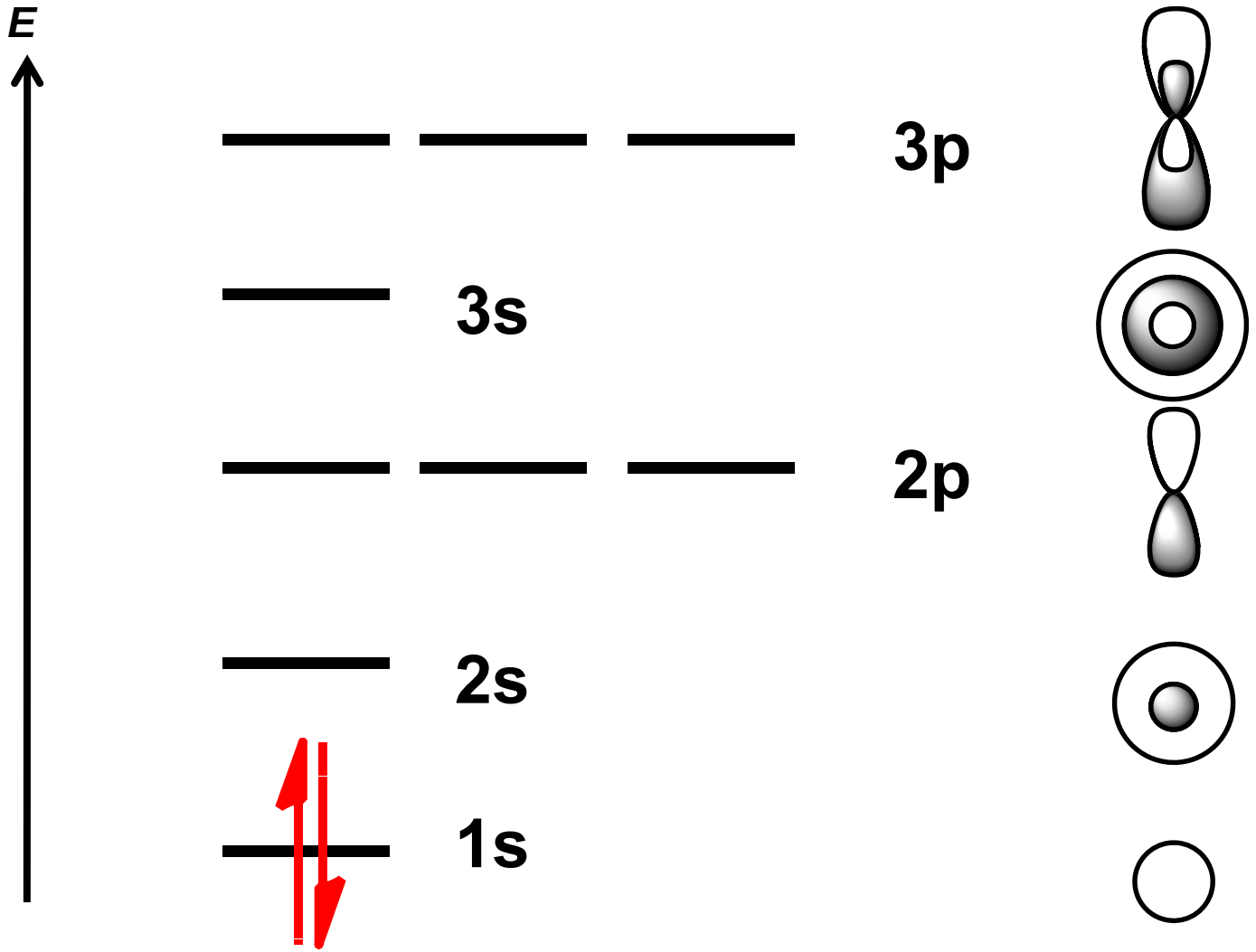
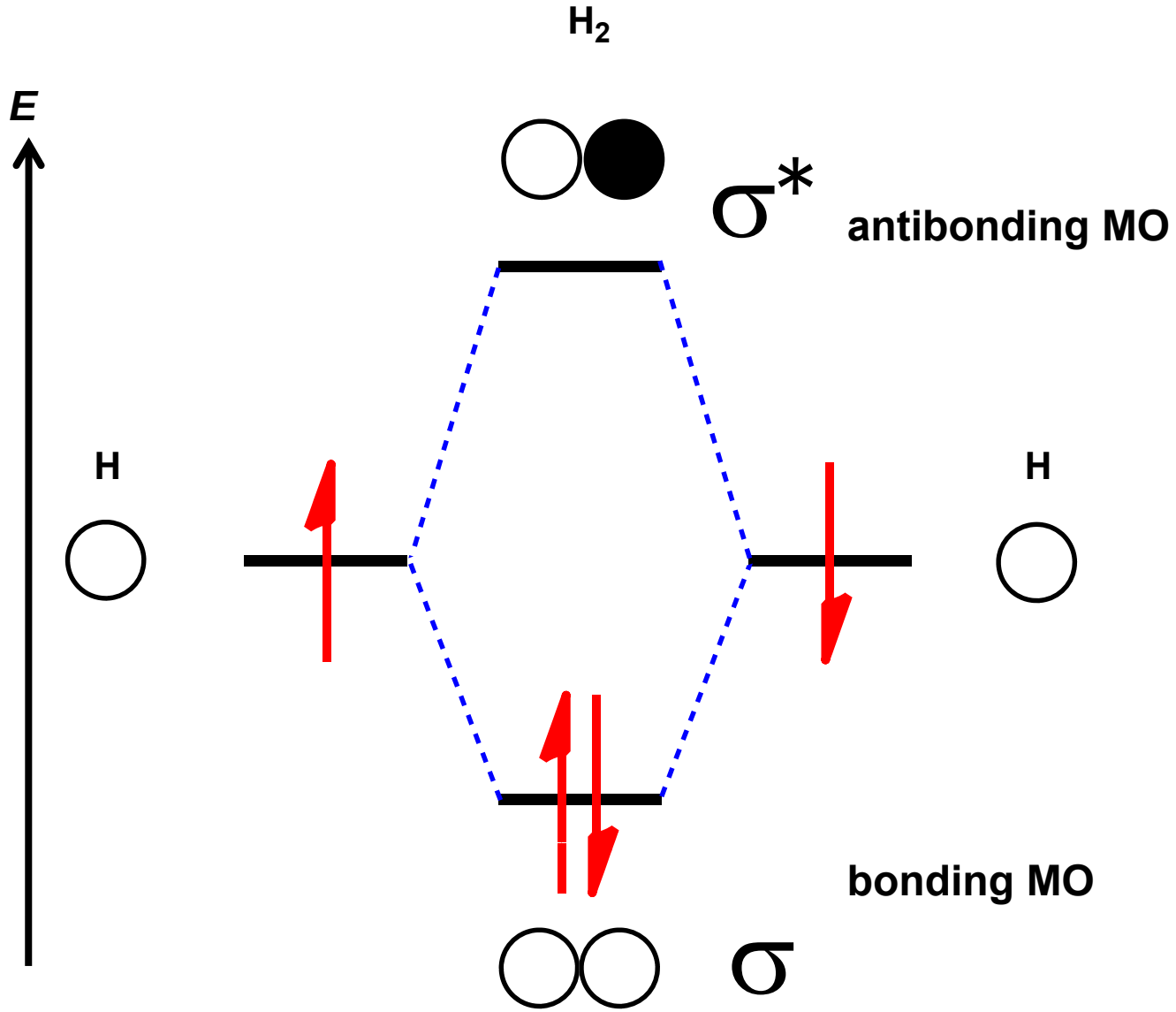
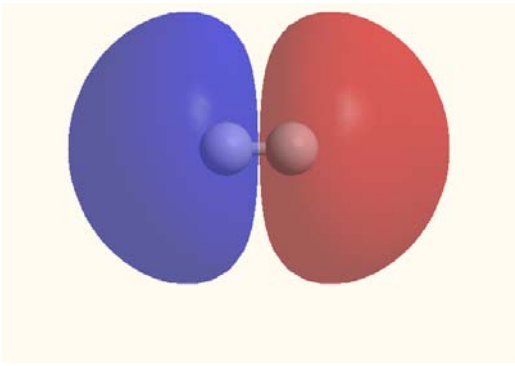
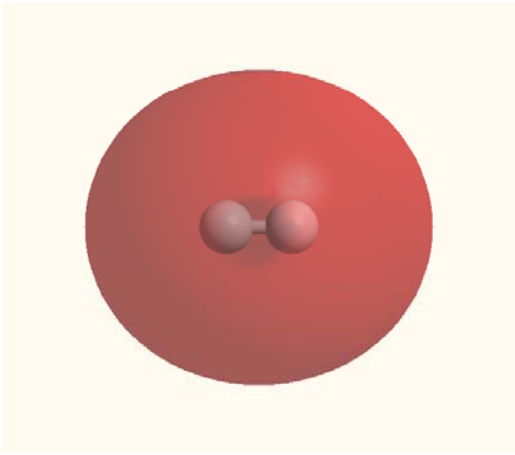
Atomic Orbital (AO)



