M.Sc. Semester-IV
Core Course-9 (CC-9)
Synthetic Organic Chemistry

II. Pericyclic Reactions

1. Molecular Orbital Symmetry

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II Pericyclic Reactions 20 Hrs

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1, 3, 5-hexatriene, allyl system, Classification of pericyclic reactions. FMO approach, Woodward-Hoffman correlation diagram method and PMO approach for pericyclic reaction under thermal and photochemical conditions.

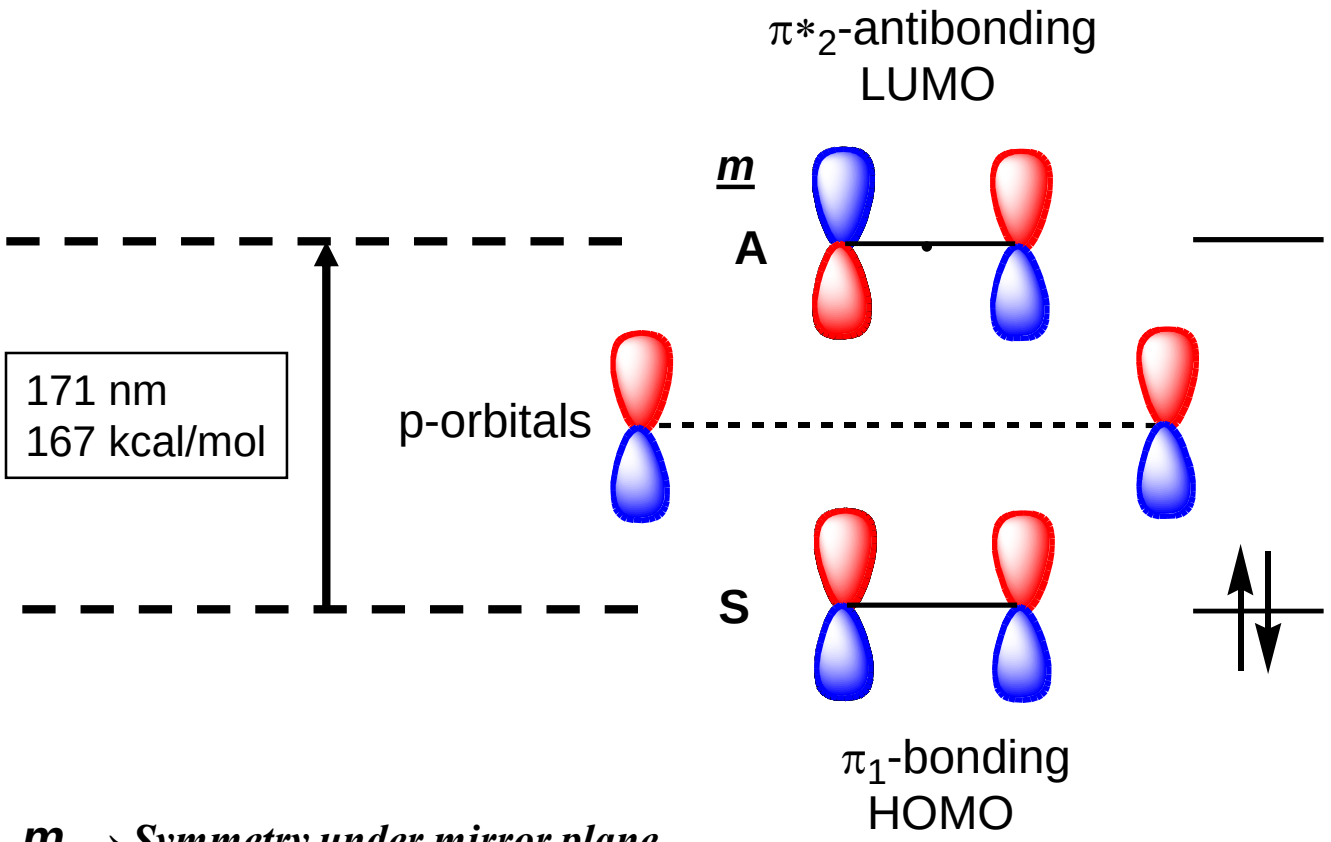
Electrocyclic reactions: Conrotatary and disrotatary motion, 4n and (4n+2) systems, Cycloaddition reaction: [2+2] and [4+2] cycloaddition reaction, Cycloaddition of ketones, Secondary effects in [4+2] cycloaddition. Stereochemical effects on rate of cycloaddition reaction, Diels-Alder reaction, 1,3-dipolar cycloaddition, Chelotropic reaction, The Nazarov reaction.

