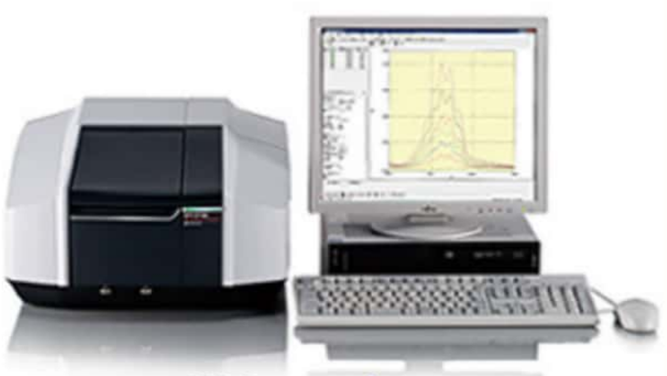
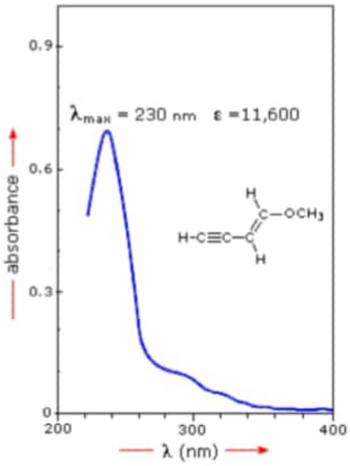
UV Spectroscopy



UV Spectrophotometer



UV Spectrum

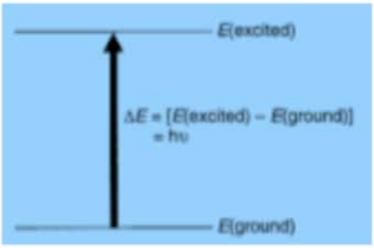
@H.G

Fundamentals of UV absorption

UV spectroscopy involves absorption spectroscopy where molecules interact with UV radiation and produce absorption spectra in the range of 200nm to 400nm.

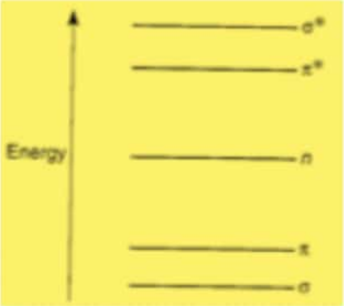
UV spectroscopy is a molecular spectroscopic method arising due to transition of valence electrons in a molecule from the ground state energy (E_e) to the higher excited state (E_e).

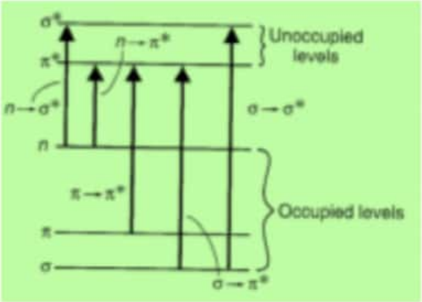
Then the difference in change of energy is $\Delta E = E_e - E_g = h\nu$



Types of Electronic Transition

Energy absorbed in the UV region by valence electrons causes transition from ground state to excited state.



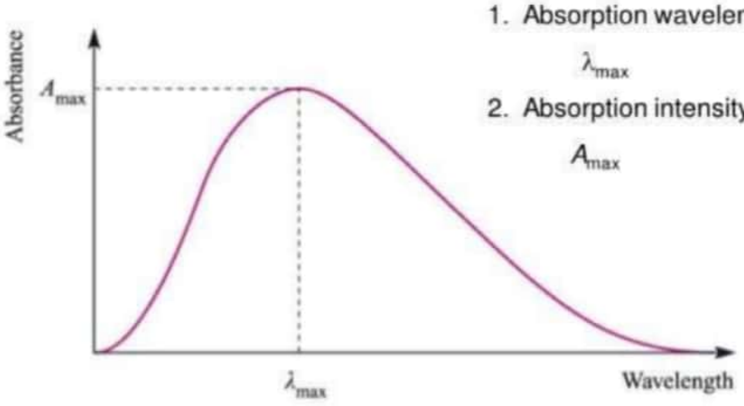


The energy required for various transitions are in the following order.

