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Ultraviolet visible spectroscopy or uv vis spectroscopy involves the measurement of absorption or transmittance of energy in the ultraviolet and visible regions of the electromagnetic spectrum. The ultraviolet visible spectroscopy principle or theory is used mainly to measure the absorption peaks (λmax) and molar absorptivity of multiple chemical bonding in organic compounds. However, ultraviolet visible (uv vis) light in absorption spectroscopy is also used to determine the colour of transition metals. On passing electromagnetic radiation in the ultraviolet and visible regions through a compound with multiple bonds. However, a portion of the radiation is normally absorbed by the compound. The amount of absorption depends on the wavelength of the radiation and the structure of the molecules. The absorption of radiation is due to the transition of electrons from lower energy orbital to higher energy orbitals. The absorption of organic compounds and transition metals is processed in two stages. In the first stage, M + hν → M∗. Ultraviolet visible spectroscopy involves the excitation of the species by absorption of photons with a limited lifetime. In the second stage, M∗ converts to a new species by photochemical reaction. Absorption in the uv visible region leads to the excitation of bonding electrons. Therefore, the absorption peaks can be correlated with the kind of bond that exists in the species. Hence absorption spectroscopy in the ultraviolet visible region is valuable for the characterization of functional groups in organic molecules. Principle of Ultraviolet Visible Spectroscopy The UV Visible spectroscopy principle is based on the absorption of ultraviolet light or visible light by chemical compounds. To occur a chemical reaction, the reacting molecules must be activated by acquiring activation energy. In photochemical reactions, the activation energy is obtained by absorption of radiation or light energy from uv visible spectroscopy. In order to study the mechanism of the photochemical reaction, we need to study the following types of electronic transition: Sigma to sigma star transition (σ → σ∗) n to sigma star transition (n → σ∗) n to pi star transition (n → π∗) Pi to pi star transition (π → π∗) Absorption Peaks Absorption peaks (λmax) and molar absorptivity (∈max) and possible electronic transition of some common compounds are given below the table, Compounds λmax (nm) ∈max (L/cm/mol) Electronic transition Alkenes 177 1.3 × 104 n → π∗ Alkyne 178 – 225 10 × 103 – 150 n → π∗ Carbonyl 186 – 280 1.0 × 103 – 16 n → π∗ Carboxyl 204 41 n → π∗ Amide 214 60 n → π∗ Azo 339 5 n → π∗ Nitro 280 22 n → π∗ Ketone 282 27 n → π∗ Water 167 1.48 × 103 n → σ∗ Methyl alcohol 184 15 n → σ∗ Benzene 204 7.9 × 103 n → σ∗ Sigma to Sigma Star Transition (σ → σ∗) A transition of an electron from a bonding sigma orbital to a higher energy antibonding sigma orbital is designated σ → σ∗ (sigma to sigma star transition in ultraviolet visible spectroscopy). In alkanes, there are only sigma bonds are available. Therefore, alkenes are showing this type of transition. In general, sigma bonds are very strong. Therefore, high energy is required for σ → σ∗ transition. n to sigma star transition (n → σ∗) n to sigma star transition (n → σ∗) involves saturated compounds with one hetero atom like oxygen, nitrogen, fluorine, chlorine, etc. Normally, saturated halides, alcohols, ethers, aldehydes, ketones, and amines participate in this type of transition. These transitions require comparatively less energy than the σ → σ∗ transition. In saturated alkyl halides, the energy required for n to sigma star transition (n → σ∗) decreases with the increase in the size of the halogen atom or decrease in electronegativity of the atom. Due to the greater electronegativity of chlorine than iodine, the n electron on the chlorine atom is comparatively difficult to excite. The n electrons on the iodine atom are loosely bound. Pi to Pi Star Transition (π → π∗) Pi to pi star transition (π → π∗) in uv vis absorption spectroscopy is available in compounds with unsaturated centers like unsaturated hydrocarbons and carbonyl compounds. It requires lesser energy than n to sigma star transition (n → σ∗). In simple alkenes several transitions are available but the n → π∗ transition requires the lowest energy. n to pi Star Transition (n → π∗) In n to pi star transition (n → π∗), an electron in an unshared pair on a hetero atom is excited to π∗ antibonding orbital. It involves the least amount of energy of all types of transition in ultraviolet visible spectroscopy. Therefore, the n → π∗ transition gives the absorption with a longer wavelength. In saturated ketones, n → π∗ transitions around 280 nm are the lowest energy transition. n → π∗ is forbidden by symmetry