Sigmotropic rearrangement: Suprafacial and antarafacial shift involving H and carbon-moieties, Peripatetic cyclopropane bridge, Retention and inversion of configuration, [3,3]-, [1,5]-, [2,3]-, [4,5]-, [5,5]-, and [9,9]-Sigmatropic rearrangements, Claisen rearrangements (including Aza-Claisen, Ireland-Claisen), Cope rearrangements (including Oxy-Cope, Aza-Cope), Sommelet-Hauser rearrangements, Group transfer reaction, Ene reaction, Mislow - Evans rearrangement, Walk rearrangement.

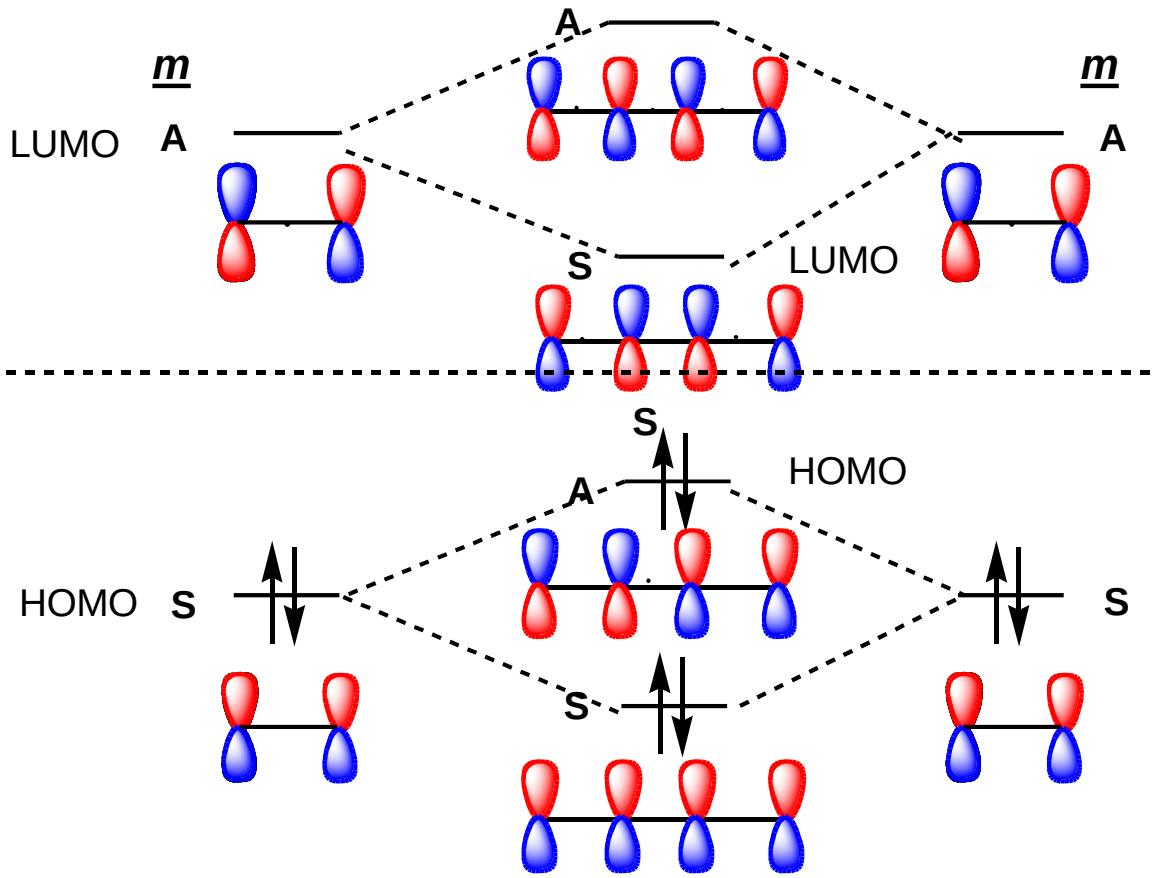
Coverage:

