

# Лекция 9

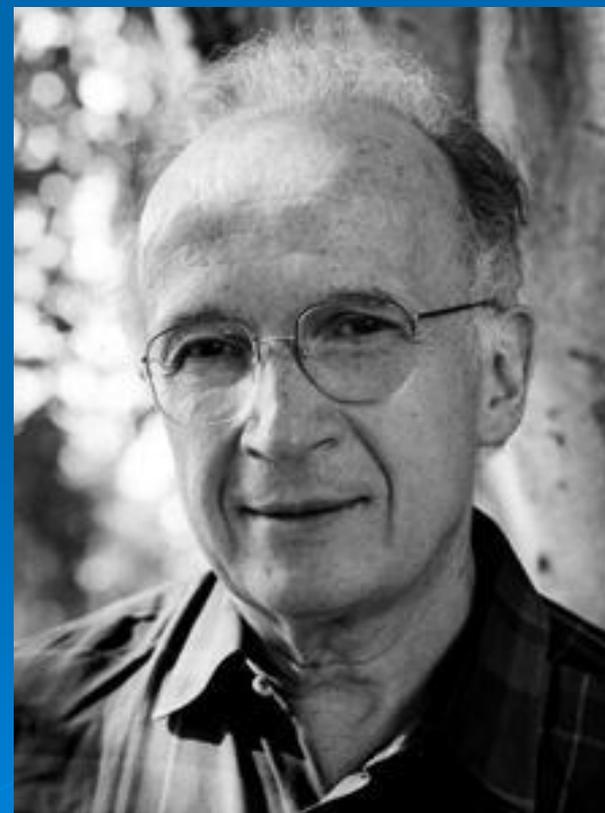
## Реакционная способность химических соединений



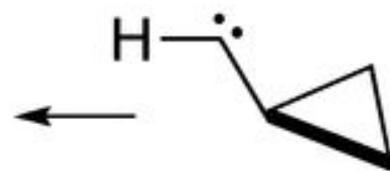
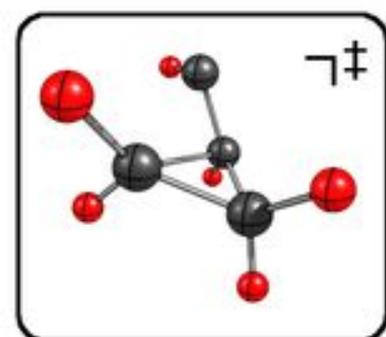
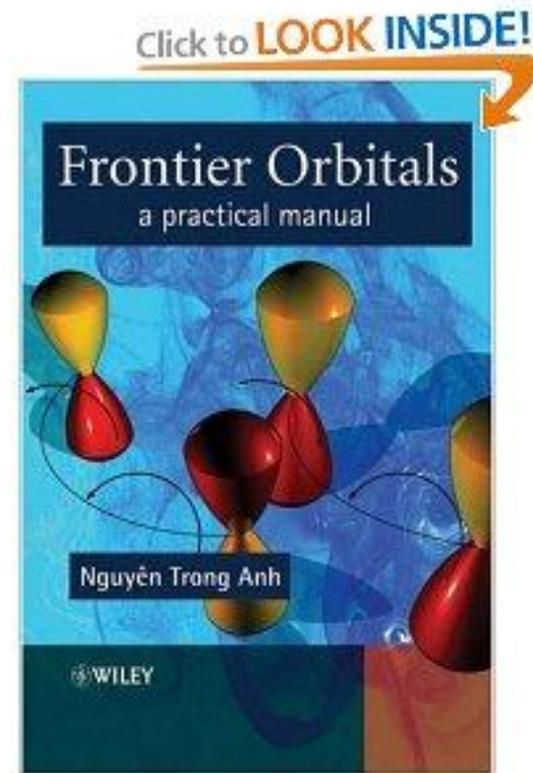
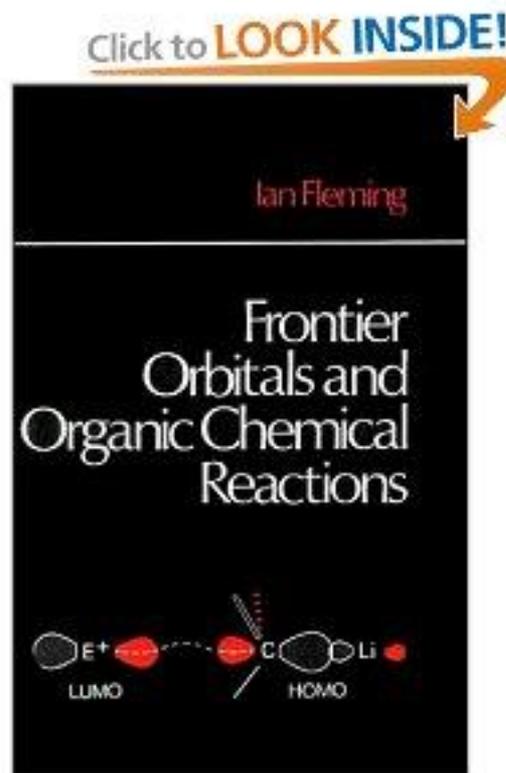
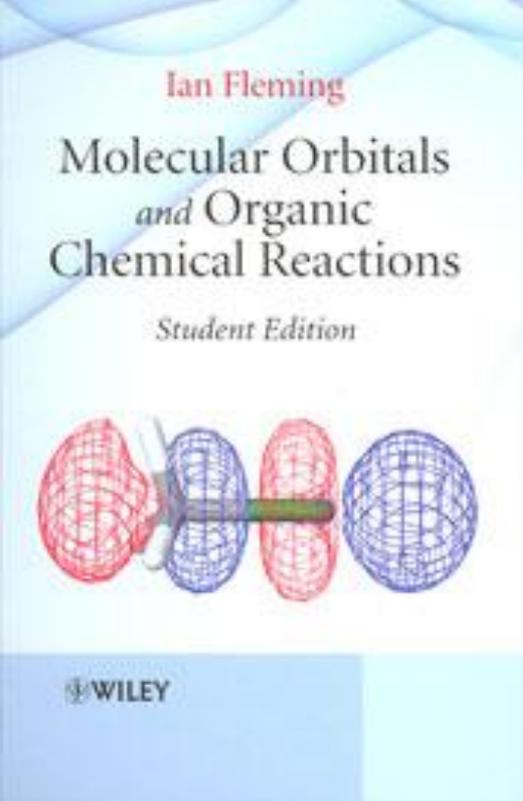
**Sir Christopher (Kelk)  
Ingold 1893-1970**



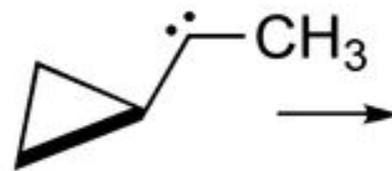
**Kenichi Fukui**



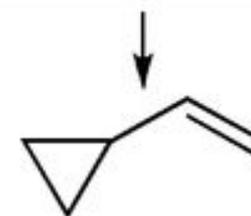
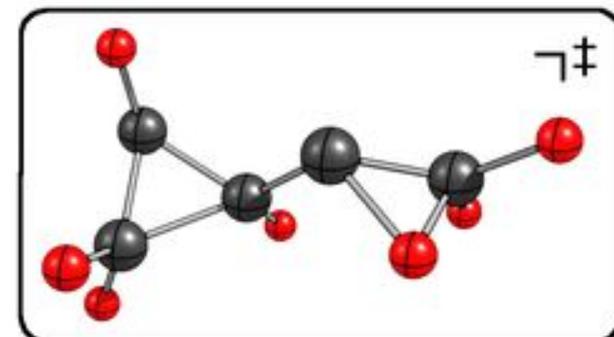
**Roald Hoffmann**