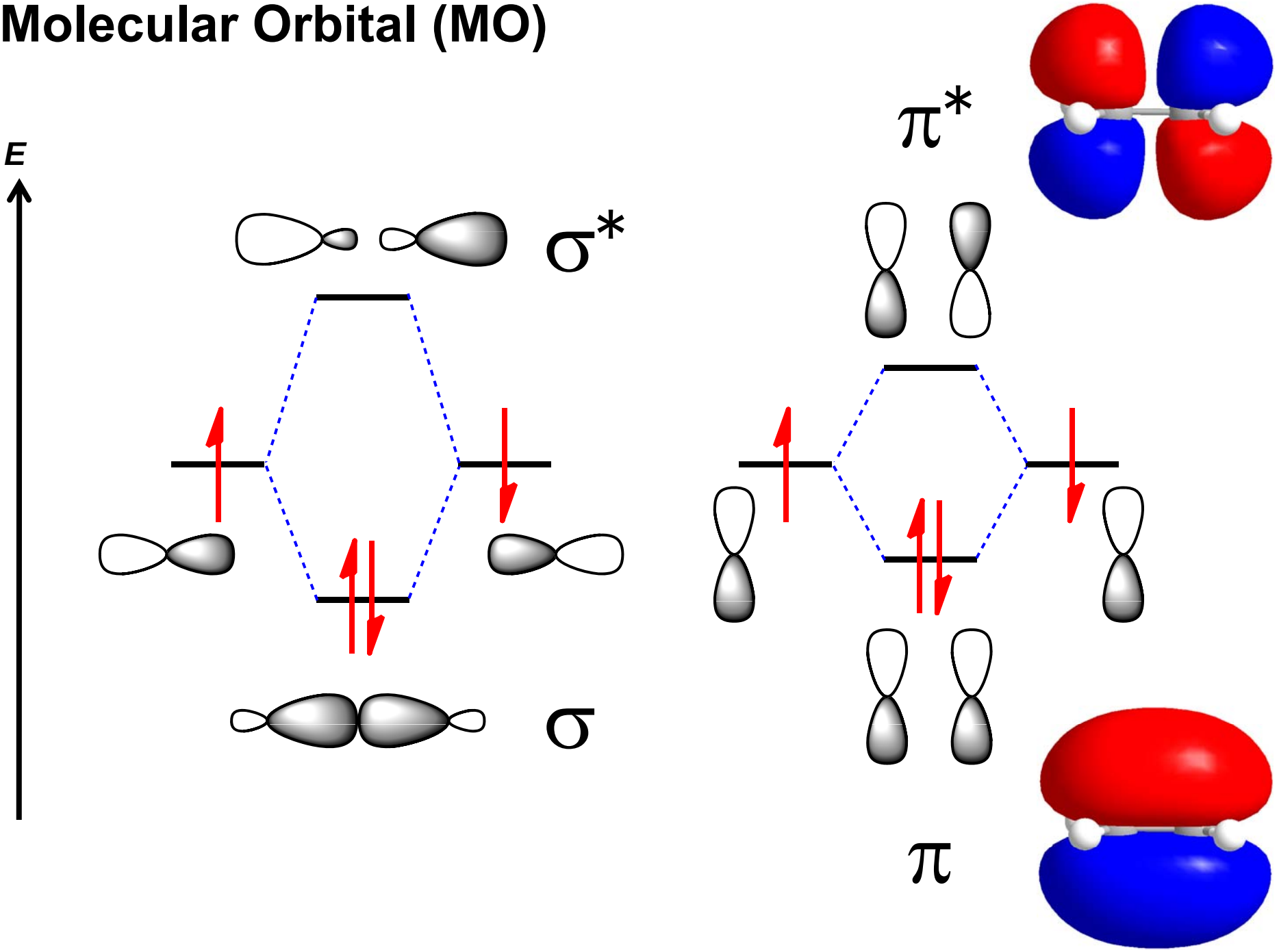
Molecular Orbital (MO)



