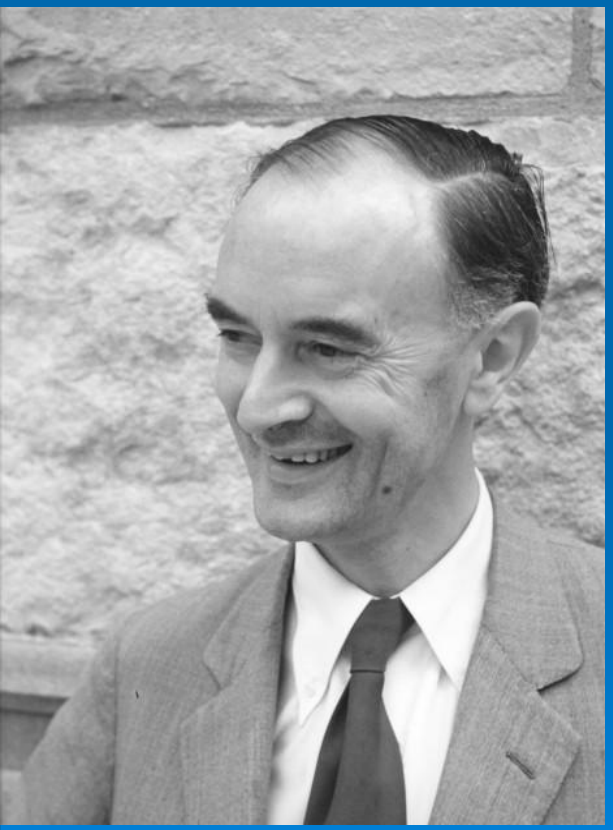
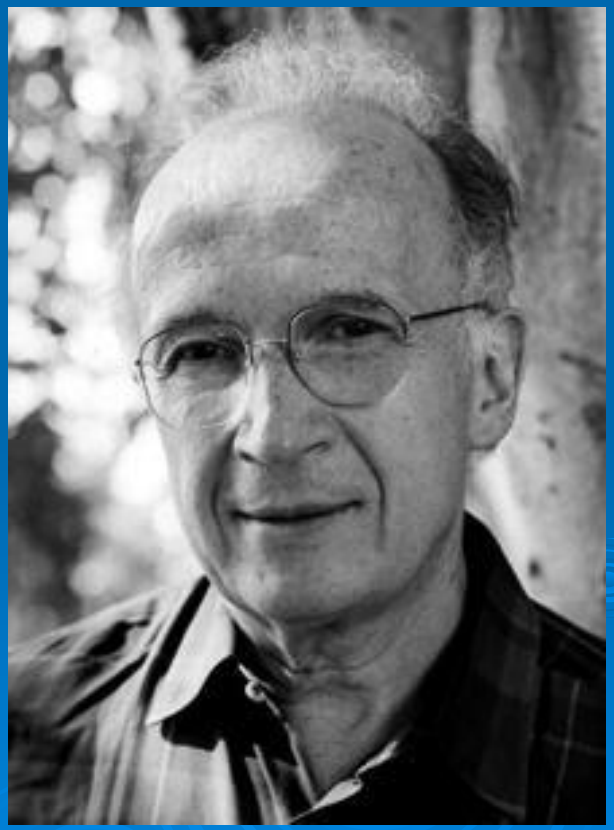
Лекция 9
Реакционная способность химических соединений

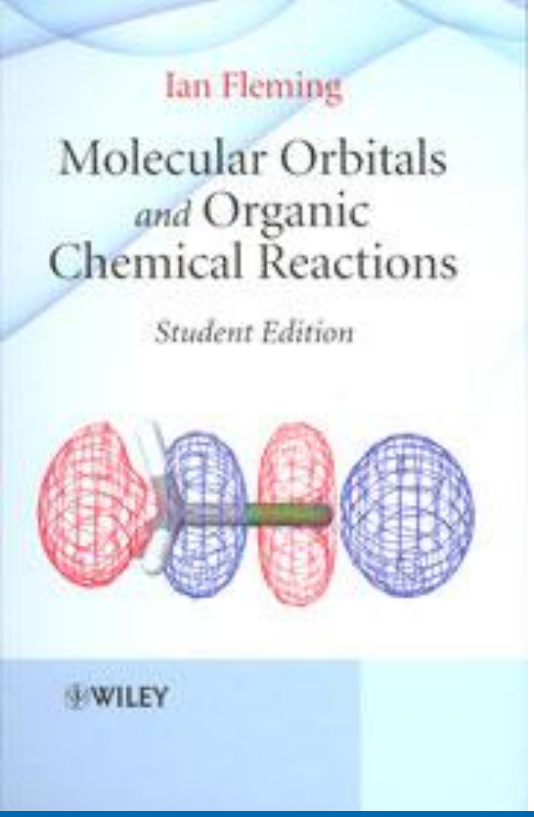


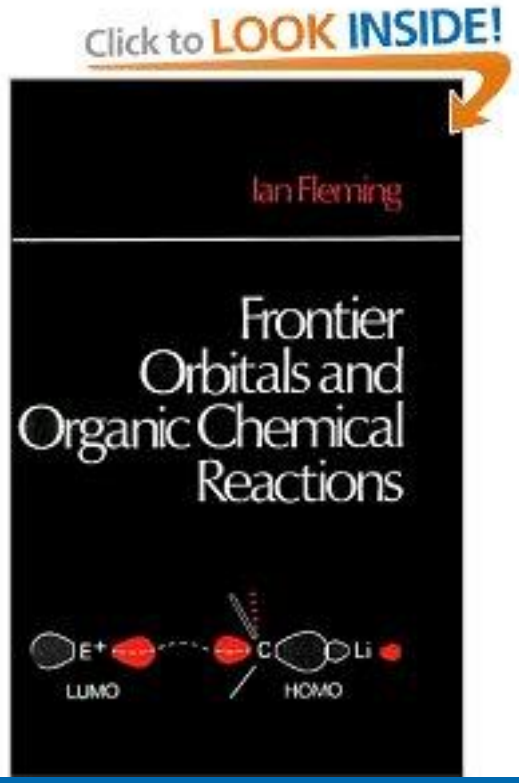
Sir Christopher (Kelk) Ingold 1893-1970

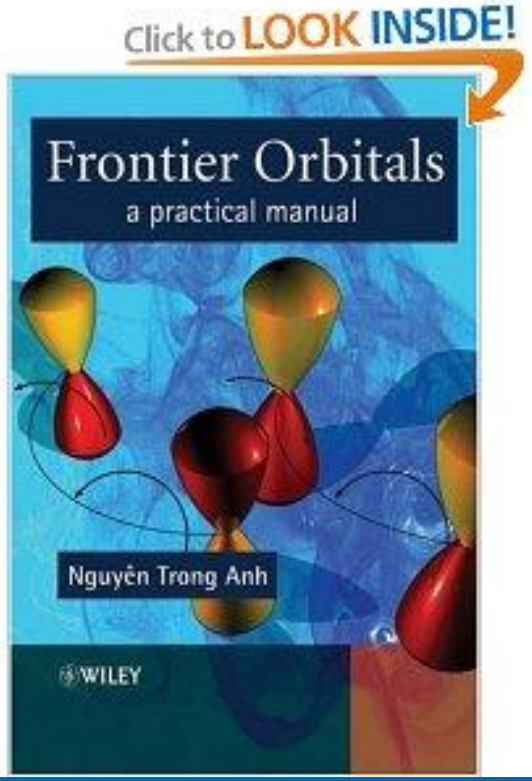
Kenichi Fukui



Roald Hoffmann


Ian Fleming
Molecular Orbitals and Organic Chemical Reactions
Student Edition
WILEY


Click to LOOK INSIDE!
Ian Fleming
Frontier Orbitals and Organic Chemical Reactions
LUMO
HOMO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a practical manual
Nguyễn Trọng Anh
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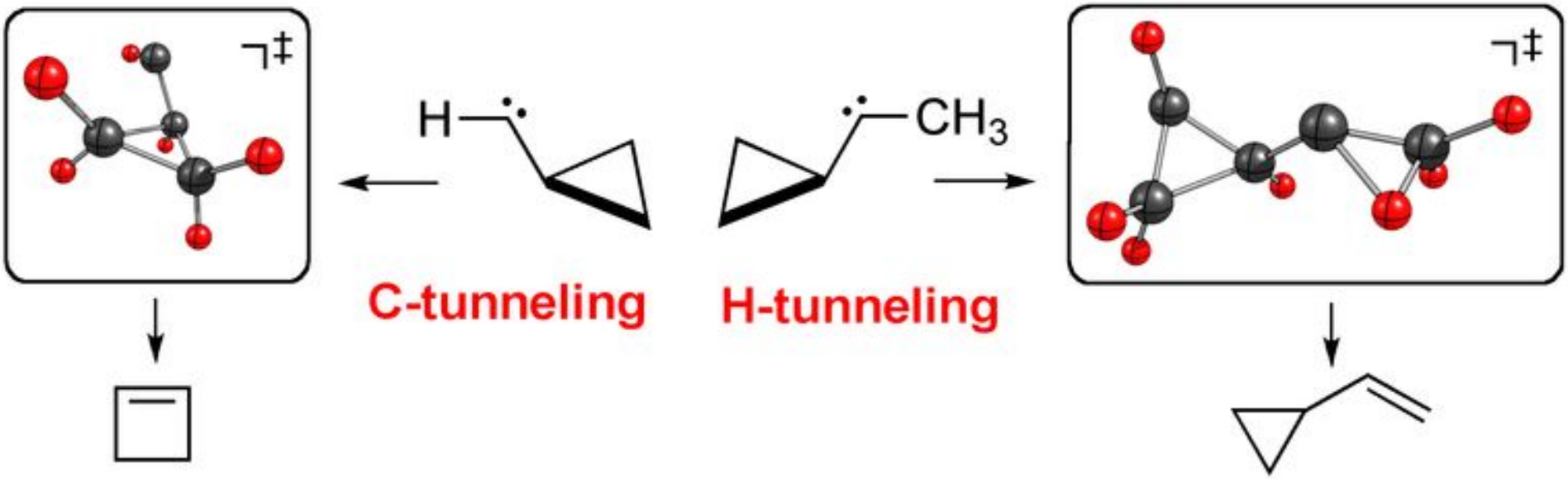
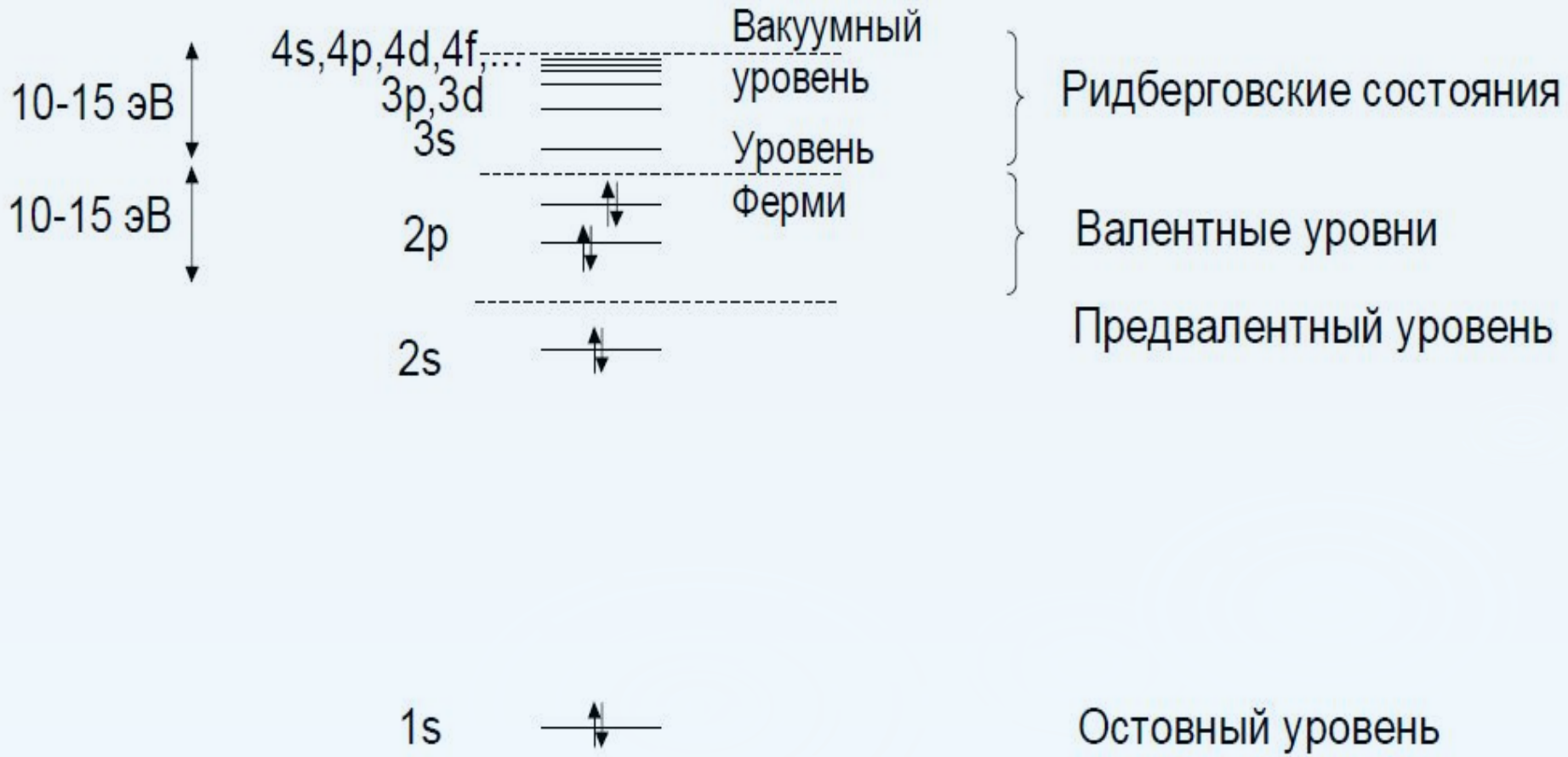
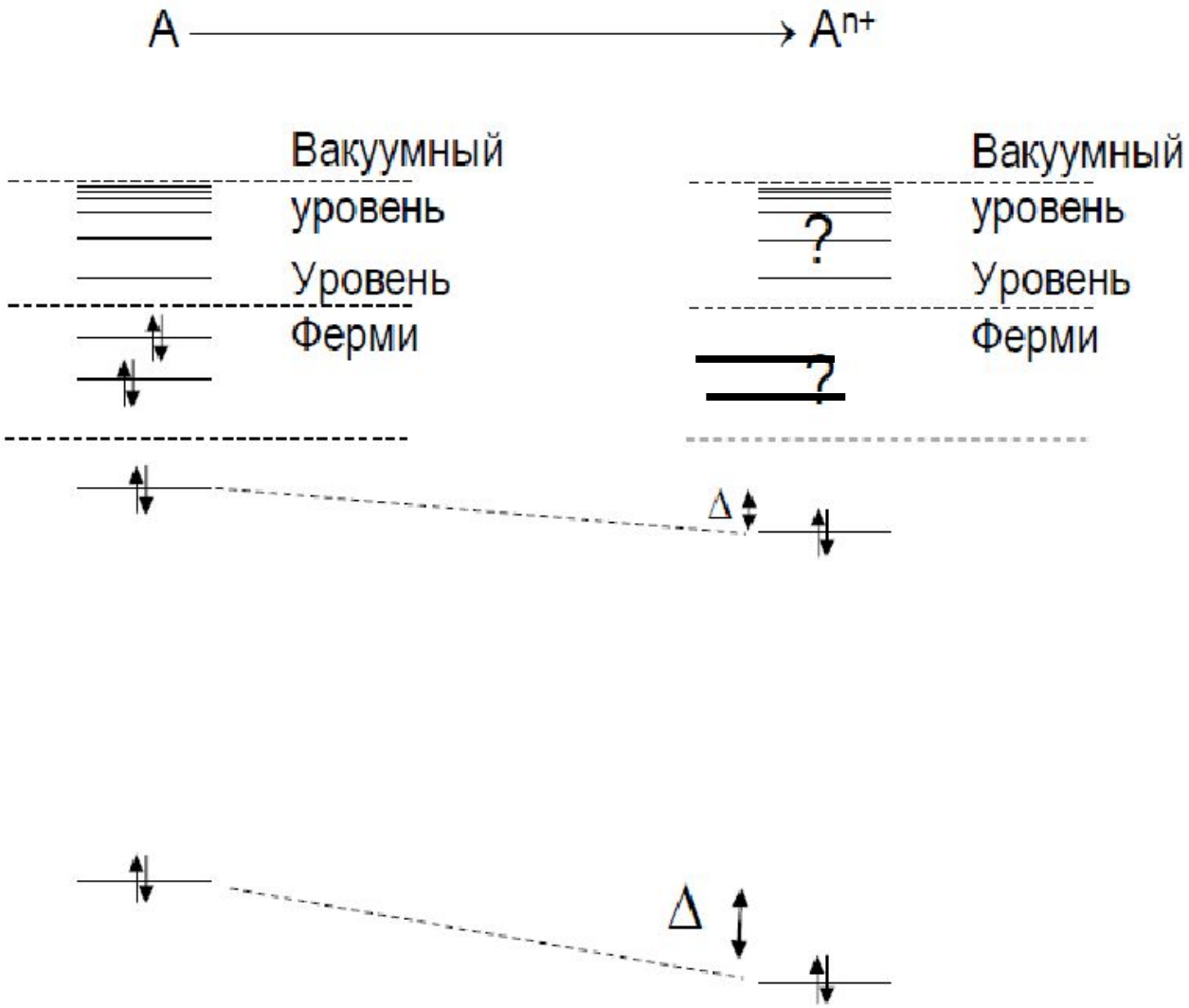

H
CH3
C-tunneling
H-tunneling

Электронные уровни атома

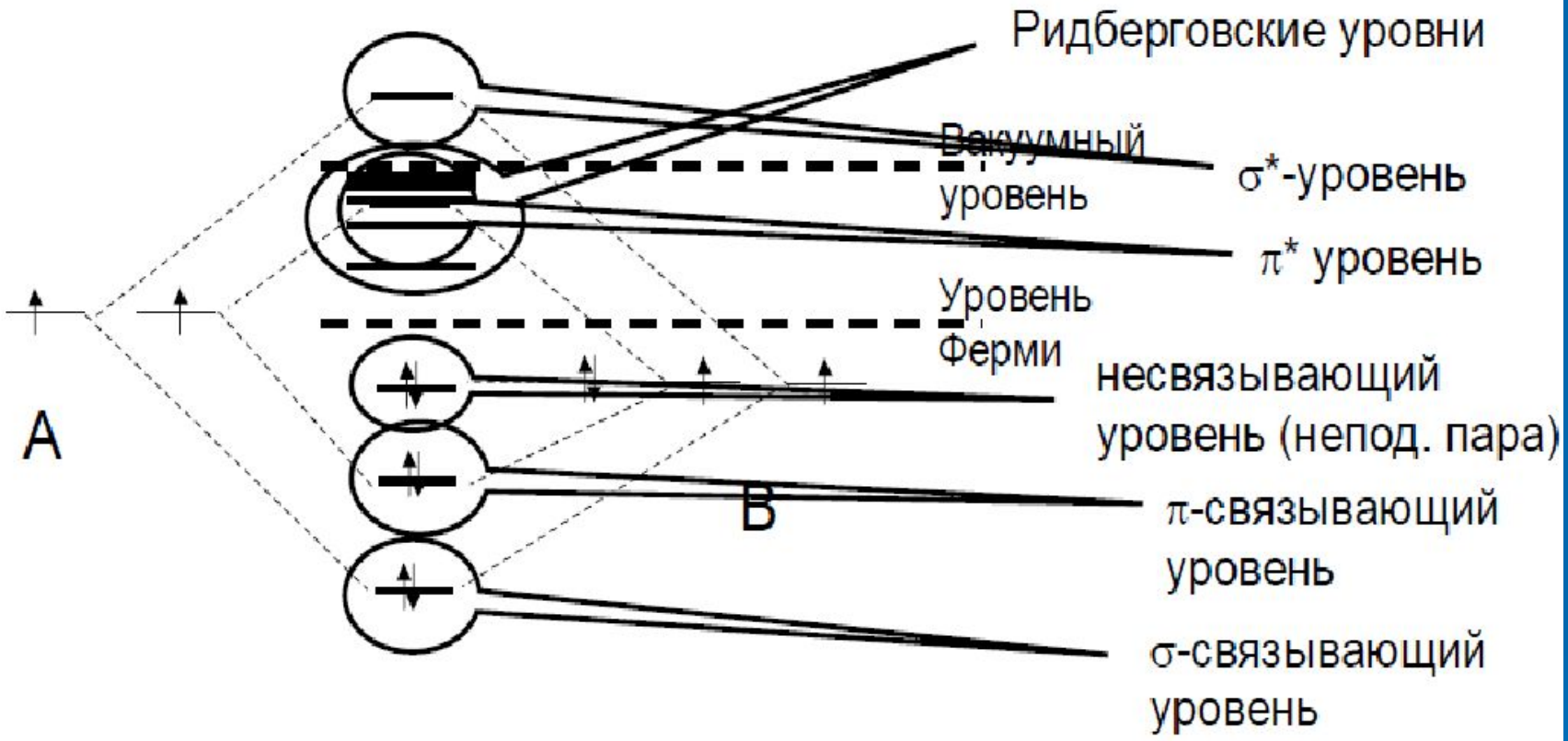
O (атом кислорода)



