

UV VISIBLE SPECTROSCOPY

Electronic transitions:

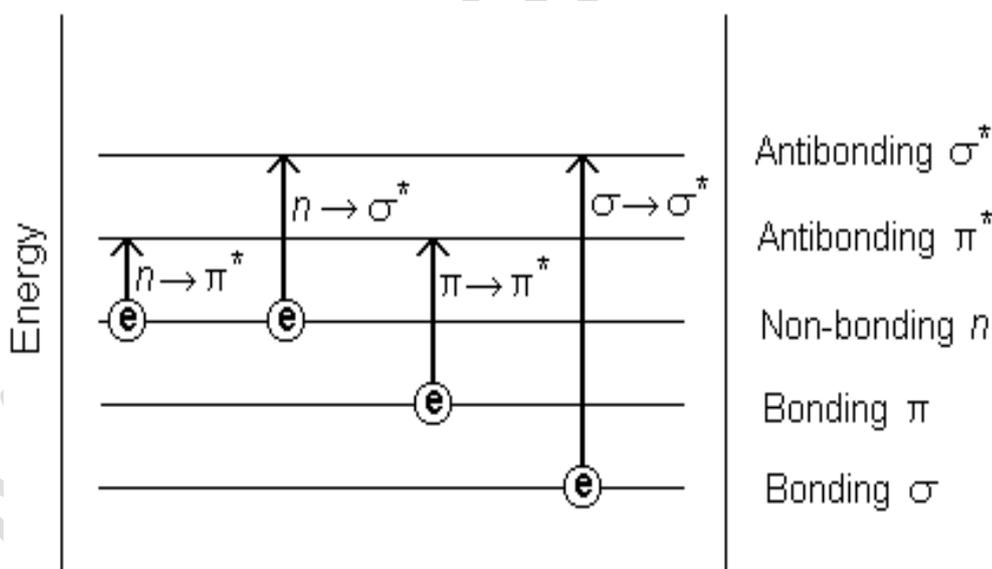
When we speak of a molecule as being raised to a higher electronic level, we mean that an electron has been changed from one orbital to another orbital of higher energy. This electron can be of any kinds we have encountered – a σ electron, a π electron or an n electron. In Ultraviolet region we are confined only to the excitation of the comparatively loosely held n and π electrons.

A rigorous discussion of transition probabilities is beyond the scope of this lab course, but one obvious factor is the overlap of the orbitals involved in the electronic excitation.

This is nicely illustrated by the two transitions of an isolated carbonyl group. The $n \rightarrow \pi^*$ transition is lower in energy ($\lambda_{\text{max}} \approx 290 \text{ nm}$) than the $\pi \rightarrow \pi^*$ transition ($\lambda_{\text{max}} \approx 180 \text{ nm}$), but the transition probability of the former is a thousand times smaller than that of the latter.

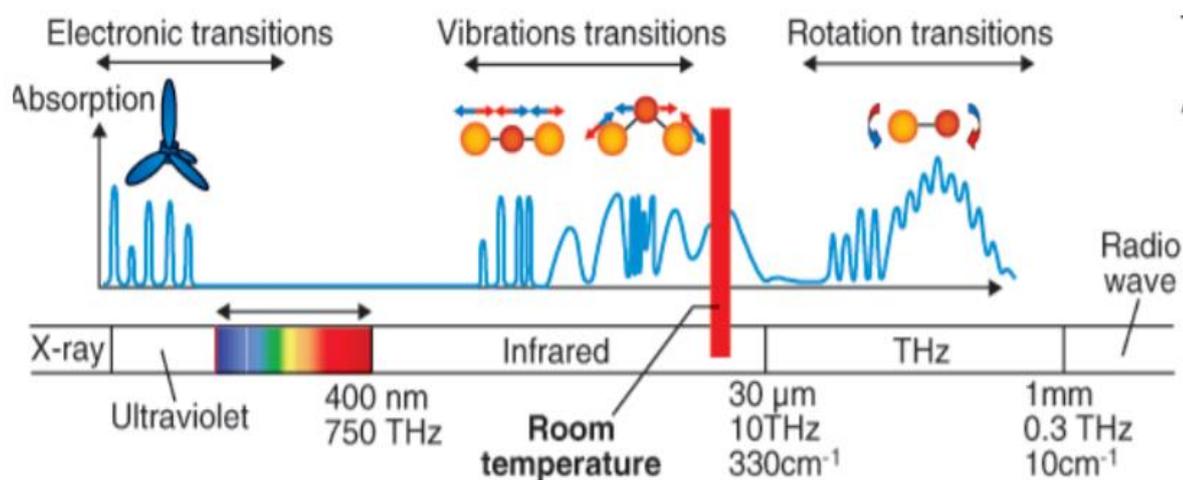
The spatial distribution of these orbitals suggests why this is so. The n -orbitals do not overlap at all well with the π^* orbital, so the probability of this excitation is small. The $\pi \rightarrow \pi^*$ transition, on the other hand, involves orbitals that have significant overlap, and the transition probability is very large.