consideration. Thus the intensity of the band due to this transition is low, although the wavelength is long. Applications of UV Visible Spectroscopy Ultraviolet (200 to 400 nm) and visible spectroscopy (400 to 750 nm) are used to detect functional groups and the nature of unsaturation in organic chemistry. The longer the conjugation give the maximum wavelength of absorption spectrum in organic compounds. A compound with sufficient conjugation becomes coloured. For example, lycopene is a compound that gives red colour due to eleven conjugated double bonds. Generally, electronic spectroscopy can differentiate conjugated diene from non-conjugated dienes and conjugated diene from conjugated trienes. The study of ultraviolet spectroscopy can be used to identify suitable tautomeric species. It is used to know the extent of strain organic molecules like 2-substituted diphenyl or acetophenones. The absorbed spectrum of d block or transition metals is an ultraviolet visible region. For f block elements transitions are possible due to f electrons. The inner transition metals have narrow peaks due to shielding electrons. On the other hand, in the case of the first and second transition series broad peaks are seen in the visible region. Spectral properties and colour of transition metal ions involve electronic transition among different energy levels of d-orbitals. In all the charge transfer metal complexes, the metals serve as electron pair acceptors. The concentration of a colour solution can find out by the absorption of light. In the visible region of the spectrum, it is possible to determine concentration by three techniques, calorimetry, photometric photometry, and spectrophotometry. Spectrophotometry is useful for determining absorbance in both ultraviolet and visible regions. In suitable cases, ultraviolet visible (uv vis) spectroscopy is used to determine reaction rates and pKa values in chemistry. Selection Rules of electronic transitions transitions. Thus, S→S, T→T are allowed, but S→T, T→S are forbidden transitions. within a given set of p- or d-orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden. What are allowed and forbidden transitions in spectroscopy? specification of selection rule Selection rules, accordingly, may specify “allowed transitions,” those that have a high probability of occurring, or “forbidden transitions,” those that have minimal or no probability of occurring. Which of the following is a forbidden transition in UV-vis region? This n→ π* transitions is “forbidden” by symmetry considerations, thus the intensity of the band due to this transition is low, although the wavelength is long (lower energy). What Is Difference Between Fluorescence And Phosphorescence?Which type of transitions are forbidden? Strong transitions are those where certain selection rules are satisfied. For example, dipole transitions can occur only between energy levels with the angular momentum parameter l differing by one. Therefore, dipole transitions between energy levels with same parity are not allowed, i.e. they are forbidden. Which transitions are not useful in UV spectroscopy? A s-s* and a n-s* are not useful for reasons discussed earlier. The n-p* transition requires low energy but the molar absorptivity is also low and transition energy will increase in presence of polar solvents. The n-p* transition is seldom used in quantitative UV-Vis spectroscopy. Do Wrestlers Wear Jockstraps Under Their Singlets?What is the meaning of forbidden transition? forbidden transition in British English noun. physics. an electronic transition in an atom, molecule, etc, that is not permitted by electric dipole selection rules. What is forbidden direct transition? Direct or indirect transition are “forbidden” transitions, if the momentum matrix element charaterizing the transition is equal to zero. Why DD transition is forbidden? In centrosymmetric complexes, d-d transitions are forbidden by the Laporte rule.Through such asymmetric vibrations, transitions that would theoretically be forbidden, such as a d-d transition, are weakly allowed. An example occurs in octahedral complexes such as in complexes of manganese(II). Which Parent Carries Twin Gene?Is pi to pi star transition allowed? It involves the least amount of energy than all types of transition in ultraviolet visible spectroscopy. Therefore, the n → π∗ transition gives the absorption with a longer wavelength. In saturated ketones, n → π∗ transitions around 280 nm are the lowest energy transition. n → π∗ is forbidden by symmetry consideration. What are the types of transitions in UV-vis spectroscopy? There are three types of electronic transition which can be considered; Transitions involving p, s, and n electrons. Transitions involving charge-transfer electrons. Transitions involving d and f electrons (not covered in this Unit) What