$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^*$ c$\rightarrow \pi^* > n \rightarrow \pi^*$

The valence electrons are exited from bonding to an antibonding orbitals (or HOMO to LUMO)

UV Spectra



The two main properties of an absorbance peak are:

1. Absorption wavelength

   λ_{max}

2. Absorption intensity

   A_{max}

Selection Rules for Electronic Transition

Not all of the transitions that at first sight appear possible are observed. Certain restrictions, called **selection rules,** must be considered. One important selection rule states that transitions that involve a change in the spin quantum number of an electron during the transition are not allowed to take place; they are called **"forbidden" transitions.** Other selection rules deal with the numbers of electrons that may be excited at one time, with symmetry properties of the molecule and of the electronic states, and with other factors

Spin Selection Rule-

Change of Spin Quantum Number is FORBIDDEN

Transition between same spin states allowed: singlet -> singlet, triplet -> triplet, others are forbidden: singlet -> triplet, doublet -> singlet, etc.

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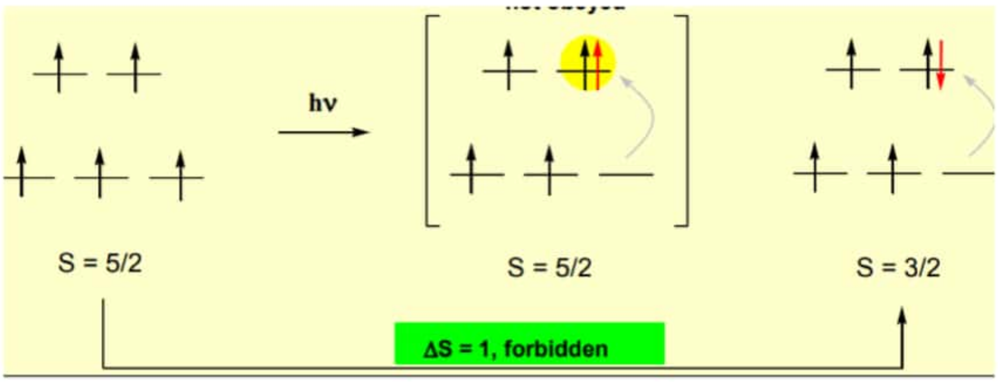
1. Spin selection rule $\Delta S = 0$ or $\Delta M^S = 0$

spin multiplicity $M^S = 2S+1$
$S = \Sigma s = n/2$ (total spin quantum number)

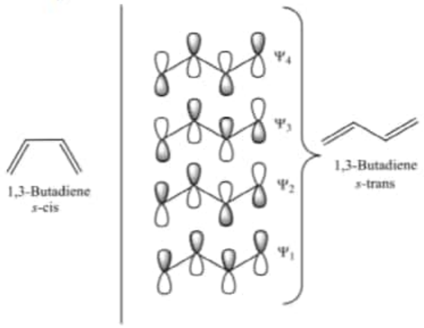


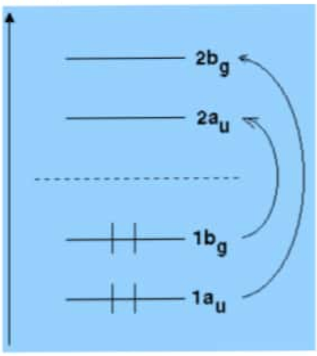
Symmetry Selection Rule

Whenever electrons change molecular orbitals due to excitation, e.g. in UV spectroscopy, the symmetry of the two involved orbitals is the criterion for a transition. We speak of symmetry-allowed and symmetry-forbidden transitions.

If the molecule has a centre of symmetry, 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.

Take the molecular orbitals of *trans*-butadiene as a first example. Figure 1 is a schematic representation of the energies of these orbitals.





There is **Laporte's rule** which states that, for any molecule possessing one centre of inversion, only transitions between g and u or vice versa are allowed.

For Details see http://www.pci.tu-bs.de/aggericke/PC4e/Kap_V/Lage_Dipolmoment.htm

Transition Dipolemoment https://en.wikipedia.org/wiki/Transition_dipole_moment

Absorption phenomenon for α,β-unsaturated carbonyl system