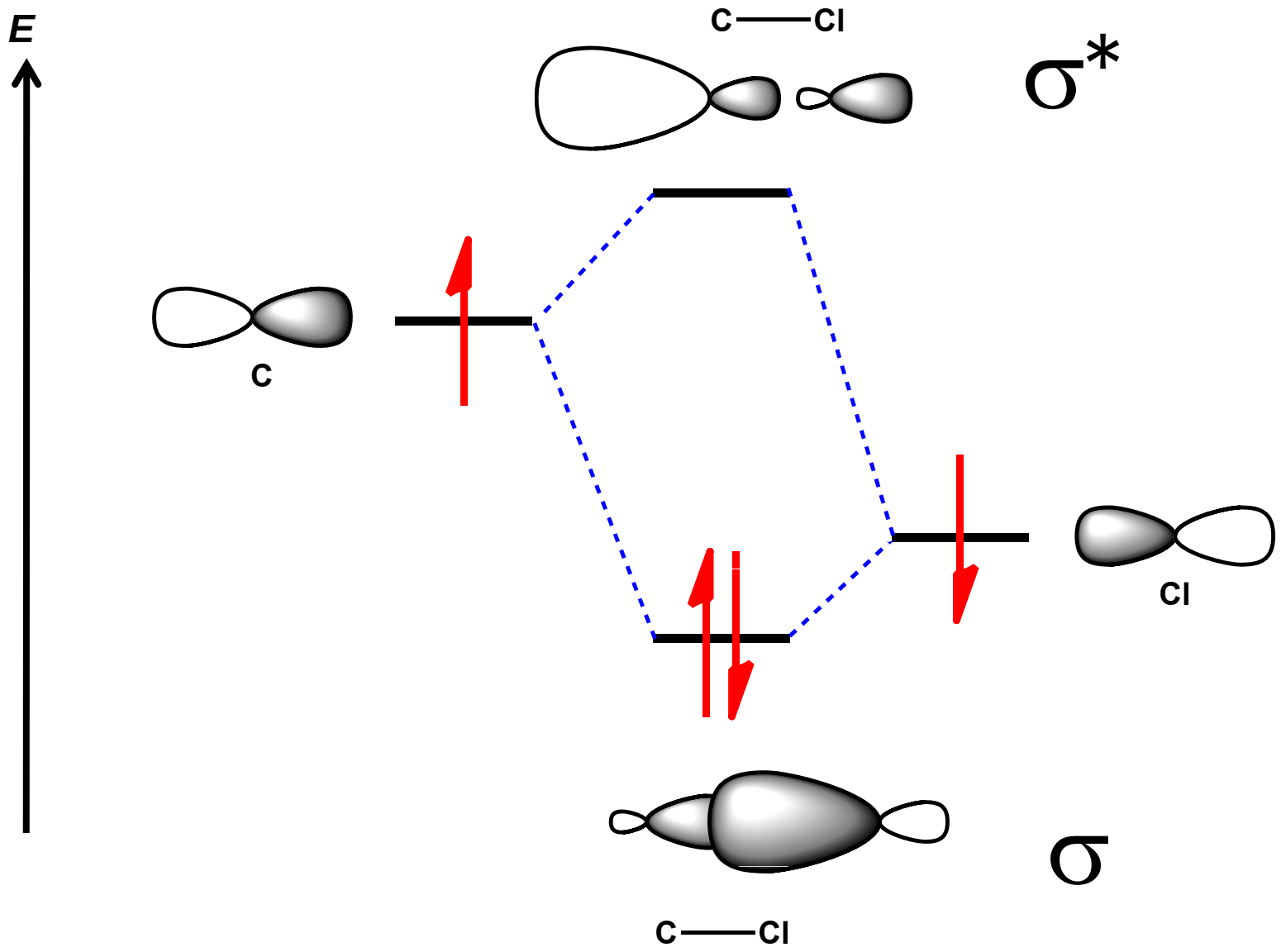


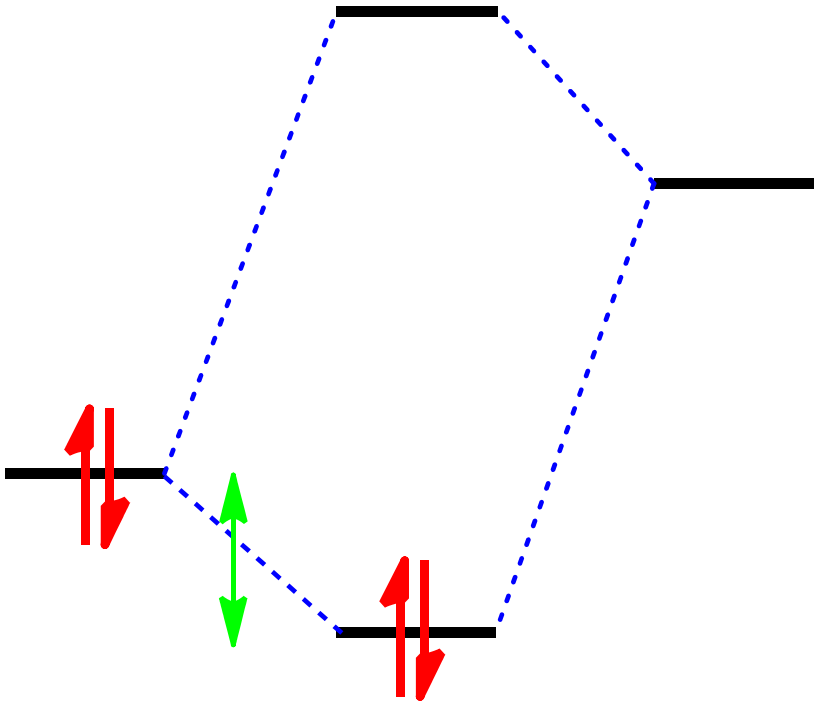


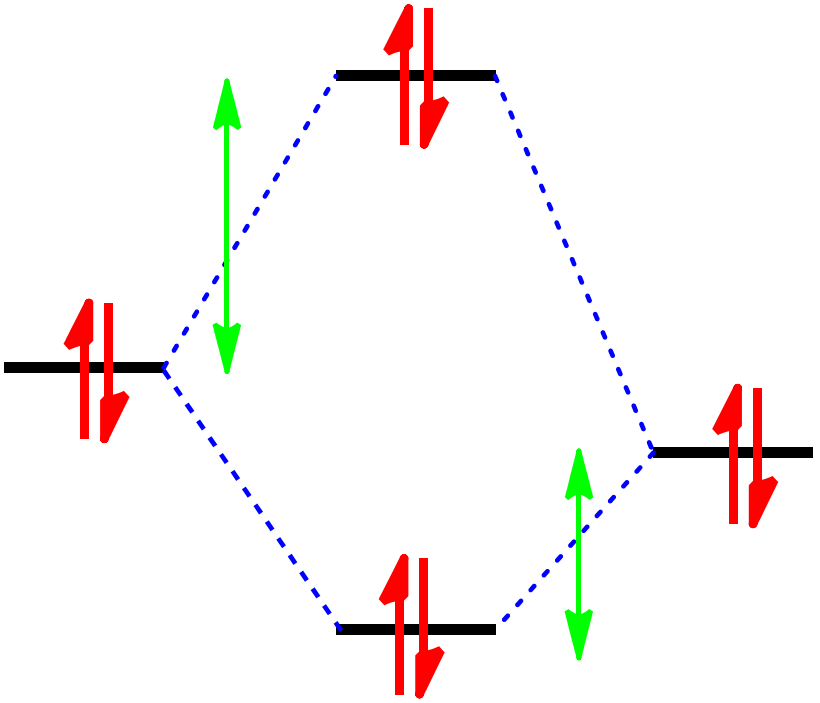
Molecular Orbital (MO)



Molecular Orbital (MO)

