2.5: Electronic State and Transitions

The symmetry requirement for observing the electronic transition is embodies in the electronic integral.

$$\int \psi_{el}^{i} H^{(1)} \psi_{el}^{f} d\Gamma$$

which **must not equal zero** to observe the transition. This can be determined by group theory by looking at the transformation properties of $H^{(1)}$ and the wavefunctions under the symmetry properties of the point group of the molecule.
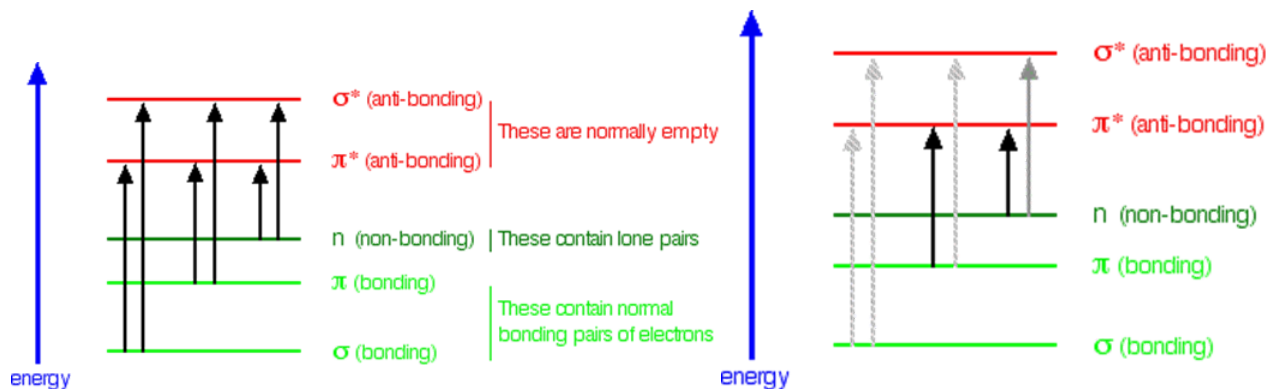
This treatment is for a diatomic but can be generalized to a polyatomic that has more than 1 degree of vibrational freedom: $3N-6$ for non-linear and $3N-5$ for linear molecules where N is the number of atoms. $V(r)$ is replace by a multi-dimensional surface $V(q_1, q_2, q_3, q_4 \ldots q_{3N-6})$ where the q's are displacements from equilibrium (often expressed as normal modes) and represent the nuclear degrees of freedom for the molecule. The normal modes are coordinates that represent combinations of bonds stretches, compressions and bends; these will be discussed later in more detail.

Electronic Transition Types

The most likely electronic transition involves the absorption of a photon by a **single electron** (as taught in general chemistry classes). Thus, if we have a one-electron MO description of the molecular electronic configuration, we can describe an electronic transition by giving the MO of the original and the MO of the state that final electron winds up in after the transition.
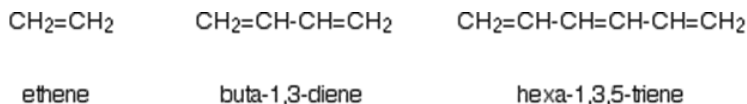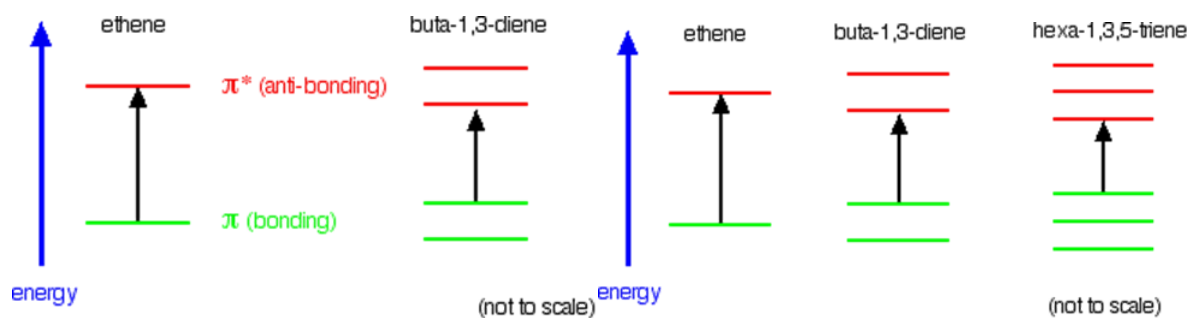
Orbital types: (Kasha)

- n: lone pair orbitals
- σ: bonding pair orbitals of σ local symmetry
- σ*: anti-bonding σ orbitals
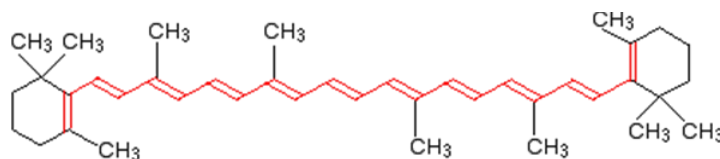- π: pi bonding MO
- π*: pi anti-bonding MO

Look again at the possible jumps. This time, the important jumps are shown in black, and a less important one in grey. The grey dotted arrows show jumps which absorb light outside the region of the spectrum we are working in.

Delocalization

$CH_2=CH_2$ $CH_2=CH-CH=CH_2$ $CH_2=CH-CH=CH-CH=CH_2$

ethene   buta-1,3-diene   hexa-1,3,5-triene

ethene — π* (anti-bonding) — π (bonding) — energy — buta-1,3-diene (not to scale) — ethene — buta-1,3-diene — hexa-1,3,5-triene — energy (not to scale)

Beta-carotene has the sort of delocalization that we've just been looking at, but on a much greater scale with 11 carbon-carbon double bonds conjugated together. The diagram shows the structure of beta-carotene with the alternating double and single bonds shown in red.

The more delocalization there is, the smaller the gap between the highest energy pi bonding orbital and the lowest energy pi anti-bonding orbital. To promote an electron therefore takes less energy in beta-carotene than in the cases we've looked at so far - because the gap between the levels is less.

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