1. Molecular Orbital Symmetry
2. Frontier Orbitals of Ethylene, 1,3-Butadiene, 1, 3, 5-Hexatriene and Allyl System

π-Molecular Orbitals of Ethylene

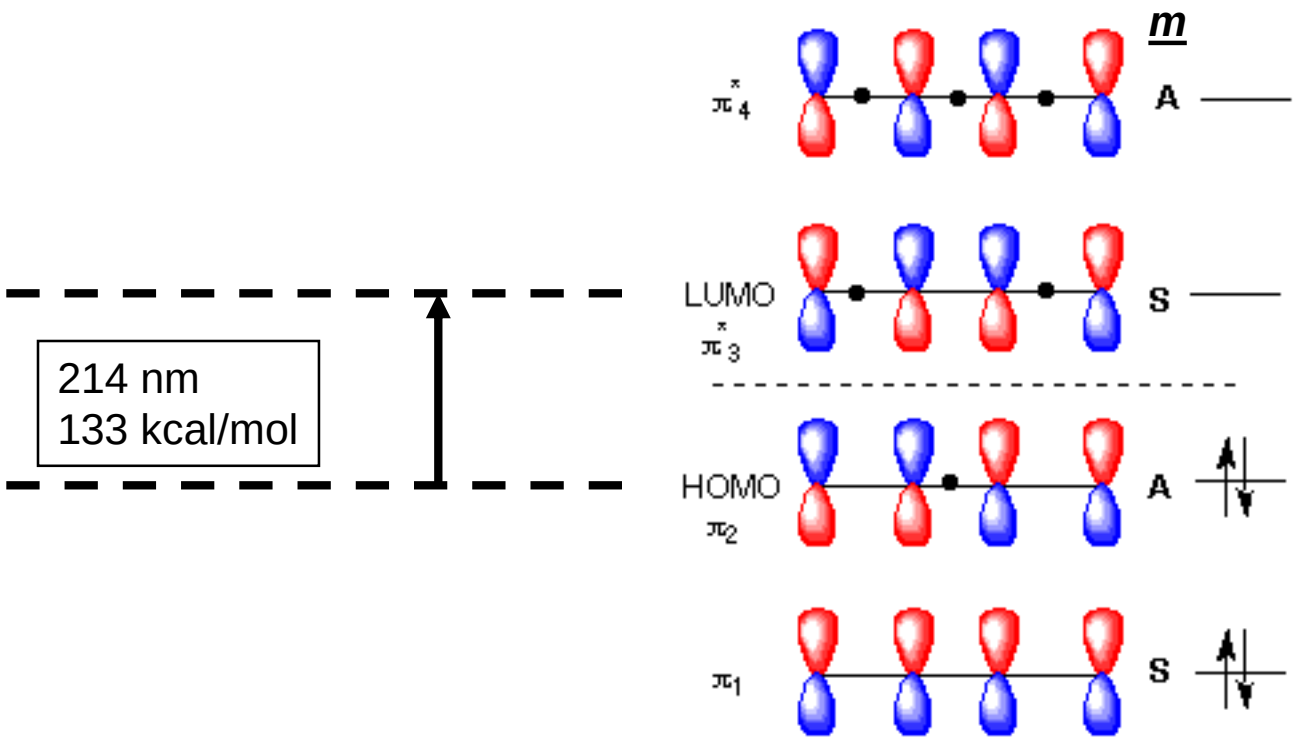


π-Molecular Orbitals of1,3-Butadiene from Ethylene