is a forbidden spectral line? forbidden lines, in astronomical spectroscopy, bright emission lines in the spectra of certain nebulae (H II regions), not observed in the laboratory spectra of the same gases, because on Earth the gases cannot be rarefied sufficiently. How Do I Import Decks In Mtg Arena?Which of the following compounds does not absorb light in UV spectrum? Chloral hydrate lacks chromophore and therefore cannot absorb UV light. Which UV transition is not possible in diethyl ether? But in diethyl ether, being a saturated compound, it has no π-bonds. This successfully dismisses the idea of having π* orbital. And, as there is no π* orbital, we can not have a transition to the π* orbital resulting in no UV-Vis absorption spectra. What is π π * transition? The π–π* transition produces a strong absorption peak around 400 nm and an absorption boundary around 460 nm, as often shown in the UV-Vis spectrum. In contrast, the n–π* transition is an excitation of a lone pair on the N atom, and its corresponding absorption peak is around 500 nm. Is Singleton A Static Class?What is Laporte allowed transition? Allowed transitions in such molecules must involve a change in parity, either g → u or u → g. The Laporte rule stipulates that s to s, p to p, d to d, etc. transitions should not be observed in centrosymmetric compounds. Practically speaking, only d-d transitions occur in the visible region of the spectrum. Can forbidden transitions occur? Transitions between energy levels in a quantum-mechanical system that are not allowed to take place because of selection rules. In practice, forbidden transitions can occur, but they do so with much lower probability than allowed transitions. What is forbidden rule? Forbidden Rules provides a comprehensive set of variant and optional rules for use with Shadow of the Demon Lord, letting you reshape the game in a variety of different ways. Whether you re looking for a points-based casting system or basic rules to kick off games beyond level 10, this supplement has it. What is the difference between direct and indirect transition? In a direct band gap semiconductor, the top of the valence band and the bottom of the conduction band occur at the same value of momentum. In an indirect band gap semiconductor, the maximum energy of the valence band occurs at a different value of momentum to the minimum in the conduction band energy. What is indirect and direct band gap? If the k-vectors are different, the material has an “indirect gap”. The band gap is called “direct” if the crystal momentum of electrons and holes is the same in both the conduction band and the valence band; an electron can directly emit a photon. Can You Breathe Singlet Oxygen?What are spin allowed transitions? Spin is directional and can be said to have odd parity. It follows that transitions in which the spin “direction” changes are forbidden. In formal terms, only states with the same total spin quantum number are “spin-allowed”. Which compound gives π → π * electronic transition? Benzene has three aromatic π → π* transitions; two E-bands at 180 and 200 nm and one B-band at 255 nm with extinction coefficients respectively 60,000, 8,000 and 215. These absorptions are not narrow bands but are generally broad because the electronic transitions are superimposed on the other molecular energy states. What Are Allowed And Forbidden Transitions In Uv Spectroscopy? Last updated: October 31st, 2022 | UV-Vis Spectroscopy Of Carbonyls (C=O Bonds) UV-Visible spectroscopy is not just about C-C pi bonds. C-O pi bonds can absorb UV light as well! Table of Contents 1. A Quick Review Of What We’ve Learned So Far About UV-Vis In our last post we showed that molecules with C-C pi (π) bonds absorb light in the UV-visible region, which promotes electrons from (bonding) π orbitals to (anti bonding) π* orbitals. We saw that the energy required for the transition depends mostly on the extent of conjugation (i.e. the number of consecutive pi bonds, roughly speaking). an alkene with little or no conjugation (e.g. ethene, CH2=CH2) possesses a large energy gap (ΔE) between the bonding and anti bonding orbitals, which requires more energetic (shorter wavelength) photons for excitation. For ethene, maximum absorbance occurs at about 170 nm, in the UV region. as conjugation increases, the energy gap ΔE decreases, pushing the wavelength of maximum absorbance (λmax) toward the visible (less energetic photons, longer wavelength) . For example, β-carotene (the orange pigment in carrots) with 11 conjugated pi bonds, absorbs in the visible (λmax = 470 nm). Because the post was so damn long, we never got around to addressing a key question: does this apply to other types of pi bonds as well? For example, do C=O pi bonds also absorb light in the UV/visible region? The short answer is: yes. The medium sized answer is: yes, but the main transition of interest is not a pi-pi* transition – it’s slightly different. The long answer is.. well, here’s the long answer. 