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Ultraviolet Spectroscopy

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Abstract – **Researches have observed that the primary and secondary bands in the spectra of polynuclear aromatic hydrocarbons shift to longer wavelength. In fact, even the second primary band, which appears at 184nm for benzenes, is shifted to a wavelength within the range of most uv spectrophotometers. This band lies at 220nm in the spectrum of naphthalene. As the extent of conjugation increases, the magnitude of the bathochromic shift also increases. The ultraviolet spectra of the polynuclear aromatic hydrocarbons possess characteristic shapes and fine structure.**

I. INTRODUCTION

When continuous radiation pass through a transparent material, a portion of the radiation may be absorbed. If that occurs, the residual radiation, when it is passed through a prism, yields a spectrum with gaps in it, called an absorption spectrum. The electromagnetic radiation that is absorbed has energy exactly equal to the energy difference between the excited and ground states. Generally, the most probable transition is from the Highest Occupied Molecular Orbital [HOMO] to the Lowest Unoccupied Molecular Orbital [LUMO].

II. THE ORIGIN OF UV BAND STRUCTURE

For an atom that absorbs in the ultraviolet, the absorption spectrum sometime consists of very sharp lines, as would be expected for a quantized process occurring between two discrete energy levels. For, molecules, however, the UV absorption usually occurs over a wide range of wavelengths because molecules normally have many excited mode of vibrations and rotation at room temperature. In fact, the vibration of molecules cannot be completely ‘frozen out’’ even at absolute zero. The rotational and vibrational levels are thus ‘superimposed’’ on the electronic levels.

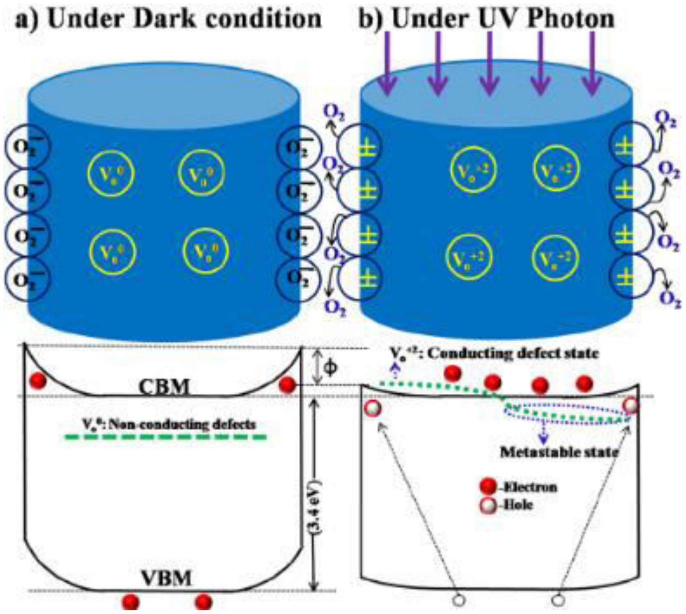

Fig 1. Model Setup

III. Principles of Absorption Spectroscopy

The greater the number of molecules capable of absorbing lights of a given wavelength the greater the extent of light absorption. The molar absorptivity is a property of the molecule undergoing on electronic transition and is not a function of the variable parameters involved in preparing a solution. The size of the absorbing system and the probity that the electronic transition will take place control the absorptivity, which ranges from 0 to 10^6. Values above 10^4 are termed high – intensity absorptions. Forbidden transitions have absorptivity in the range from 0 to 1000.

Fig 2. Lab View

IV. INSTRUMENTATION

The typical ultraviolet- visible spectrophotometer consists of a light source, a monochromator and a detector. The light source is usually a deuterium lamp, which emits electromagnetic radiation in the ultraviolet region of the spectrum. In a typical double – beam instrument, the light emanating from the light source is split into two beams, the sample beam and the reference beam. The sample cell must be constructed of a material that is transparence to the electromagnetic radiation being used in the experiment. For spectra in the visible range of the spectrum, cells composed of glass or plastic are generally suitable. Instead, cells made of quartz must be used since quartz does not absorb radiation in this region.

IV. PRESENTATION OF SPECTRA

The ultraviolet visible spectrum is generally recorded as a plot of absorbance versus wavelength. It is customary to then report the data with either Plotted on the ordinate and wavelength plotted on the abscissa. However, very few electronic spectra are reproduced in the scientific literature; most are described by indications of wavelength maxima and absorptivity of the principle absorption peaks.