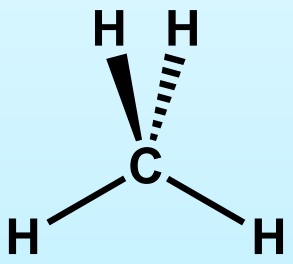


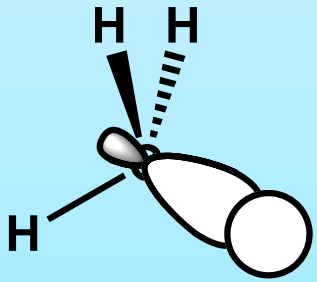


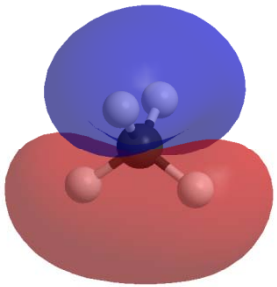


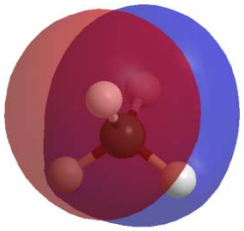
Hybridization

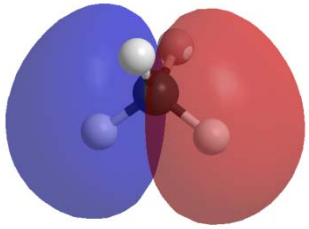
sp^3

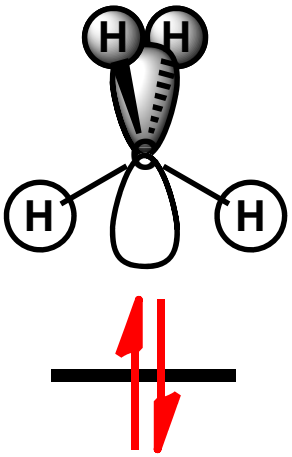


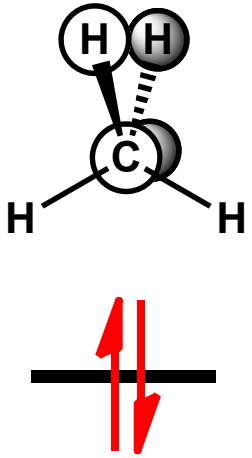


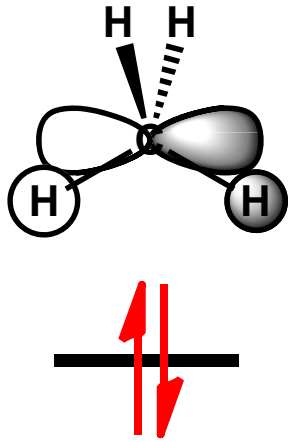