**C-tunneling**

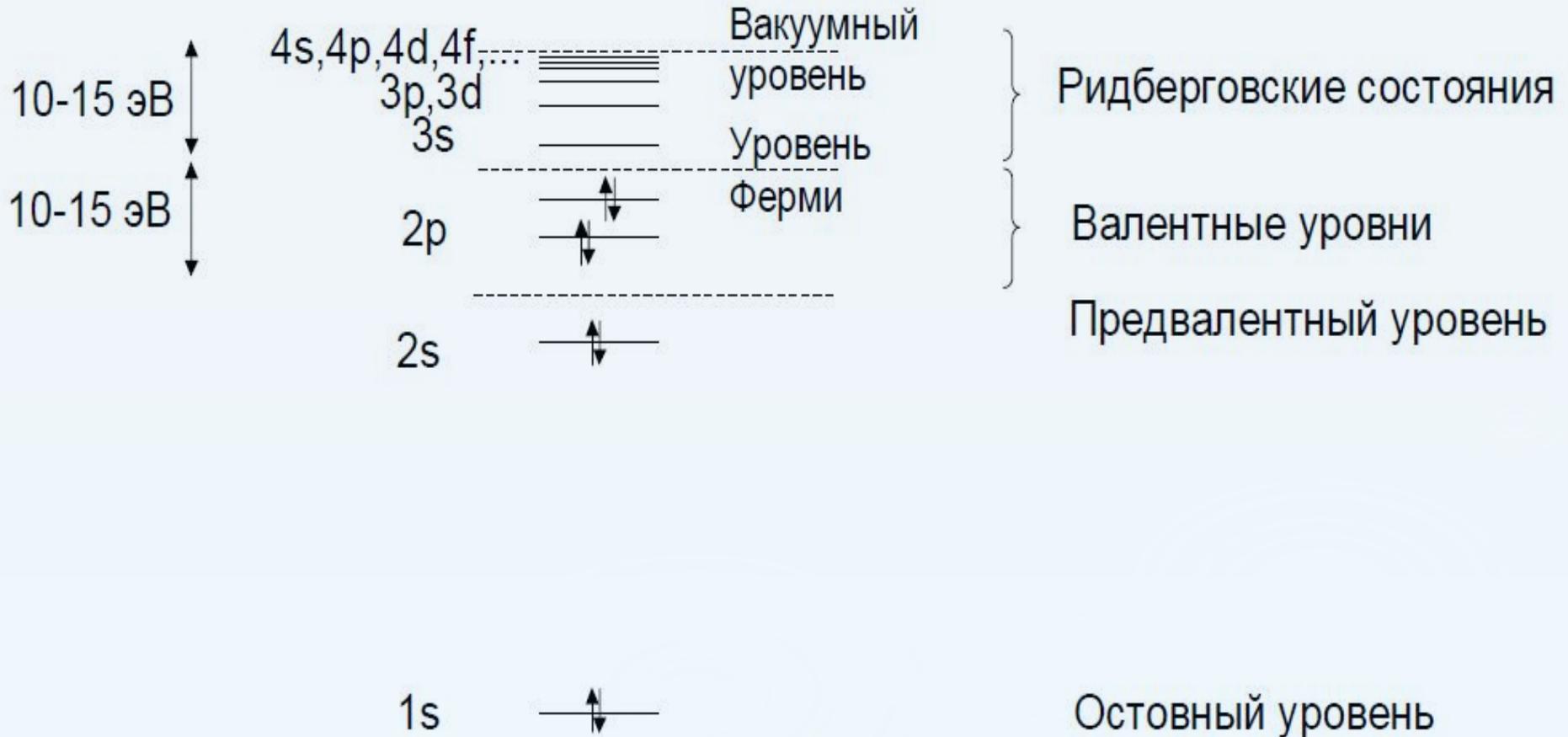


**H-tunneling**

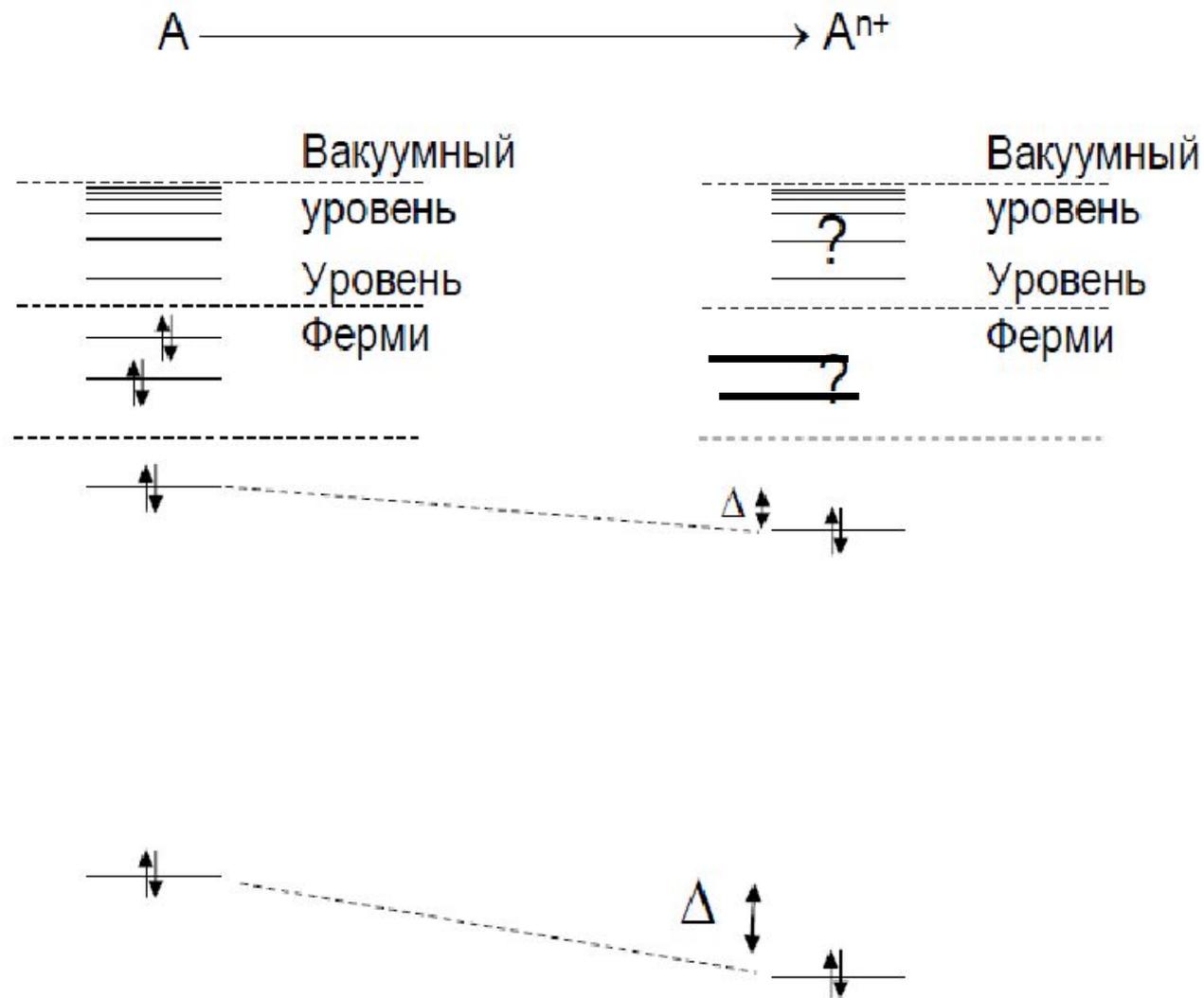


# Электронные уровни атома

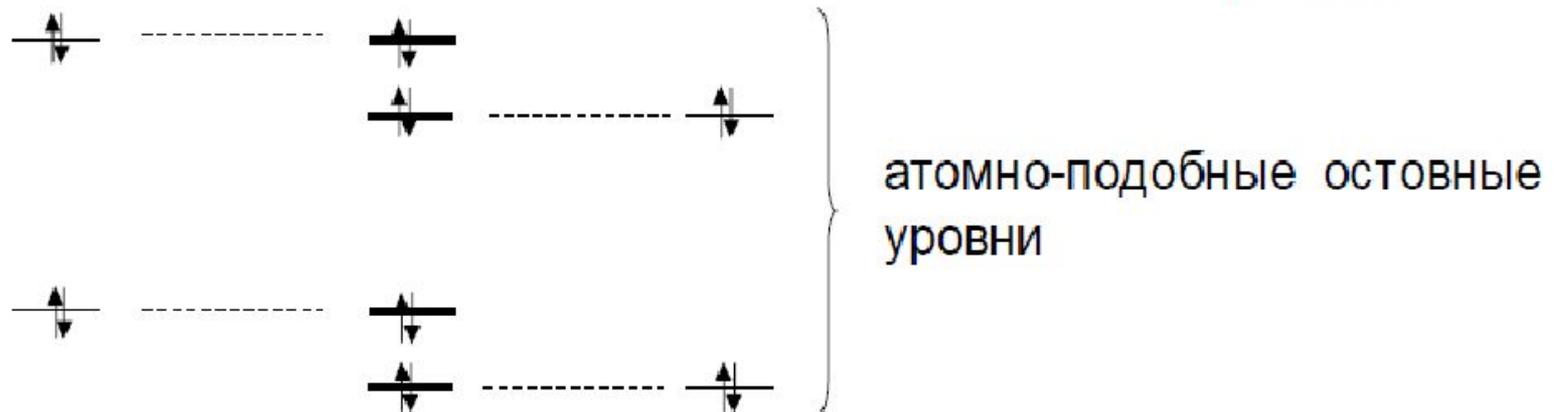