m → *Symmetry under mirror plane*

π-Molecular Orbitals of1,3-Butadiene



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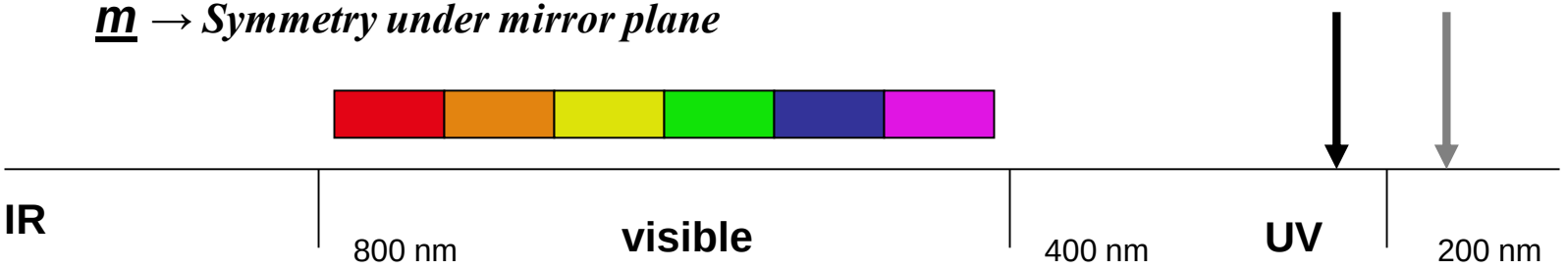
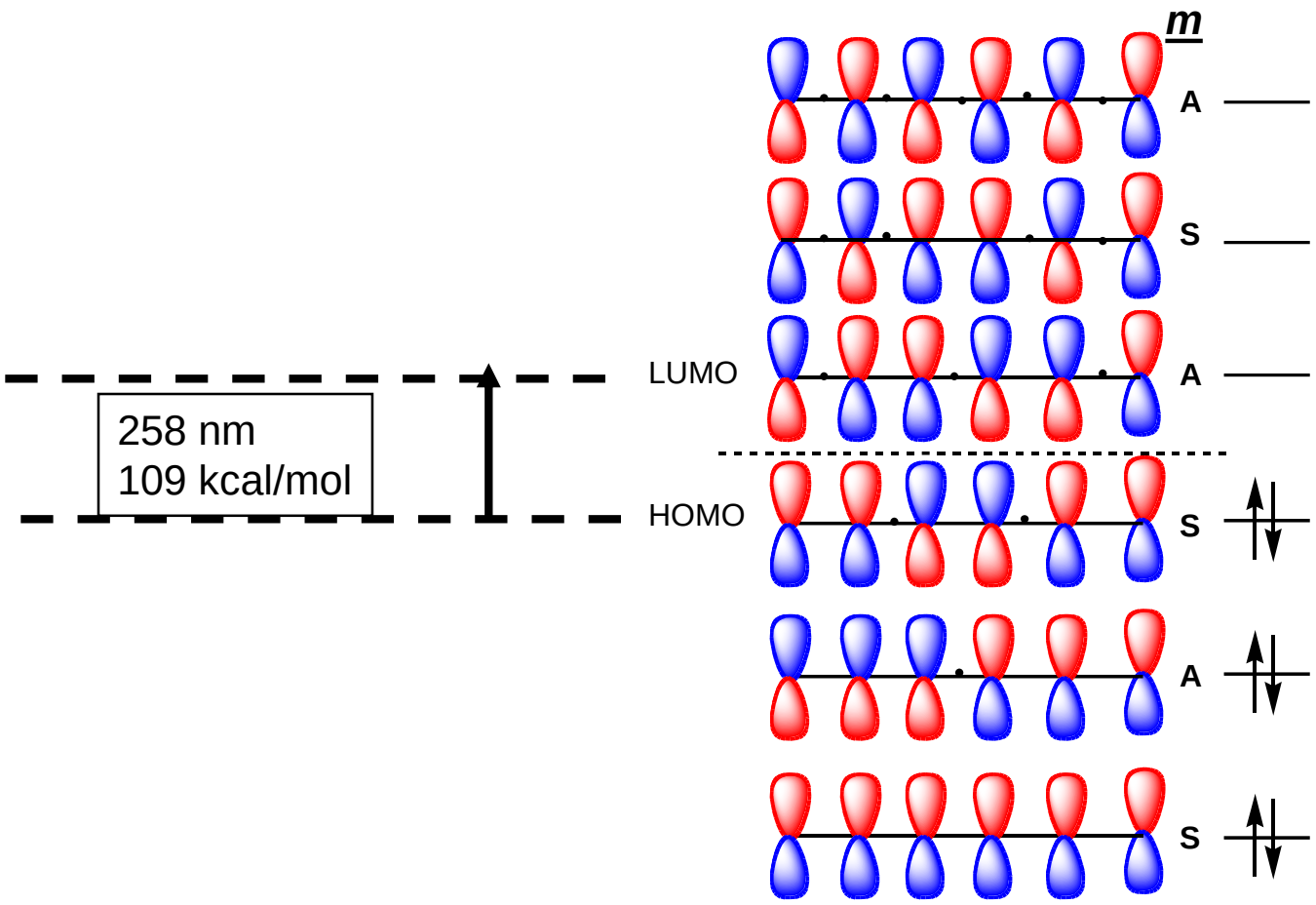