2. Absorbance of C=O bonds Show A Maximum Around 300 nm Let’s start with one of the simplest compounds with a C=O bond: 2-propanone, otherwise known as acetone. Question: Does acetone absorb UV or visible light? Answer: You betcha. Here’s the UV-Vis absorption spectrum for 2-propanone (acetone). [The key piece of information to glean from that spectrum is that there is an absorbance maximum at about 275 nm, in the ultraviolet.] If you have an astonishingly good memory you may recall from the last post (or from my introduction above) that the absorption max for ethene (CH2=CH2) is about 170 nm. An absorption around 275 nm means that longer wavelength and therefore less energetic photons are required for this transition. Doesn’t that seem weird? If anything, C=O π bonds are stronger than C=C π bonds. [You can look it up]. Wouldn’t you reasonably expect *more* energy to be required to promote an electron from pi(π) to pi* (π*)? What gives? Now: as we’ll see in a minute, there is a pi to pi* (π→π*) transition for acetone in the UV, but that peak at 275 nm is NOT a pi to pi* transition. It’s a transition from a non-bonding orbital (n) to the pi* orbital (n→π*). 3. Carbonyl (C=O) Groups Tend To Show Weak Absorbances At (Roughly) 300 nm That Correspond To Transitions Between Non-Bonding Orbitals and Pi* Orbitals Huh? Let’s look at a simple molecular orbital drawing of acetone. [This is a somewhat simplified picture. For a more detailed MO diagram for that also includes a more thorough discussion about the nature of the non-bonding orbitals, I highly recommend Reusch’s online textbook entry here.] A few important things to note: Carbonyl groups contain non-bonding electrons that are in an orbital intermediate in energy between the bonding pi orbital and the anti bonding pi* orbital. These orbitals are absent in typical alkenes such as ethylene [CH2=CH2] [note 1] Being higher in energy, transitions between electrons in the non-bonding orbital to the pi* orbital have a smaller ΔE and therefore absorb at longer wavelength. It is this (n→π*) transition which is responsible for the peak at around 275 nm. 4. What About Pi to Pi* Transitions for C=O? So what about the pi to pi* transition? Doesn’t that happen too? Glad you asked. If you take a quick look back at the UV-Vis absorption spectrum of acetone, above, you’ll note that the X-axis gets cut off around 240 nm or so. There’s a reason for that (mwah-ah-ah). If you zoom out, you’ll see that there’s a much stronger transition around 190 nm. [I went looking for a decent full-size UV spectrum of acetone, and the diagram below is the best I could find. I didn’t make this image and it is not my intellectual property. I found it here.] So as it turns out, that “peak” at 275 nm (n→π*) we were looking at turns out to be a molehill, next to the (π→π*) mountain at about 195 nm in the deeper UV. In other words, the (n→π*) transition at 275 nm that we’ve spent so much time talking about is very weak relative to the (π→π*) transition. [sometimes a term called “epsilon, ε” is used to denote this difference in magnitude of absorption]. Why might that be? It has to do with differences in orbital overlap. In order for an electron to transition from one orbital to another, two conditions must be met. First, as previously discussed, the orbital has to interact with a photon of appropriate energy ΔE. Second, there has to be significant overlap between the orbitals in space. We generally don’t discuss this for (π→π*) and (σ→σ*) transitions because each pair of bonding and anti bonding orbitals occupies the same region of space. If you look back to the diagram for the location of the n orbitals in acetone compared to the location of the pi* orbitals, you might notice that they are essentially at right angles to each other. Poor orbital overlap means that even if the electron has sufficient energy ΔE to make the transition, the transition is considerably less likely to occur since the excited electron will be less likely to be occupying an area of space corresponding to the higher-energy orbital. [Extra detail: you might recall that orbitals are 3-dimensional volumes where the probability of encountering an electron is 95%. Therefore, there is some electron density outside of the volumes we typically consider “orbitals”] 5. Carbonyls Also Participate in Conjugation Carbonyls can also participate in conjugation with C-C pi bonds. This leads to an increase in the overall λmax of the molecule. For instance, the absorbance of the alkene 2-methyl pent-2-ene is below 200 nm, as is the π→π* absorbance of 4-methyl pentane-2-one (below). In mesityl oxide, where the alkene and C=O group are in conjugation with each other, the absorption maximum moves to longer wavelength at 228 nm. This is similar to the difference between the absorbance of ethene (174 nm) and butadiene (217 nm). NoteThe absorbance maximum can be sensitive to the identity of the solvent as well as the identity of the substituents on the alkene. [Note 2]. 