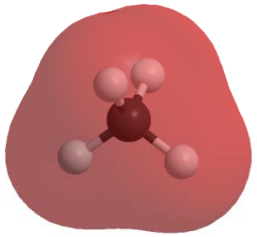


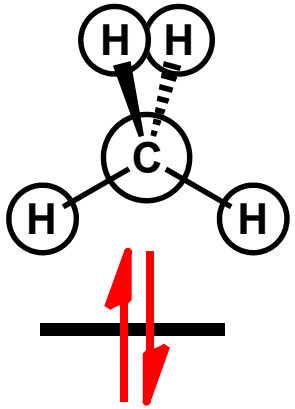




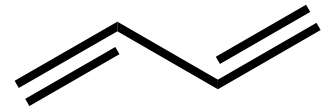


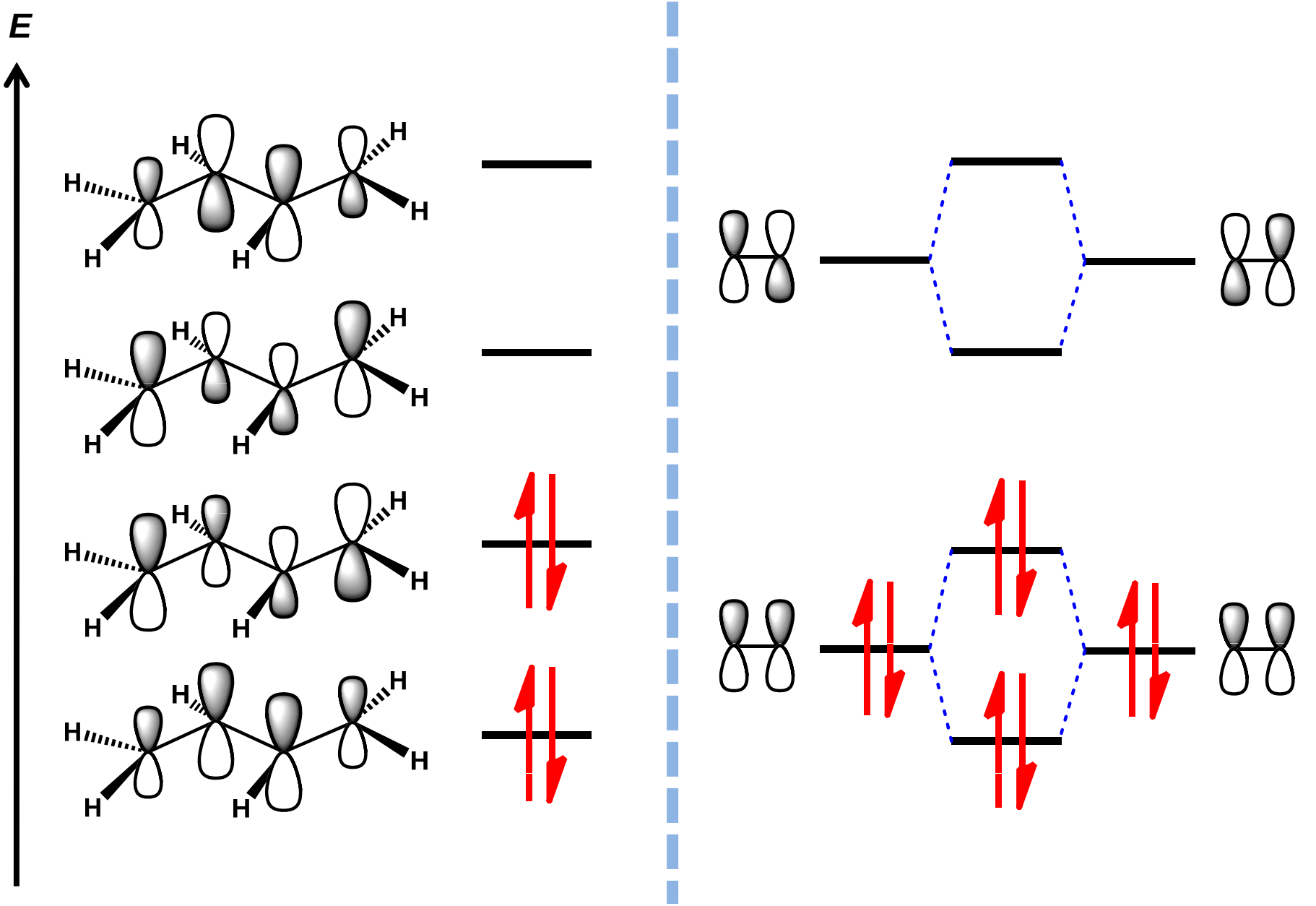




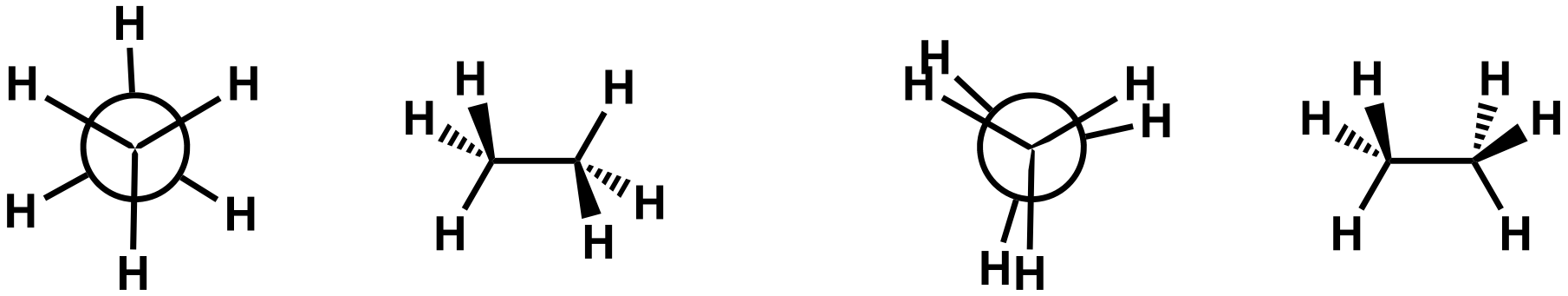


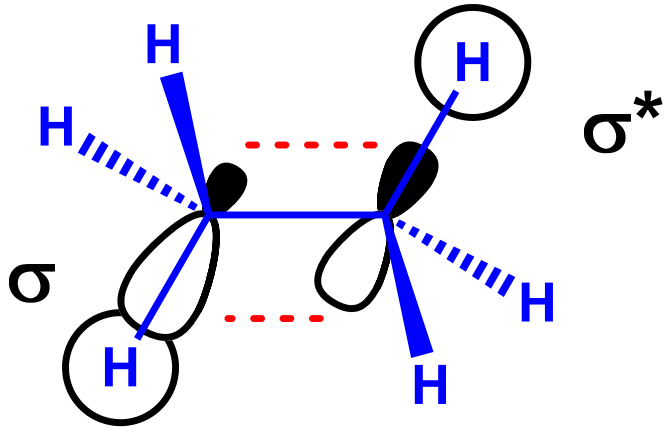
Butadiene

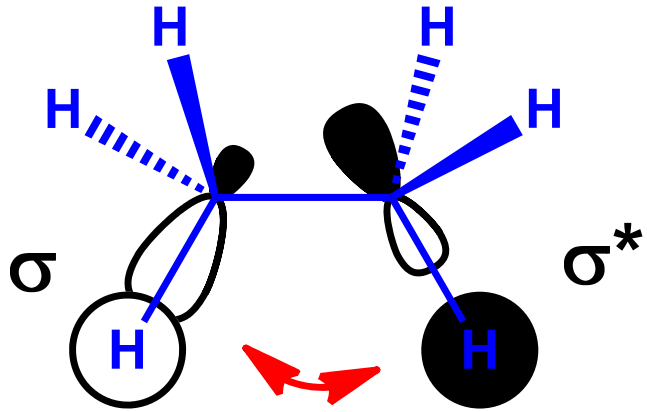




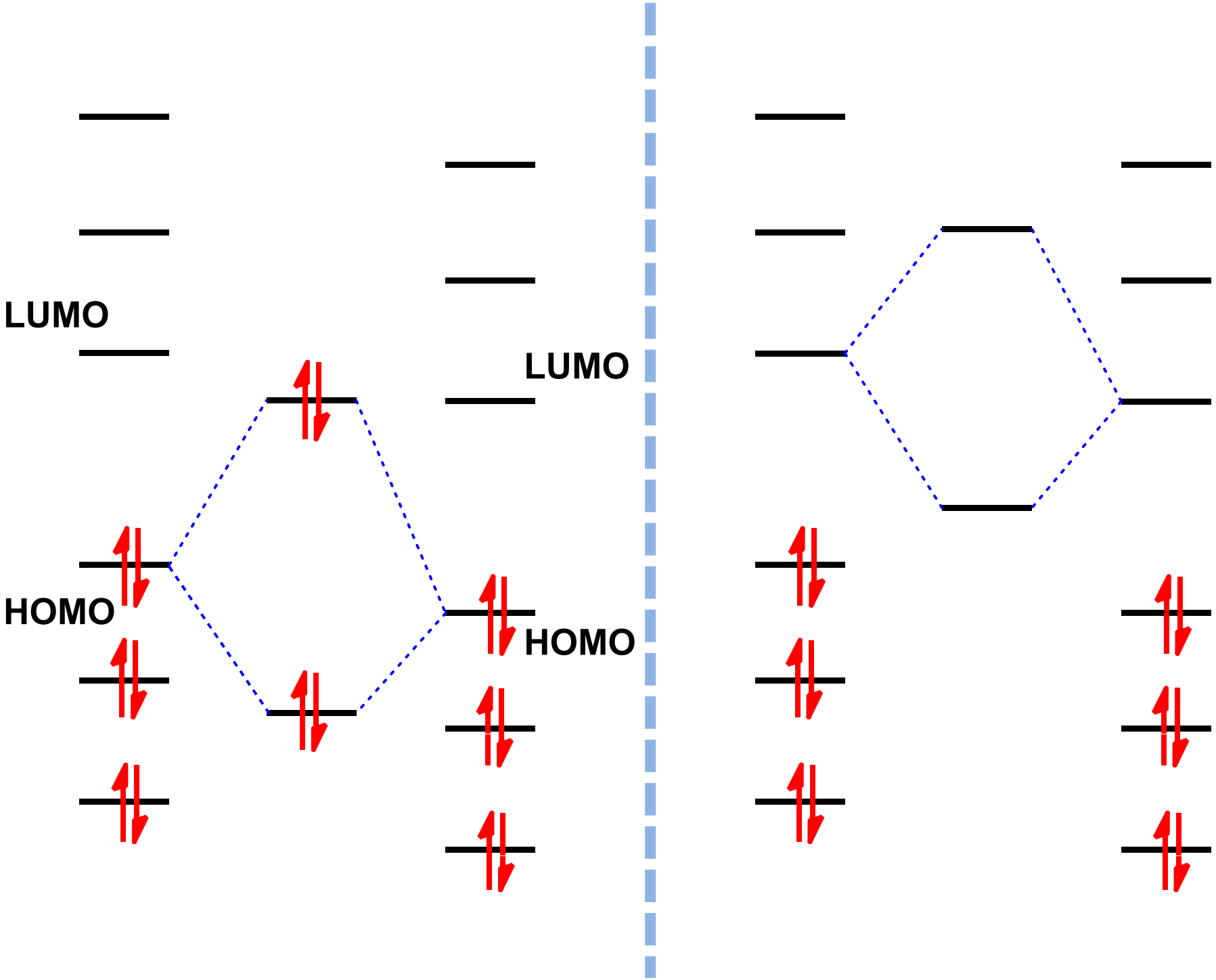
Staggered vs. Eclipsed Conformation of Ethane

