formed metal ion in solution}}{M^{n+}} + \underset{\text{ejected electrons from metal.}}{ne^-}$$

A potential difference is created between the metal and solution due to the accumulation of electrons in solution. This potential is called

the electrode potential and tends to retard the the dissolution of more metal ions and encourage the deposition of the already dissolved metal ions back to the surface of the metal. This is naturally the reverse reaction[60] of what was originally observed:

$$M^{n+} + ne^- \longrightarrow M$$

metal ion in solution — ejected electrons from metal — atom of metal back on the surface.

A stable state is reached where the potential of the solution, resulting from the rate of dissolution of the metal becomes equal to the rate of deposition of the metal ion. This stable potential is called the reversible potential, E_r and its values depend on the concentration of the dissolved metal ions and the standard reversible potential, E_o for unit activity of the dissolved metal ions, a_{ij} or for the reversible reaction

$$M^{n+} + ne^- \rightleftharpoons M$$

metal ion in solution — ejected electrons from metal — atom of metal back on the surface

$$E_{r,Mn+/M} = E^{\circ}_{Mn+/M} + RT\,nF \ln a_{Mn+}$$

R stands for the universal gas constant, T the absolute temperature, F the Faraday constant and n the number of electrons transferred per metal ion. At the reversible potential no further dissolution occurs.

Surface chemistry mainly involves adsorption on the surface and several researchers have worked on the principles that are involved and promulgated laws to support their findings. The most widely used phenomena are those of Langmuir and Freundlich. It is important to note that in this discussion our concern will be mainly geared to physisorption which is a physical concept and involves interaction of the electrons of the adsorbate and those of the adsorbent as demonstrated by van der Waals forces. On the other hand,

chemisorption involves real chemical bonding between the adsorbate and the adsorbent.

Again corrosion can be defined as a process where a metal or its alloy is transformed from the metallic form to the combined state by interaction with the environment. Corrosion processes may be mainly chemical or electrochemical and cause deterioration or destruction of the metal structure[60]. Most metals on exposure tend to arrive at a chemically stable state through a chemical or an electrochemical process. This is true because the combined state is energetically more stable than the uncombined state. This transition is electrochemical in nature:

$$2M \longrightarrow 2M^{+} + 2e^{-}$$

$$O_2 + 2e^{-} \longrightarrow O^{2-}$$

$$2M + O_2 \longrightarrow 2M^{+} + O^{2-}$$

This transition is in line with the second law of thermodynamics which states that "All naturally occurring processes always tend to change spontaneously to the direction which will lead to equilibrium and their motivation lie at the heart of thermodynamics with special emphasis on entropy."[63] Another way in which we can see the activity of the electron is when a speck attaches itself to your body.

This is as a result of gain or loss of electrons by the speck and now in spontaneous reaction, wanting to be in a stable state is attracted to a body of opposite charge. Infact, in the entire study of corrosion inhibition carried out by my students[60-62, 64-72] it is all about electrons. There is nowhere one can talk about corrosion without mention of electrons. A corrosion cell consists of an anode and a cathode in a corrodent. The anode dissolution of the metal is the beginning of corrosion process and this process shown below involves loss of electrons.

$$M \longrightarrow M^{n+} + ne^-$$

In the electrochemical cell the anode is positive and since electrons are produced at the anode (anion electrode) which make the overall reaction to be an oxidation reaction. Similarly, the cathodic process is involved with consumption of electrons and this is termed a reduction reaction. Typical cathodic reactions in aqueous corrosion processes involve hydrogen evolution as in the reactions below:

a. Electronation of hydrogen ion

$$2H^+_{(aq)} + 2e_{(aq)} \longrightarrow H_{2(g)}$$

b. Electronation of water molecule

$$H_2O_{(l)} + e_{(aq)} \longrightarrow [H] + OH$$

c. Oxygen reduction in acidic medium

$$\tfrac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e_{(aq)} \longrightarrow H_2O_{(l)}$$

d. Oxygen reduction in neutral medium

$$\tfrac{1}{2}O_{2(g)} + H_2O_{(l)} + 2e_{(aq)} \longrightarrow 2OH\ (aq)$$

e. Metal ion reduction

$$Mn^+_{(aq)} + ne_{(aq)} \longrightarrow M_{(s)}$$

The metal ion reduction can be examplified by the deposition of copper in soil.

$$Cu^{2+}_{(aq)} + 2e^-_{(aq)} \longrightarrow Cu_{(s)}$$

Anodes and cathodes can arise from two different metals in contact with one another.[74-79] Here the surface of one metal becomes anodic with respect to the other metal.

In some sulphate containing soils which are generally poorly aerated, sulphate reducing bacteria are found in electron manipulation by depolarising the cathodic reaction as shown:

$$SO_4^{2-}{}_{(aq)} + 4H_{2\,(g)} \longrightarrow S^{2-}{}_{(aq)} + 4H_2O_{(l)}$$

which results in rapid attack on iron with formation of a non-protective iron sulphide.