Изменение электронных уровней атома при образовании хим. связей

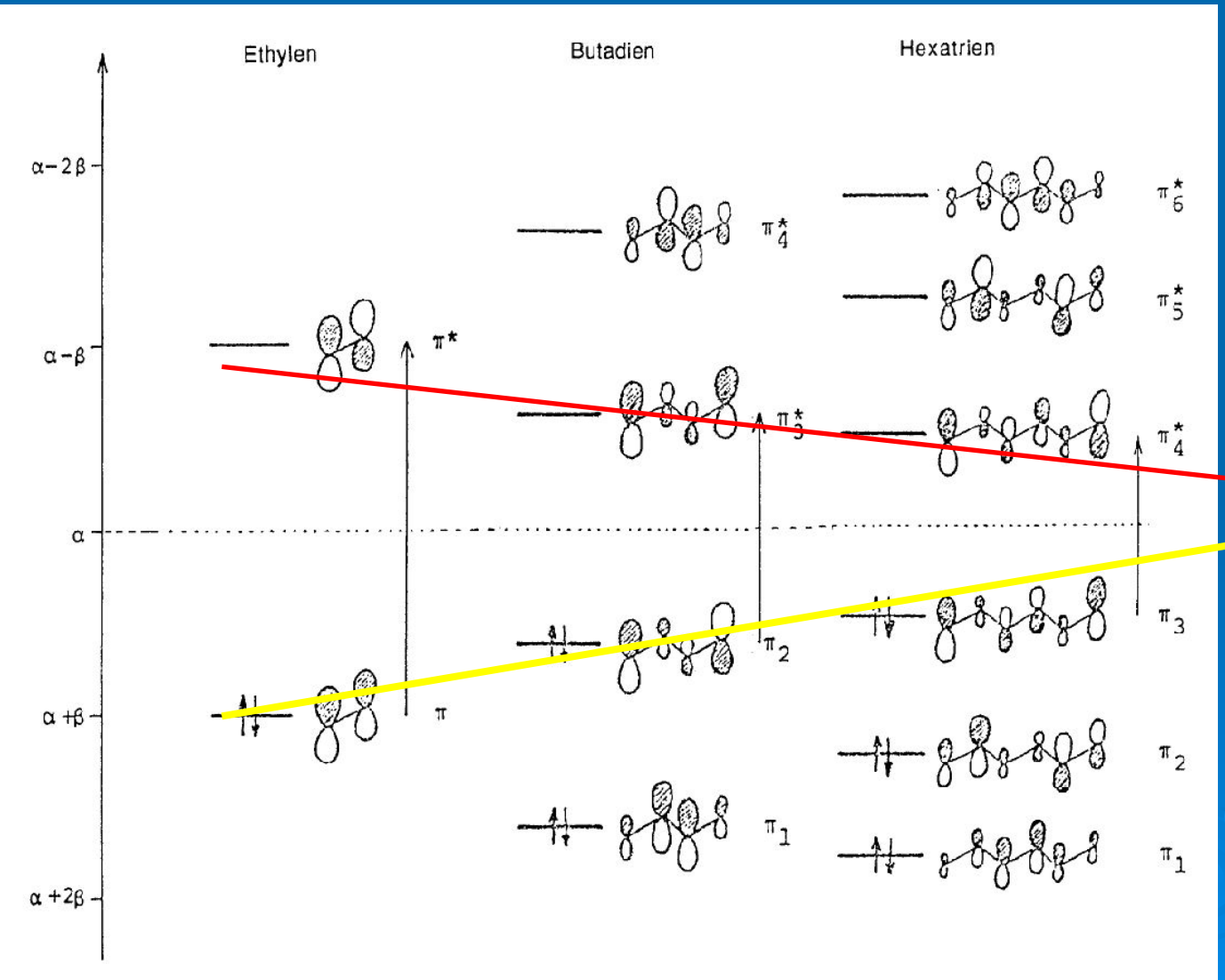


Молекулярные орбитали



Электронные зоны

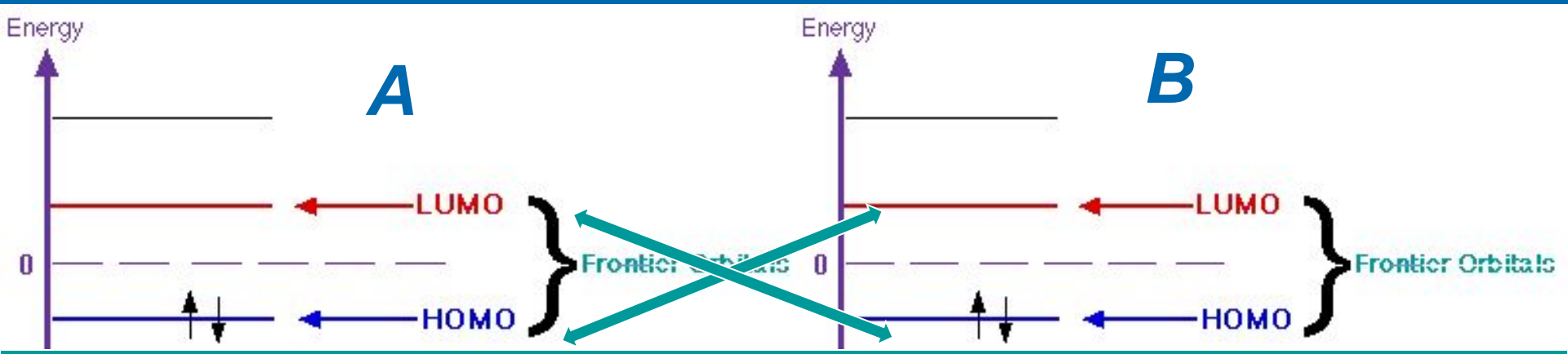
Электронные зоны «органических» металлов



полупроводники

Органические металлы

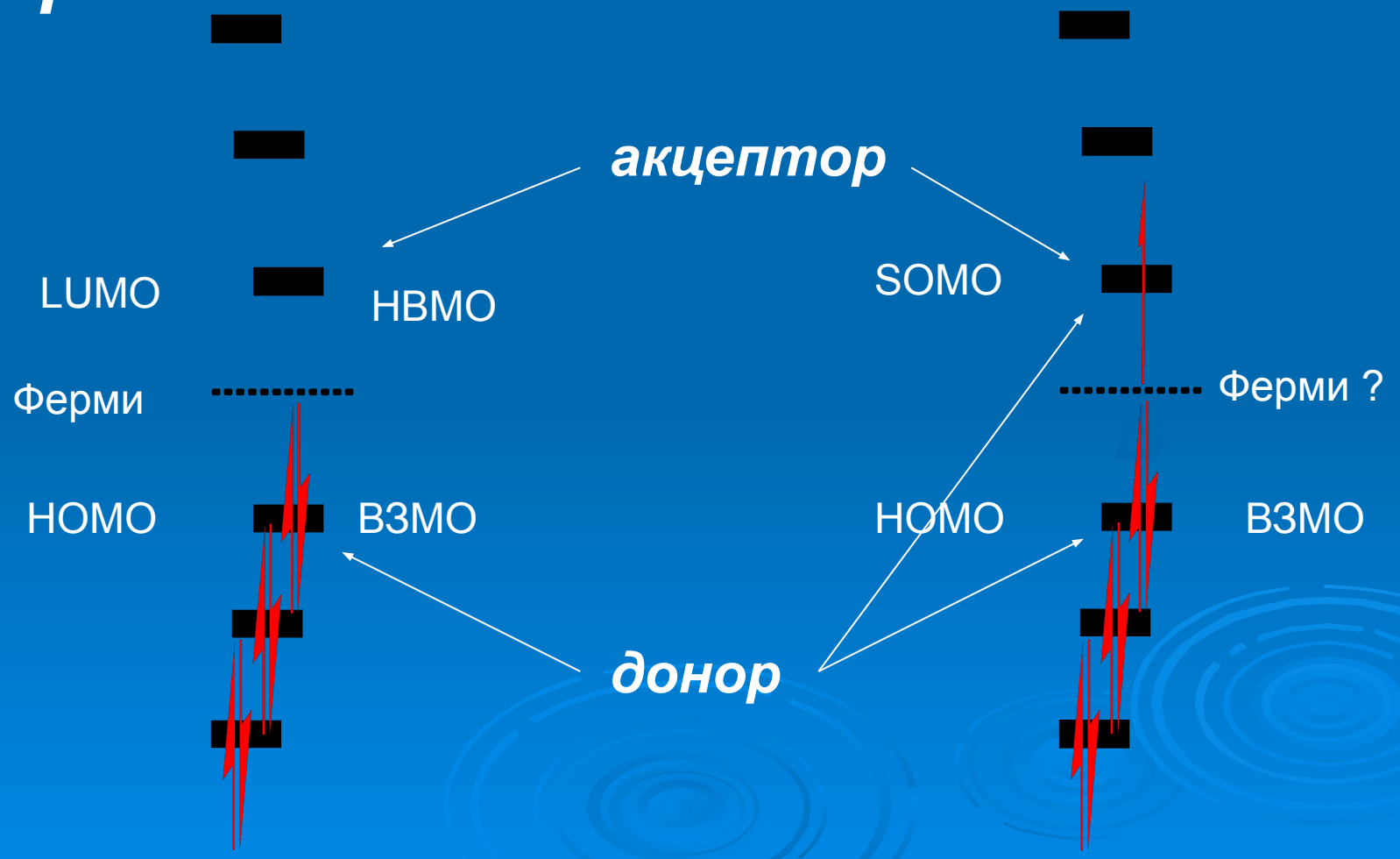
Реакция характеризуется взаимным переносом электронной плотности от одной молекулы (атома) к другой молекуле (атому)



В случае только ***«одностороннего»*** переноса электронной плотности, говорят о

донорно – акцепторном взаимодействии

Реакционная способность определяется подвижностью электронов по орбиталям и в основном расположенными в области ***уровня Ферми***



Свойства валентных электронных уровней (10 – 15 эВ ниже ***уровня Ферми***) и вакантных электронных уровней (10 – 15 эВ выше ***уровня Ферми***) определяют большинство практически важных свойств атомов, молекул и веществ –

- реакционная способность,

- электрофизические свойства,

- магнитные свойства,

- окраска и т.д.

Очевидно,

что реакционная способность молекул зависит от расположения (т.е. энергии) МО

надо только освободить молекулу, «отпустить» привязь

энергию переходов между МО можно оценить по спектральным данным

- Для основного состояния – самая стабильная электронная конфигурация
- Фотоны UV , VIS и ИК области возбуждают молекулу

High energy UV, X-ray photons may cause e- emission (ionization)

IR photons have much less energy, vibrate molecules

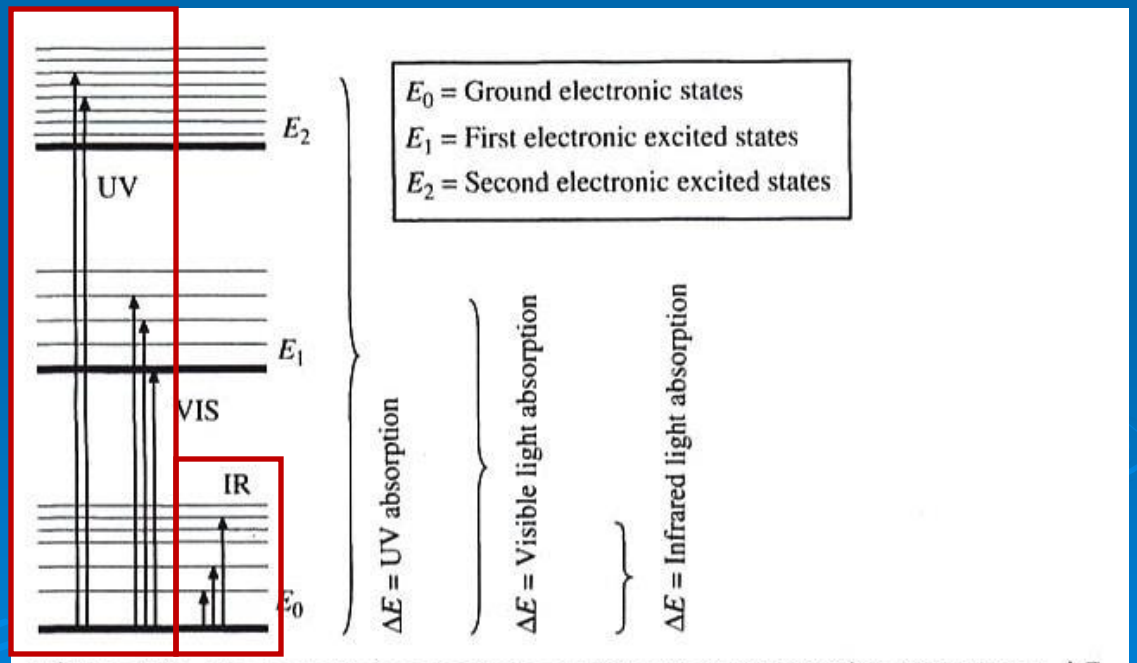
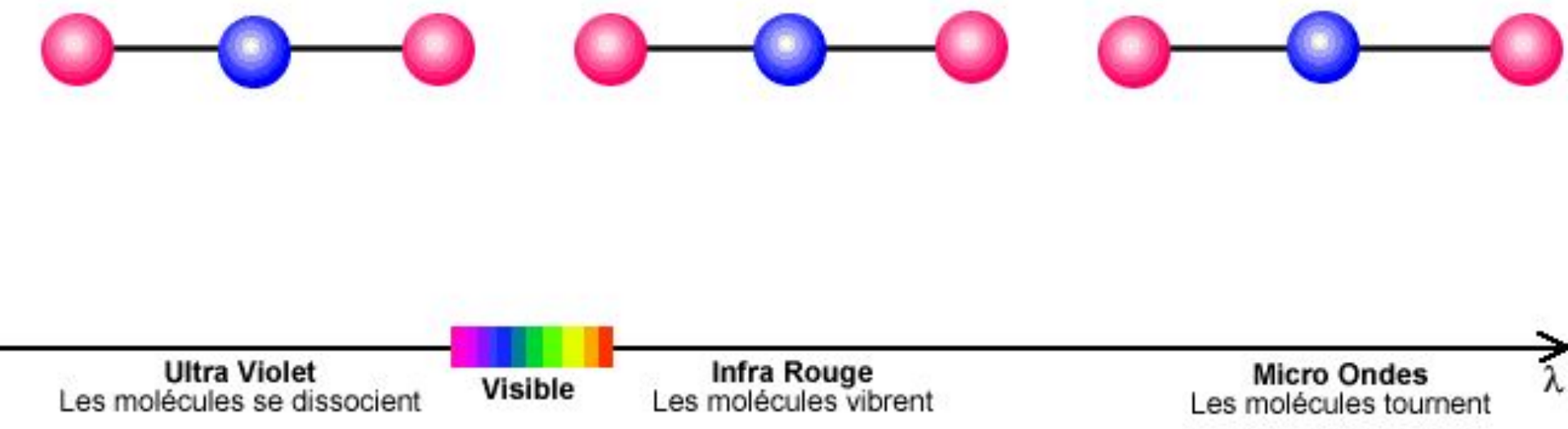
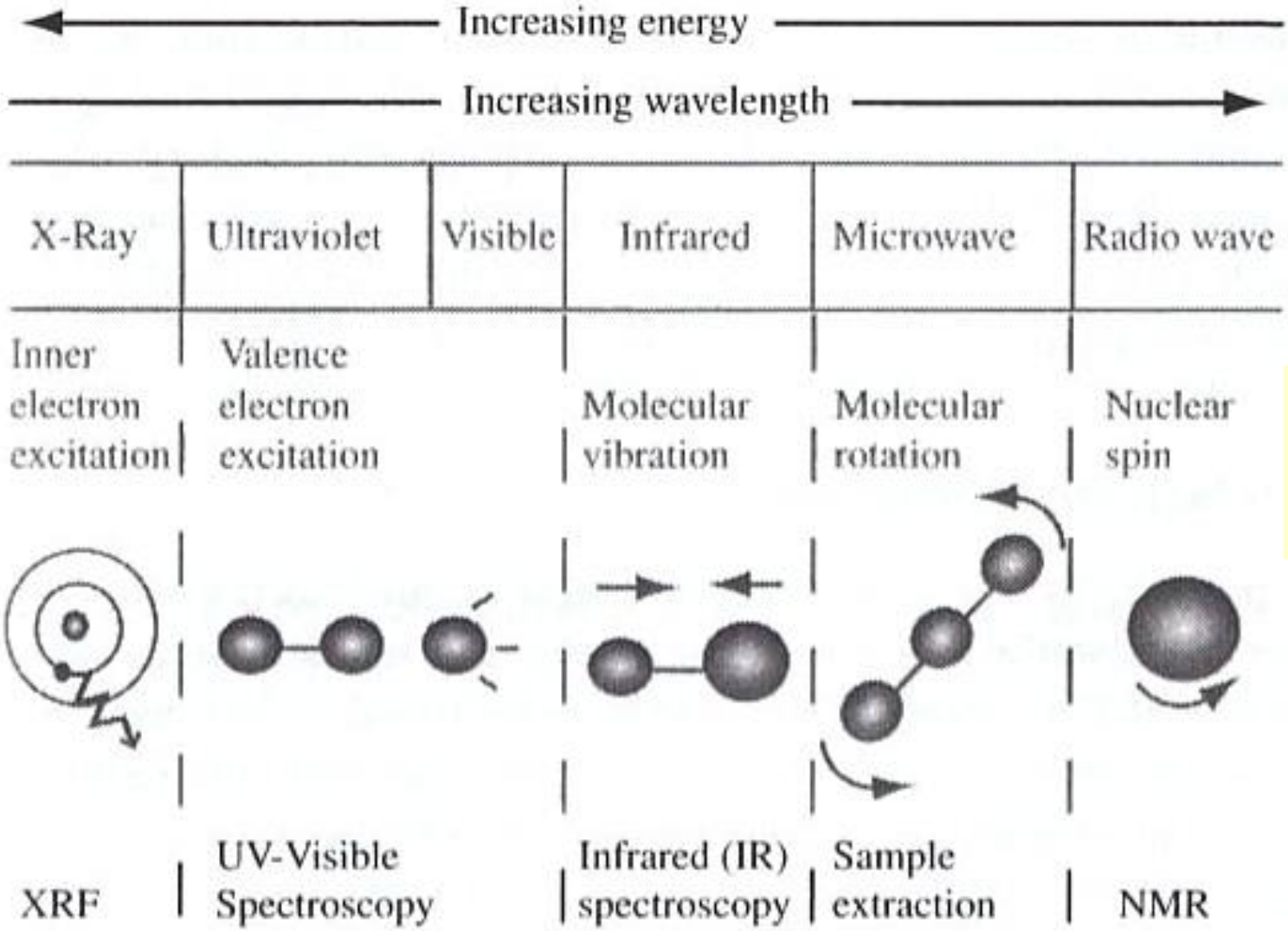


Figure 8.2 Energy levels in a molecule and three types of absorption spectrometry. ΔE is the radiation absorbed by a molecule

UV-Visible + IR Spectroscopic Methods

Introduction to the Principles of Spectroscopy

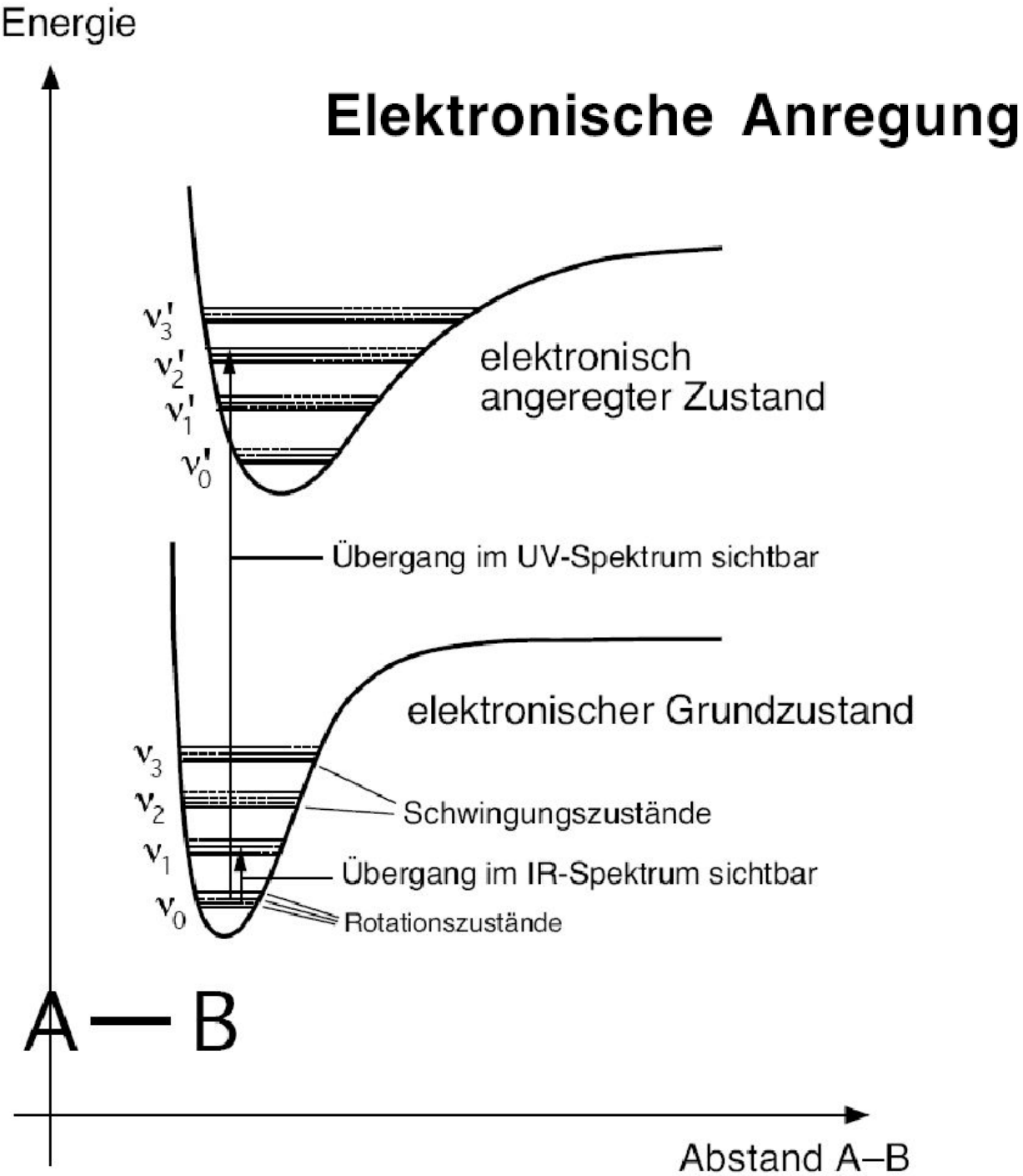




Ionization occurs under high energy UV radiation

MW least energetic, does not vibrate

Figure 8.3 Molecular responses to radiations of various wavelength ranges (not to scale)