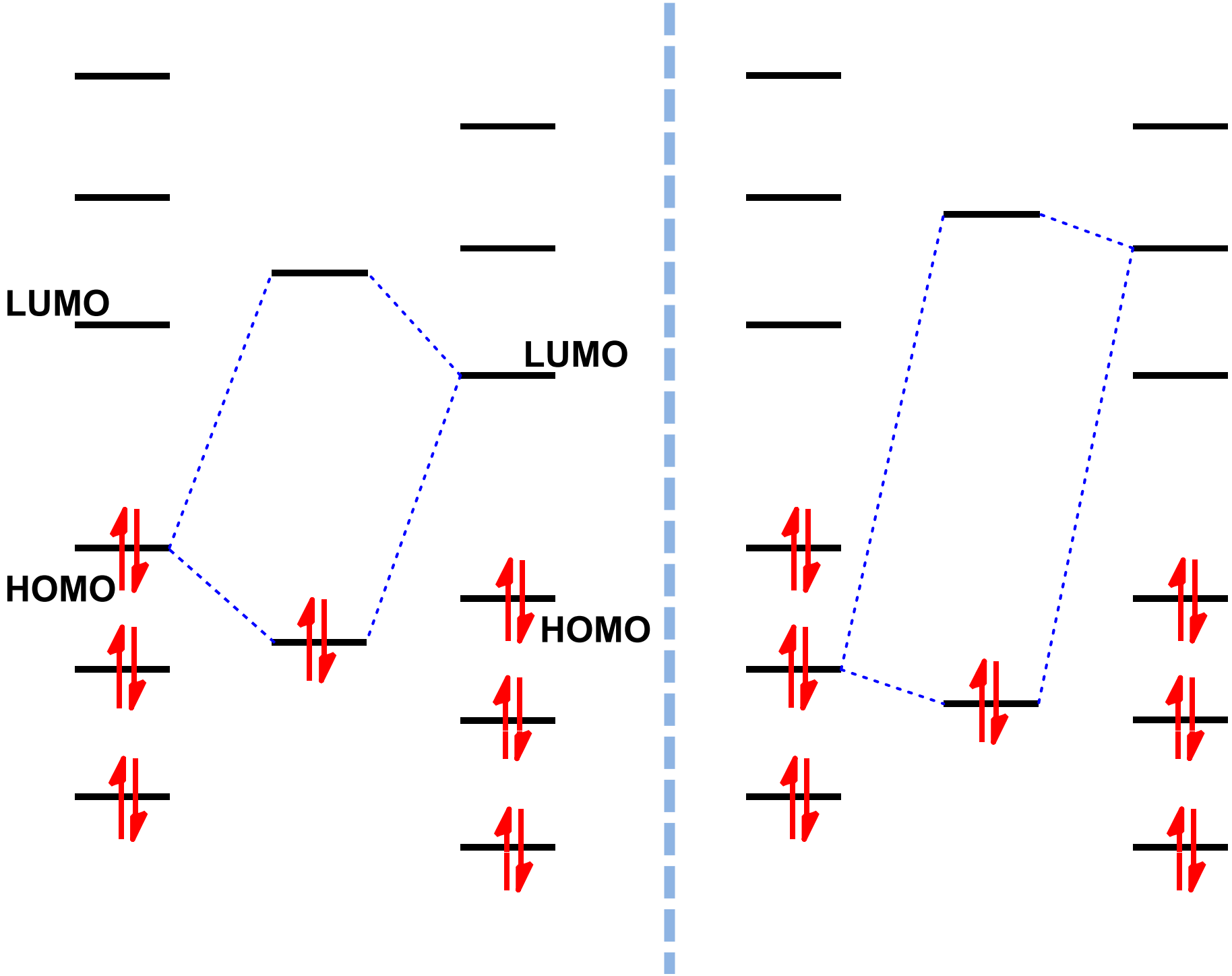




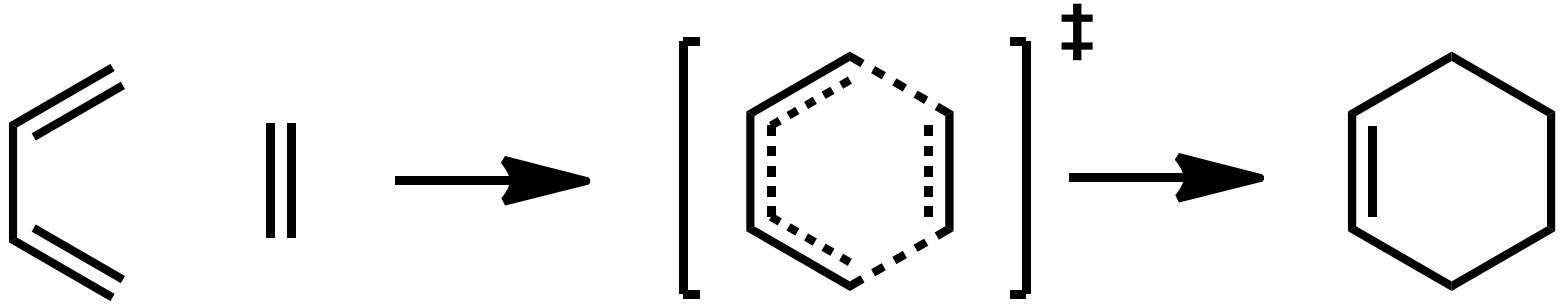


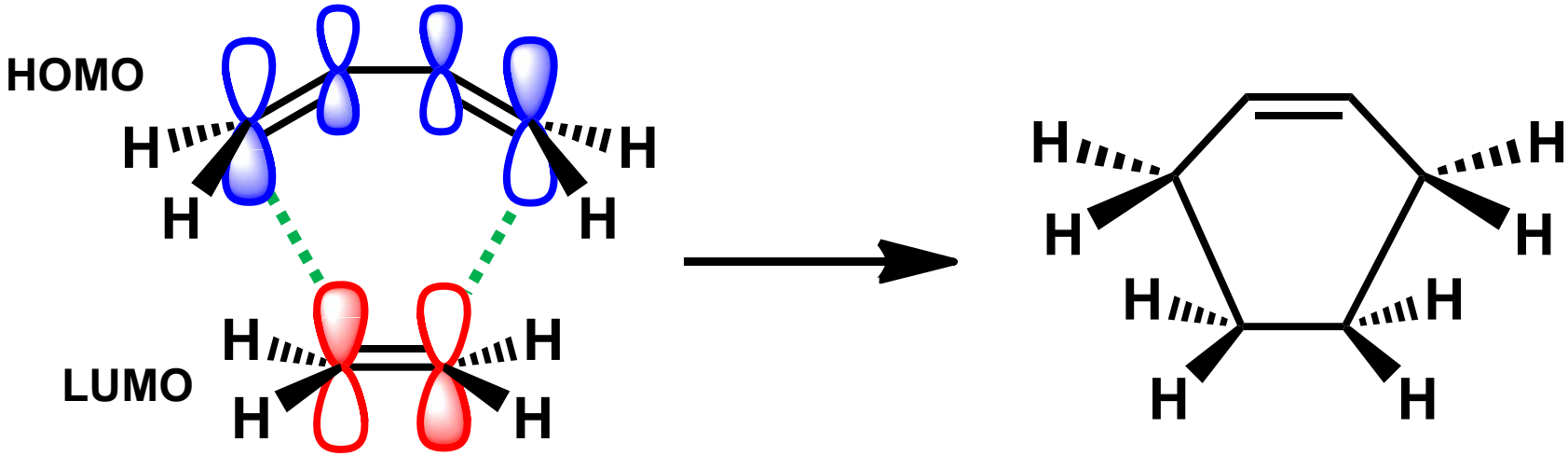
See: Pophristic V.; Goodman, L. *Nature* **2001**, *411*, 565.
See also: Bickelhaupt, M.; Baerends, E. J. *Angew. Chem. Int. Ed.* **2003**, *42*, 4183.
Weinhold, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 4188.
Mo, Y.; Gao, J. *Acc. Chem. Res.* **2007**, *40*, 113.


LUMO
HOMO
LUMO
HOMO


LUMO
HOMO
LUMO
HOMO

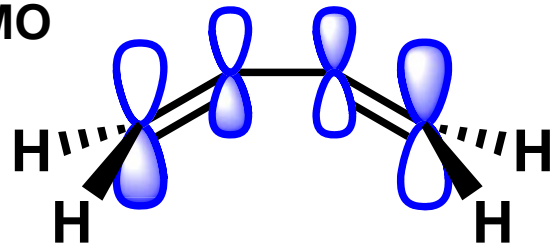
Diels–Alder Reaction



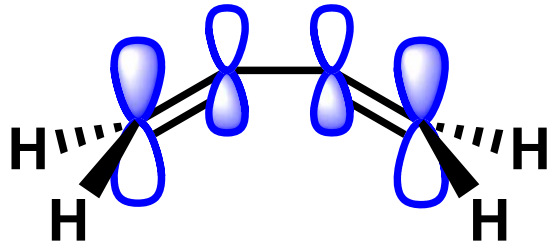


[4 + 2]

HOMO



LUMO



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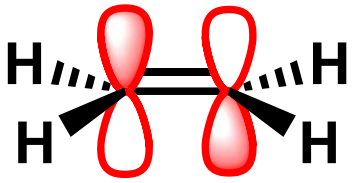

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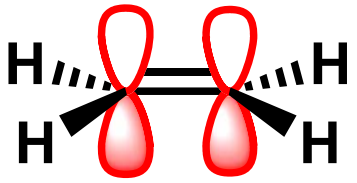

[2 + 2]

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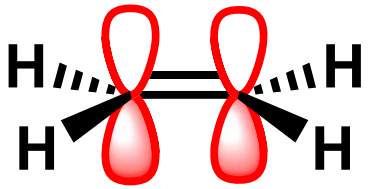
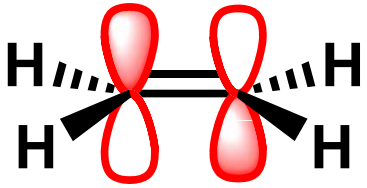


LUMO



Salem–Klopman Equation

occ-occ *Coulomb*

$$\Delta E = -\sum_{ab}(q_a+q_b)\beta_{ab}S_{ab} + \sum_{k<l}\frac{Q_kQ_l}{\varepsilon R_{kl}}$$

$$+\sum_{r}^{occ}\sum_{s}^{unocc} - \sum_{s}^{occ}\sum_{r}^{unocc} \frac{2(\sum_{ab} c_{ra}c_{sb}\beta_{ab})^2}{E_r - E_s}$$

occ-unocc

Hard and Soft Acids and Bases (HSAB)

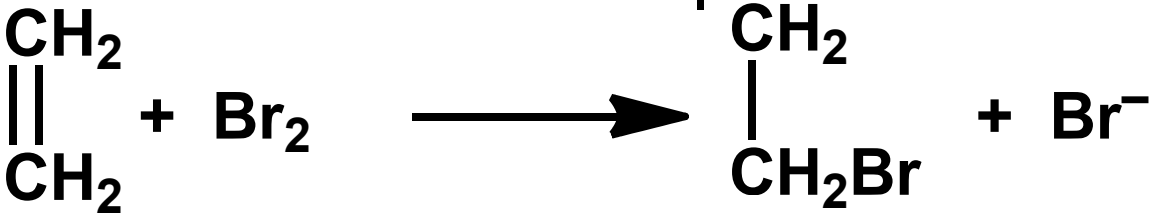
	hard	borderline	soft
acid	H^+ Li^+, Na^+ Mg^{2+}, Ca^{2+} Al^{3+} Fe^{3+} Si^{4+} BF_3 $AlCl_3$ etc.	Fe^{2+} Cu^{2+} Zn^{2+} R_3C^+ etc.	Cu^+, Ag^+, Au^+ Hg^+, Hg^{2+} BH_3 RS^+ I^+, Br^+, I_2, Br_2 nitrobenzene metal(0) carbene etc.
base	F^- H_2O, OH^- $CH_3CO_2^-$ Cl^- NO_3^- ROH, RO^- NH_3, RNH_2 etc.	aniline pyridine Br^- NO_2^- etc.	R_2S, RSH, RS^- I^- SCN^- R_3P CN^- CO ethene benzene H^-, R^- etc.

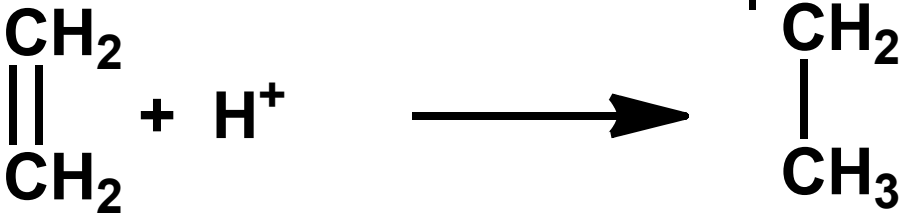
Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
Fleming, I.（竹内敬人, 友田修司　訳）, フロンティア軌道法入門, 講談社サイエンティフィク, **1978**.