π-Molecular Orbitals of1,3,5-Hexatriene



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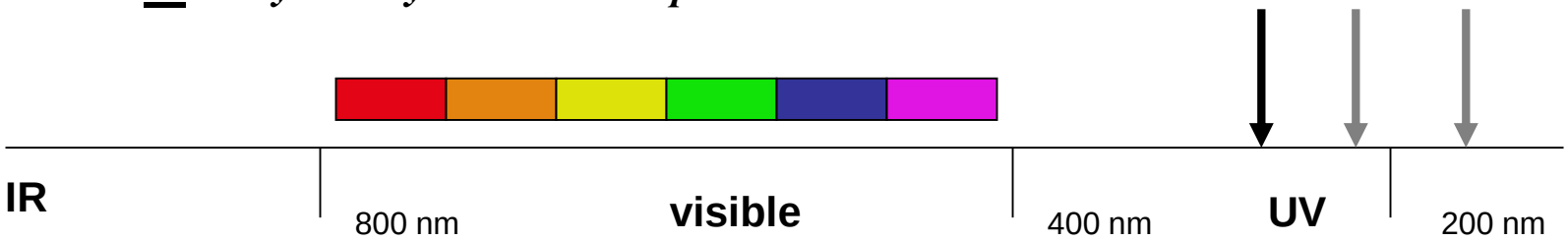
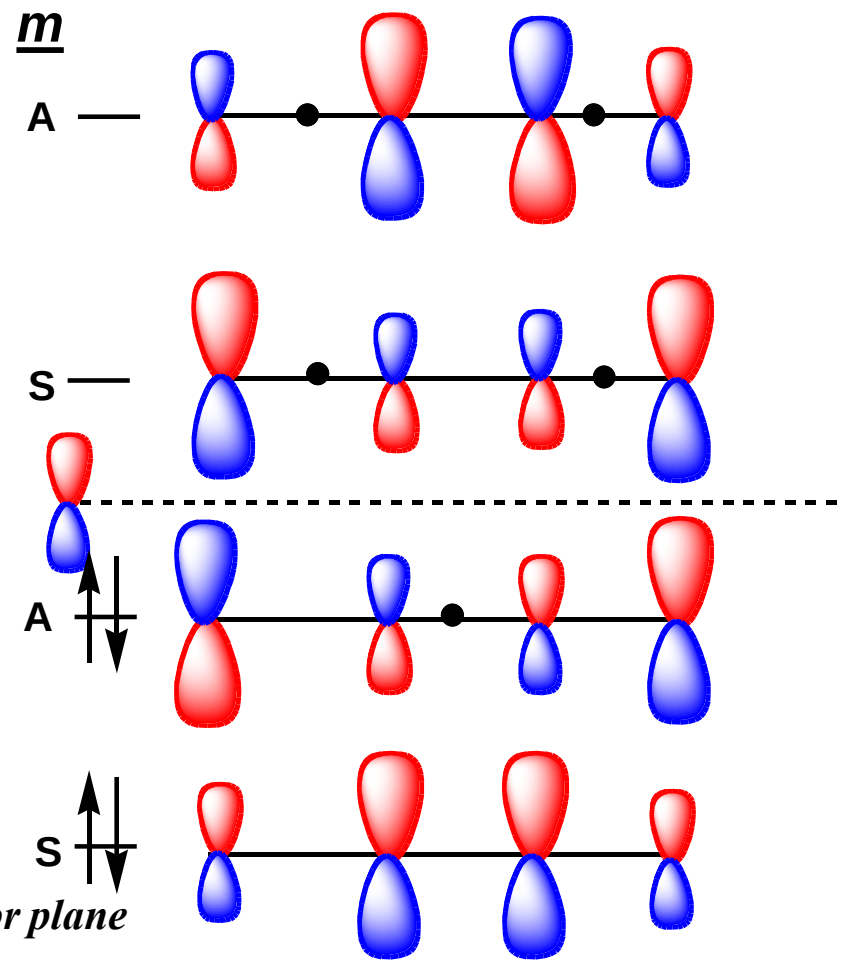