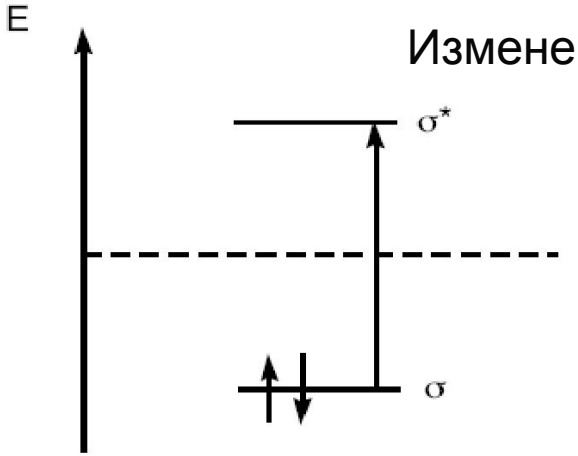
Энергия системы =

E(электронная)+

E(колебательная)

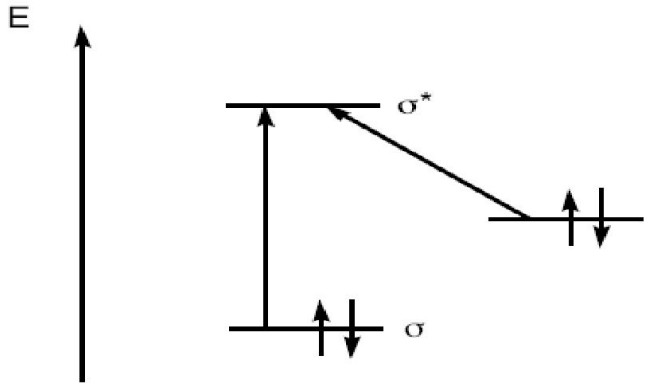
E(вращательная)

Изменение E (электронная)



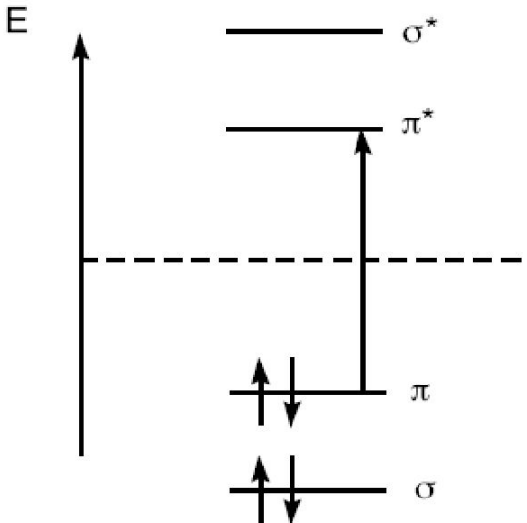
$\sigma \rightarrow \sigma^*$-Übergang : z.B. CH_4 122 nm

z.B. $CH_3–CH_3$ 135 nm



$n \rightarrow \sigma^*$-Übergang : z.B. $CH_3–O–H$ 177 nm

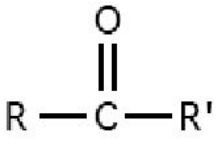
z.B. $CH_3–O–CH_3$ 184 nm

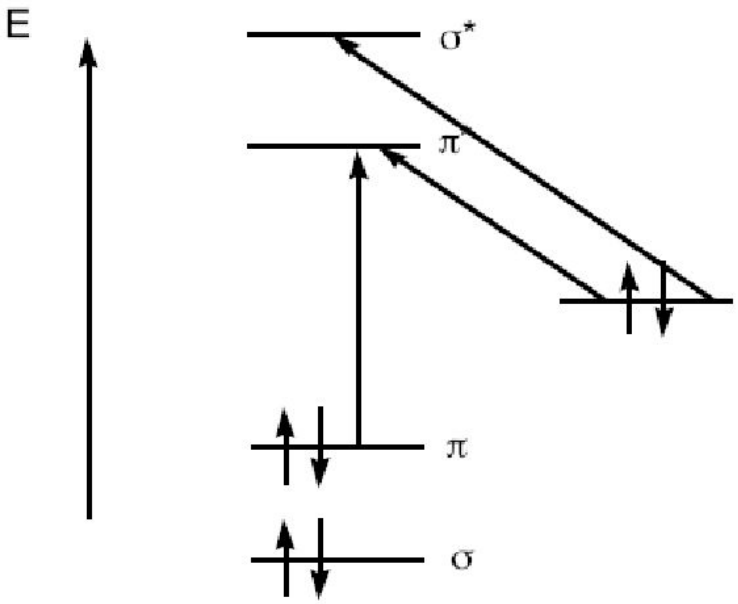


$\pi \rightarrow \pi^*$-Übergang

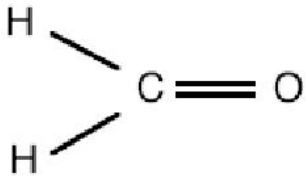
	λ_{max} [nm]	ε_{max}
z.B. $CH_2=CH_2$	163	15'000
$(CH_3)_2C=C(CH_3)_2$	197	11'000

Изменение E (электронная)

Hypothetische **Carbonylgruppe** 



z.B.

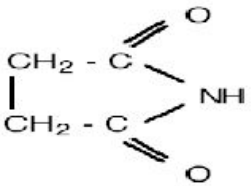


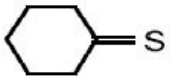
$n \rightarrow \pi^*$ -Übergang: 304 nm ($\varepsilon = 18$)

$\pi \rightarrow \pi^*$ -Übergang: 208 nm

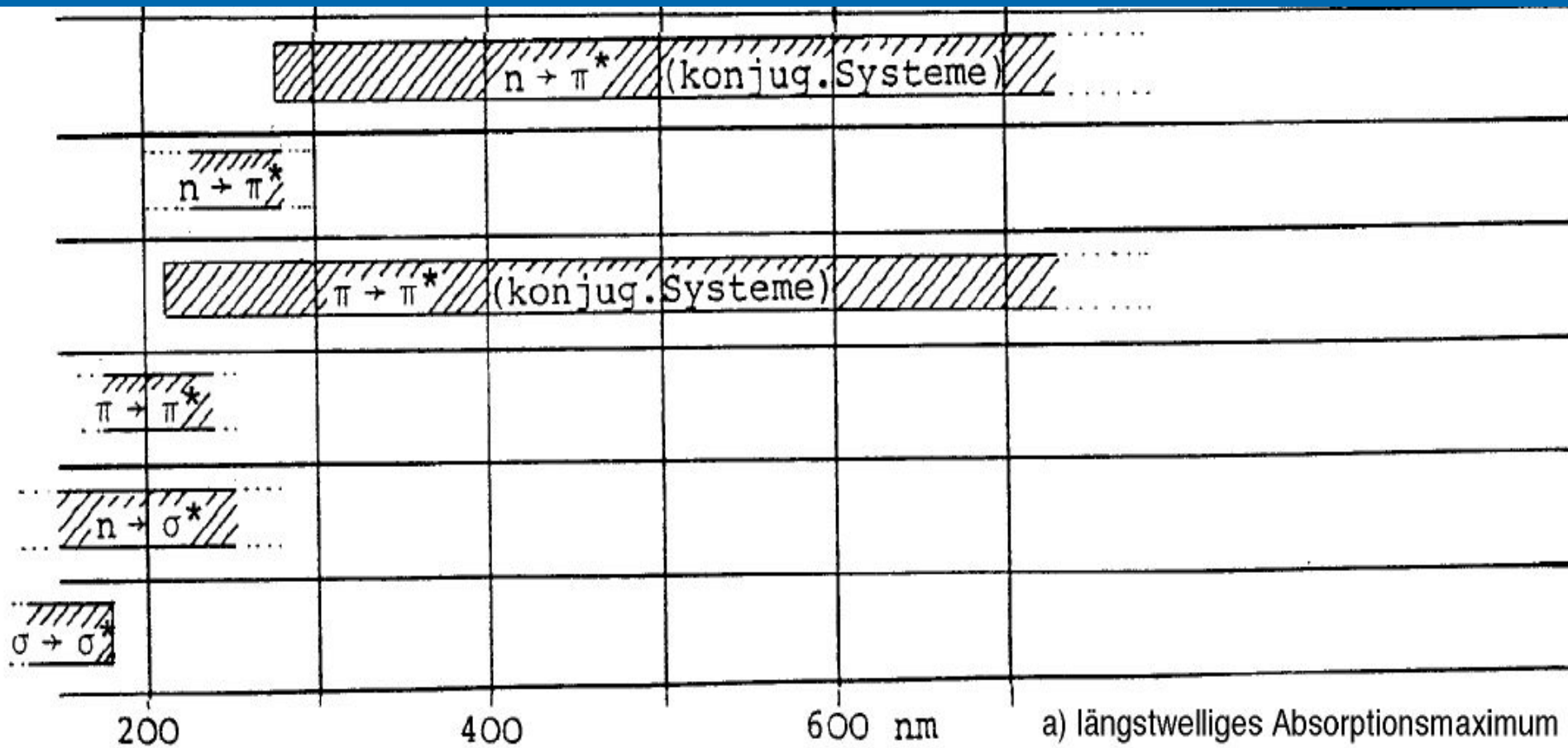
$n \rightarrow \sigma^*$ -Übergang: vermutlich um 180 nm

4.4.2. UV-Absorption einfacher Chromophore

Chromophor	Verbindung	Übergang	λ_{max} [nm]	ε_{max}	Lösungsmittel
C–C	$CH_3–CH_3$	$\sigma \rightarrow \sigma^*$	135	stark	Gas
C–H	CH_4	$\sigma \rightarrow \sigma^*$	122	stark	Gas
C–O	$CH_3–OH$	$n \rightarrow \sigma^*$	177	200	Hexan
	$CH_3–O–CH_3$	$n \rightarrow \sigma^*$	184	2500	Gas
C–N	$(C_2H_5)_2NH$	$n \rightarrow \sigma^*$	193	2500	Hexan
	$(CH_3)_3N$	$n \rightarrow \sigma^*$	199	4000	Hexan
C–S	CH_3SH	$n \rightarrow \sigma^*$	195	1800	Gas
		$n \rightarrow \sigma^*$	235	180	Gas
	$C_2H_5–S–C_2H_5$	$n \rightarrow \sigma^*$	194	4500	Gas
		$n \rightarrow \sigma^*$	225	1800	Gas
S–S	$C_2H_5–S–S–C_2H_5$	$n \rightarrow \sigma^*$	194	5500	Hexan
		$n \rightarrow \sigma^*$	250	380	
C–Cl	CH_3Cl	$n \rightarrow \sigma^*$	173	200	Hexan
C–Br	$n\text{-}C_3H_7Br$	$n \rightarrow \sigma^*$	208	300	Hexan
C–I	CH_3I	$n \rightarrow \sigma^*$	259	400	Hexan
C=C	$CH_2=CH_2$	$\pi \rightarrow \pi^*$	162.5	15000	Heptan
	$(CH_3)_2C=C(CH_3)_2$	$\pi \rightarrow \pi^*$	196.5	11500	Heptan
C=O	$(CH_3)_2C=O$	$n \rightarrow \sigma^*$	166	16000	Gas
		$\pi \rightarrow \pi^*$	189	900	Hexan
		$n \rightarrow \pi^*$	279	15	Hexan
	$CH_3–C(=O)–OH$	$n \rightarrow \pi^*$	200	50	Gas
	$CH_3–C(=O)–OC_2H_5$	$n \rightarrow \pi^*$	210	50	Gas
	$CH_3–C(=O)–ONa$	$n \rightarrow \pi^*$	210	150	Wasser
	$CH_3–C(=O)–NH_2$	$n \rightarrow \pi^*$	220	63	Wasser
		$n \rightarrow \pi^*$	191	15200	Acetonitril

Chromophor	Verbindung	Übergang	λ_{max} [nm]	ε_{max}	Lösungsmittel
C=N	$H_2N-\overset{\overset{NH}{\|}}{C}-NH_2 \cdot HCl$		265	15	Wasser
	$(CH_3)_2C=NOH$		193	2000	Ethanol
	$(CH_3)_2C=NONa$		265	200	Ethanol
N=N	$CH_3-N=N-CH_3$	$n \rightarrow \pi^*$	340	16	Ethanol
N=O	$(CH_3)_3C-NO$	$n \rightarrow \pi^*$	300	100	Ether
			665	20	
	$(CH_3)_3C-NO_2$		276	27	Ethanol
	$n\text{-}C_4H_9-O-NO$		218	1050	
			313-384	20-40	Ethanol
	$C_2H_5-O-NO_2$		260	15	Ethanol
C=S	$CH_3-\overset{\overset{S}{\|}}{C}-CH_3$		460	schwach	
			495	schwach	Ethanol
C=C	HC=CH		173	6000	Gas
	$n\text{-}C_5H_{11}-C\equiv C-CH_3$		177.5	10000	Hexan
			196	2000	
			222.5	160	
C≡N	$CH_3-C\equiv N$		<190		
X=C=Y	$CH_2=C=CH_2$		170	4000	
			227	630	
	$(C_2H_5)_2C=C=O$		227	360	
			375	20	
	$C_2H_5-N=C=N-C_2H_5$		230	4000	
			270	25	
	$C_2H_5-N=C=S$		250	1200	Hexan

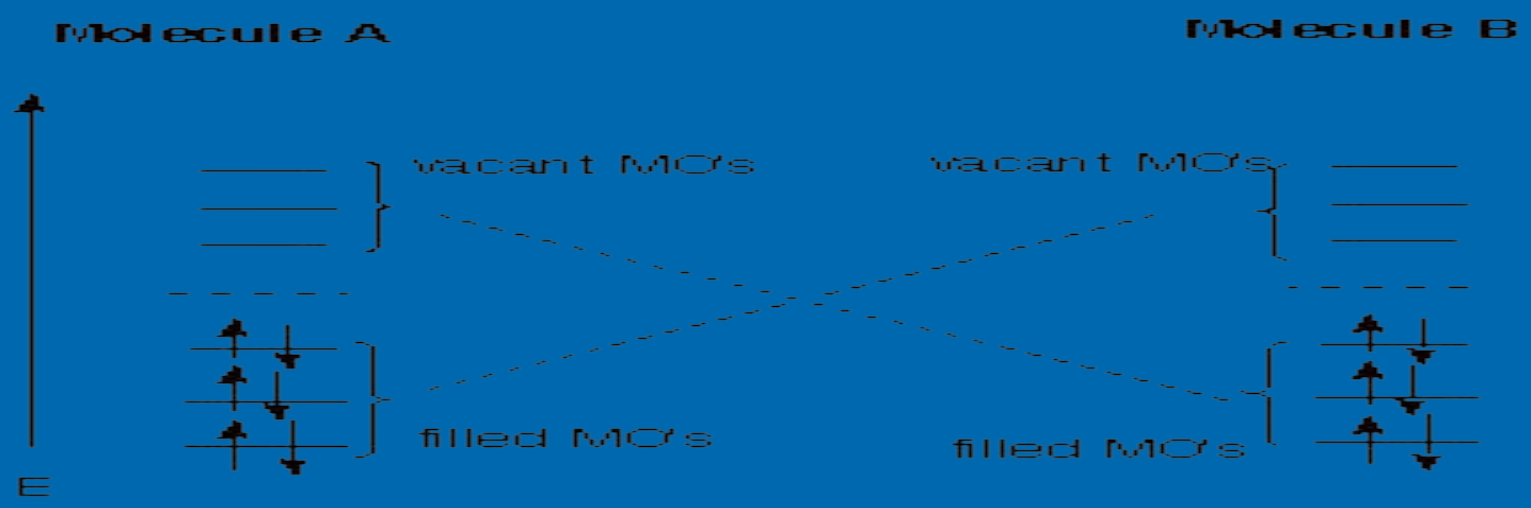
Изменение E (электронная)



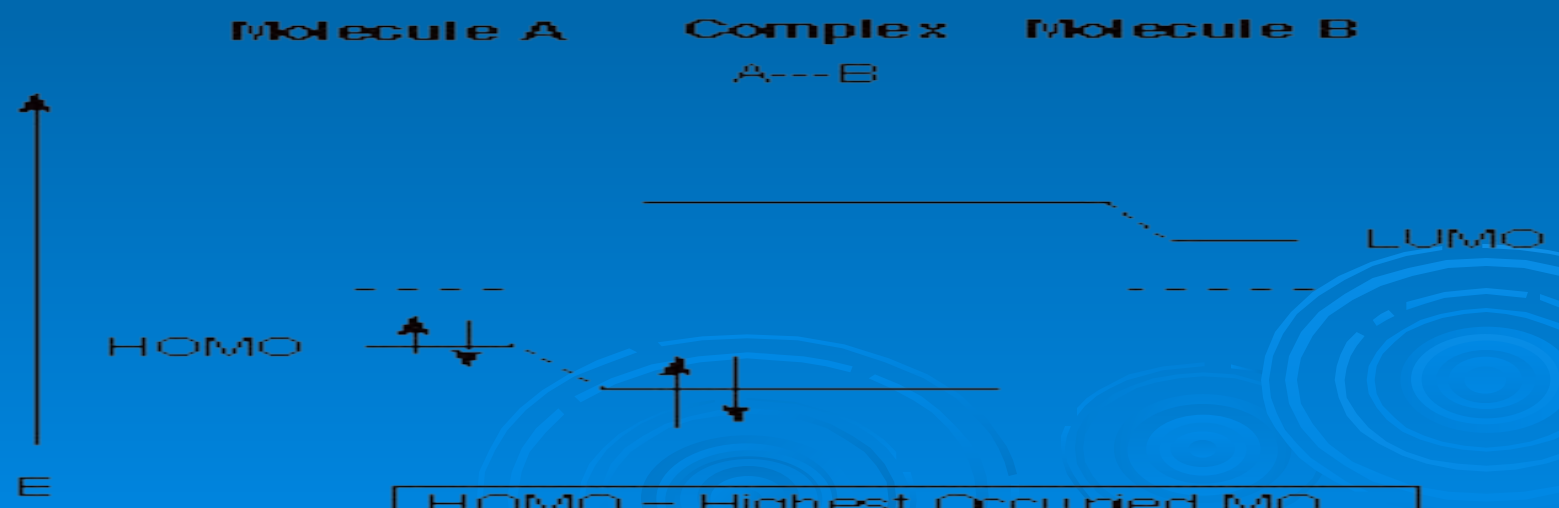
E = hv

Евращ = (v1 + ½) hv mit v = 0, 1, 2...

Еколеб = (v2 + ½) hv mit v = 0, 1, 2...



