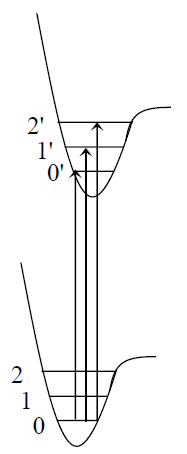
**Electronic Spectroscopy**

**Electronic Excitation: Frank-Condon Principle**

The electronic excitation corresponds to transition between different potential energy (PE) curves (fig. 2). Note, the equilibrium bond distances are not same in all electronic states. Usually, the bond distances in the excited electronic state is slightly larger and hence, in fig. 2 the PE curve in the excited state is displaced slightly to the right. The time needed for an electronic transition is very fast. Therefore, during electronic transition the e slower moving nuclei do not undergo any displacement and hence, the inter-nuclear distances remain fixed during an electronic transition. This is the famous Frank-Condon principle. Thus, the electronic transitions are represented by vertical lines (i.e. with no change in the inter-nuclear distance). Such an electronic transitions is referred to as a Frank-Condon transitions or vertical transitions.

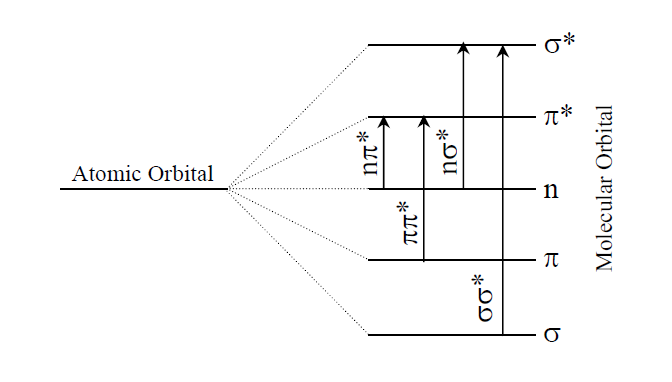


**Fig. 2. Electronic transition between different potential energy curves**.

It may be noted that at room temperature most of the molecules are in the lowest (n=0) vibrational level. Thus for absorption the transitions start from n=0 level. However, on excitation the molecule may be excited to the lowest vibrational level (n'=0) of the upper electronic states as well as higher vibrational levels (n'=1, 2 3, …) as shown. Evidently, the energy gap between successive absorption lines gives vibrational energy in the excited electronic state. It should be emphasized that the vibrational energy gap in the excited state is usually lower than that in the ground electronic state. Such a transition which involves change of both electronic and vibrational energy is called a vibronic transition. A vibronic transition is often very broad because of the large number of transitions involving vibrational and rotational states. Thus electronic transition in most cases appear as a band.

**Nature of Molecular Orbitals**

In a molecule there are different kinds of molecular orbitals (MO-s)- σ, π and n (non-bonding) ones. Out of these the non-bonding MO-s have energies roughly equal to the energy of the atomic orbitals (AO-s). The bonding MO-s are lower in energy compared to the atomic orbitals while energy of an anti-bonding orbital is higher than that of the corresponding atomic orbitals. The σ MO-s and π MO-s arise respectively, from axial and lateral overlap of the atomic orbitals. The σ bonding MO-s are the lowest in energy while the σ anti-bonding MO-s (σ\*) posses the highest energy. The π bonding MO-s possess higher in energy compared to the σ bonding MO-s while the π anti-bonding MO-s (π\*) possesses lower energy than a σ anti-bonding MO. The relative energies of the σ, π and n bonding MO-s and also the corresponding anti-bonding MO-s are shown in fig. 3. From fig. 3 it is easy to see that the relative energies of different transitions are of the order, nπ\* < ππ\*~nσ\*<σσ\*.



**Fig. 3. Different kinds of molecular orbitals.**