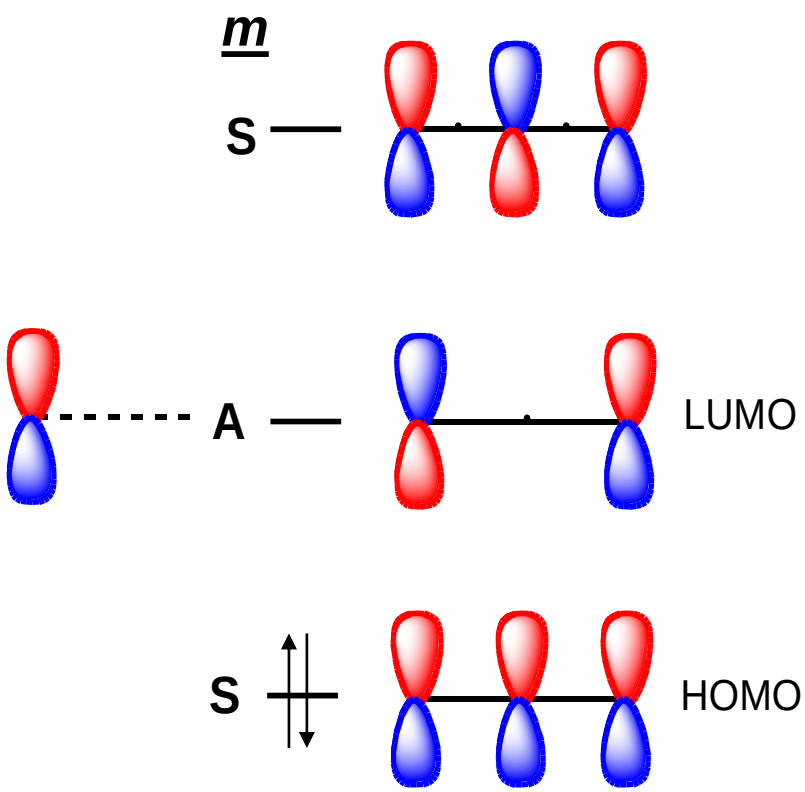
Butadiene: Orbital Coefficients

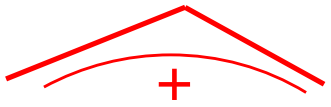


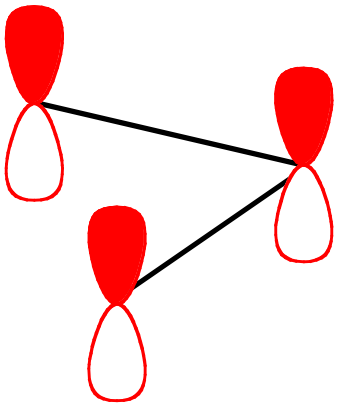
Frontier Molecular Orbitals FMOs

m → *Symmetry under mirror plane*

The Allylic System: Allyl Cation







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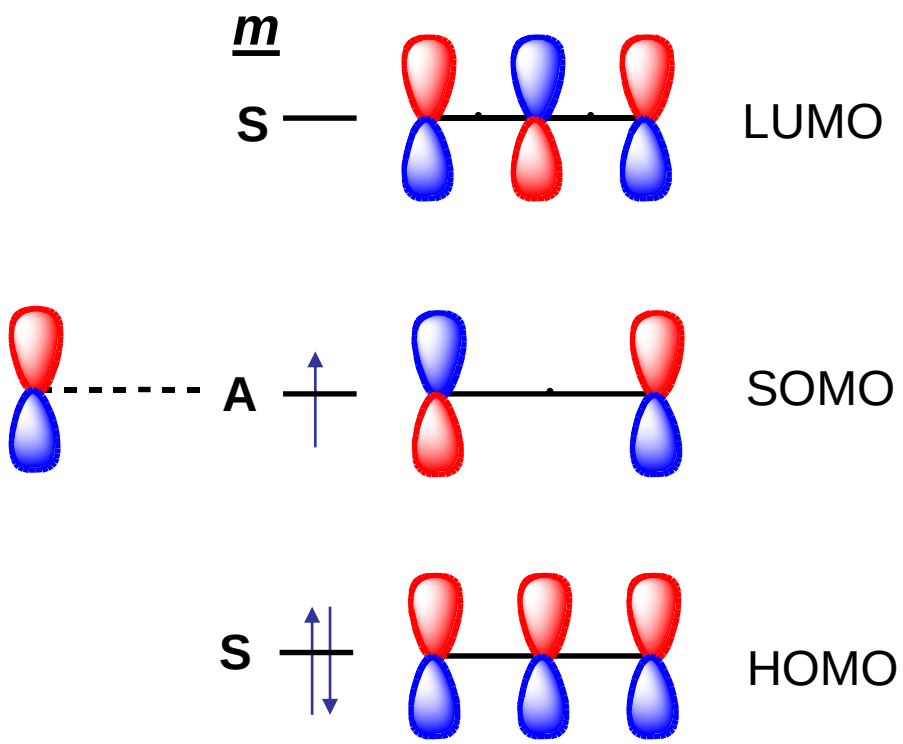
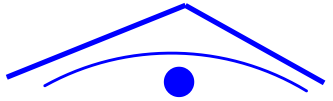
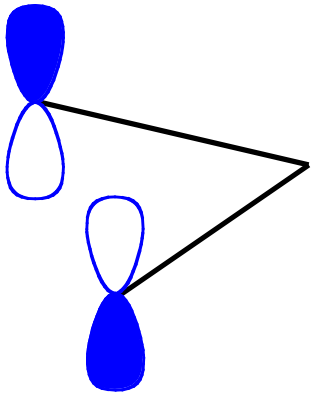
The Allylic System: Allyl Radical