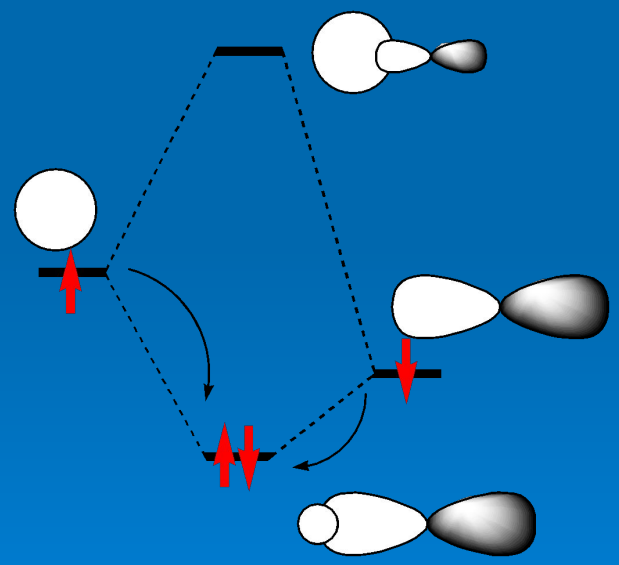
Filled MO's interact with **vacant MO's** to give complex MO's in which the stablized complex MO has two electrons; consider as one example, the interaction of the highest energy filled MO of **A** with the lowest energy vancant MO of **B:**



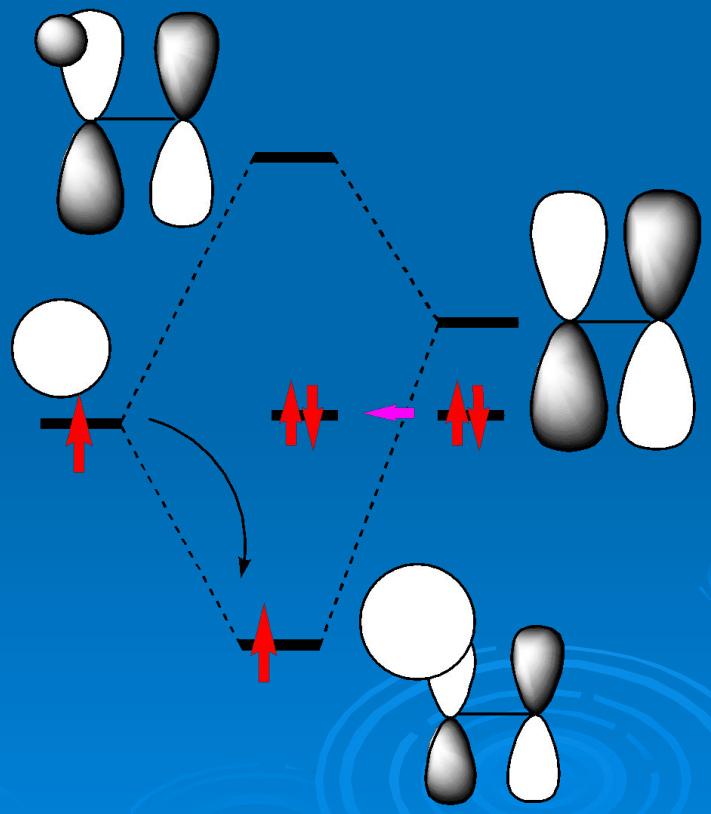
HOMO = Highest Occupied MO
LUMO = Lowest Unoccupied MO

некоторые примеры протекания реакций без изменения структуры МО

$H\cdot + Cl\cdot \Rightarrow HCl$



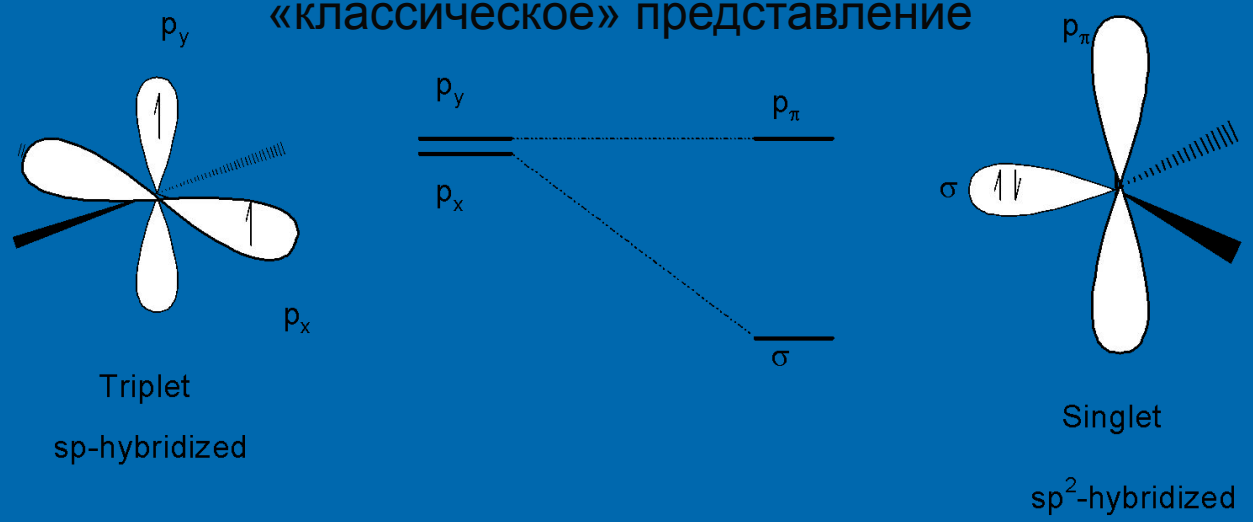
$H\cdot + CH_2{=}CH_2$



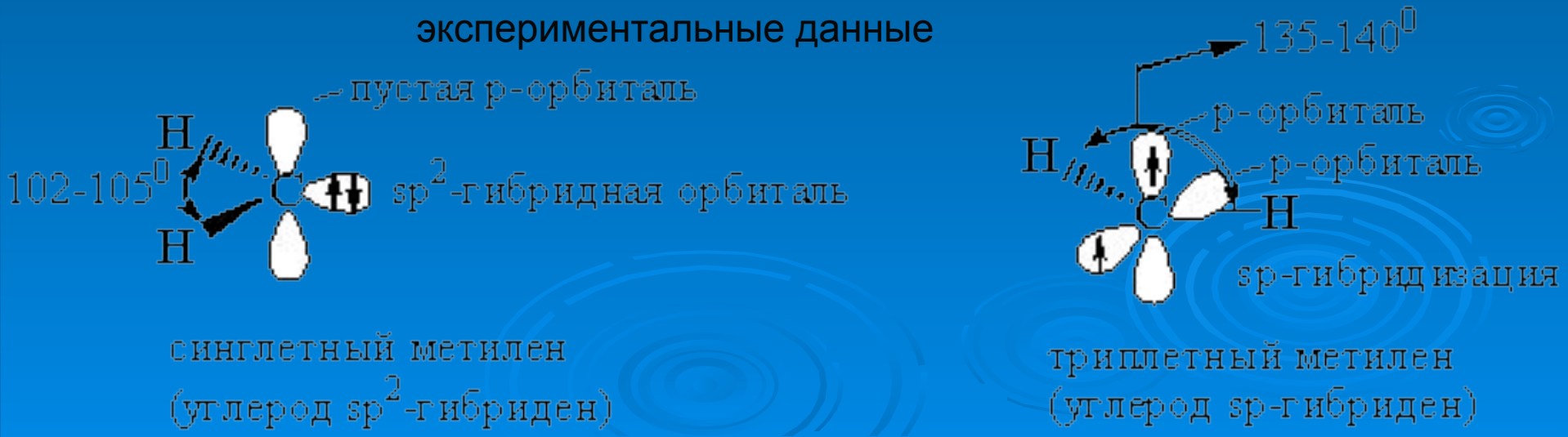
$\Rightarrow \{CH_3\text{-}CH_2\cdot\}^*$

Метилен (карбен) как реакционная частица

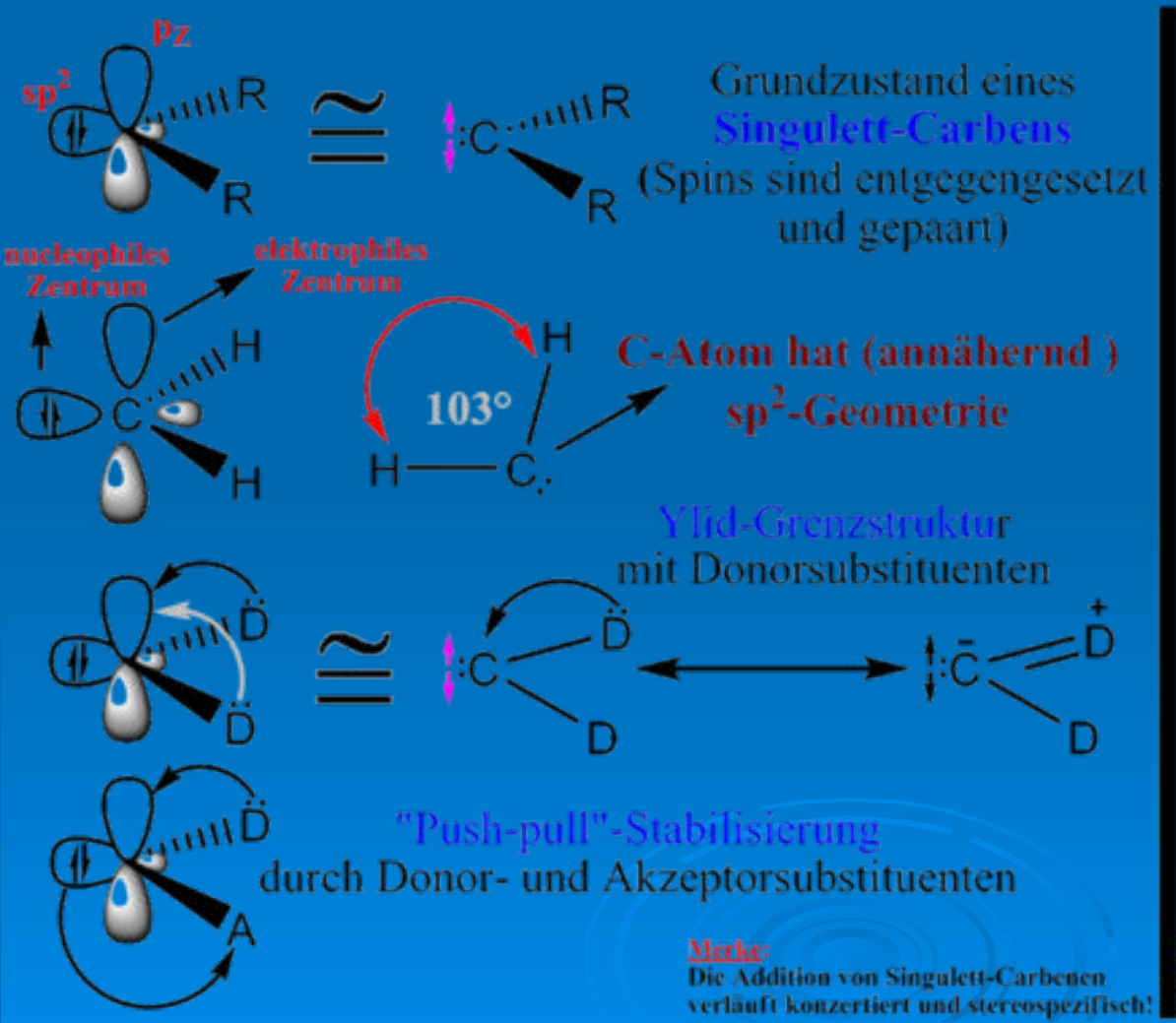
«классическое» представление

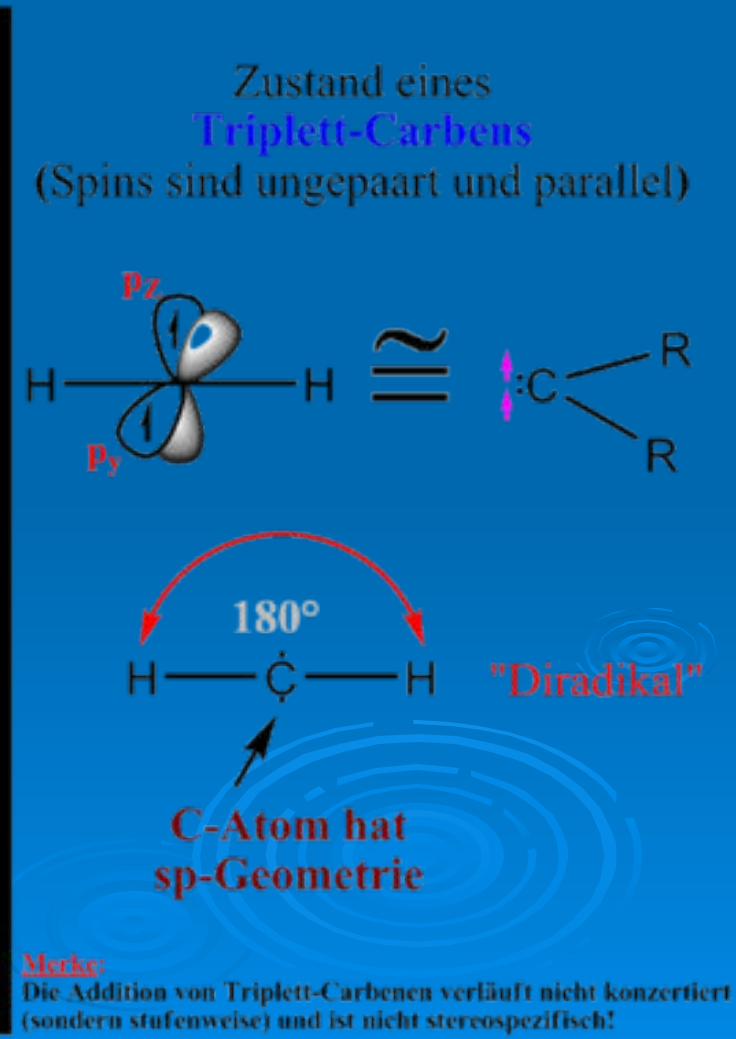


экспериментальные данные

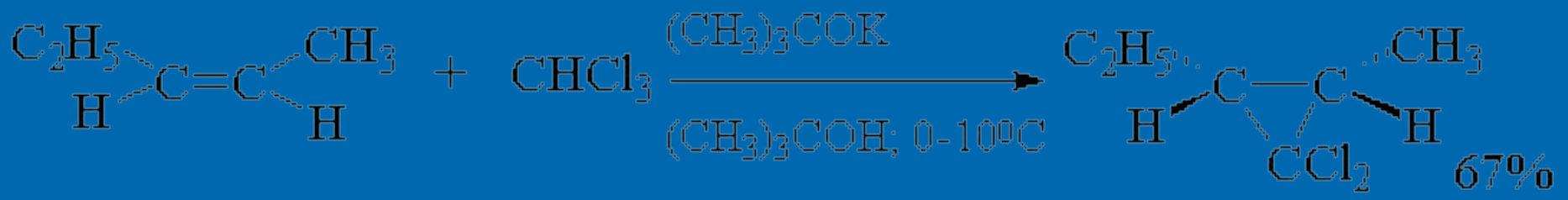


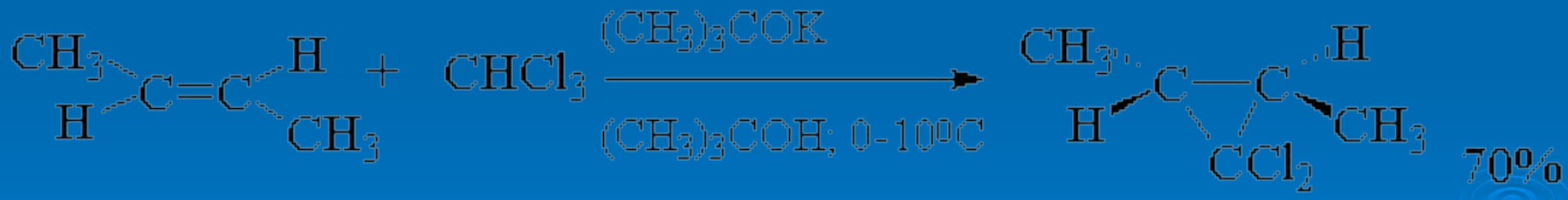
Метилен (карбен) как реакционная частица



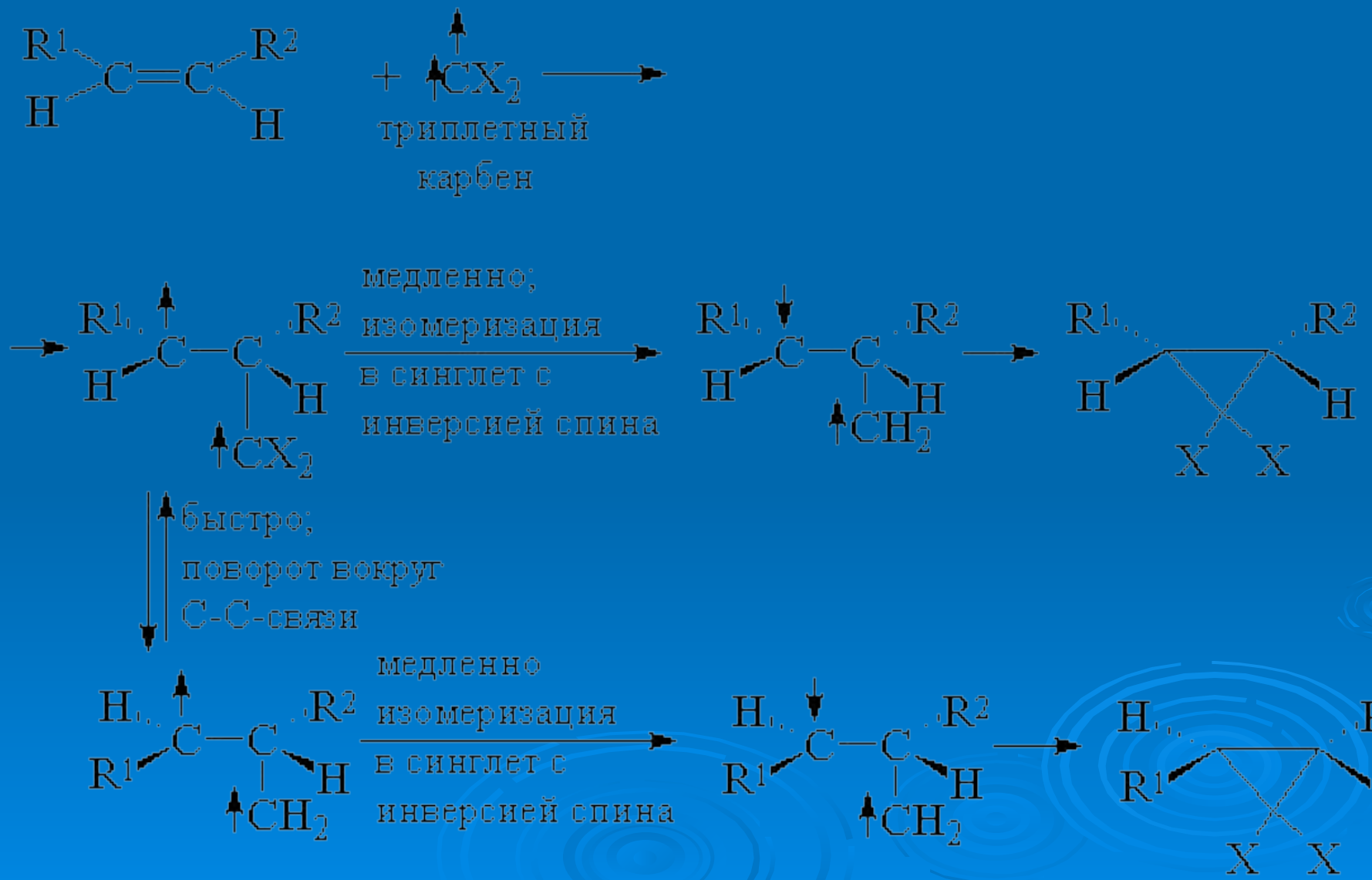


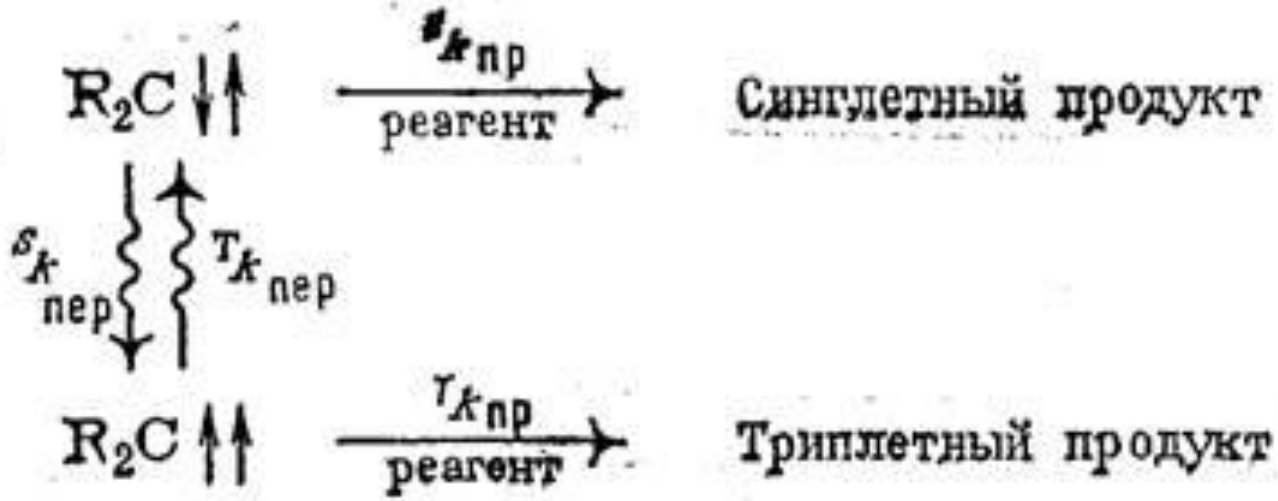
Присоединение синглетной формы карбена по двойной связи происходит, строго стереоспецифично.

