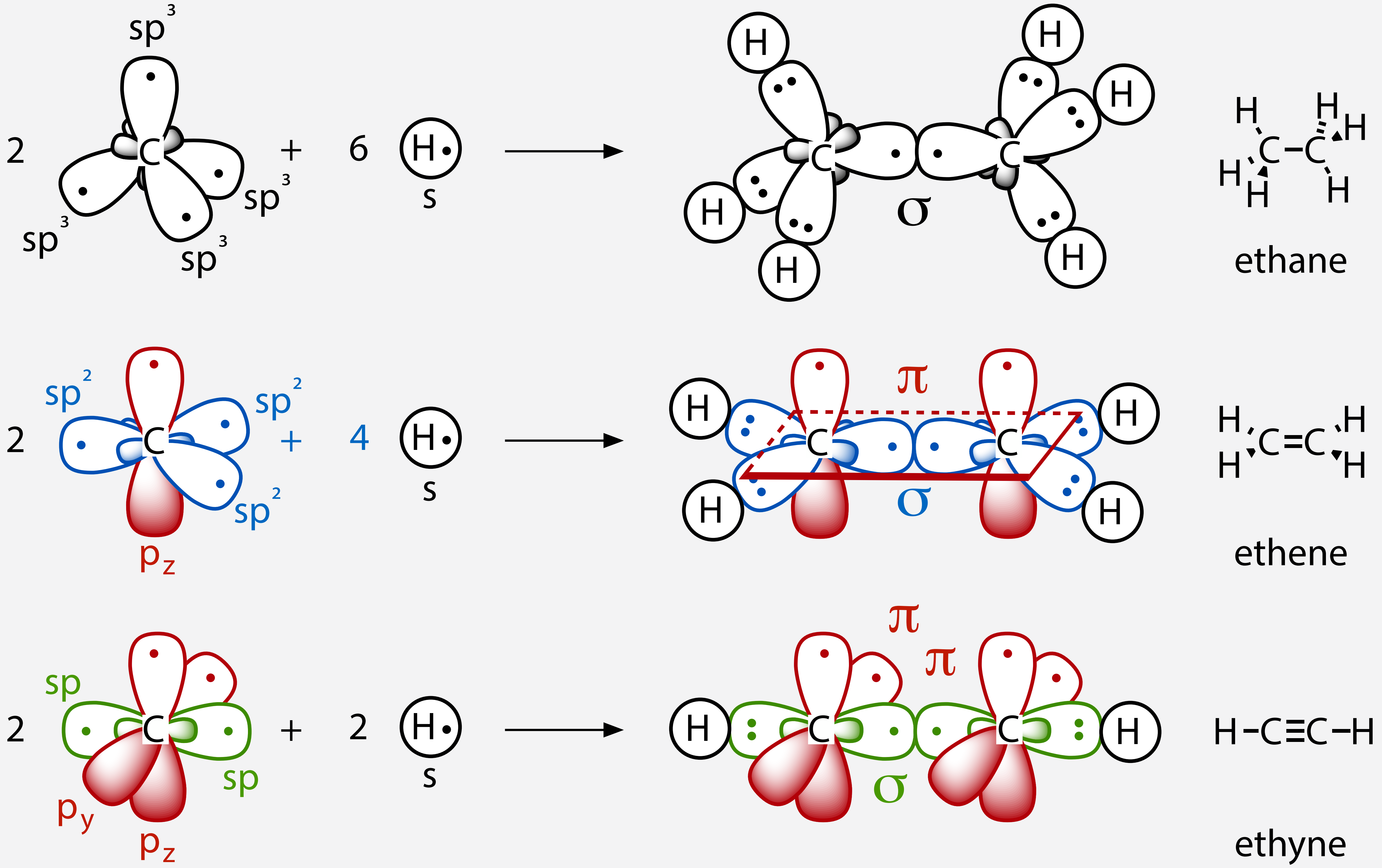
2.4 Formation of Multiple Bonds

Reading Recommendations

- Clayden, Greeves, Warren, *Organic Chemistry*, Oxford University Press, 2^{nd} ed., **2012**, *pp* 99–106.
- Jamart, Bodiguel, Brosse, *Les cours de Paul Arnaud - Cours de chimie organique*, Dunod, 19^{th} ed., **2015**, *pp* 79–86.