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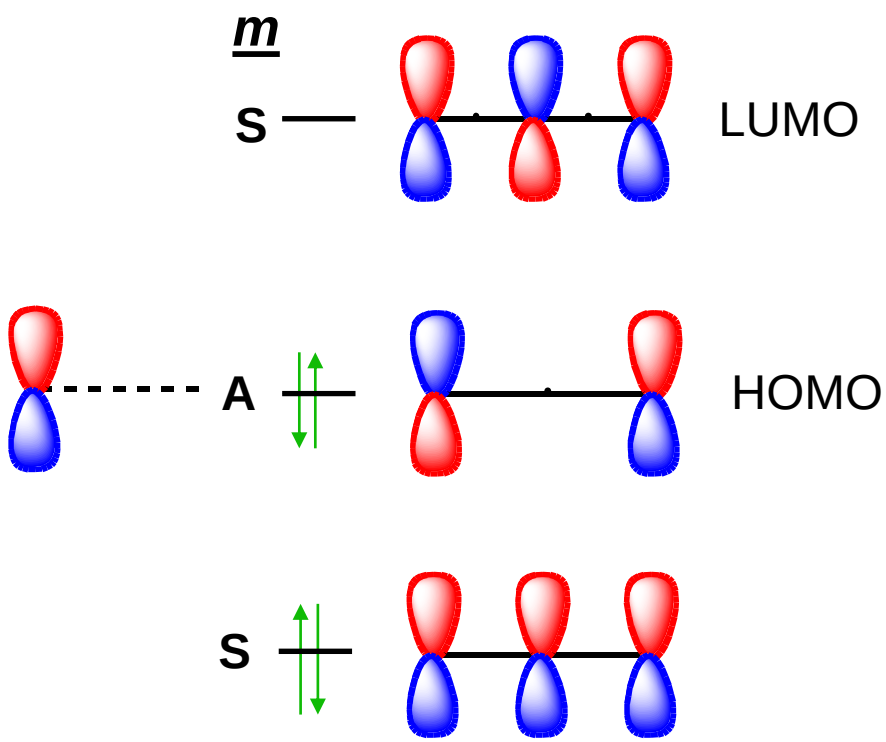
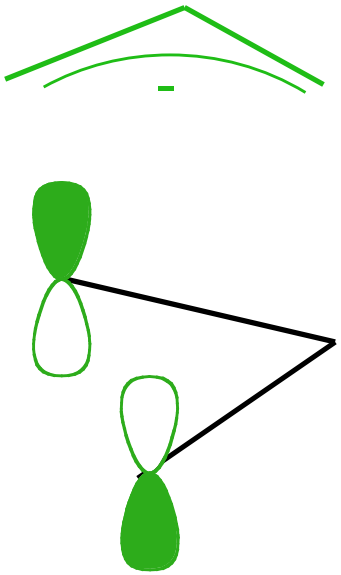
The Allylic System: Allyl Anion