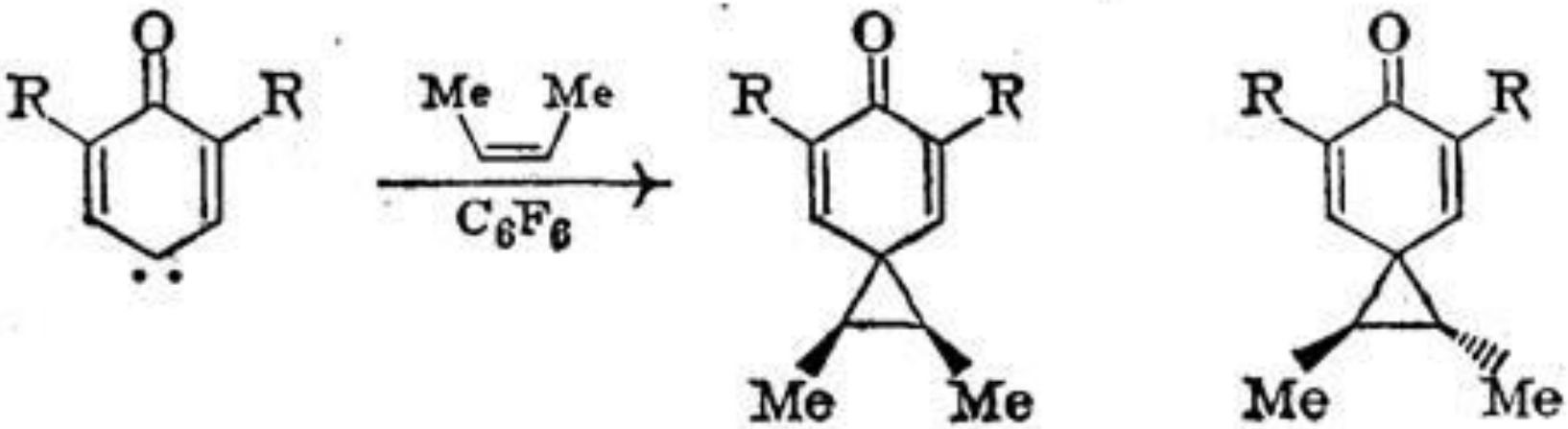




Присоединение триплетной формы карбена по двойной связи происходит, не стереоспецифично.

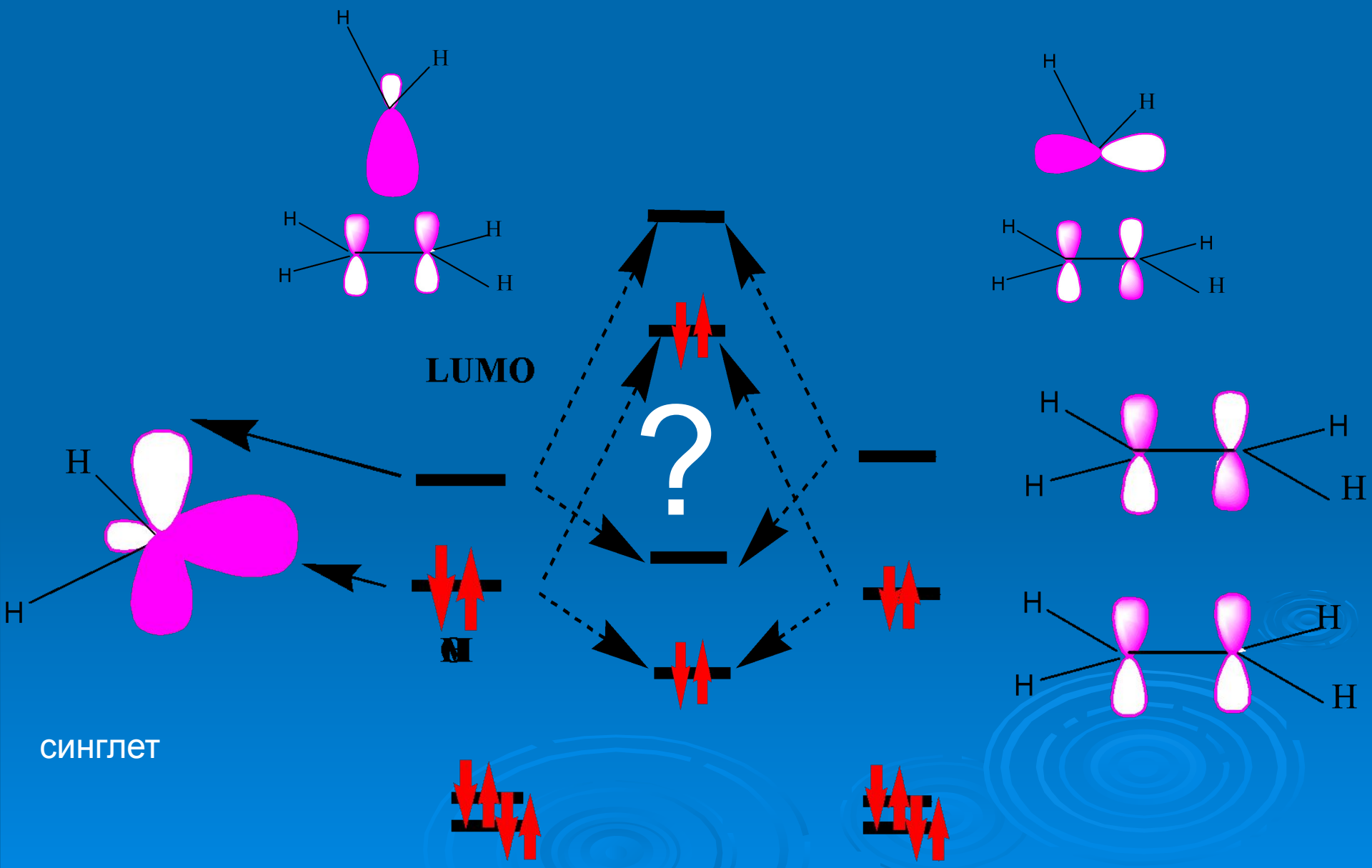




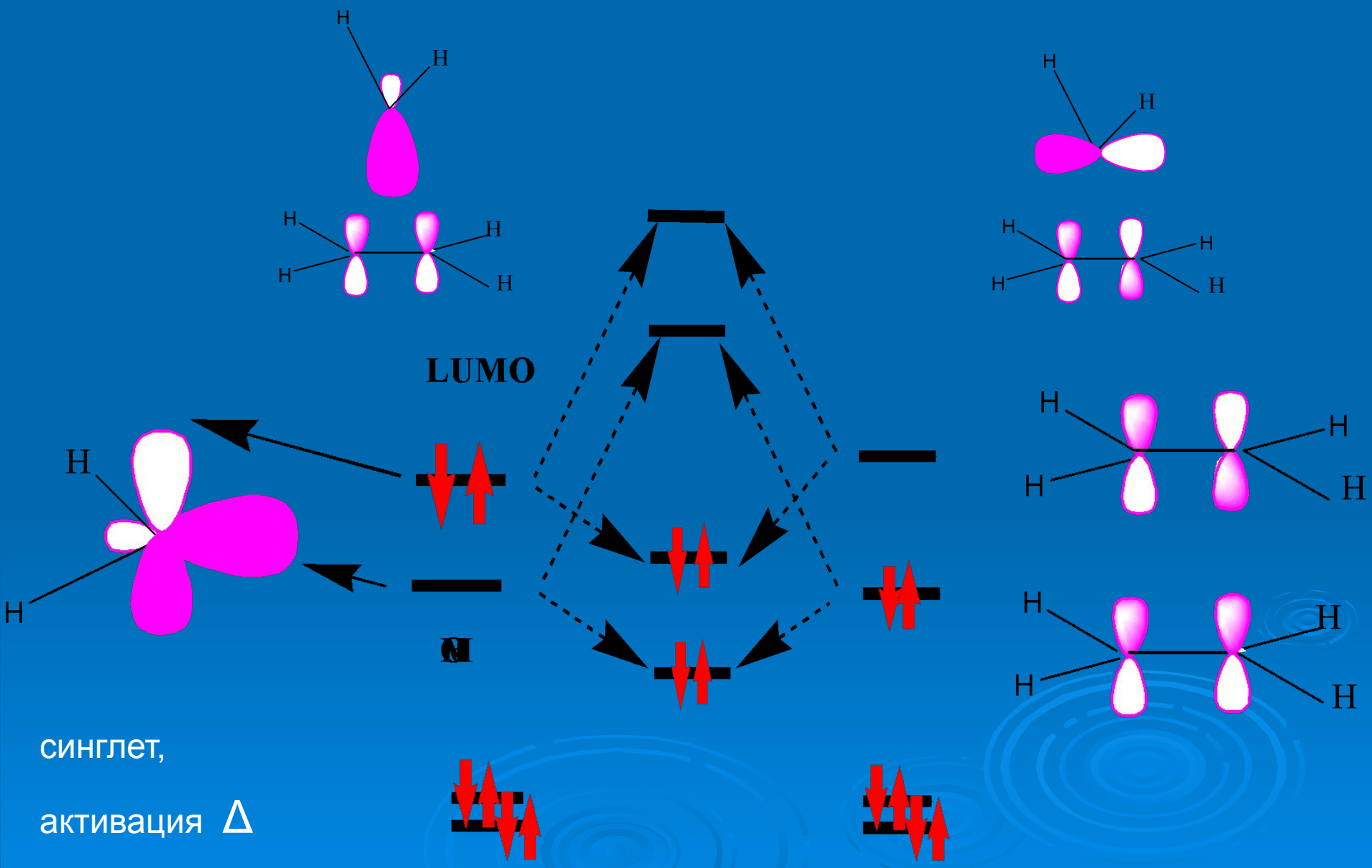


C_6F_6		
0%	95%	5%
90%	66%	33%

Взаимодействие этилена с метиленом (карбеном)



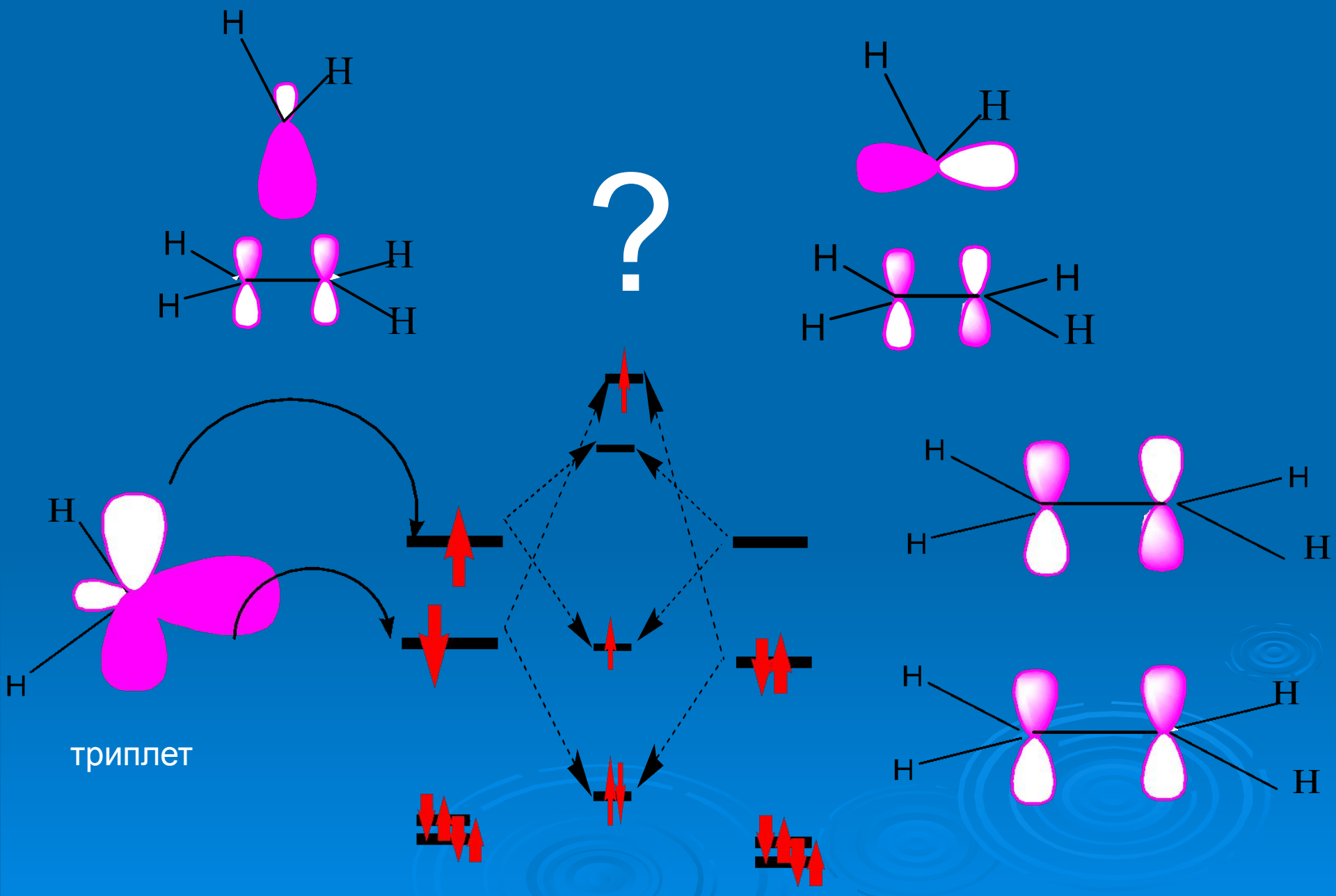
Взаимодействие этилена с метиленом (карбеном)

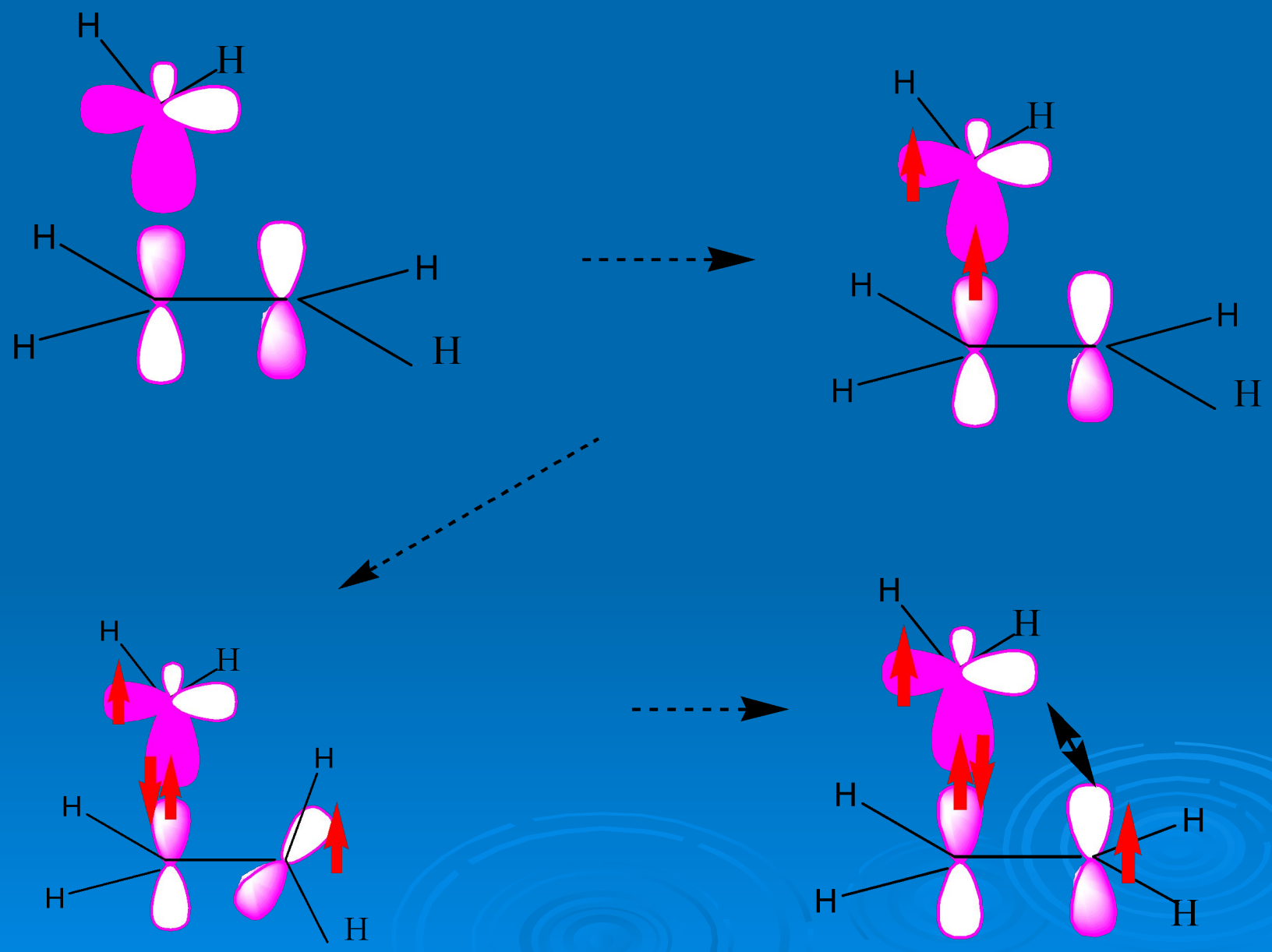


синглет,

активация Δ

Взаимодействие этилена с метиленом (карбеном)