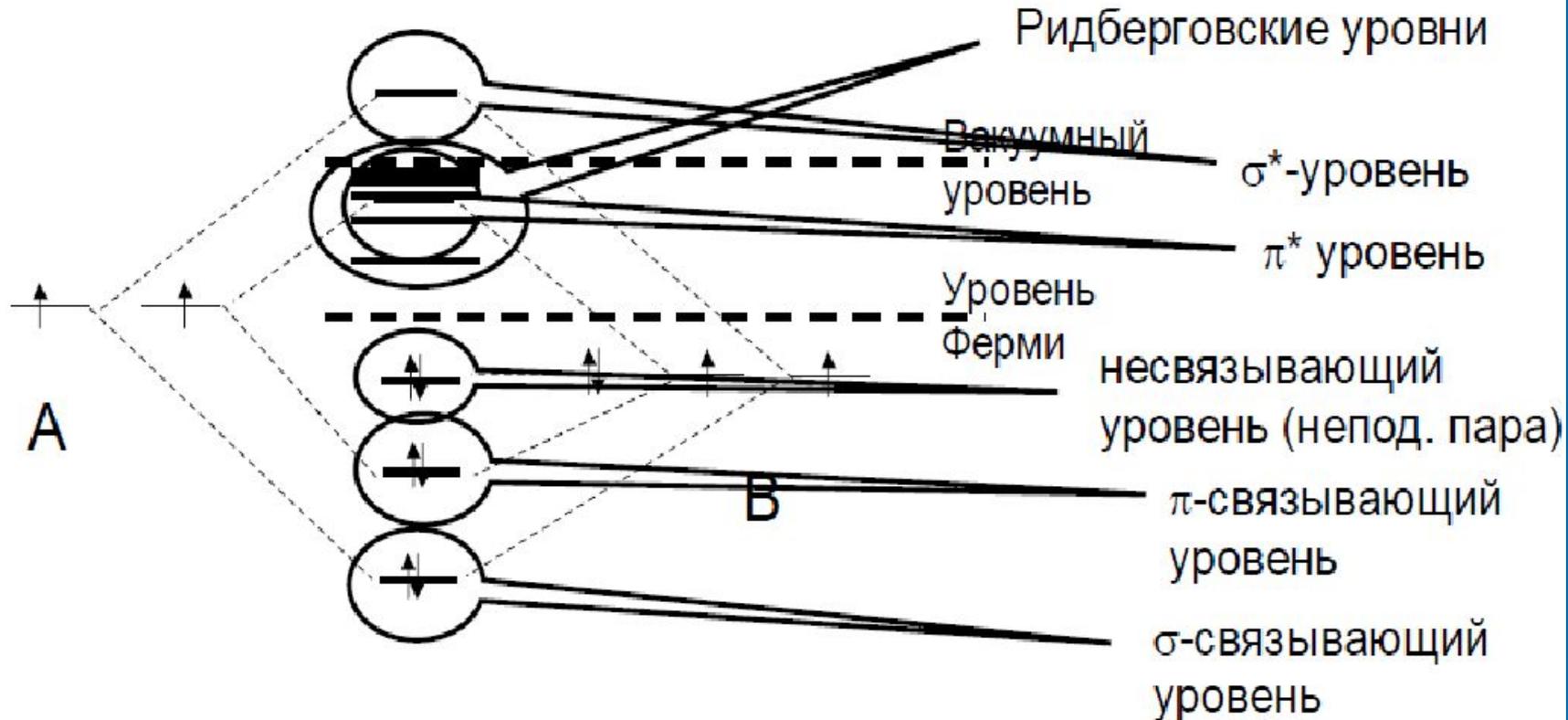
O (атом кислорода)



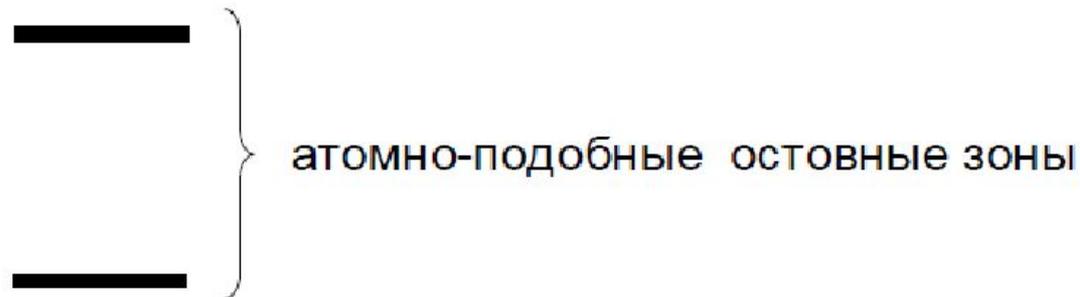
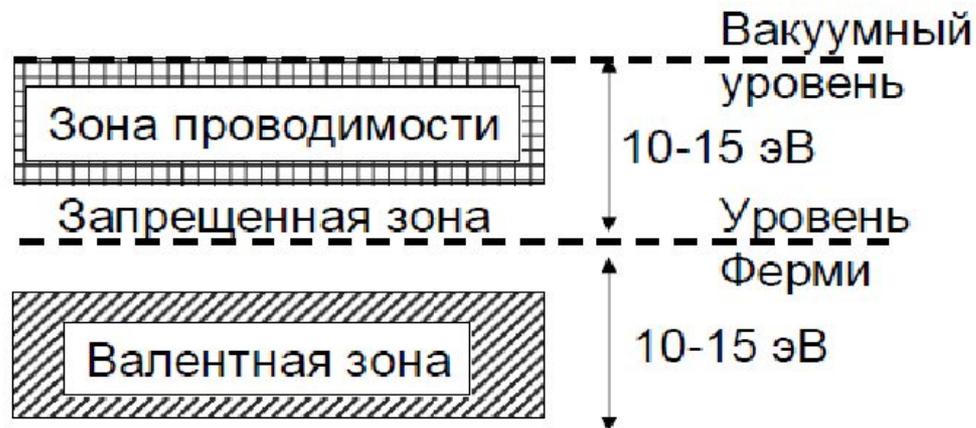
# Изменение электронных уровней атома при образовании хим. связей