Formation of Carbon-Carbon Multiple Bonds

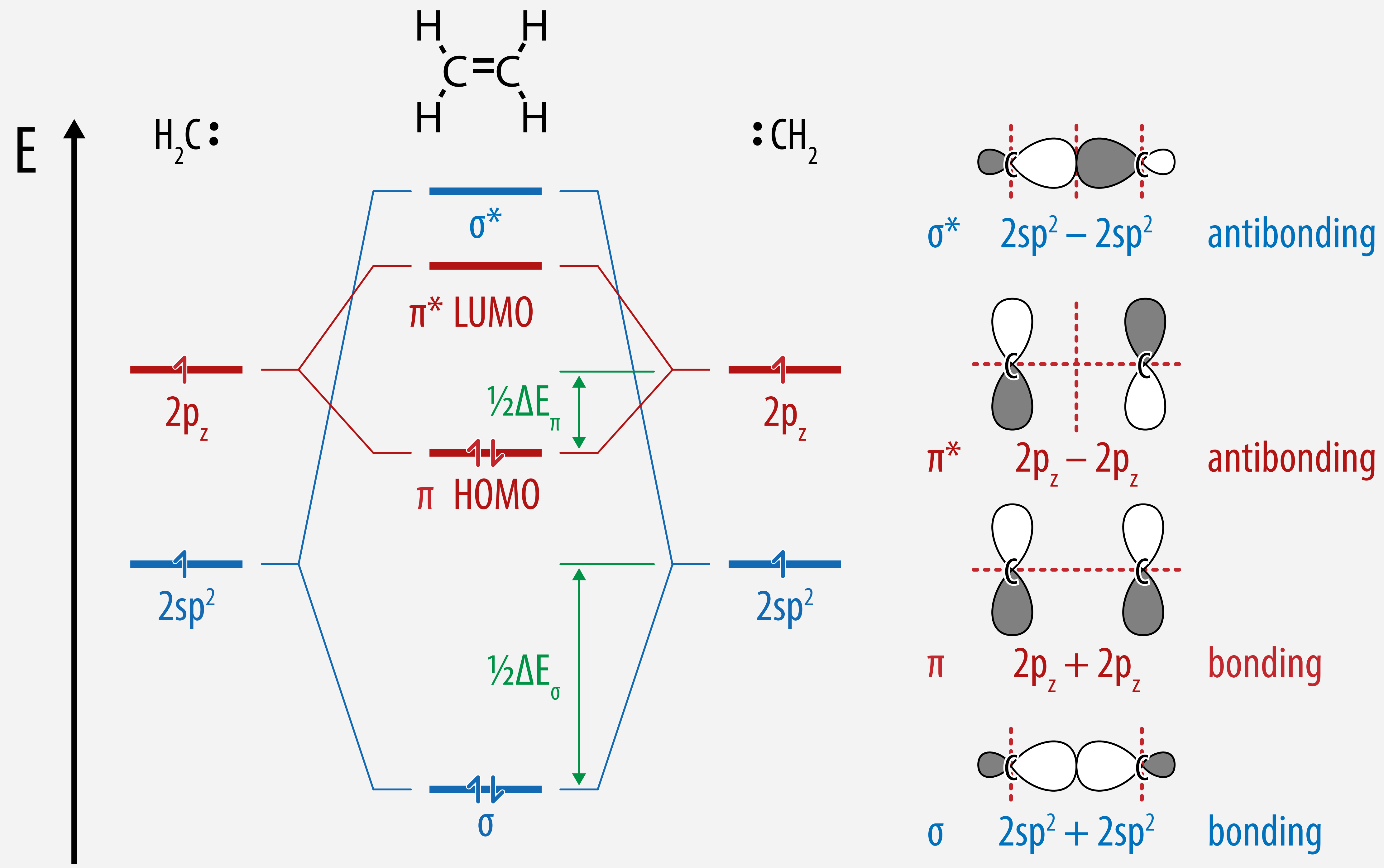


	length	energy
ethane	1.54 Å	347 kJ/mol
		Δ*E* = 267 kJ/mol
ethene	1.34 Å	614 kJ/mol
		Δ*E* = 225 kJ/mol
ethyne	1.21 Å	839 kJ/mol

- **double or triple bonds are one σ bond plus one or two π-bonds, respectively**