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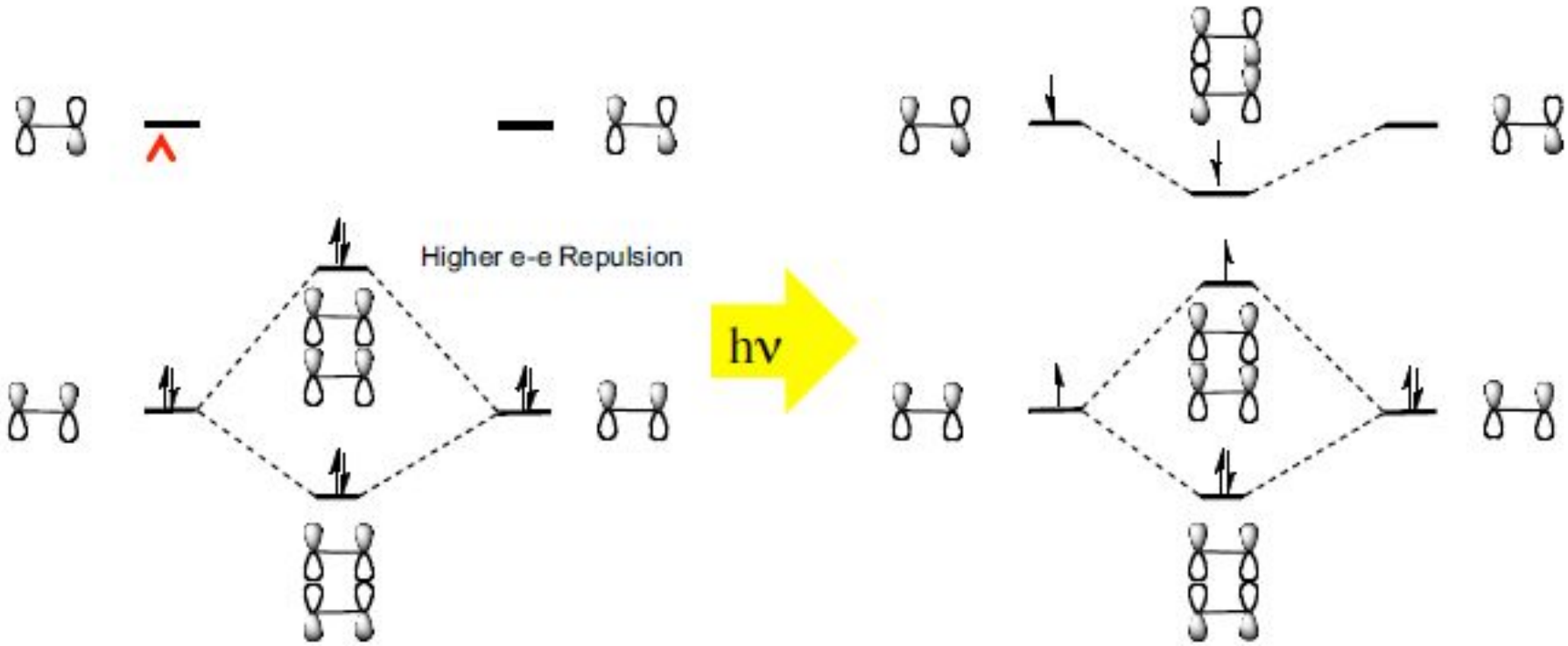
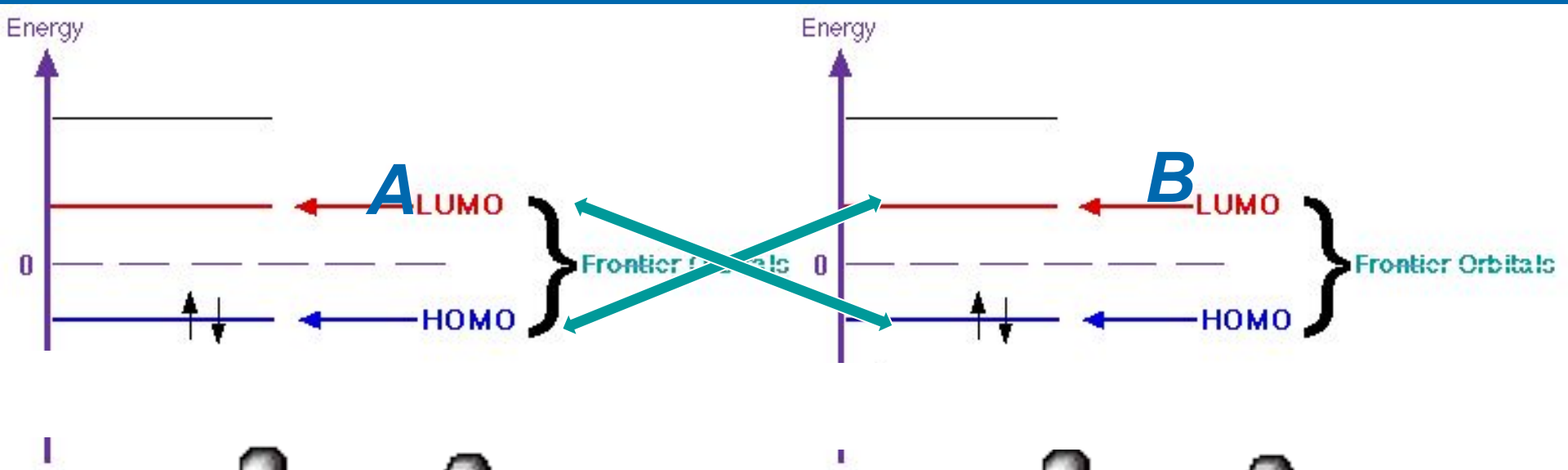
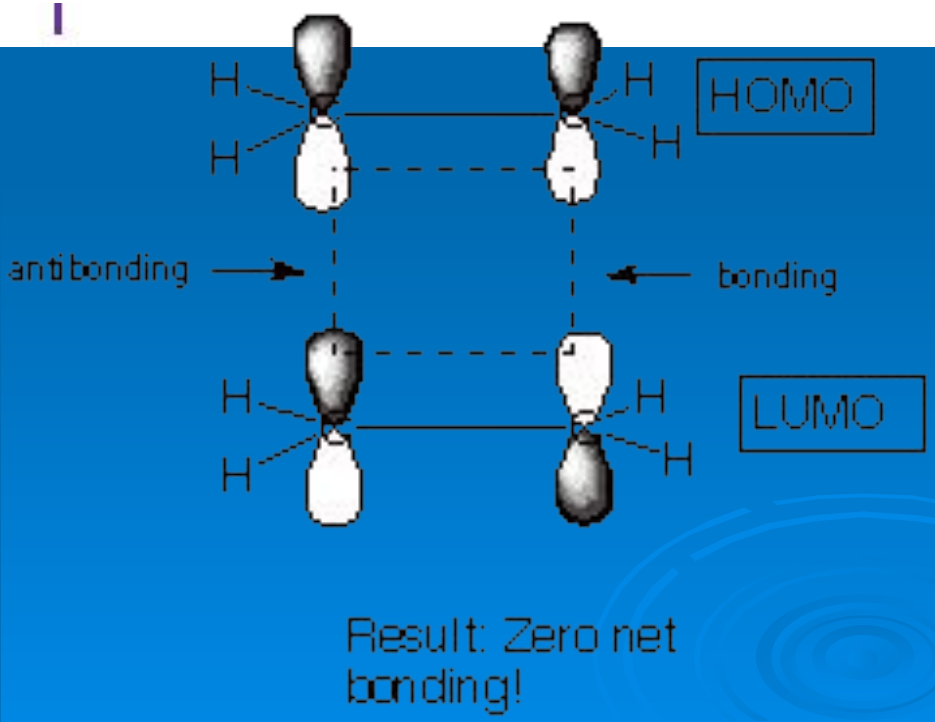
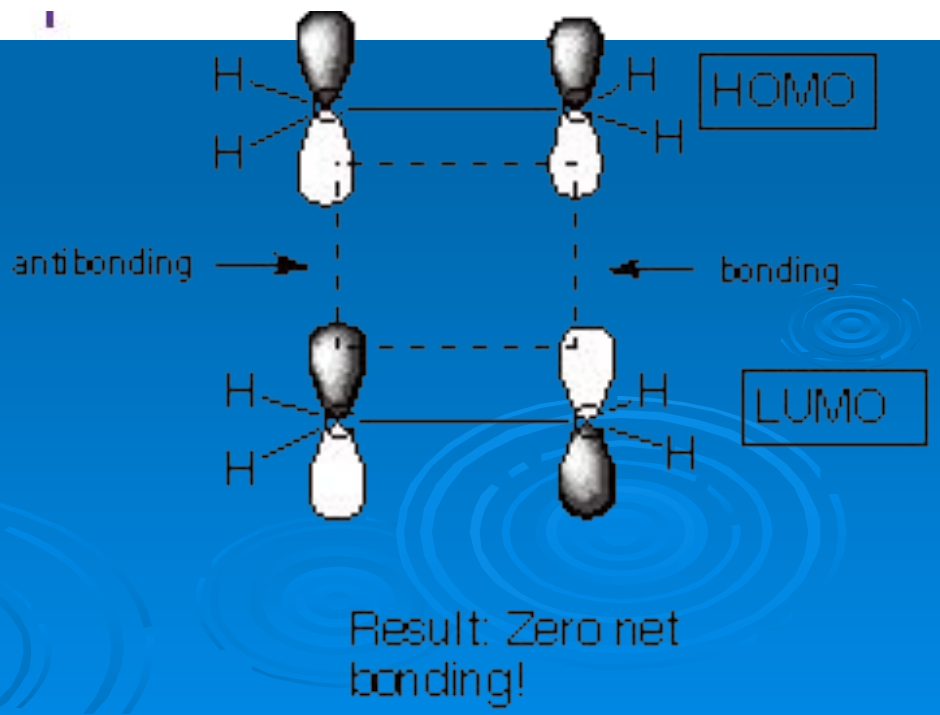
Dimerization of Ethylene



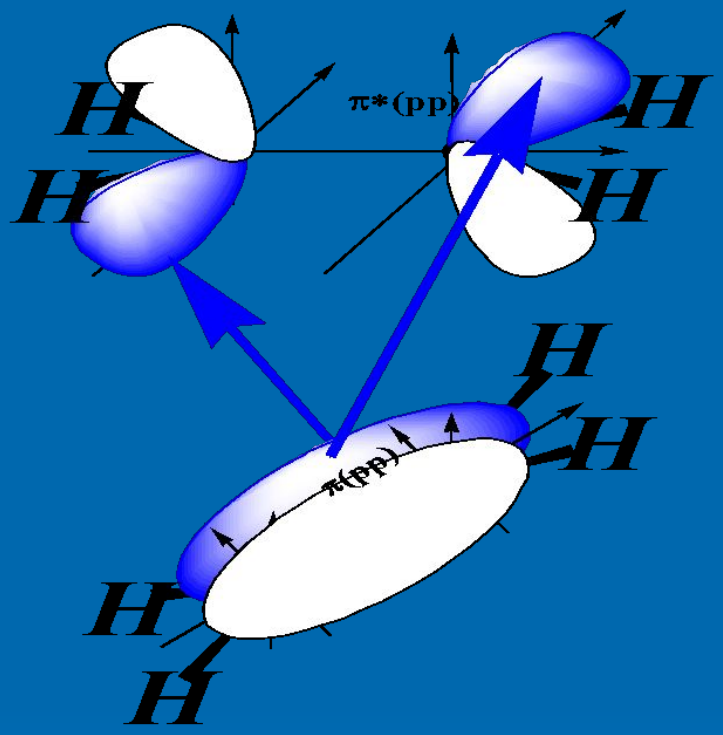
Димеризация этилена

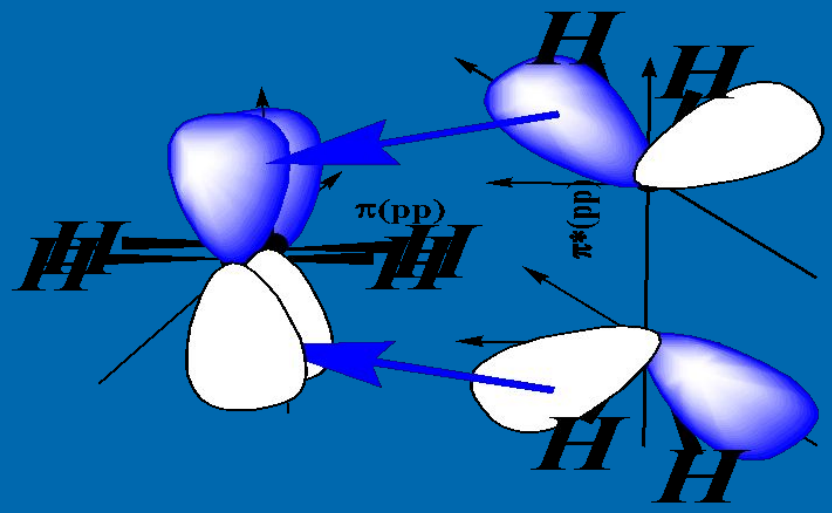




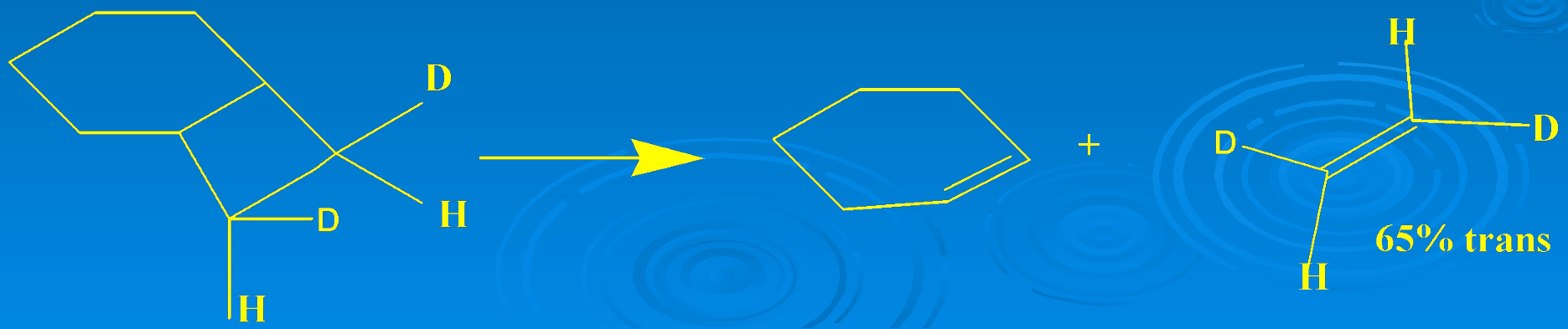


The rate of the thermal reaction of ethylene to form cyclobutane has been measured over the temperature range 723°–786°K and at pressures between 300 and 1300 torr.

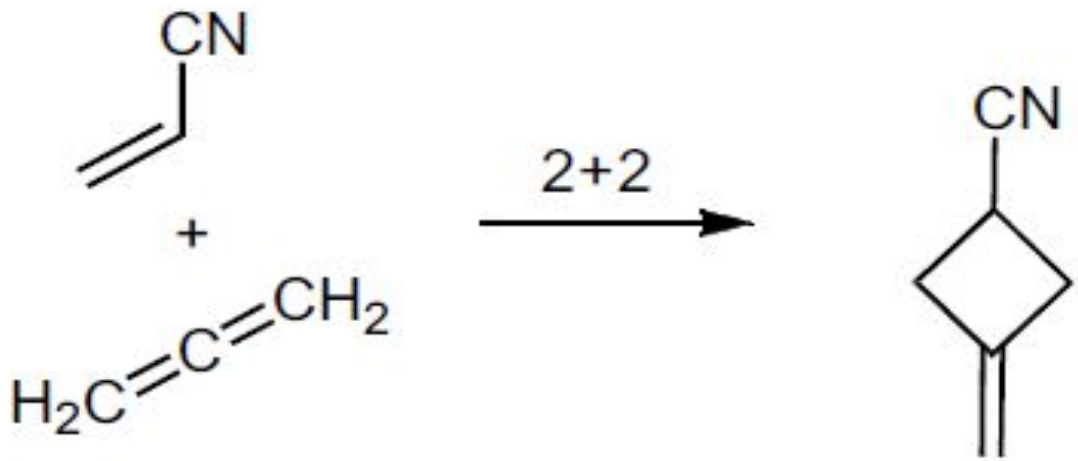




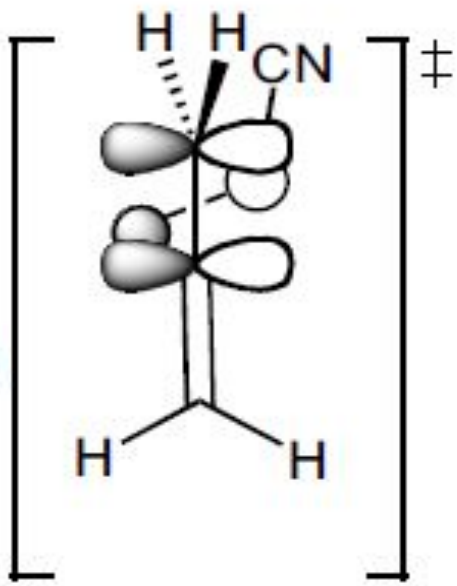
доказательство



Example of a Thermally Allowed 2+2

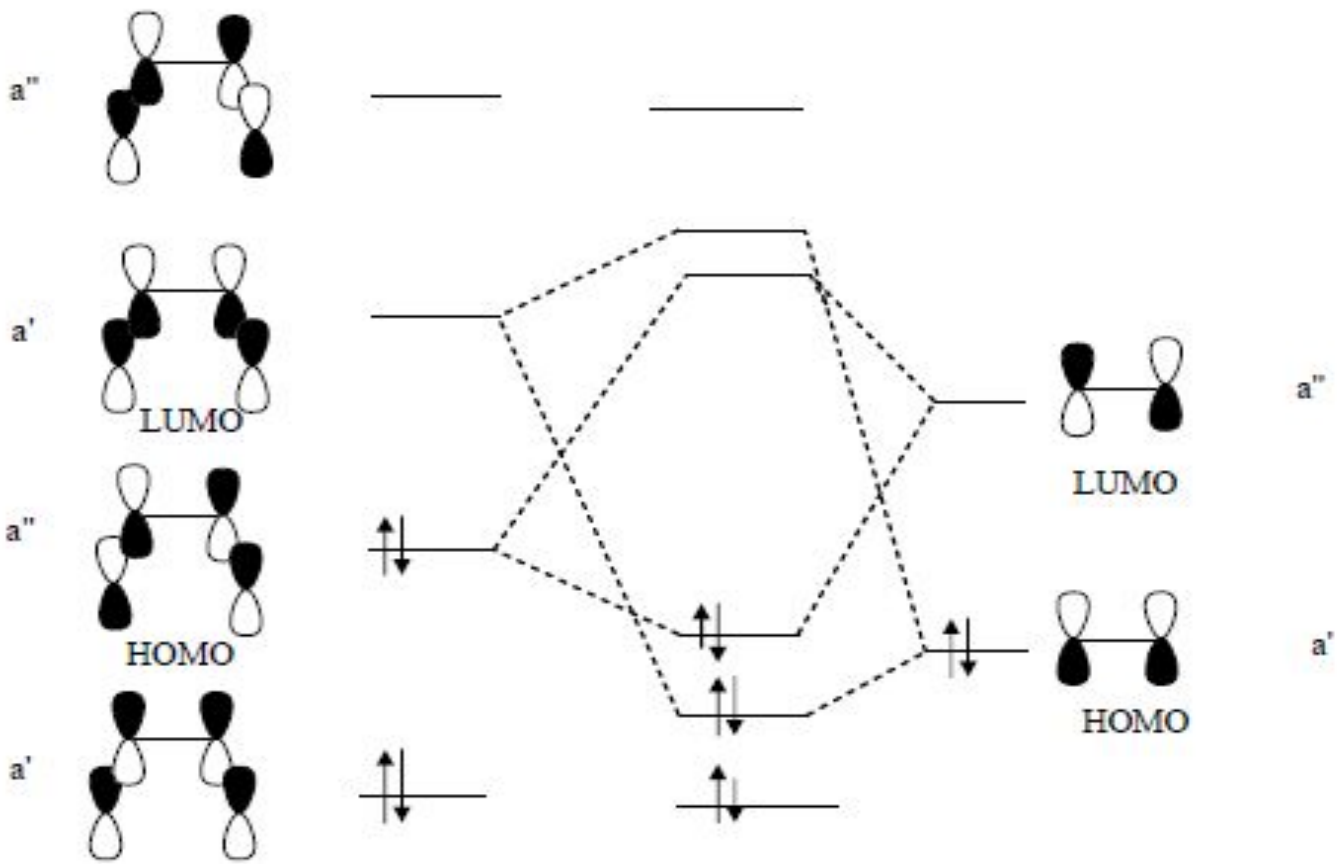


Allene HOMO
Acrylnitrile LUMO



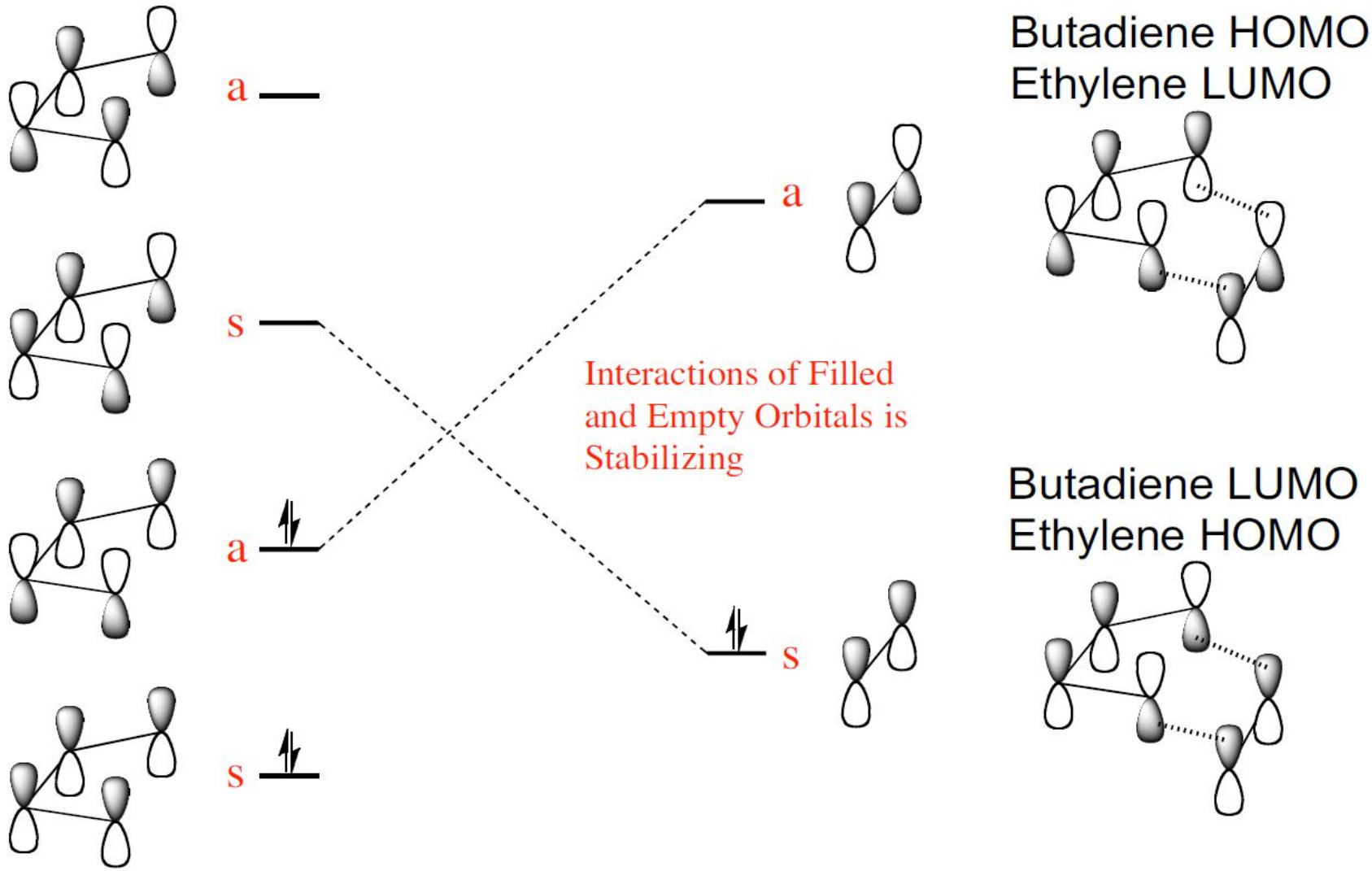
Bonding in the Tranisition State

Цикдоприсоедиенение этилена к бутадиену

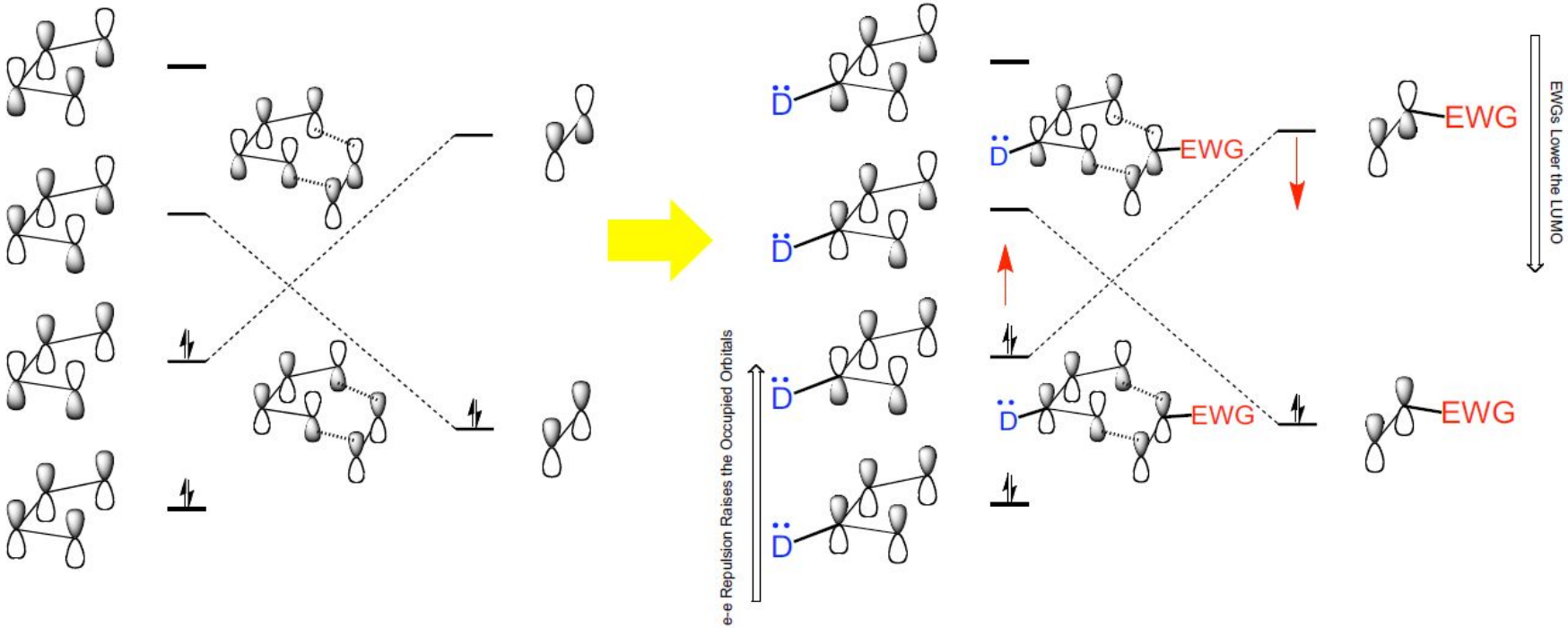


Reaction will proceed thermally.