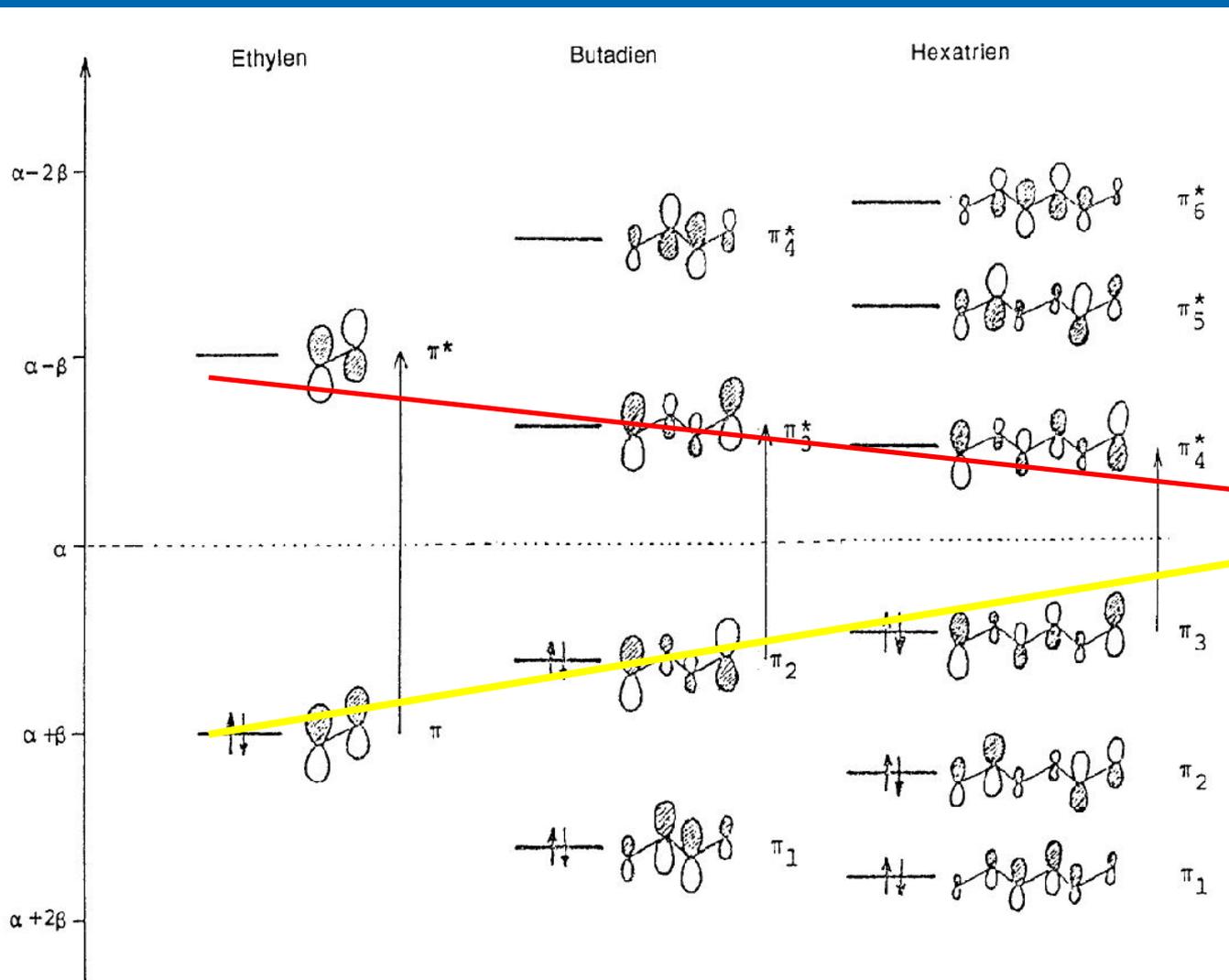
# Молекулярные орбитали



# Электронные зоны



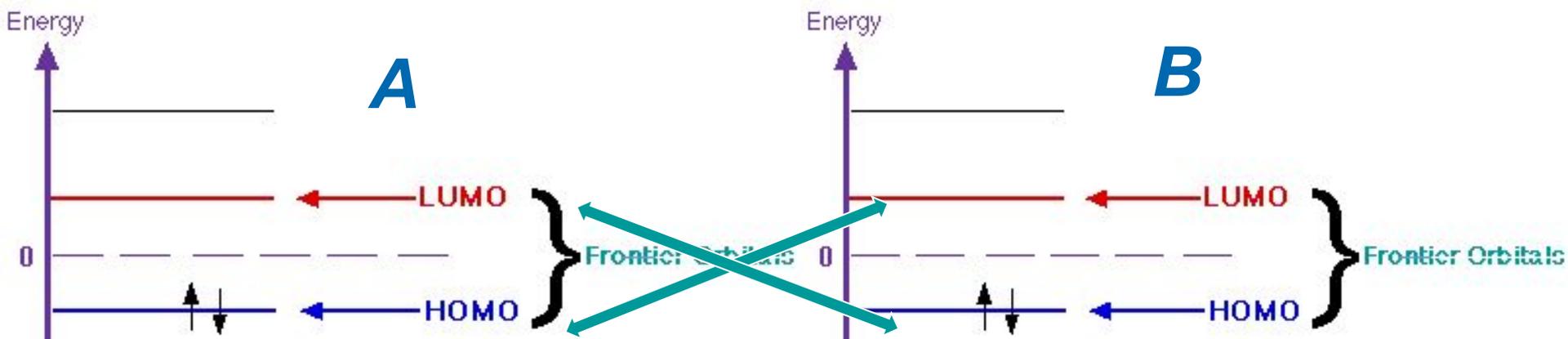
# Электронные зоны «органических» металлов