- **π bonds between residual p orbitals, node plane along bond, no rotational symmetry**
- **rotation around π-bonds requires breaking them, energetically too costly at r. t.**

Molecular Orbital View of the Carbon-Carbon Double Bond

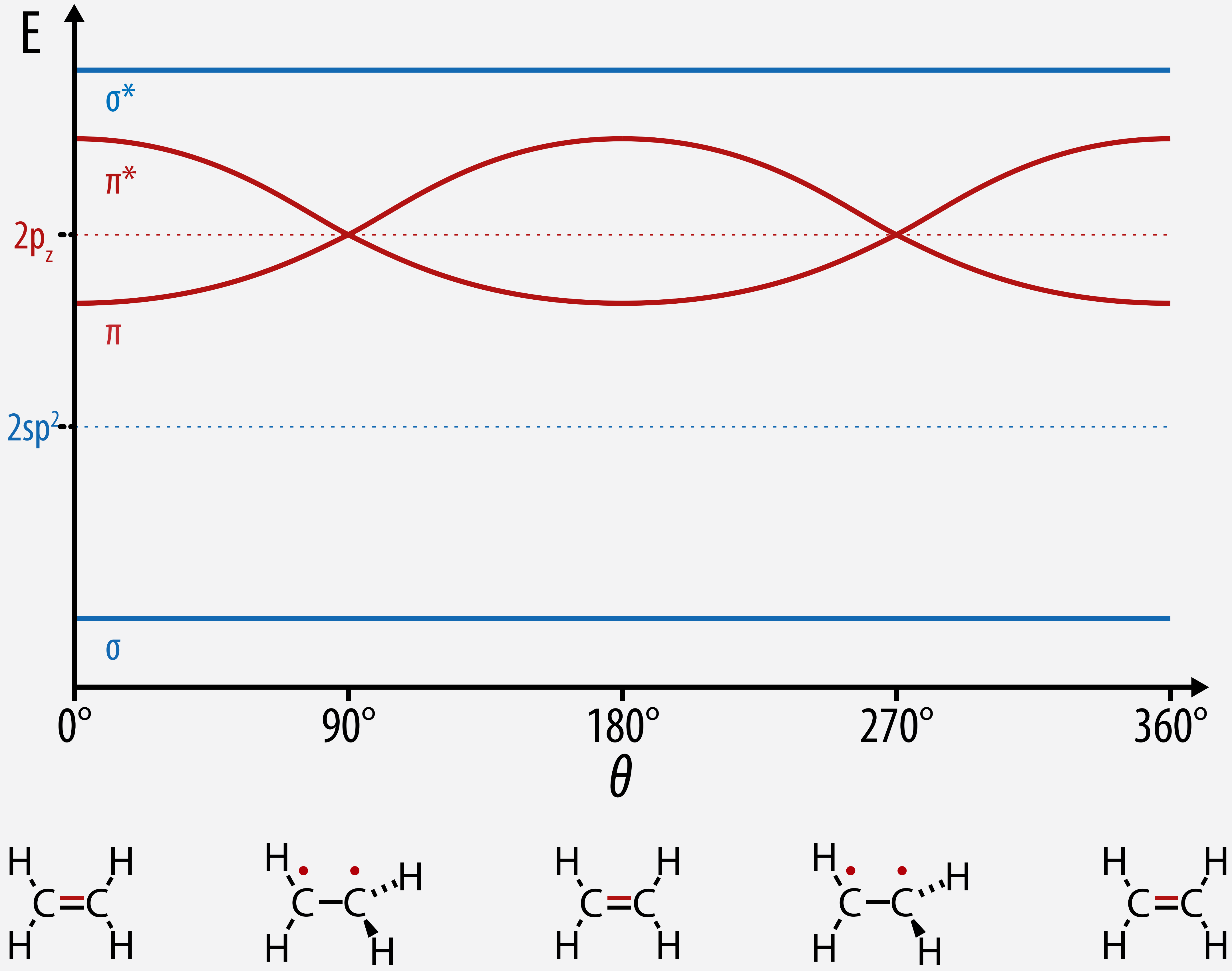
- simplified and schematic molecular orbital energy diagram of the ethene molecule

