



Lectures of Molecular spectroscopy
Second Semester, Scholar year 2024-2025
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Lecture No. 5 : Electronic Transitions Spectroscopy

1-Introduction:

- Electronic changes have been occurs in this region, since the energy limits equal to 8000Cm^{-1} frequency (ranged from 750nm into less 200nm).
- It is classify into three different region (A, B, and C), since
 - i- The visible is C-region, which is range from 750nm into400nm.
 - ii- The near UV-region (B) is range from 400nm into 200nm.
 - iii- Last region-A is the vacuumed UV-region that has ranged from 200nm and less than (oxygen absorbed).
- The energy value limits reach the outer shell electrons of chemical species and promotion to higher energy levels.

They found some assumption of the electronic transitions in molecule since nuclei remain frozen (R unchanged):-

- 1- Vertical transitions between potential energy curves.
- 2- There is no selection rule governing the allowed vibrational changes accompanying an electronic transition.
- 3- The probability of undertaking a $v'' \rightarrow v'$ transition is governed by Franck-Condon factors.

2- Features of Electronics spectroscopy:

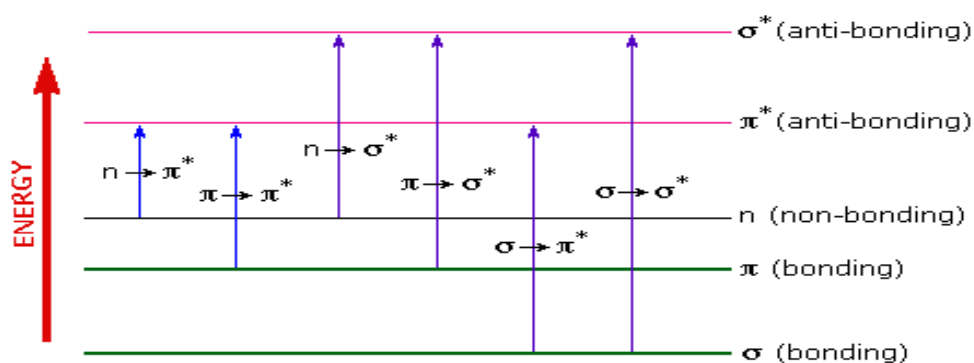
- Gives information about electronics structures of molecules, electronics energies at different molecular levels, and the know emission and absorption spectra for colored chemical compounds.
- A large change in energy is coming from electronic transitions also rearrangements of electrons that has produced change in electrostatic power on nuclei.
- At the same time of electronic transition there are vibrational and rotational; so, can be analysis the vibrational structure from electronic transition spectra.
- If sample spectra at gas phase, there are confused in spectral lines as one-band width broad peaks and cannot be analysis. Therefore, the spectra in gas phase are very complexes than other phases (at solid phase and liquid phase).

- In some time, absorption energy is so enough to dissociation the molecules.
 $E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}}$

3- UV-Visible spectra:

- In organic molecules, most bonding electrons are excited by $\lambda < 185$ nm (Vacuumed-UV).
- Most functional groups have lone pairs whose energies place them in the near UV and visible range. These groups are call “chromophores”, although this is a bit odd, since all molecules are “chromophores” under the right conditions.
- The visible region of the spectrum comprises photon energies of 36 to 72 kCal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kCal/mole.
- Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis. The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital.
- Absorption spectroscopy carried out in this region is sometimes call "electronic spectroscopy".

A diagram showing the various kinds of electronic excitation that may occur in chemical species shown on the left. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an excited state.



- All chemical species are active and they have electronic spectra because the change in electronic distribution produced the change in dipole moment. All semi diatomic molecules can be having electronic spectra also within rotation & vibration like N₂, H₂, and Br₂.
- According to the theory of molecular orbital, there are different types of transitions occurs due electron promotion from lower energy orbital levels into higher molecular orbital energy levels, or transitions can be represented by transition from atomic character orbital into higher energy molecular orbital.

4- The Importance of Conjugation

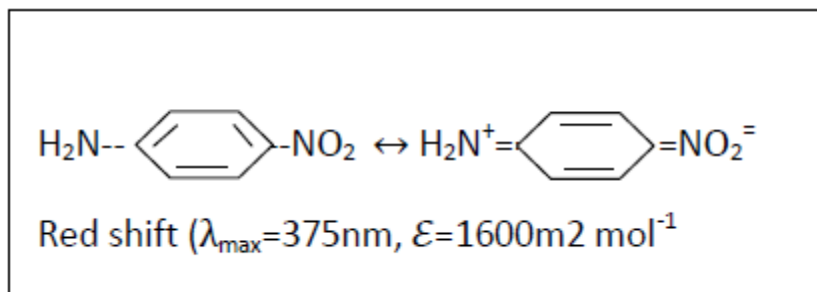
A comparison of the absorption spectrum of 1-pentene, $\lambda_{\text{max}} = 178 \text{ nm}$, with that of isoprene clearly demonstrates the importance of chromophore conjugation. The spectrum on conjugation of double and triple bonds also shifts the absorption maximum to longer wavelengths. From the polyene spectra displayed, it is clear that each additional double bond in the conjugated pi-electron system shifts the absorption maximum about 30 nm in the same direction. In addition, the molar absorptivity (ϵ) roughly doubles with each new conjugated double bond.

Extending conjugation generally results in bathochromic and hypochromic shifts in absorption. The appearance of several absorption peaks or shoulders for a given chromophore is common for highly conjugated systems, and is often solvent dependent. This fine structure reflects not only the different conformations such systems may assume, but also electronic transitions between the different vibrational energy levels possible for each electronic state. **Terminology for Absorption Shifts**

Nature of Shift	Descriptive Term
To Longer Wavelength	Bathochromic
To Shorter Wavelength	Hypochromic
To Greater Absorbance	Hyperchromic
To Lower Absorbance	Hypochromic

C- Effect of complementary groups (Charge transfer spectrum)

When they found more than one substituted group into aromatic ring with different effect, (one of them is electron donating and the other is electron drawing) in Para position for each other's, these groups can be calling complementary groups.



The transition is call Charge transfer, this phenomenon is due the resonance exchange effect. If the two substituted groups into the aromatic ring have the same electronic effect (both of them drawing or donating) the resultant spectrum as individual spectrum of one group and there are not complementary groups. The same thing occurs if they are not in Para position from each other's.

D- Effect of hydrogen bonded (inter & intra).

This reason is come out from hydrogen bond formation in two different cases, the first is inter hydrogen bonding formation in the same chemical species moiety like in salicylic acid, the second case is intra hydrogen bonding formation between two chemical species moieties in bulk solution like ethanol and acetone. Both types will alter the transition into blue shift (shorter wavelength).

6-Rules of Electronic transitions

1. Not all transitions are possible to observe.
2. For an electron to transition, certain quantum mechanical constraints apply – these are call “selection rules”.
3. An electron cannot change its spin quantum number during a transition – these are “forbidden”.
4. To further complicate matters, “forbidden” transitions are sometimes observed (albeit at low intensity) due to other factors