полупроводники

Органические металлы

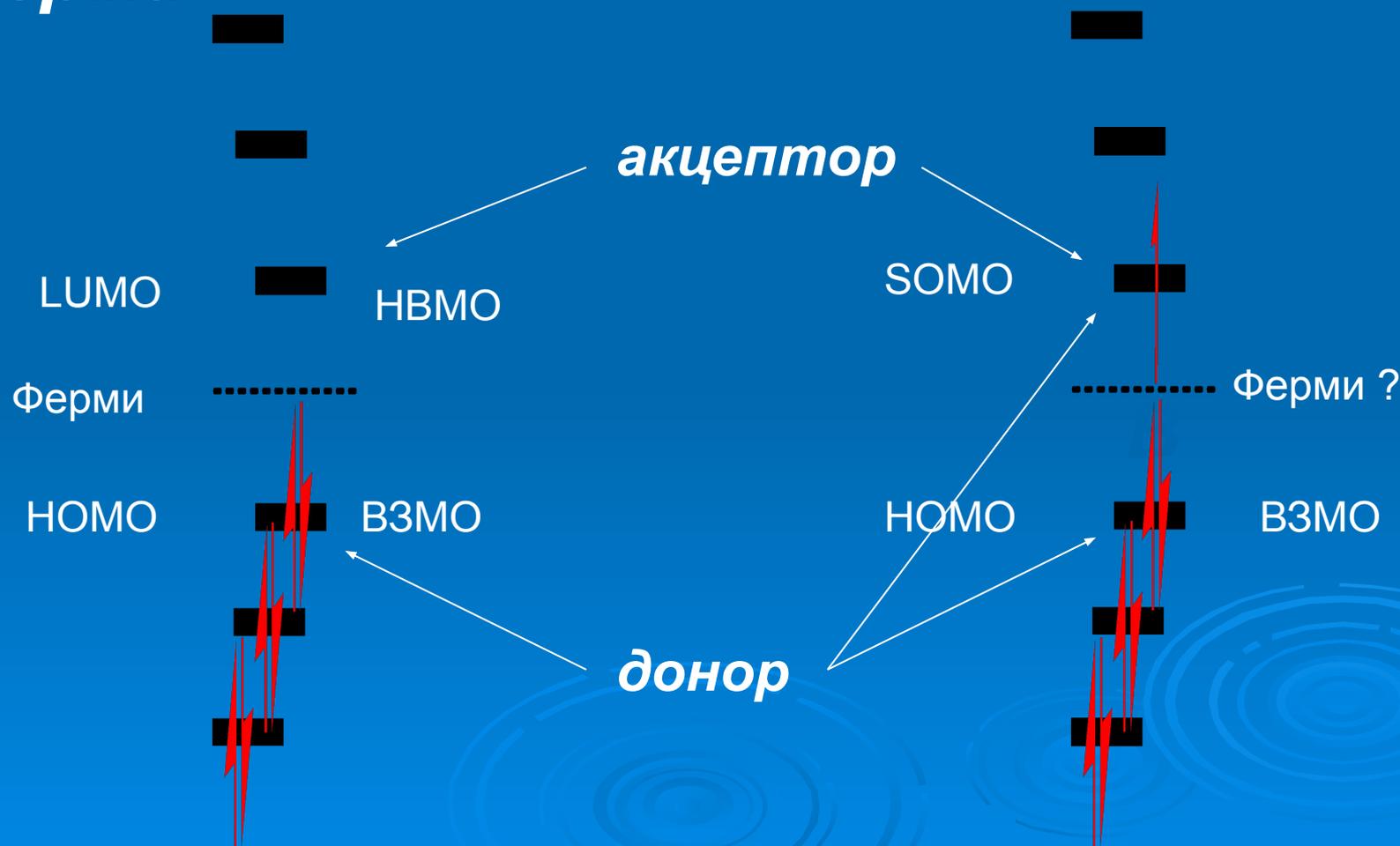
*Реакция характеризуется взаимным переносом электронной плотности от одной молекулы (атома) к другой молекуле (атому)*



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

**донорно – акцепторном** взаимодействии

Реакционная способность определяется подвижностью электронов по орбиталям и в основном расположены 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.**

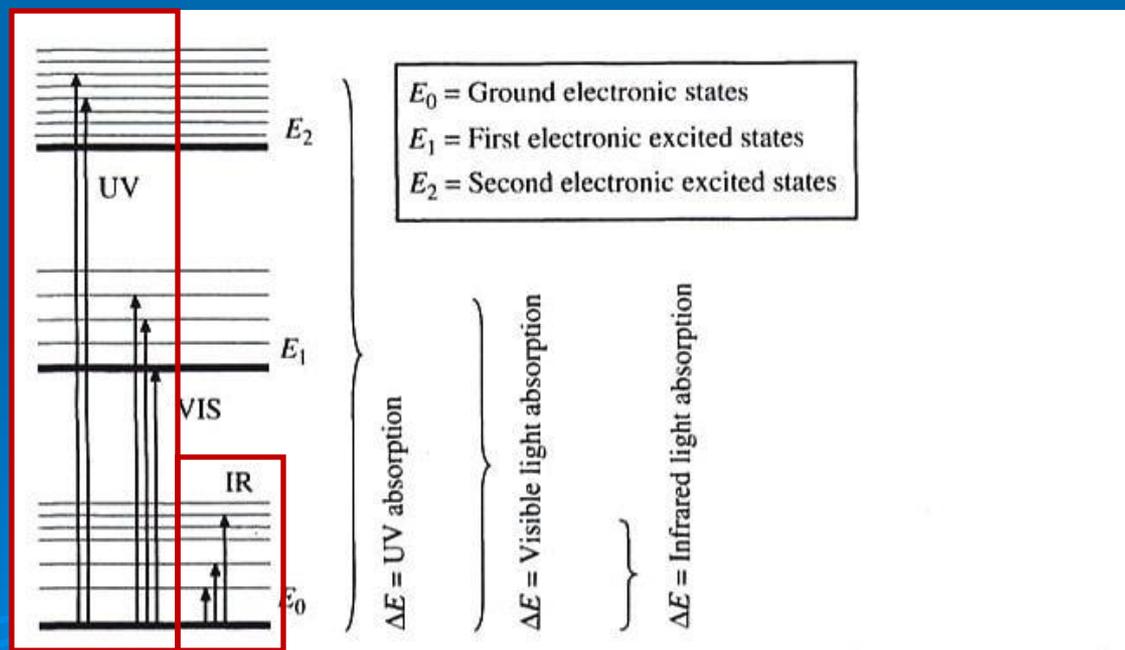


# энергию переходов между МО можно оценить по спектральным данным

- 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)

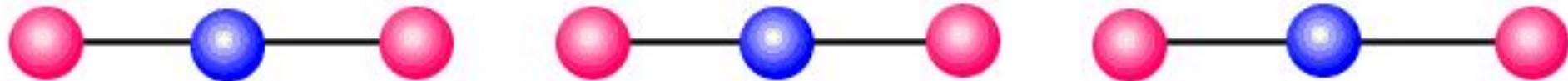
IR photons have much less energy, vibrate molecules



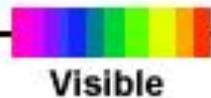
**Figure 8.2** Energy levels in a molecule and three types of absorption spectrometry.  $\Delta E$  is the radiation absorbed by a molecule