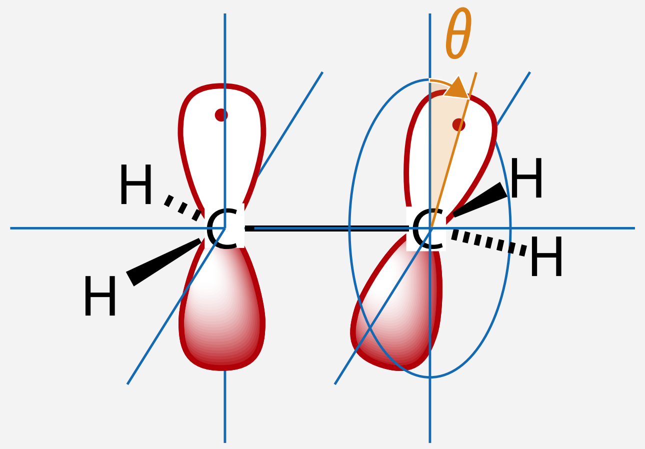


- **only orbitals of matching symmetry & orientation interact, sp^2 with sp^2, and p_z with p_z**
- **distinct σ bond (from two sp^2) and π bond (from two p_z) with different energy, symmetry**
- **chemistry ruled by highest occupied, lowest unoccupied molecular orbitals (HOMO, LUMO)**

Rotation Around a Double Bond

- σ bond has rotational symmetry relative to carbon.carbon bond axis, but π bond does not