6. Summary: UV-Vis Spectroscopy Of Carbonyls Absorbance in the rough neighbourhood of 270-300 nm is common for molecules containing a C=O group (such as ketones and aldehydes) and this corresponds to a (n→π*) transition. These absorbances tend to be weak, relative to (π→π*) transitions. Still, observing this absorbance can be an important clue in the structure determination of unknown compounds. In the next post we’ll go into practical details of using UV-Vis in structure determination. [Again, for a more in depth look on the subject of C=O absorbance, go to Reusch. We’re really skimming the surface here, but it is enough for our purposes.] Notes Note 1. It should be noted that non-bonding orbitals are present in species such as the allyl cation, allyl anion, and other ions of odd-numbered pi systems. Note 2. For carbonyls, generally more polar solvents lead to higher λmax values, as does the presence of substituents (such as methyl groups) on the alkene. Bonus Topic: Azo Dyes Since we’re on the subject, let’s briefly explore another system where both n→π* and π→π* transitions are observed: azo dyes. Azo dyes are the kind of thing that you’ve likely seen a million times without specifically knowing what they are. For example, the yellow color of highway markings? That’s Pigment Yellow 10. Azo dyes are commonly used in colouring textiles, plastics, and many other substances not intended for human consumption (they’re generally banned as food additives). The key structural feature of an azo compound is a N=N linkage. One of the simplest azo compounds is azobenzene, where each nitrogen is connected to an aromatic ring. Slight modifications to the benzene ring can dramatically modify the color of the molecule. Aniline Yellow, discovered in 1861, was the first azo compound to find commercial use as a dye, and countless derivatives of azobenzene have been synthesized since then. [The synthesis is via diazo coupling – we won’t get into that here]. Here’s the UV-Vis spectrum of Aniline Yellow, as calculated by ChemTube 3D. Note how it is qualitatively similar to that of acetone: a strong absorbance on the left (towards the UV) and a weak absorbance on the right (towards the visible). In contrast to acetone, however, where the weak absorbance is at 260 nm, the weak absorbance in Aniline Yellow is in the visible region of the spectrum at about 460 nm. It is this absorbance at 460 nm that is responsible for the color of Aniline Yellow. By analogy to acetone, the weak transition is an (n→π*) transition and the strong transition around 360 nm is a π→π* transition. Photoisomerization What’s even more interesting about azobenzenes and their derivatives (e.g. Aniline Yellow) is the phenomenon of photoisomerization, where absorption of specific frequencies of light can lead to isomerization of trans isomers to cis isomers and vice-versa. Absorbance of UV light by trans-azobenzene (a π→π* transition) leads to isomerization to cis-azobenzene. Contrariwise, absorbance of visible light (blue light) by cis-azobenzene (the n→π* transition) results in conversion back to the trans-isomer [so does leaving cis-azobenzene in the dark, a process known as thermal relaxation]. The mechanism for this process is still not completely settled. Pretty neat that you can target a specific isomer merely by changing the frequency of light. A process which determined the absorption or transmission of light in the ultraviolet region of the electromagnetic spectrum is known as UV (ultraviolet) spectroscopy. In uv spectroscopy light absorbed is used to shift electron from low energy level to high energy level. ALLOWED TRANSITION High probability transitions that are seen as powerful absorption bands are considered to be allowed transitions. The transitions that entail the promotion of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) are those that are permitted in UV spectroscopy. These transitions are also referred to as π → π* and n → π* transitions. The π → π* transition involves the excitation of electrons from a non-bonding orbital to an anti-bonding orbital causes the π* transitions. As part of the n → π* transitions, electrons are excited from a lone pair (n) orbital to an anti-bonding π* orbital. FORBIDDEN TRANSITION On the other hand forbidden transitions have a limited likelihood of happening and are seen as weak or nonexistent absorption bands. In UV spectroscopy, transitions that go against the selection rules are considered forbidden. These transitions, which have a