# UV-Visible + IR Spectroscopic Methods

## Introduction to the Principles of Spectroscopy



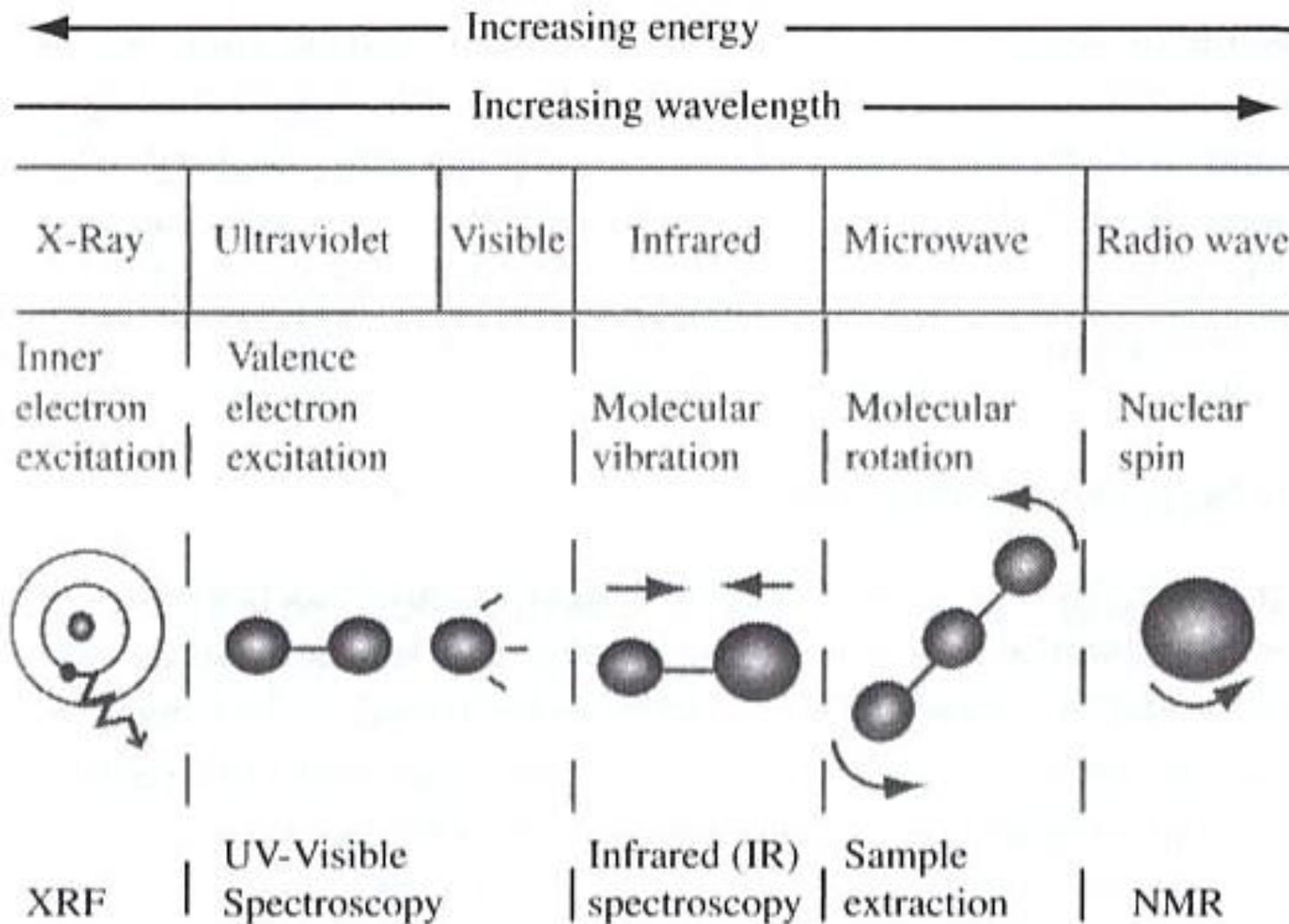
**Ultra Violet**  
Les molécules se dissocient



**Infra Rouge**  
Les molécules vibrent

**Micro Ondes**  
Les molécules tournent

$\lambda$



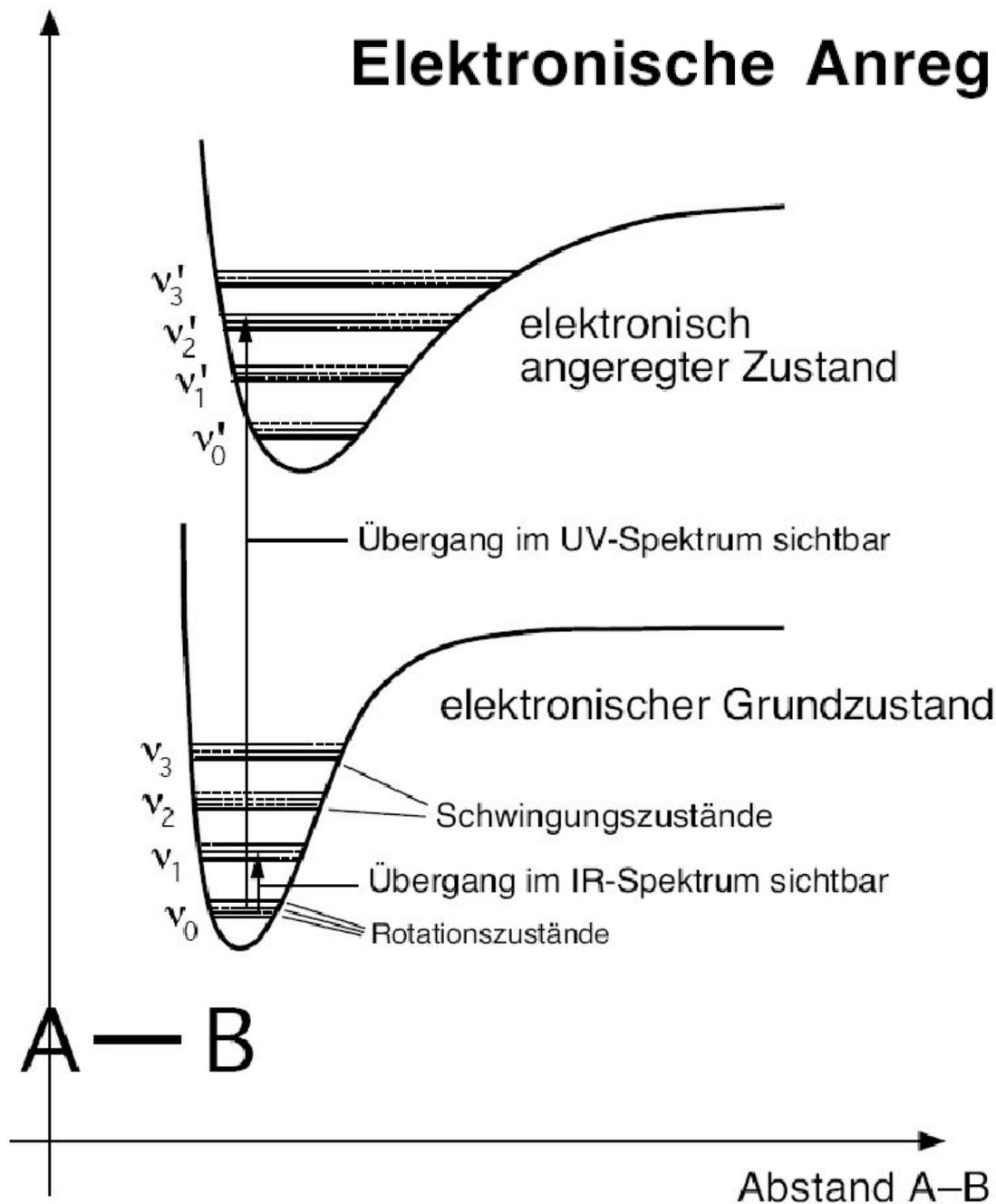
Ionization occurs under high energy UV radiation

MW least energetic, does not vibrate

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

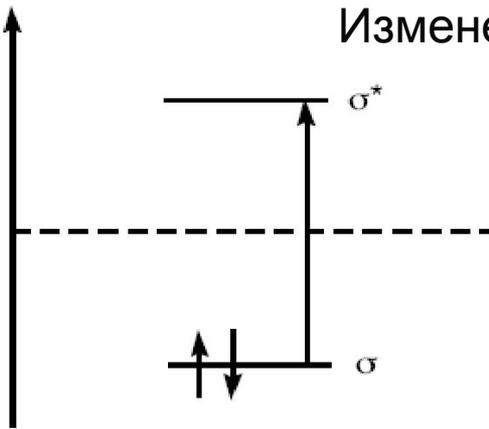
Energie

# Elektronische Anregung



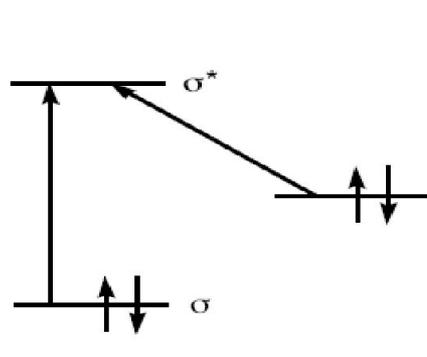
Энергия системы  
=  
E(электронная)+  
E(колебательная)  
E(вращательная)