Orbitals of the Same Symmetry Can Interact



Purturbation Theory:
Orbitals Closer in Energy, Interact Stronger



Electron withdrawing groups EWG

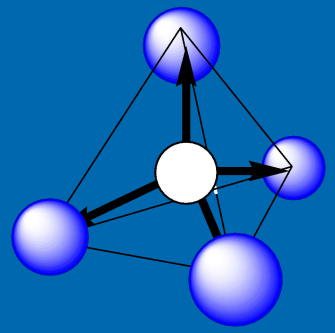
Однако,

реакционная способность молекул зависит не только от расположения МО, но и от их строения

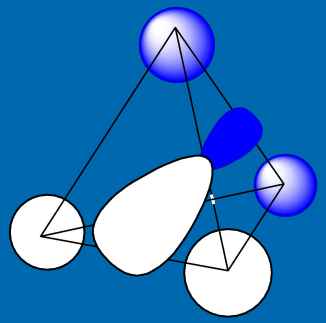
необходимо дополнительное возбуждение для перестройки МО

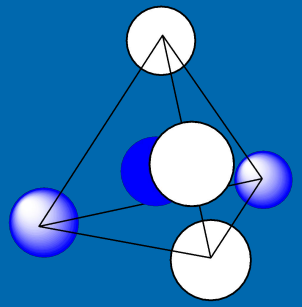
некоторые примеры протекания реакций с изменением структуры МО

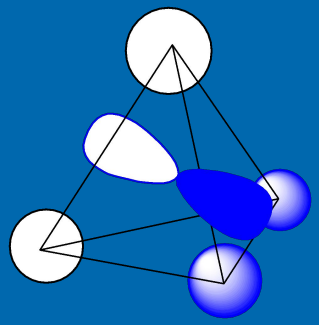
Реакционная способность метана



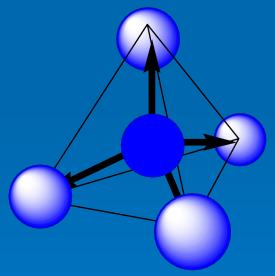
LUMO







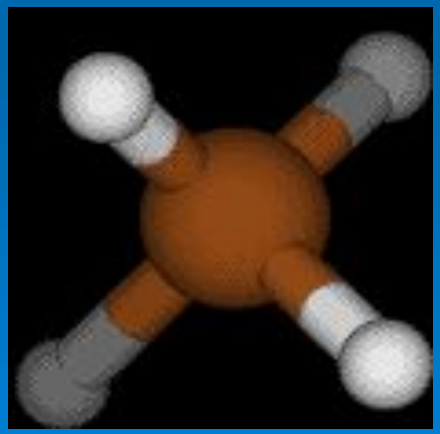
HOMO



«фронтальные» («граничные» орбитали слишком диффузны, поэтому перекрывание их с локализованными орбиталями реагента слишком мало, т.е. мал выигрыш в энергии при образовании «активированного» комплекса, молекуоа в основном состоянии инертна.

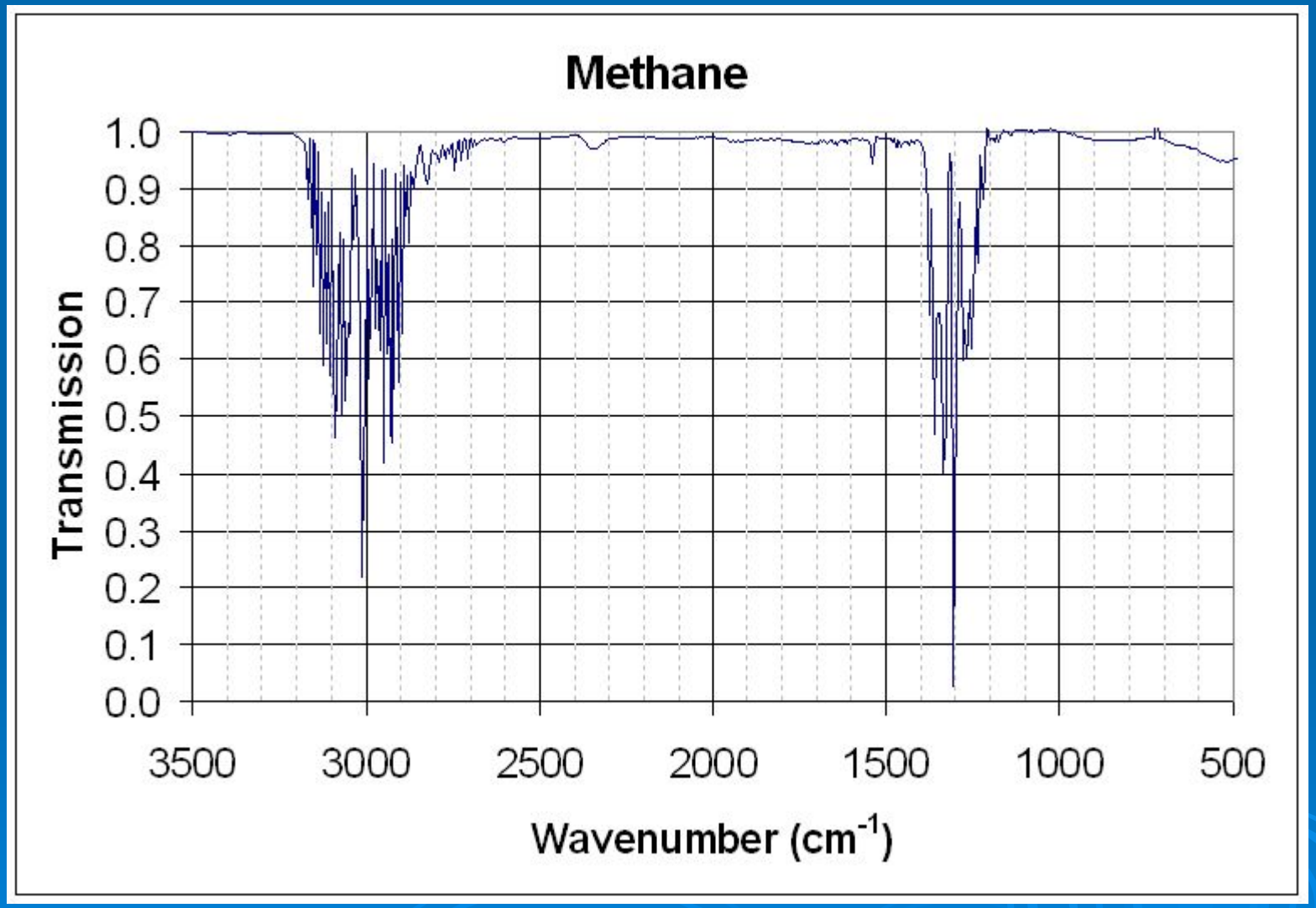
Реакционная способность метана

Вращение молекулы не может вызвать изменение геометрии орбиталей (в данном случае – изменение их диффузности

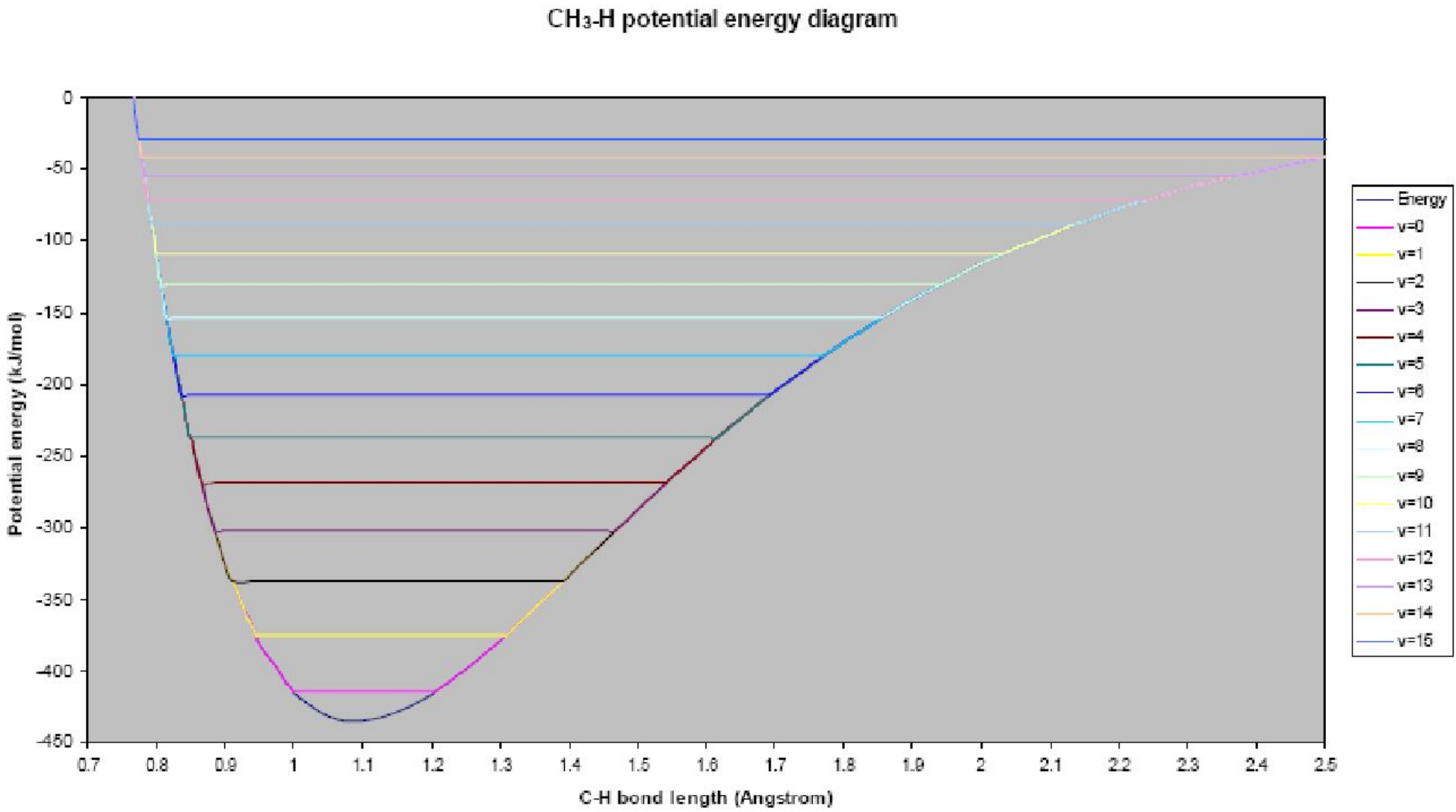


Однако колебания частей молекулы должно приводить к изменению строения орбиталей

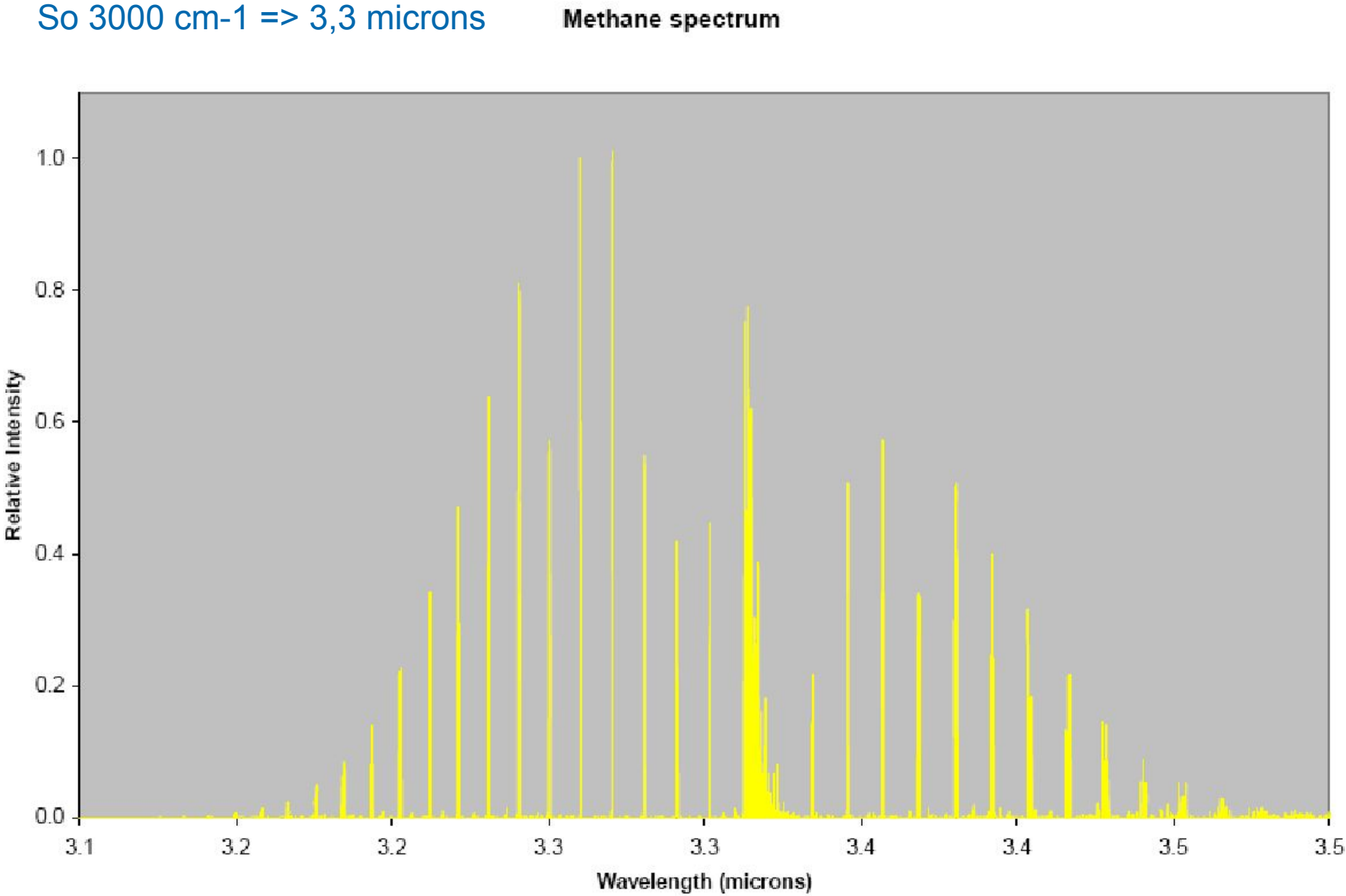
Энергию изменения геометрии орбиталей модно оценить по спектральным данным



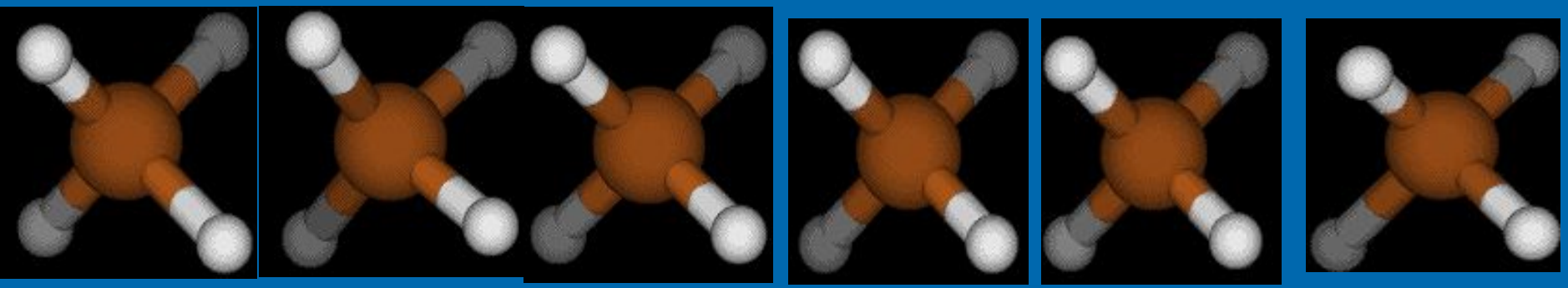
So 3000 cm-1 => 3,3 microns

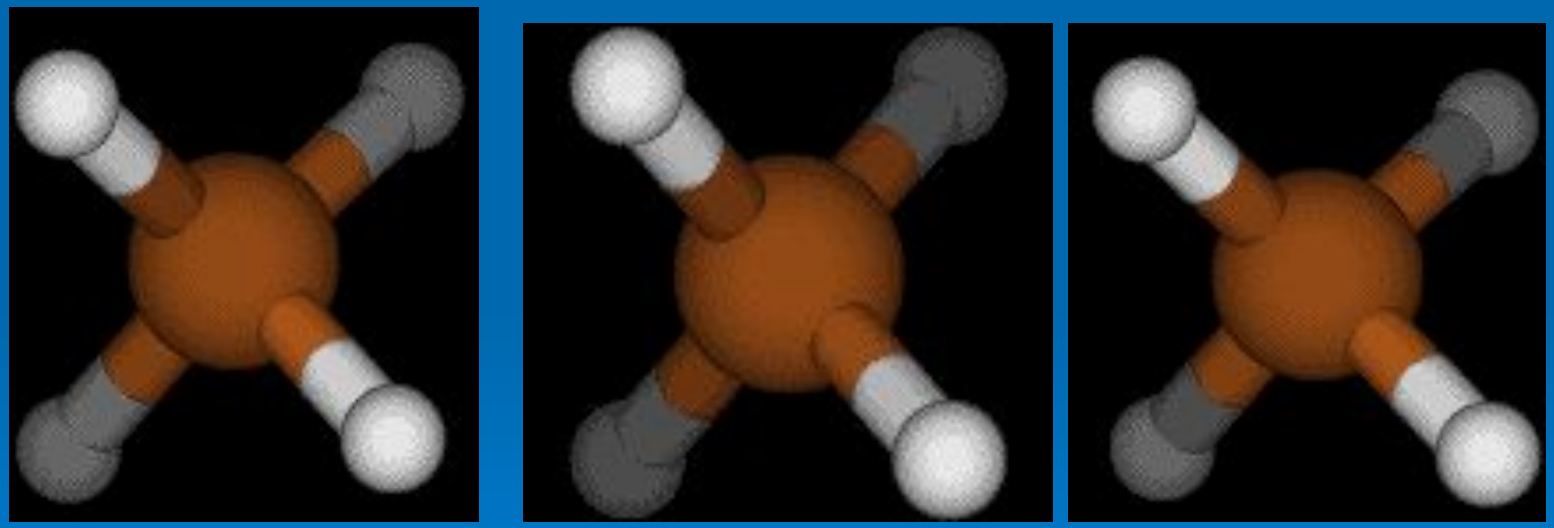

CH3-H potential energy diagram
Potential energy (kJ/mol)
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
2.2
2.3
2.4
2.5
C-H bond length (Angstrom)
Energy
v=0
v=1
v=2
v=3
v=4
v=5
v=6
v=7
v=8
v=9
v=10
v=11
v=12
v=13
v=14
v=15