(A) $HO^- + Br_2 \longrightarrow HOBr + Br^-$

(B) $HO^- + H^+ \longrightarrow H_2O$

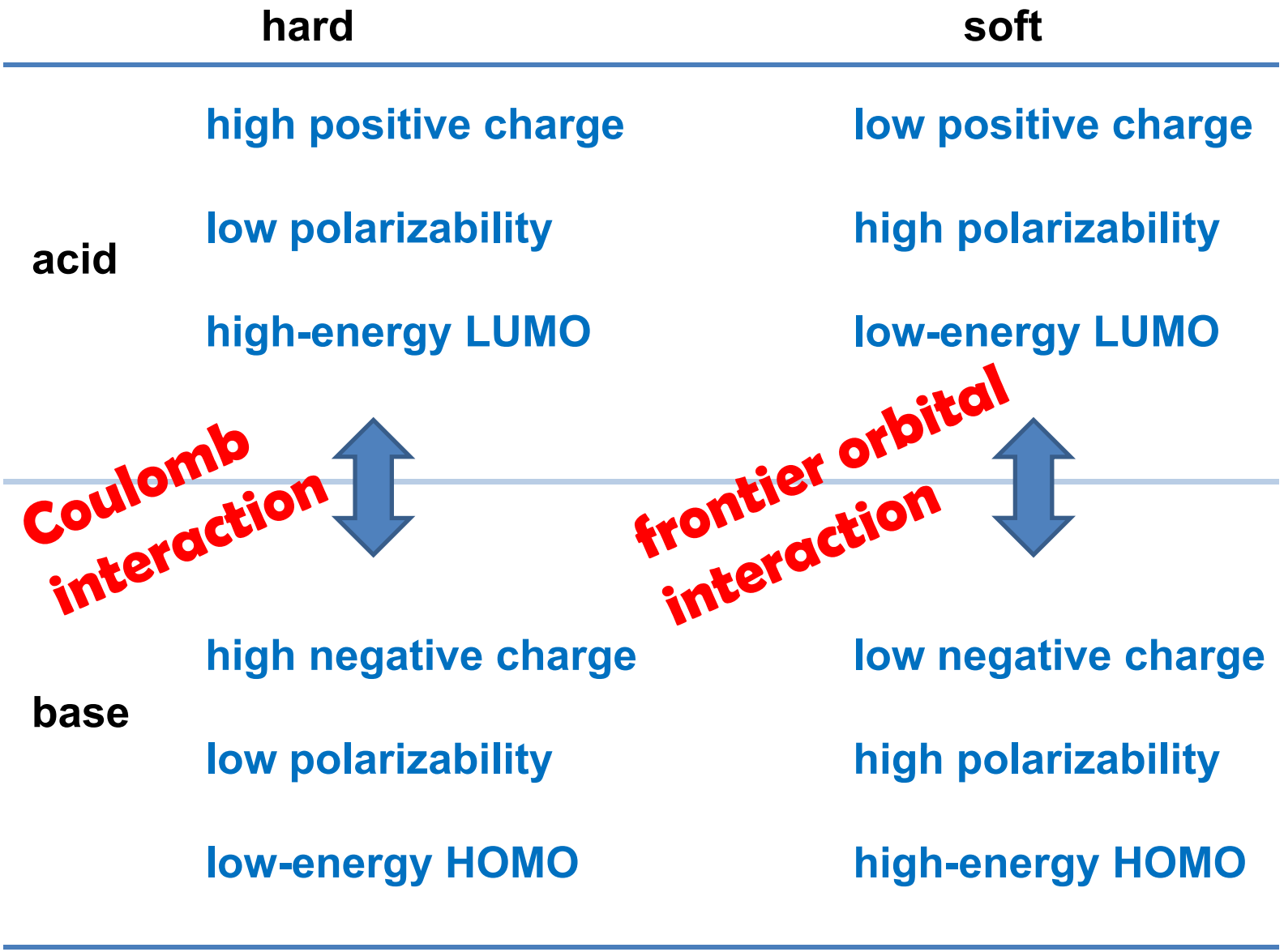
(A) < (B)

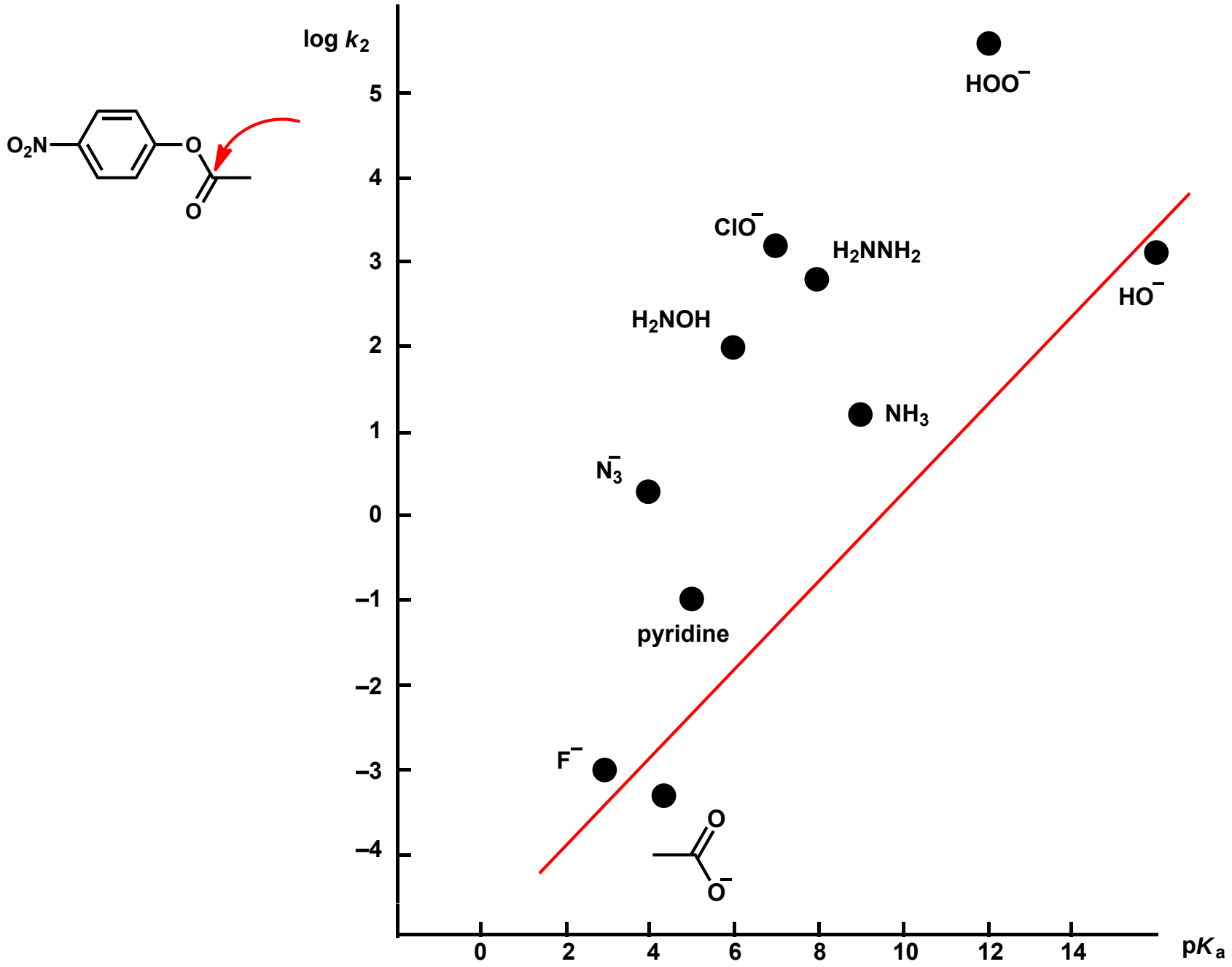
(C) 

(D) 

(C) > (D)

Hard and Soft Acids and Bases (HSAB)





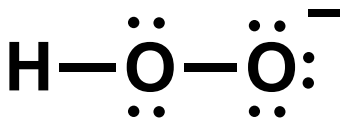
Jencks, W. P.; Carriuolo, J. *J. Am. Chem. Soc.* **1960**, *82*, 1778.