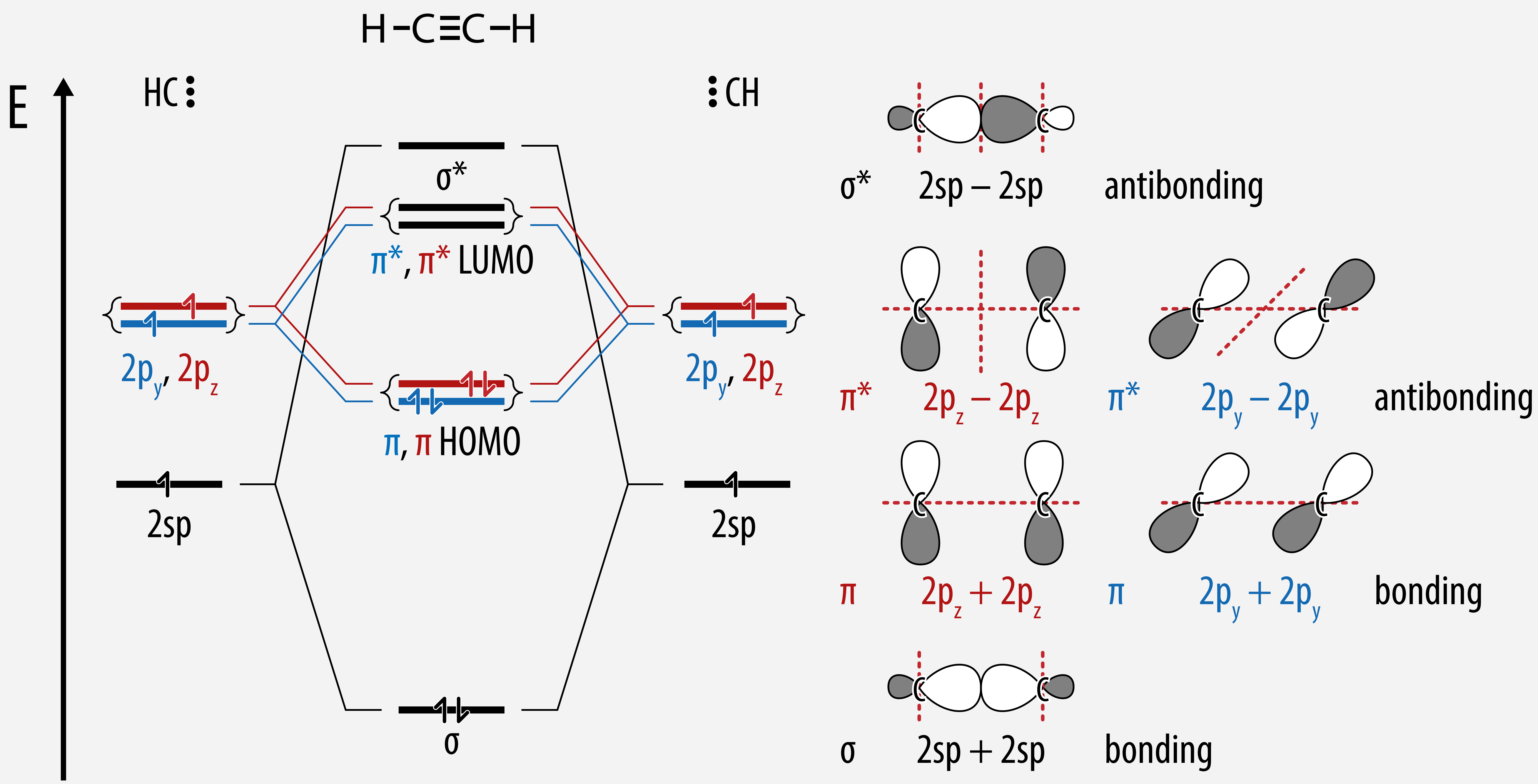




- **rotating π orbitals by 90° requires π bond breaking (≈260 kJ/mol), disfavorable at room temperature**