Transitions between electronic states can be divided into the following categories:



$\pi \rightarrow \pi^*$ transitions: For molecules that possess π bonds like alkenes, alkynes, aromatics, acryl compounds or nitriles, light can promote electrons from a π bonding molecular orbital to a π anti-bonding molecular orbital. This is called a $\pi \rightarrow \pi^*$ transition and is usually strong (high extinction coefficient). Groups of atoms involved in π bonding are thus often called chromophores. The transition energy (or absorption wavelength) can be an indication for different types of π bonds (carbon-carbon, carbon oxygen or carbon-nitrogen in a nitrile group).

- $n \rightarrow \pi^*$ transitions: Lone pair electrons that exist on oxygen and nitrogen atoms may be promoted from their non-bonding molecular orbital to a π anti-bonding molecular orbital. This is called an $n \rightarrow \pi^*$ transition and requires less energy (longer wavelength) compared to a $\pi \rightarrow \pi^*$ transitions within the same chromophore. However, the transition probability is usually much lower.
- $n \rightarrow \sigma^*$ transitions: Saturated compounds with substituents containing lone-pairs such as water, ammonia, hydrogen disulfide only have $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions in the UV-visible range.
- d-d transitions: Many transition metal ion solutions are coloured as a result of their partially filled d-levels, which allows promotion of an electron to an excited state (change of d-level occupation) by the absorption of relatively low energy visible light. The bands are often broad and strongly influenced by the chemical environment. They are also usually very weak.
- Charge transfer transitions: Much stronger absorption is found when complexing the metal ion with some suitable organic chelating agent to produce a charge-transfer complex. Electrons may be transferred from the metal to the ligand or vice versa. The high transition probability is exploited to quantitatively detect ions in solution. There are numerous chelating agents available which may or may not complex selectively where there is more than one type of metal ion present.



Chromophore

The term chromophore was previously used to denote a functional group of some other structural feature of which gives a colour to compound.

For example- Nitro group is a chromophore because its presence in a compound gives yellow colour to the compound.

But these days the term chromophore is used in a much broader sense which may be defined as “any group which exhibit absorption of electromagnetic radiation in a visible or ultra-visible region “It may or may not impart any color to the compound.

Some of the important chromophores are: ethylene, acetylene, carbonyls, acids, esters and nitrile groups etc.

A carbonyl group is an important chromophore, although the absorption of light by an isolated group does not give rise to any colour in the ultra-violet spectroscopy.

Types of chromophores:

Two types of chromophores are known.

1. Chromophores in which the groups have π electrons undergo π - π^* transitions.

For examples: -ethylene, acetylenes etc.

2. Chromophores having both π - electrons and n (non-bonding) electrons undergo two types of transitions. i.e., π - π^* and n- π^* , for examples: - carbonyls, nitriles, azo compounds and nitro compounds etc.

Identification of chromophores:

There is no set rule for the identification of a chromophore. The change in position as well as the intensity of the absorption depends upon a large number of factors.

Following points may be useful.

1. Spectrum having a band near 300 m μ may possess two or three conjugated units.
2. Absorption bands near 270-350 m μ with very low intensity ϵ max 10-100 are because of n- π^* transitions of carbonyl group.
3. Simple conjugated chromophores like dienes or α β -unsaturated ketones have ϵ max values, i.e., from 10,000 to 20,000.
4. The absorption with ϵ max value between 1, 000-10,000 reveals the presence of an aromatic system. If aromatic nucleus is substituted with groups which can extend the chromophore, the absorption takes place at still higher value of extinction coefficients.

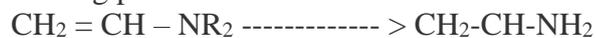
Auxo chromes:

It is a group which itself does not act as a chromophore but when attached to a chromophore, it shifts the adsorption towards longer wavelength along with an increase in the intensity of absorption.

Some commonly known auxo chromic groups are: -OH, -NH₂, -OR, -NHR, and -NR₂. For example:
When the auxo chrome -NH₂ group is attached to benzene ring. Its absorption changes from λ max 225 (ε max 203) to λ max 280 (ε max 1430)

All auxo chromes have one or more non-bonding pairs of electrons.

If an auxo chromes is attached to a chromophore, it helps in extending the conjugation by sharing of non-bonding pair of electrons as shown below.



The extended conjugation has been responsible for bathochromic effect of auxo chromes.

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