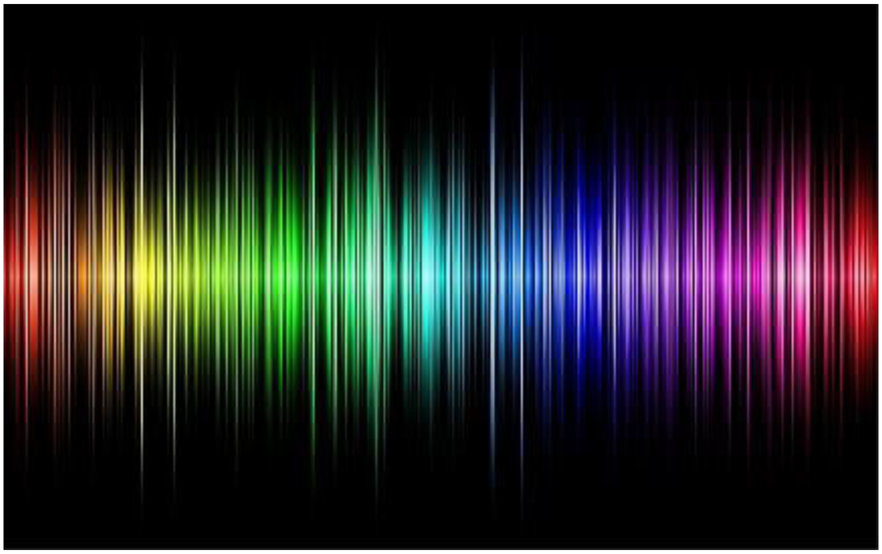

Fig 3. Model Spectra

V. SOLVENTS

The choice of the solvent to be used in ultraviolet spectroscopy is quite important. The first criterion for a good solvent is that it should not absorb ultraviolet radiation in the same region as the substance whole spectrum is being determined. Usually solvents that do not conjugated systems are most suitable for this purpose, although they vary regarding the shortest wavelength at which they remain transparent to ultraviolet radiation. A second criterion for a good solvent is its effect on the fine structure of an absorption band.

What is A Chromophore?

Although the absorption of ultraviolet radiation results from the excitations of electrons from ground to excited states, the nuclei that the electrons hold together in bonds play on important role is determining which wavelength of radiations absorbed are properties of a group of atoms rather than of electron themselves. The group of atoms producing such as absorption is called a chromophore. Very often, it is extremely difficult to predict from theory how the absorption will change as the structure of the chromophore is modified, and it is necessary to apply empirical working guides to predict such relationships.

VI. THE EFFECT OF CONJUGATION

One of the best ways to bring about a bathochromic shift is to increase the extent of conjugation in a double bounded system. In the presence of conjugated double bonds, the electronic energy levels of a chromophores not only results in a bathochromic shift but increases the intensity of the absorption. These two effects are of prime importance in the use and interpretation of electronic spectra of organic molecules because conjugation shift the selective light absorption isolated chromophore from a region of the spectrum that is not readily accessible to a region that is easily studied with commercially available Spectro photometer

VII. THE EFFECT OF CONJUGATION OF ALKENES

The bath chromatic shift that results from on increase in the length of a conjugated system implies that an increase in conjugation decreases the energy for electronic excitations. This is true and can be explained most easily by the used of molecular orbital theory. According to molecular orbital [MO] theory, the atomic orbitals on each of the carbon atoms combine to make π molecular orbitals. The new bonding orbital, a molecular orbital, has an energy lower than that of either of the original p orbitals; likewise, the antibonding orbital has on elevated energy.

VIII. AROMATIC COMPOUNDS

The absorption that results from transitions within the benzene chromosphere can be quite complex. The ultraviolet spectrum contains three absorption bands, which sometimes contain a great deal of fine structure. If you were to attempt a simple explanations for the electronic transitions in benzene, you would conclude that there are four possible transitions, but each transitions has the same energy.

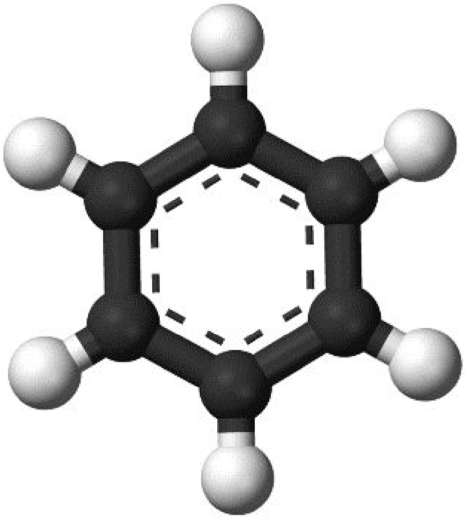

Fig 4. Model diagram

IX. SUBSTITUENTS WITH UNSHARED ELECTRONS

Substituents that carry nonbonding electrons can cause shifts in the primary and secondary absorption bands. The nonbonding electrons can increase the Length of the π system through resonance. The more available these n electrons are for interactions with the π system of the aromatic ring, the greater the shift will be .Interactions of this type between the n and π electrons usually cause shift in the primary and secondary benzene absorption bands to longer wavelength. In addition, the presence of n electrons in these compounds gives the possibility of n to π* transitions.

Substituents Capable of π- Conjugation:

Substituents that are themselves chromophores usually contain π electrons. Just as in the case of n electrons, interaction of the benzene – ring electrons and the π electrons of the substituents can produce a new electron transfer band. At times, this new band may be so intense as so to obscure the secondary band of the benzene system. However, the magnitudes of the shifts are somewhat smaller in the case of benzoate ion, the conjugate base of benzoic acid.