E ↑ **Изменение E (электронная)**



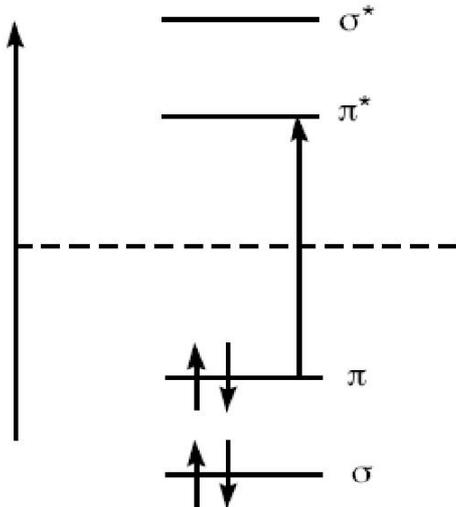
$\sigma \rightarrow \sigma^*$ -Übergang : z.B. CH4 122 nm  
z.B. CH3-CH3 135 nm

E ↑



$n \rightarrow \sigma^*$ -Übergang : z.B. CH3-O-H 177 nm  
z.B. CH3-O-CH3 184 nm

E ↑

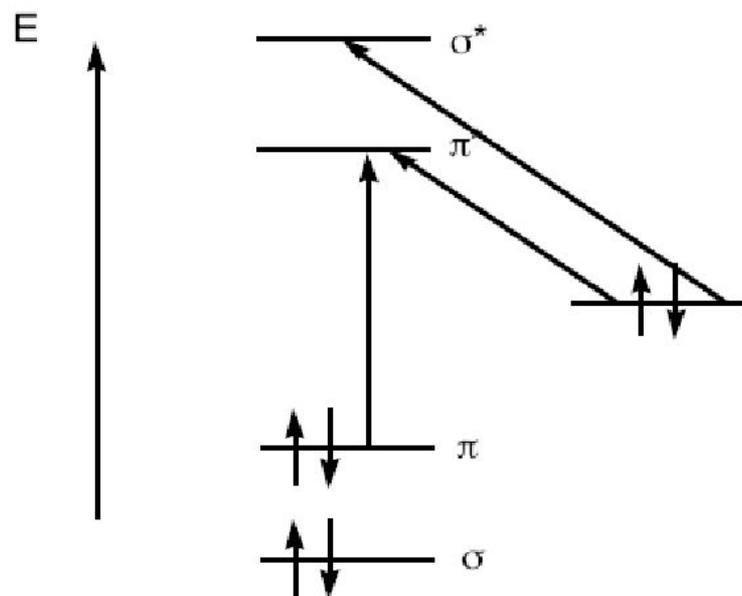


$\pi \rightarrow \pi^*$ -Übergang

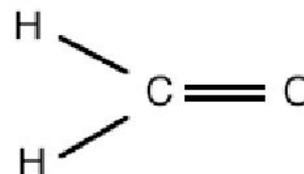
	$\lambda_{\max}$ [nm]	$\epsilon_{\max}$
z.B. <chem>CH2=CH2</chem>	163	15'000
<chem>(CH3)2C=C(CH3)2</chem>	197	11'000

# Изменение E (электронная)

Hypothetische Carbonylgruppe  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$



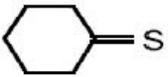
z.B.



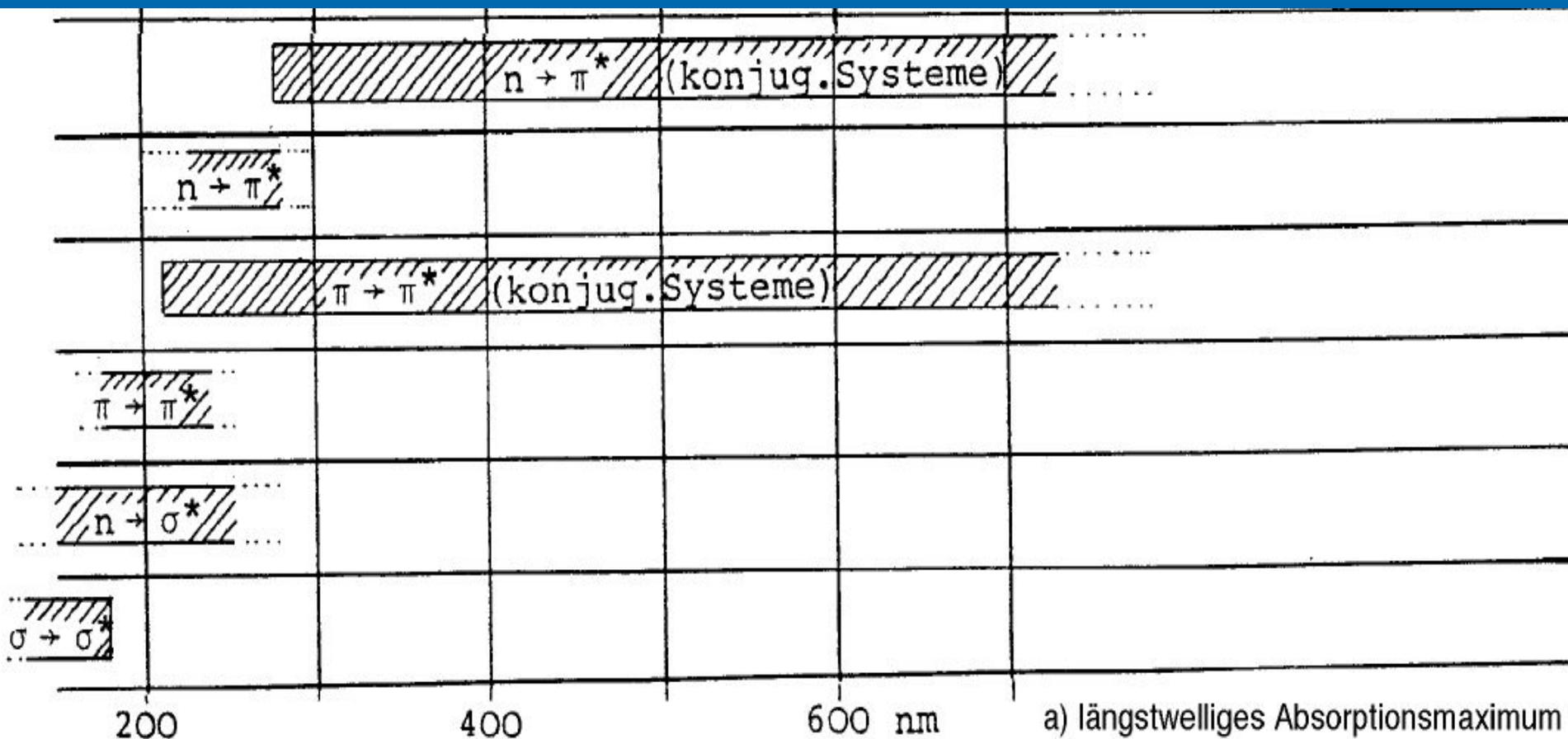
- |                                     |                            |
|-------------------------------------|----------------------------|
| $n \rightarrow \pi^*$ -Übergang:    | 304 nm ( $\epsilon = 18$ ) |
| $\pi \rightarrow \pi^*$ -Übergang:  | 208 nm                     |
| $n \rightarrow \sigma^*$ -Übergang: | vermutlich um 180 nm       |