limited probability of happening, entail modifications to the molecule’s spin or parity. They thus tend to be weak or missing in the UV spectrum. scoresvideosteachers About Authors: Tarun Patel , Prof. Dr. Vipin Kukkar, Nilesh Sovasia Seth G.L. Bihani S.D. College of Technical Education, Institute of Pharmaceutical Sciences and Drug Research, Sri Ganganagar, Rajasthan, INDIA INTRODUCTION When we speak of a molecule as being raised to a higher electronic level we mean that an electron has been changed from one orbital to another orbital of higher energy. This electron can be of any kinds we have encountered –a σelectron, a π electron or an n electron. In Ultraviolet region we are confined only to the excitation of the comparatively loosely held n and πelectrons.2 [adsense:336x280:8701650588] Reference Id: PHARMATUTOR-ART-1249 IMPORTANT IN THIS ARTICLE: * CONCEPT OF MOLECULAR ORBITALS * POSSIBLE HOMO-LUMO COMBINATIONS Out of the above mentioned transitions only n→ π* and π→ π* are of use to the analytical chemist working on the ultraviolet spectrophotometer. When light – either visible or ultraviolet – is absorbed by valence (outer) electrons. These Electrons are promoted from their normal (ground) states to higher energy (excited) states .The energies of the orbitals involved in electronic transitions have fixed values. Because energy is quantised, It seems safe to assume that absorption peaks in a UV/visible spectrum will be sharp peaks. However, this is rarely, if ever, observed. Instead the spectrum has broad peaks .This is because there are also vibrational and rotational energy levels available to absorbing materials. Ultraviolet- visible spectroscopyor ultraviolet - visible spectrophotometery (UV-Vis or UV/Vis) involves the spectroscopy of photons in the UV-visible region. There is an interaction between UV visible light and sample which is in solution form. As a result of this interaction some photons (photons of UV-Vis EMR) are absorbed and this absorption of UV visible is measured by an instrument named UV visible spectrophotometer. UV visible is low energy EMR hence generally no ionization is take place but electronic transition of lone pair and π electron take place (200-800 nm).6 QUANTUM MECHANICS Quantum mechanics (QM) is a set of scientific principles describing the known behavior of energy and matter that predominate at the atomic and subatomic scales. QM gets its name from the notion of a quantum, and that quantum value is the Planck constant. The wave–particle duality of energy and matter at the atomic scale provides a unified view of the behavior of particles such as photons and electrons. While the notion of the photon as a quantum of light energy is commonly understood as a particle of light that has an energy value governed by the Planck constant, what is quantized for an electron is the angular momentum it can have as it is bound in an atomic orbital.Electrons have certain properties of particles and certain properties of waves. Electrons have mass and charge like particles. Because they are so small and are moving so fast, electrons have no defined position. Their location is best described by wave mechanics (i.e. a three dimensional wave) and a wave equation called the Schrödinger equation. Solutions of the Schrödinger equation are called wave functions and are represented by the Greek letter psi. Each wave function describes a different orbital. There are many solutions to the Schrödinger equation for a given atom. Atomic orbitals:- The region in space where an electron is likely to be found called an orbital. There are different kinds of orbitals, which have different sizes and different shapes, and which are disposed about the nucleus in specific ways. The particular kind of orbital that an electron occupies depends upon the energy of the electron.5 NOW YOU CAN ALSO PUBLISH YOUR ARTICLE ONLINE. SUBMIT YOUR ARTICLE/PROJECT AT articles@pharmatutor.org Subscribe to Pharmatutor Job Alerts by Email FIND OUT MORE ARTICLES AT OUR DATABASE CONCEPT OF MOLECULAR ORBITALS Theory of molecular orbitals comes under the preview of quantum mechanism. Erwin schrodinger formulated a wave equation which has a series of solutions called wave functions, each corresponding to a different energy level for the electron. In molecules, as an isolated atoms, electrons occupy orbitals and in accordance with much the same “rules”. These molecular orbtials are considered to be centered about many nuclei, perhaps covering the entire molecule; the distribution of nuclei and electrons is simply the one that results in the most stable molecule. Constructive interference of two wave function leads to high probability density between the nuclei, leading to bonding orbital while in antibonding MOs wave function interfare destructively leading to low electron density that is