So 3000 cm-1 => 3,3 microns

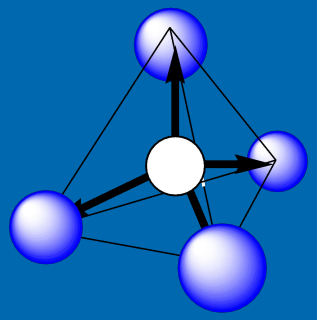


Основные колебания в метане

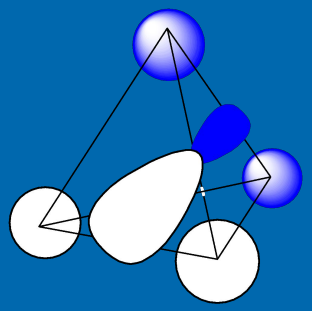


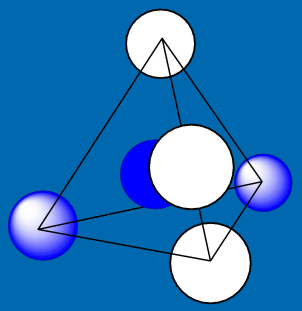


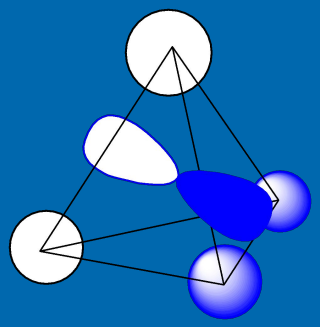
Образование треугольной пирамиды



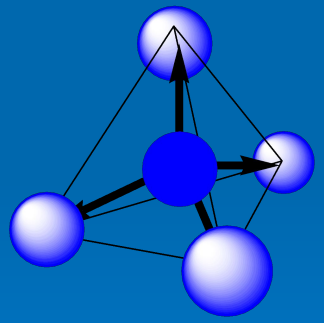
LUMO

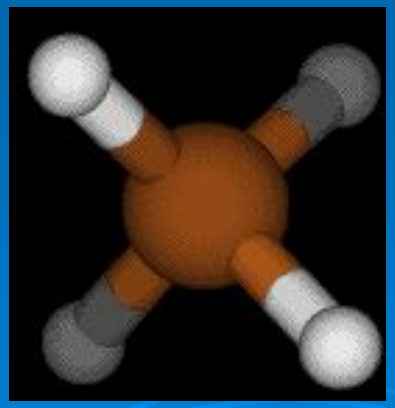


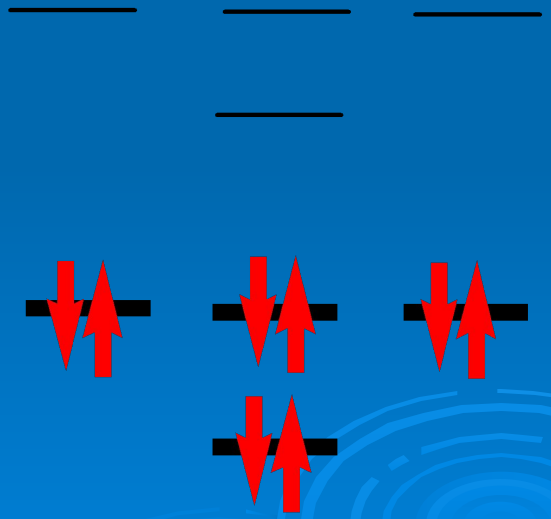




HOMO

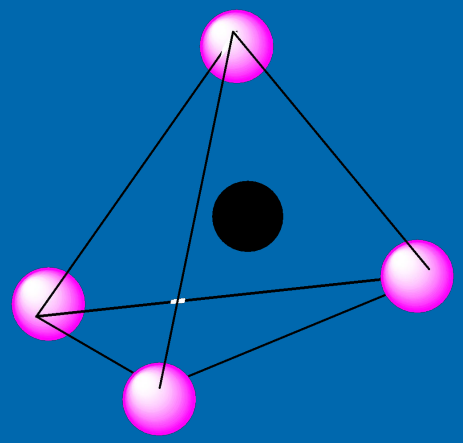


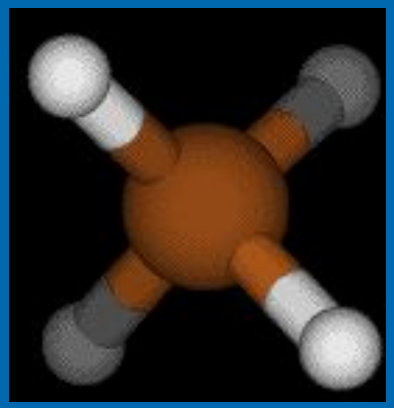


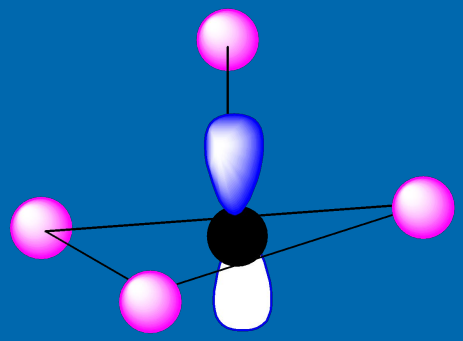


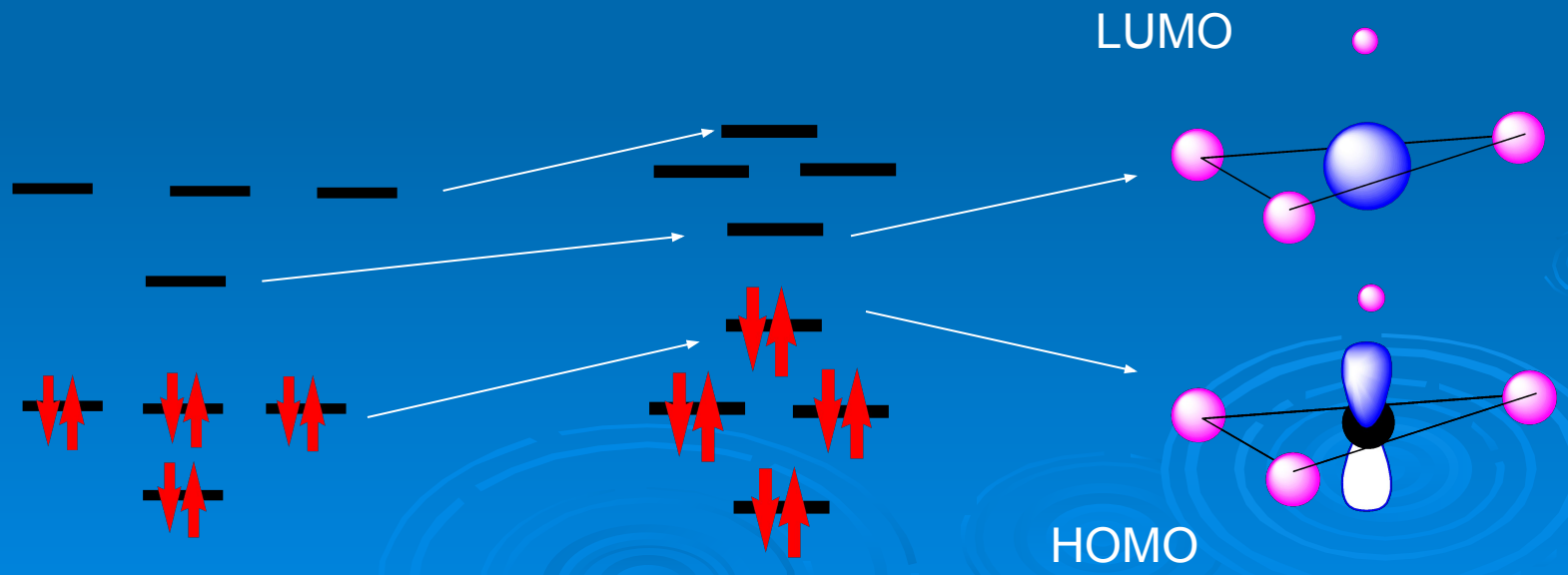
Что происходит с орбиталями?

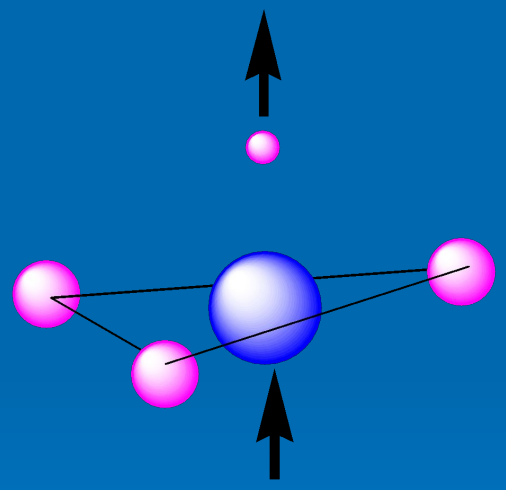
Образование треугольной пирамиды

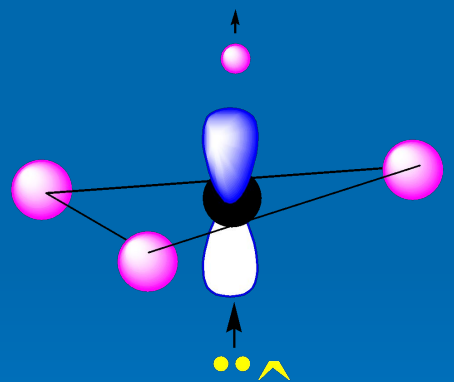




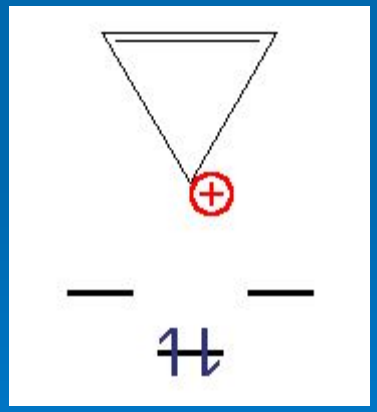


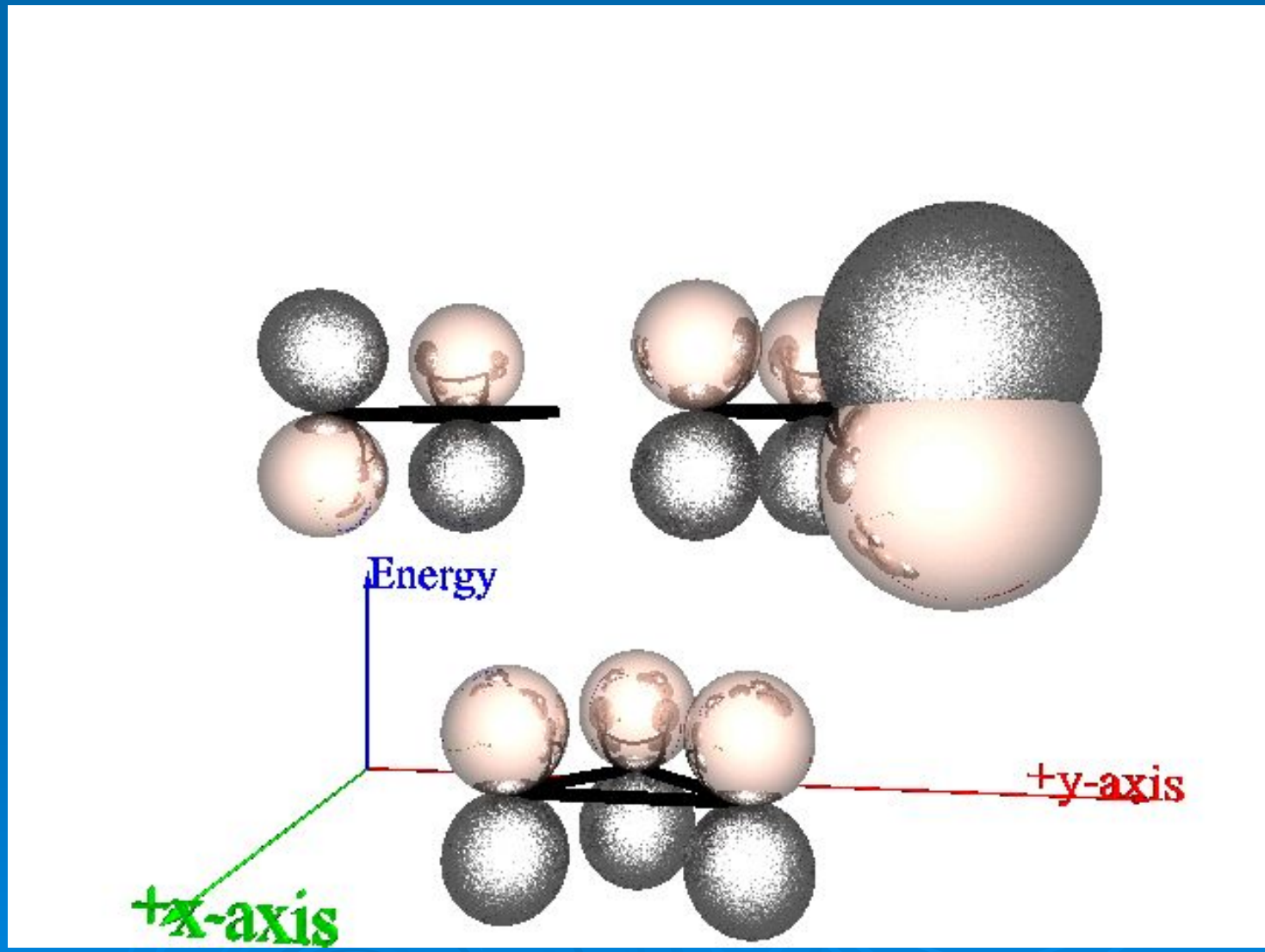


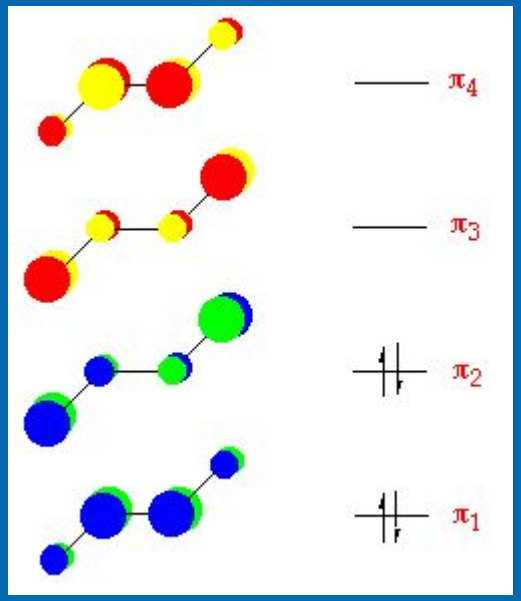

Nu

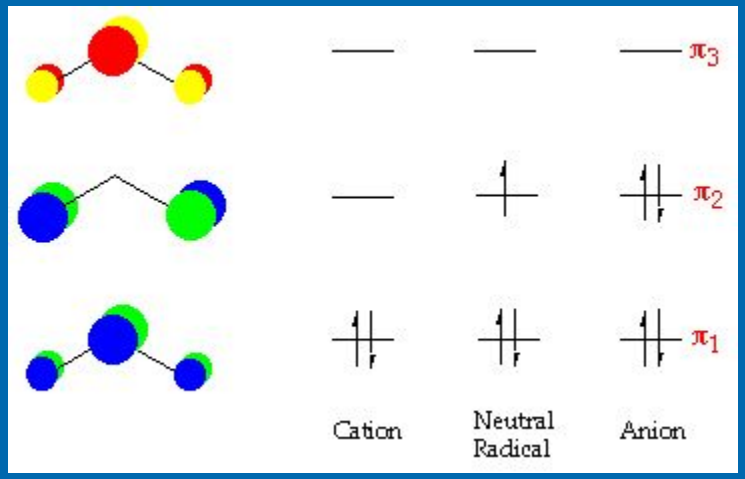

Ê

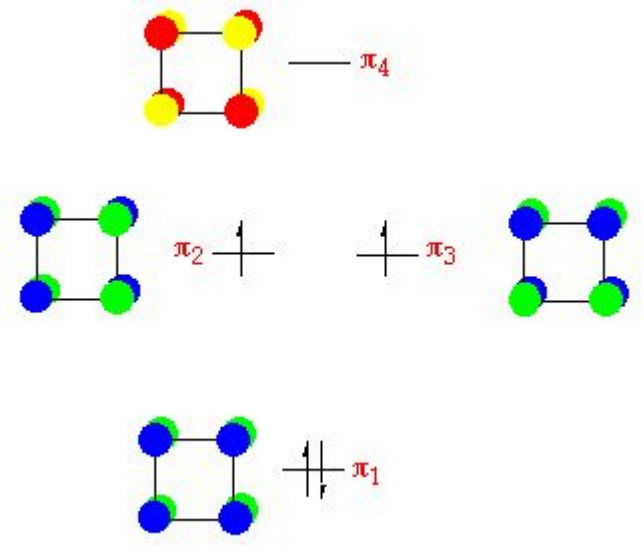
Некоторые реакционные орбитали органических молекул

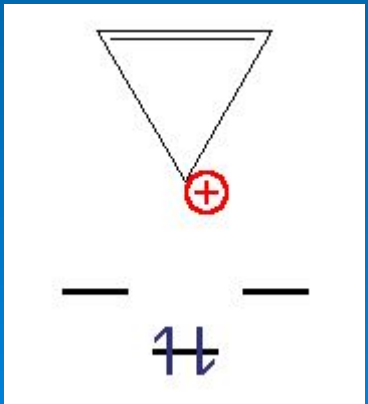


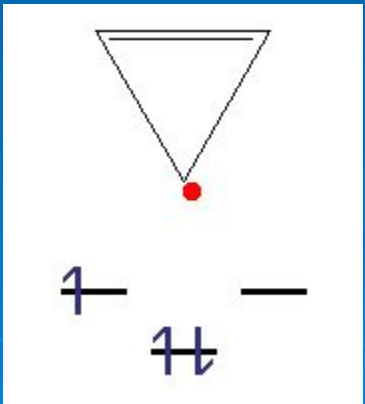


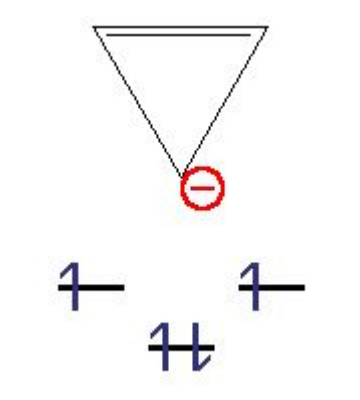

π4
π3
π2
π1

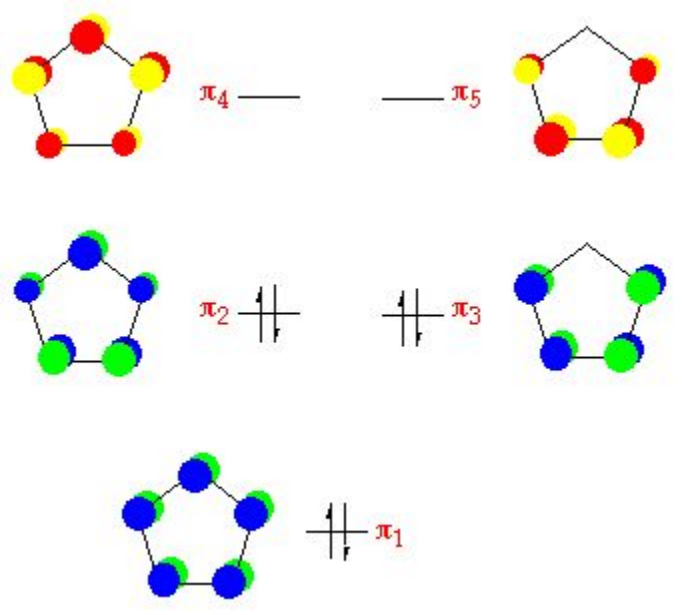

π3
π2
π1
Cation
Neutral Radical
Anion

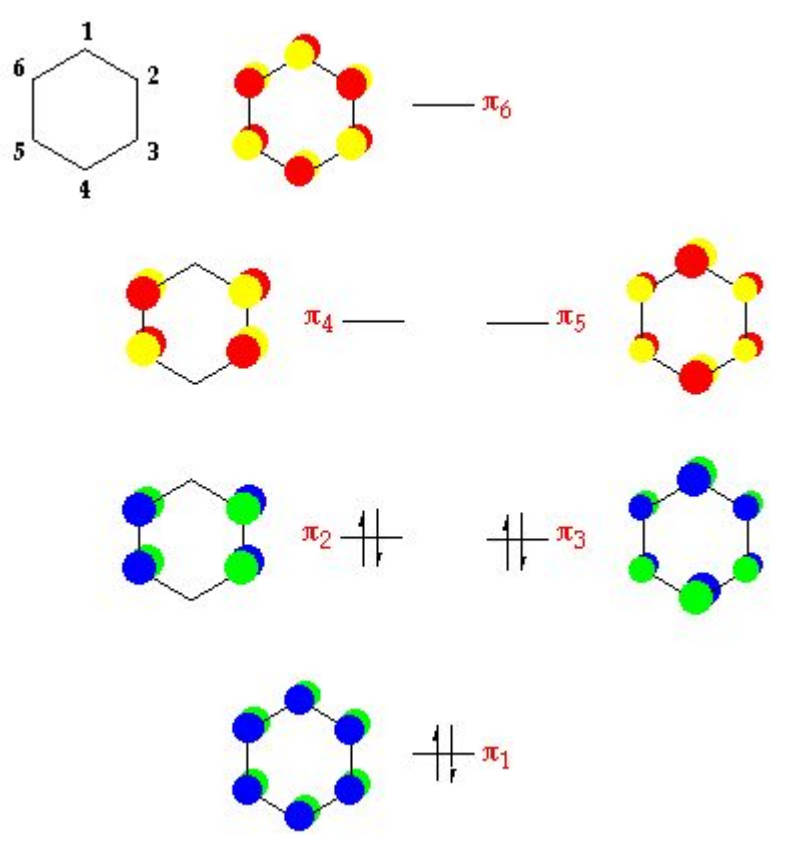

π4
π2
π3
π1








π4
π5
π2
π3
π1


1
2
3
4
5
6
π6
π4
π5
π2
π3
π1

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