X. ELECTRON – RELEASING AND ELECTRON – WITHDRAWING EFFECTS

Substituents may have differing effects on the positions of absorption maxima, depending whether they are electron with drawing. Any substituent, regardless of its influence on the electron distribution elsewhere in the aromatic molecule, shifts the primary absorption band to longer wave length. Electron – withdrawing. Any substituents, regardless of its influence on the electron distribution elsewhere in the aromatic molecule, shifts the primary absorption band to longer wave length. Electron – withdrawing groups have essentially no effect on the position of the secondary absorption band unless, of course, the electron – withdrawing group is also capable of acting chromophore.

Di-substituted Benzene Derivatives:

With di-substituted benzenes, two possibilities exist. If both groups are electron releasing or if they are both electron withdrawing, they exert effects similar to those observed with mono-substituted benzenes. The group with the stronger effect determines the extent of shifting of the primary absorption band with substitution of these types, there is no opportunity for the kind of direct resonance interaction between substituent groups that is observed with para substituents. In the case of ortho substituents, the steric inability of both groups to achieve coplanarity inhibits resonance.

Poly Nuclear Aromatic Hydrocarbons and Heterocyclic Compounds:

Researches have observed that the primary and secondary bands in the spectra of polynuclear aromatic hydrocarbons shift to longer wavelength. In fact, even the second primary band, which appears at 184nm for benzenes, is shifted to a wavelength within the range of most UV spectrophotometers. This band lies at 220nm in the spectrum of naphthalene. As the extent of conjugation increases, the magnitude of the bathochromic shift also increases. The ultraviolet spectra of the polynuclear aromatic hydrocarbons possess characteristic shapes and fine structure.

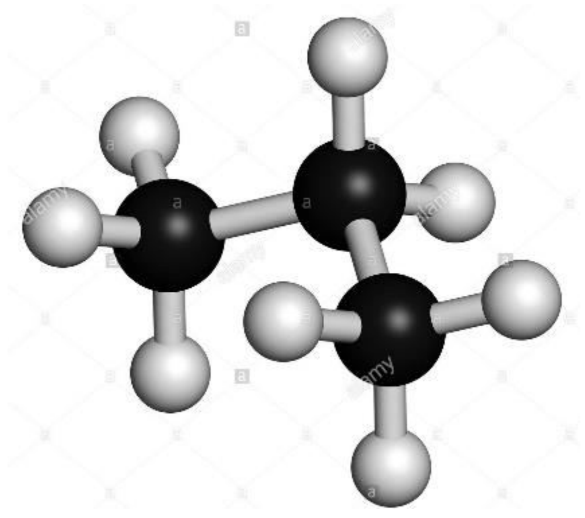

Fig 5. Model diagram

XI. MODEL COMPOUND STUDIES

Very often, the ultraviolet spectra of several members of a particular class of compounds are very similar. Unless you are thoroughly familiar with the spectroscopic properties of each member of the class of compounds, it is very difficult to distinguish the substitution patterns of individual molecules by their ultraviolet spectra. By comparing the uv spectrum of an unknown substance with that of a similar but less highly substituted compound, you can determine whether or not they contain the same chromophore. The spectra of model compounds can be obtained from published catalogues of ultraviolet spectra.

Visible Spectra: Colour in Compounds:

The portion of the electromagnetic spectrum lying between about 400 and 750nm is the visible region. Light waves with wavelengths between these limits appear colored to the human eye. As anyone who has seen light diffracted by a prism or the diffraction effect of a rainbow knows, one end of the visible spectrum is violet and the other is red. Light wavelengths near 400nm is violet, while that with wavelengths near 750nm is red. If a substance absorbs visible light, it appears to have a colour; if not, it appears white. There is an inverse relationship between the observed colour and colour absorbed.

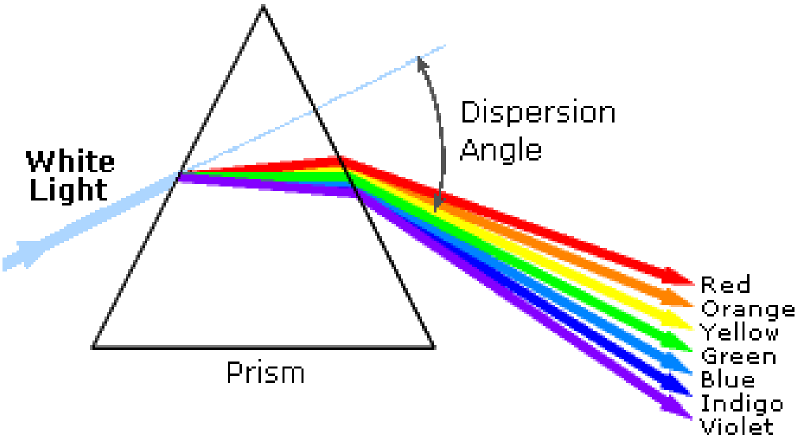

Fig 6. Visible Spectra: Colour in Compounds

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