greater repulsions Thus electrons in a bonding MOs tend to hold the atoms together and electrons in antibonding tend to force atoms apart.8 Linear Combination of Atomic Orbitals [LCAO] As we know that the number of formed molecular orbitals is equal to the number of component atomic orbitals. AOs may overlap either axially or collaterally. This can be understood diagrammatically as shown below Axial Overlapping Axial Overlapping Figure 3 Co-lateral overlapping lateral Overlaping ENERGY LEVELS OF BONDING AND ANTI-BONDING MOLECULAR ORBITALS The two P atomic orbitals combine to form two molecular orbitals, one bonding and one antibonding .5 ELECTRONIC CONFIGURATION OF SOME MOLECULES Ethylene configuration of π electrons in the ground state and the excited state For the π electrons of ethylene, there are two molecular orbitals since there are two linear combinations of the two component p orbitals. The broken line in the figure indicates the non-bonding energy levels. Below it lies the bonding orbitals, π and above it lies the antibonding orbitals π*. Normally a molecule exists in the state of lowest energy, the ground state. But absorption of light of the right frequency in the ultraviolet region rises a molecule to an excited state, a state of higher energy, in the ground state of ethylene both πelectrons are in the π orbital, this configuration is specified as π2, where the superscript tells the no. of electrons in the orbital. In the excited state one electron is in the πorbital and the other still of opposite spin- is in the π*orbital, this configuration, ππ*is naturally the less stable since only one electron helps to hold the atoms together, while other tend to force them apart. 1,3- butadiene .configuration of π electrons in the ground state and the first excited state For 1,3-butadiene,with 4 component p orbitals, there are 4 MO for π electrons. The ground state has the configuration ψ12 ψ22, i.e. there are two electrons in each of the bonding orbitals ψ1 & ψ2.the higher of these ψ2, resembles two isolated π orbitals, although it is of somewhat lower energy, orbital ψ1 encopasses all four carbons, this delocalization provides the net conjugated system. Absorption of light of the right frequency rises one electron to ψ3 hv ψ12 ψ22 ----------> ψ12 ψ2 ψ3 ground state lowest excited state HOMO refers to Highest Occupied Molecular Orbital LUMO refers to Lowest Unoccupied Molecular Orbital The two orbitals best matched in energy will be the highest occupied molecular orbitals or HOMO. on one reactant, and the lowest energy unoccupied MO,or LUMO on the other. NOW YOU CAN ALSO PUBLISH YOUR ARTICLE ONLINE. SUBMIT YOUR ARTICLE/PROJECT AT articles@pharmatutor.org Subscribe to Pharmatutor Job Alerts by Email FIND OUT MORE ARTICLES AT OUR DATABASE POSSIBLE HOMO-LUMO COMBINATIONS Table-1 HOMO LUMO RESULT An occupied n orbital An empty n orbital Bond formation only An occupied n orbital A σ*orbital Bond formation and bond rupture An occupied n orbital A π*orbital Bond formation and bond rupture A πorbital An empty orbital Bond formation and bond rupture A π orbital A σ*orbital Bond formation and bond rupture A π orbital A π* orbital Bond formation and bond rupture A σ orbital An empty orbital Bond formation and bond rupture A σ orbital A σ* orbital Bond formation and bond rupture A σ orbital A π* orbital Bond formation and bond rupture Transition probability It is not essential that exposure of a compound to ultraviolet or visible light must always gives to an electronic transition. On the other hand, the probability of a particular electronic transition has found to depend €d upon the value of molar extinction coefficient and certain other factors. According transitions can be divided into two categories. (i) Allowed transitions (ii) Forbidden transitions (i) Allowed transitions – these are transitions having molar coefficient 104 or more. These are generally designated as π→ π transitions. For example in 1,3-butadiene which exhibits absorption at 217nm has €max value 21000 represents an allowed transition. These transition are mainly favoured due to symmetry relationship. For e.g. 1,3- butadiene absorbs at 217nm and has molar absorptivity of 21000 (ii) Forbidden transitions – these are transitions for which €max is generally less than 104 . for example transition of saturated aldehyde showing weak absorption near 290nm and having €max 100 has been a forbidden transition. For e.g. Carbonyl group absorbs at 300nm and a molar absorptivity of 10-100.5 TRANSITIONS IN ULTRAVIOLET SPECTROSCCOPY Electronic transitions in UV-visible spectroscopy which are important are n→ π* & π→ π*transitions. (a) n→ π* transitions. - In this transition, an electon of unshared electron pair on a hetero atom is excited to π* antibonding orbital. This transition involves least amount of energy than