Formation of Carbon-Carbon Triple Bonds

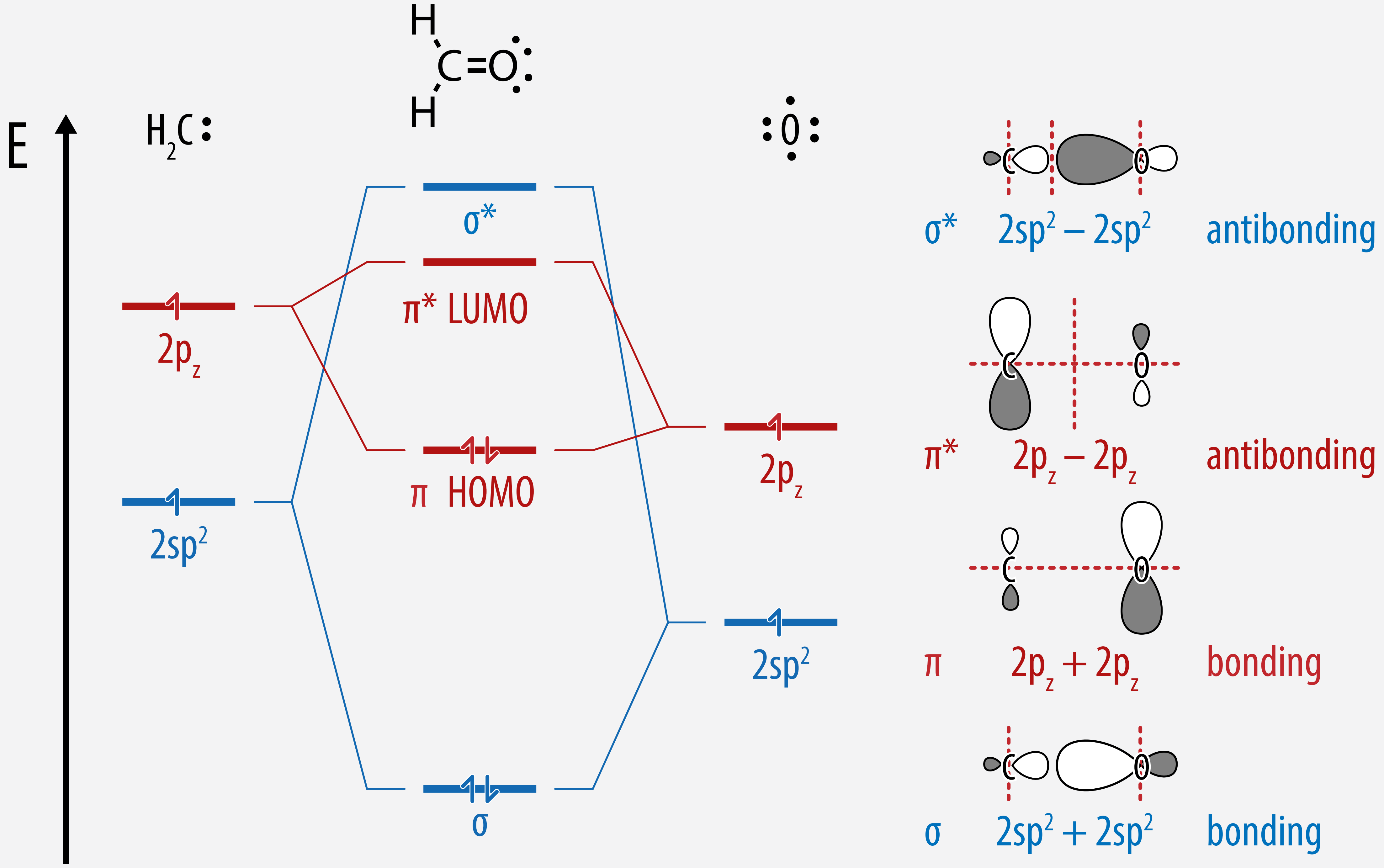
- simplified and schematic molecular orbital energy diagram of the ethyne molecule



- **only orbitals of matching symmetry & orientation interact (sp with sp, p_z with p_z, p_y with p_y)**
- **distinct σ-bond (from two sp^2) and two *independent* π-bonds (each from two p_z and two p_y)**
- **the two π-bonds are identical in energy, symmetry, just different in orientation**

Molecular Orbital View of the Carbon-Oxygen Double Bond in the Carbonyl Group

- simplified and schematic molecular orbital energy diagram of the carbon-oxygen double bond



- **σ bond from sp^2(C) with sp^2(O), π-bond from p_z(C) with p_z(O) with different bond energies**
- **oxygen orbitals lower in energy due to electronegativity difference of carbon and oxygen**
- **bonding σ orbital and, in particular, bonding π orbital "look like" oxygen orbitals**

Learning Outcomes

- **multiple bonds can be described as distinct σ bond plus one or two π bonds**
  - σ bond has rotational symmetry with respect to carbon-carbon bond axis
  - π bond does not have rotational symmetry; rotation requires breaking it
- **chemistry & physics dominated by frontier orbitals: π HOMO and π* LUMO**