α-Effect

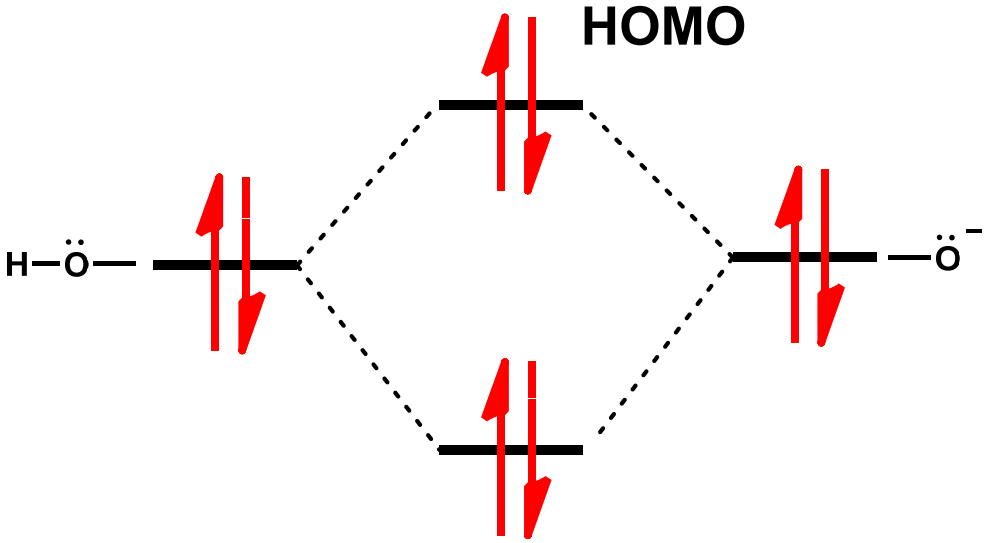
HOO^- vs. HO^-

	k_{HOO^-} / k_{HO^-}		K_{HOO^-} / K_{HO^-}
Ph—C≡N	10^5	H_3O^+	10^{-4}
$Ph—CH_2Br$	50		

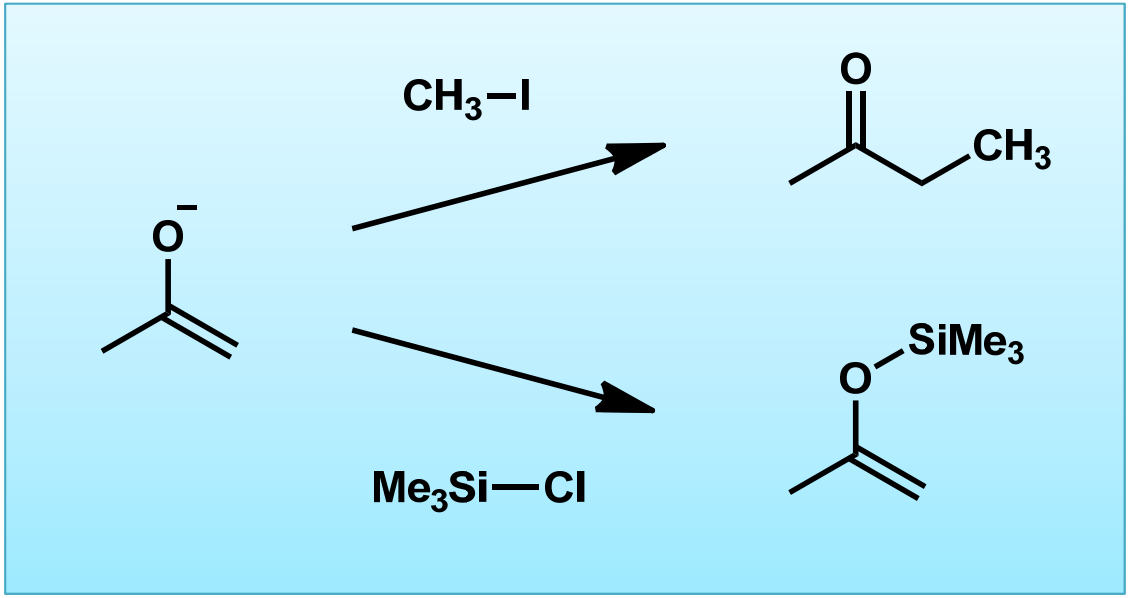
Fleming, I. Molecular *Orbitals and Organic Chemical Reactions,* John Wiley & Sons: West Sussex, 2009.



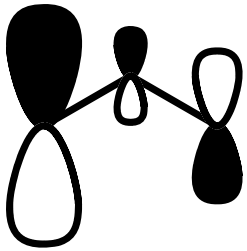
$H_2N—NH_2$ $HO—NH_2$



Ambident Nucleophile

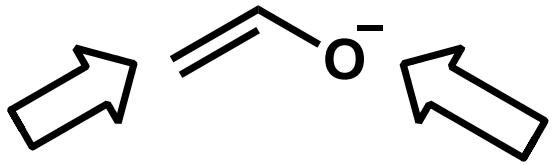


large coefficient



HOMO

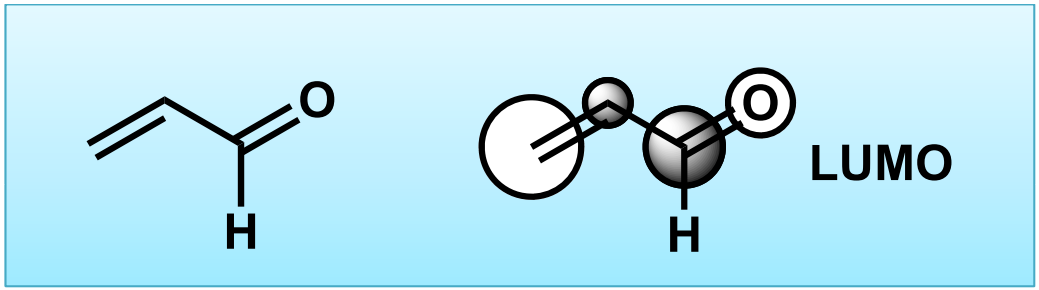
frontier orbital control



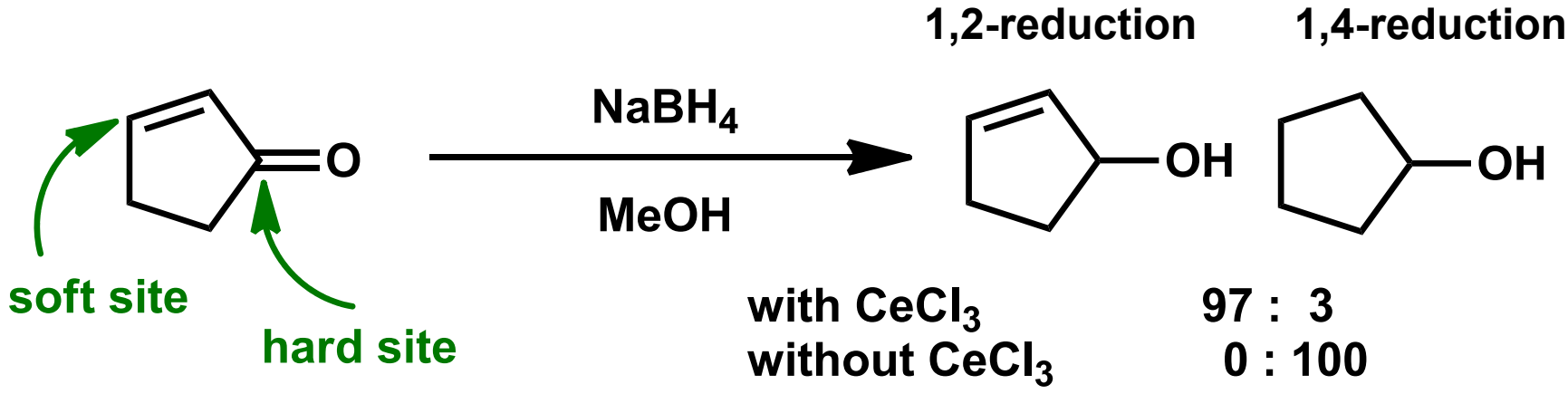
charge control

soft nucleophilic center

hard nucleophilic center



Luche Reduction（ルーシュ還元）



$NaBH_n(OMe)_{4-n}$ .... harder than $NaBH_4$

"From the hard and soft acids and bases (HSAB) theory, it was deduced that the substitution of hydrides in BH_4^- by alkoxy groups increases the hardness of the reagent. The attack of the conjugate enone system is then enhanced at the hard site, i.e., carbon 2."

Gemal, A. L.; Luche, J.-L. *J. Am. Chem. Soc.* **1981**, *103*, 5454.