all the transitions and therefore, this transition gives rise to an absorption band at longer wavelengths. In saturated aliphatic ketones, e.g., the n→ π*transitions around 280 nm is the lowest energy transitions. This n→ π* transitions is “forbidden” by symmetry considerations, thus the intensity of the band due to this transition is low, although the wavelength is long (lower energy). (b) π→ π* transitions - This transition is available in compounds with unsaturated centres, e.g., simple alkenes, aromatics, carbonyl compounds, etc. this transition requires lesser energy then transition in a simple alkene, although several transitions are available , the lowest energy transition is the π→ π*transition and a absorption band around 170nm-190nm in unconjugated alkenes is due to this transition in the case of , e.g., saturated ketones, the most intense band around 150nm is due to π→ π*transition.7 DESIGNATION OF BANDS K- Band One may designate the UV absorption bands by using electronic transitions or the letter designation. The band due to π→ π* transitions in a compound with conjugated π system is usually intense (€max.>10000) and is frequently referred to as the k-band (german- konjugierte). The examples of the compounds in which k-band appears are butadiene, Mesityl oxide. Benzene itself displays three absorption bands at 184,204 and 256nm and of these the band at 204nm is often designated as k-band, and this used in other benzenes as well. Eg. Conjugated diene, triene, polyene, enones and aromatic rings R- Band The n→π* transition (R-band german radikalartig) in compounds with single chromatographic groups i.e., carbonyl or nitro are forbidden with € value less than 100. In conjugated systems the energy separation between the ground and excited states is reduced and the system then absorbs at longer wavelengths and with a greatly increased intensity (k-band is intense and at longer wavelength). Moreover, due to the lessening of the energy gap, the n→ π* transition due to the presence of the heteroatom and lone pair i.e. the r-band also undergoes a red shift with little change in intensity. Eg. Acetone, acroline, methyl vinyl ketone, acet aldehyde, acetophenone, croton aldehyde B-Band These bands are observed in aromatic compounds and hetero aromatic compounds. Here B refers to Benzenoid bands Eg. Benzene, tolune, acetophenone, benzoic acid, napthelene, styrene E- Bands Such band originate due to electronic transition in the benzenoid system of the ethylinic part enclosed in cyclic conjugation. Here E refers to Ethylinic. These are further classified as E1 and E2 Eg. Benzene, nepthelene, anthracene, quinolene7 DIFFERENT EFFECTS 1. Effect of solvent The transitions of polar bonds, like c=o but not ethylene, are affected by solvent polarity as solvent polarity is increased, π→ π*bands undergo red shifts. This is so since excited state is more polar than the ground state and hence stabilization is greater relative to the ground state with two n electrons receives greater stabilization than the excited state with only n electron. These opposite trends are clear by examining the data of mesityl oxide. There is more on shift of bands with solvents. 2. Effect of conjugation Absorption in near UV that is above 200 nm is invariably associated with the presence of unsaturated groups or atoms with unshared pairs of electrons the saturated hydrocarbon which do not have these structural elements observe below 200nm reason, not of much significance for structural study of organic compounds. Thus interstically a complex steroid molecule cholest-4-ene-3 one is easily recognized to have an α-ß unsaturated keton moiety, similar to that in mesityl oxide by their spectral resemblance.5 3. Effect of PH In alkaline PH π → π* transition is more favoured and in acidic PH n → π* transition is more favoured. For eg. (1) P- nitrophenol ---> p- nitrophenol (+M effect increased) Alkaline PH π → π* transition more favoured less energy is required absorption would take place at longer wavelength (2) p-amino phenol ---> P-amino phenol Acidic PH n → π* transition is more favoured More energy required Blue shift Absorption at shorter wavelength REFERENCES 1. Carry F.A., “organic chemistry”, fourth ed., new York, McGraw hill. 2. Chatwal gurdeep R. and Anand sham K., “instrumental methods of chemical analysis”, edited by M. Arora, published by Himalaya publishing house, new delhi, 2005, page no.-2.150-2.154 3. Dr. Shankar ravi, “textbook of pharmaceutical analysis”, third edition, Rx publication, page no.-2.2-2.5 4. Jag Mohan, “organic analytical chemistry theory and practice”, published by Narosa publication house, new delhi. Page no.-347-350. 5.Kalsi P.S., “spectroscopy of organic compound”, sixth edition, new delhi. New age international Pvt. 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