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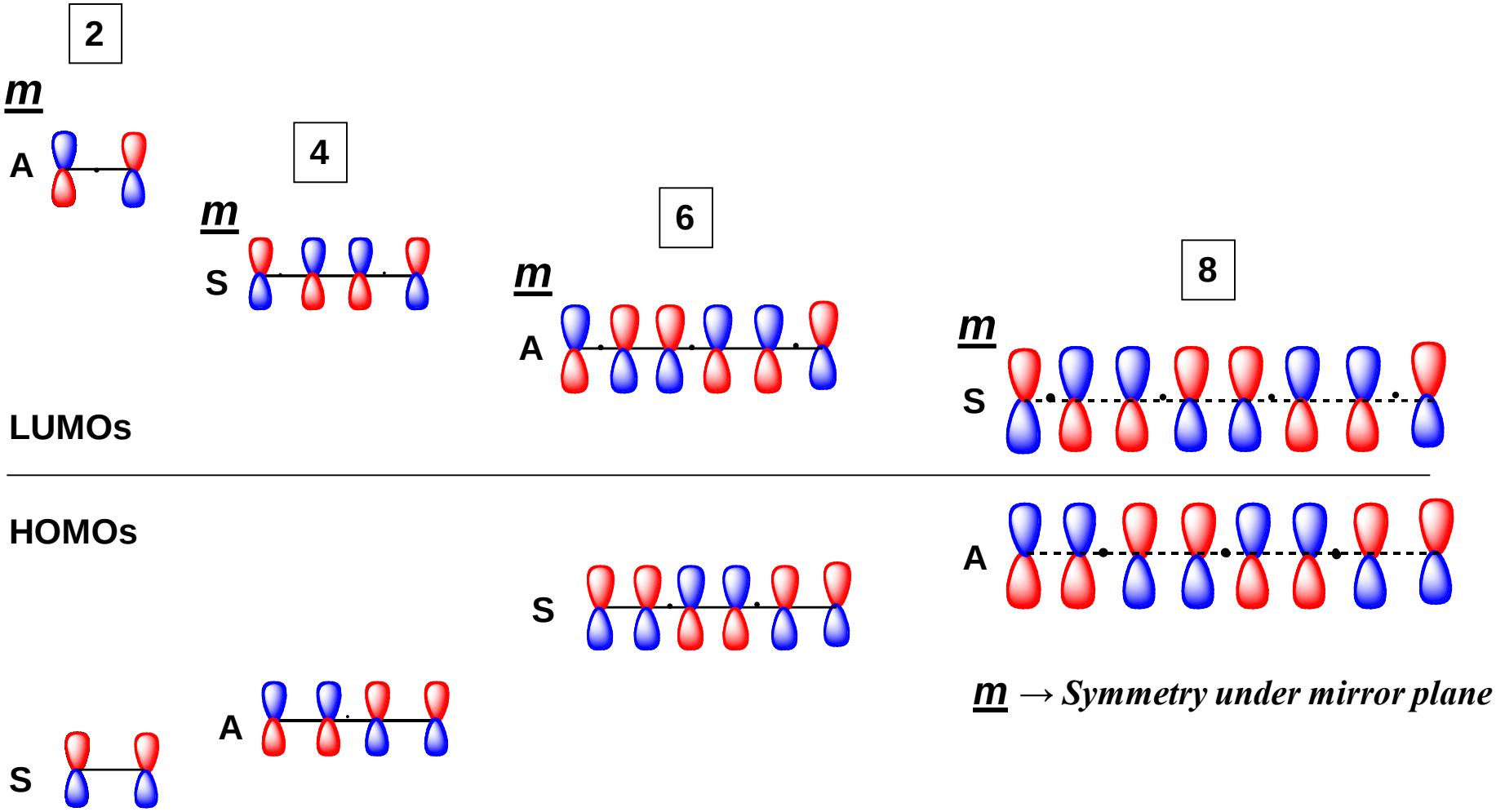
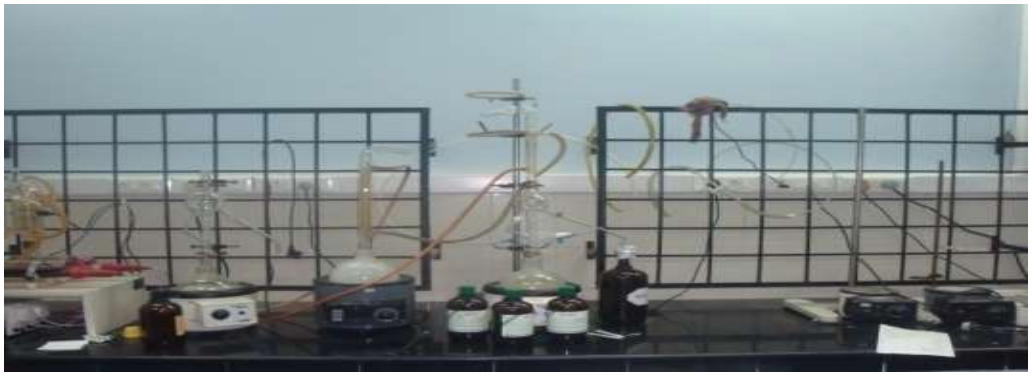
Energy Gap Between HOMO and LUMO



Thank You



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