In a microbial environment with pH $\leq$ 0 or pH $\leq$ 14 we have reactions of the sort:

$$H_2S_{(g)} + e^- \longrightarrow [H] + HS^- \xrightarrow{e^-} [H] + S^{2-}$$

The S^{2-} can now react with Fe^{2+} to give :

$$Fe^{2+} + S^{2-} \longrightarrow FeS$$

In acid environment, pH < 7, we have the following reaction steps:

$$Fe \longrightarrow Fe^{2+}{}_{(aq)} + 2e^-{}_{(aq)}$$

$$H_3O^+{}_{(aq)} + e^-{}_{(aq)} \longrightarrow [H] + H_2O_{(l)}$$

$$[H] + [H] \longrightarrow 2H_{2\,(g)}$$

In neutral environment, with pH = 7, we have the following reaction procedure:

$$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^{-}_{(aq)}$$

$$H_2O_{(l)} + e^{-}_{(aq)} \longrightarrow [H] + OH^{-}_{(aq)}$$

$$Fe_{(s)} + 2H_2O_{(l)} \longrightarrow Fe(OH)_{2\,(aq)} + 2[H]$$

$$[H] + [H] \longrightarrow H_{2\,(g)}$$

Finally, if Fe^{3+} ion does diffuse to the region of the cathode where OH group is in abundance, the reaction follows this pattern:

$$2Fe^{3+}_{(aq)} + 6OH^{-}_{(aq)} \longrightarrow \underset{\text{(rust)}}{Fe_2O_{3\,(s)}} + 3H_2O_{(l)}$$

An insoluble solid iron oxide or rust is precipated.

CONCLUSION:

An inaugural lecture is one that details the works of the lecturer that gave her/him the opportunity and privilege to be called a professor.

No mention has been made of electrons in solid state as this phenomenon is comparatively younger than in gaseous and liquid states. In addition, electrons found in solid states as in material science, electrical and electronic engineering, mother boards in computer science and physics are obvious and thought by the general public to be the only electrons in existence. Indirect existence of the electron in the liquid state has been shown.

As a result, I have detailed the experimental findings that gave a near suggestion of the existence of the electron. In the lecture "**The Question of the electron: Its origin & Impact on Chemical Processes**", attempt has been made to introduce the beginnings and the discovery of the electron starting with JJ Dalton, GJ Stoney and JJ Thomson. It did not end there as attempts were also made to show the contributions of Ernst Rutherford and Niels Bohr. It was also shown how the electron possessed corpuscular character and how the electron in its particle character revolved round the nucleus of the atom. The controversy as to whether an electron is a particle or a wave has though been resolved by both chemists and physicists alike was mentioned.

It is the electron in nature (electron-light falling on the skin to give a sensation of heat and on the eye to give the sensation of sight as recorded by John Falk) photosynthesis and the process that gives rise to sight that interested the presenter. He also showed through his research of the existence of a second "anomalous" fluorescence band a phenomenon which he tried to explain with the principle of electron transfer. In this principle an electron leaves a donor moiety in a conjugated electron system of a molecule to the acceptor moiety of the same molecule. This was further clarified by the frontier-orbitals of the HOMO-LUMO molecular orbitals of the molecule. The happenings in surface chemistry were also investigated to show that electrons were also involved. In electrochemistry as the name implies, it is controlled totally by electrons. One can see that there is no place in this world where the electron is not futured. Rightfully therefore the topic "**The Question of the electron: Its origin & Impact on Chemical Processes**" has no specific area of research nor is there any limit to its search.

I would want to conclude in the words of whom I consider the father of the electron, Niels Bohr. He says "Every great and deep difficulty bears in itself its own solution. It forces us to change our thinking in order to find it."[9]

Acknowledgements:

It will be improper if I do not give thanks to my **"doctor-father"** Prof. Dr. rer. nat. Ernst B. Lippert who introduced me to the existence of dual fluorescing compounds. I will also not forget my senior colleague Prof. Dr. rer. nat. Wolfgang Rettig and my colleague Dr. rer. nat. Gunther Wermuth. My thanks also goes to Prof. Robin M. Hochstrasser, Prof. Eugene Nixon, Dr. Thomas Cellucci and all the staff of the Laser Laboratory of the University of Pennsylvania. Here attempt was made to determine the rotational relaxation time of the rotating dimetylamino group which could have given me an edge like my predicessor in the same lab, the 1999 Nobel Laureate Ahmed H. Zewail . At home I will not forget the encougraing discussions with both Prof. AI Onuchukwu and Prof. EE Oguzie. To all the members of the Chemistry Department, especially Prof. GN Onuoha , I say thank you for being there as a friend.

Thank you all for Listening and God Bless.

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