#### 4.4.2. UV-Absorption einfacher Chromophore

Chromophor	Verbindung	Übergang	$\lambda_{\max}$ [nm]	$\epsilon_{\max}$	Lösungsmittel
C-C	CH <sub>3</sub> -CH <sub>3</sub>	$\sigma \rightarrow \sigma^*$	135	stark	Gas
C-H	CH <sub>4</sub>	$\sigma \rightarrow \sigma^*$	122	stark	Gas
C-O	CH <sub>3</sub> -OH	$n \rightarrow \sigma^*$	177	200	Hexan
	CH <sub>3</sub> -O-CH <sub>3</sub>	$n \rightarrow \sigma^*$	184	2500	Gas
C-N	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	$n \rightarrow \sigma^*$	193	2500	Hexan
	(CH <sub>3</sub> ) <sub>3</sub> N	$n \rightarrow \sigma^*$	199	4000	Hexan
C-S	CH <sub>3</sub> SH	$n \rightarrow \sigma^*$	195	1800	Gas
		$n \rightarrow \sigma^*$	235	180	Gas
	C <sub>2</sub> H <sub>5</sub> -S-C <sub>2</sub> H <sub>5</sub>	$n \rightarrow \sigma^*$	194	4500	Gas
		$n \rightarrow \sigma^*$	225	1800	Gas
S-S	C <sub>2</sub> H <sub>5</sub> -S-S-C <sub>2</sub> H <sub>5</sub>	$n \rightarrow \sigma^*$	194	5500	Hexan
		$n \rightarrow \sigma^*$	250	380	
C-Cl	CH <sub>3</sub> Cl	$n \rightarrow \sigma^*$	173	200	Hexan
C-Br	n-C <sub>3</sub> H <sub>7</sub> Br	$n \rightarrow \sigma^*$	208	300	Hexan
C-I	CH <sub>3</sub> I	$n \rightarrow \sigma^*$	259	400	Hexan
C=C	CH <sub>2</sub> =CH <sub>2</sub>	$\pi \rightarrow \pi^*$	162.5	15000	Heptan
	(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub>	$\pi \rightarrow \pi^*$	196.5	11500	Heptan
C=O	(CH <sub>3</sub> ) <sub>2</sub> C=O	$n \rightarrow \sigma^*$	166	16000	Gas
		$\pi \rightarrow \pi^*$	189	900	Hexan
		$n \rightarrow \pi^*$	279	15	Hexan
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{OH} \end{array}$	$n \rightarrow \pi^*$	200	50	Gas
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{OC}_2\text{H}_5 \end{array}$	$n \rightarrow \pi^*$	210	50	Gas
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{ONa} \end{array}$	$n \rightarrow \pi^*$	210	150	Wasser
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{NH}_2 \end{array}$	$n \rightarrow \pi^*$	220	63	Wasser
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2 - \text{C} \\ \quad \quad \quad \backslash \\ \quad \quad \quad \text{NH} \\ \quad \quad \quad \parallel \\ \text{CH}_2 - \text{C} \\ \quad \quad \quad \backslash \\ \quad \quad \quad \text{O} \end{array}$	$n \rightarrow \pi^*$	191	15200	Acetonitril

Chromophor	Verbindung	Übergang	$\lambda_{\max}$ [nm]	$\epsilon_{\max}$	Lösungsmittel
C=N	$\text{H}_2\text{N}-\overset{\text{NH}}{\parallel}{\text{C}}-\text{NH}_2 \cdot \text{HCl}$		265	15	Wasser
	$(\text{CH}_3)_2\text{C}=\text{NOH}$		193	2000	Ethanol
N=N	$(\text{CH}_3)_2\text{C}=\text{NONa}$	$n \rightarrow \pi^*$	265	200	Ethanol
	$\text{CH}_3-\text{N}=\text{N}-\text{CH}_3$		340	16	Ethanol
N=O	$(\text{CH}_3)_3\text{C}-\text{NO}$	$n \rightarrow \pi^*$	300	100	Ether
	$(\text{CH}_3)_3\text{C}-\text{NO}_2$		665	20	
	$n-\text{C}_4\text{H}_9-\text{O}-\text{NO}$		276	27	Ethanol
	$\text{C}_2\text{H}_5-\text{O}-\text{NO}_2$		218	1050	
			313-384	20-40	Ethanol
			260	15	Ethanol
C=S	$\text{CH}_3-\overset{\text{S}}{\parallel}{\text{C}}-\text{CH}_3$		460	schwach	
			495	schwach	Ethanol
C=C	$\text{HC}=\text{CH}$		173	6000	Gas
	$n-\text{C}_5\text{H}_{11}-\text{C}=\text{C}-\text{CH}_3$		177.5	10000	Hexan
C≡N			196	2000	
	$\text{CH}_3-\text{C}\equiv\text{N}$		222.5	160	
X=C=Y	$\text{CH}_2=\text{C}=\text{CH}_2$		<190		
	$(\text{C}_2\text{H}_5)_2\text{C}=\text{C}=\text{O}$		170	4000	
			227	630	
			227	360	
	$\text{C}_2\text{H}_5-\text{N}=\text{C}=\text{N}-\text{C}_2\text{H}_5$		375	20	
			230	4000	
			270	25	
	$\text{C}_2\text{H}_5-\text{N}=\text{C}=\text{S}$		250	1200	Hexan

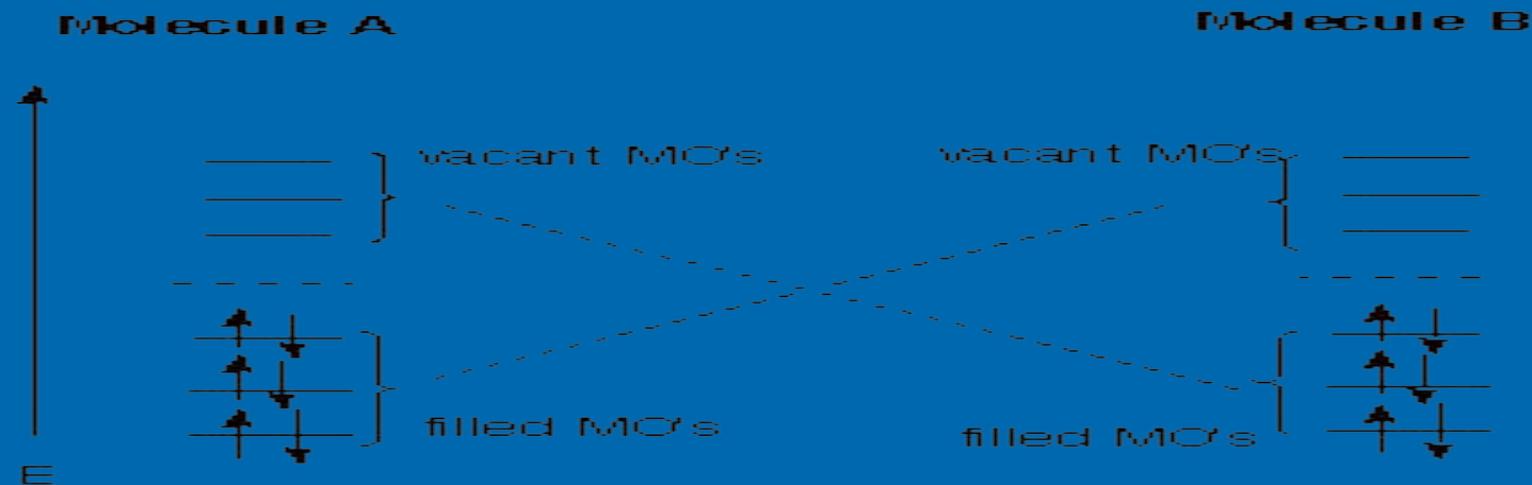
# Изменение E (электронная)



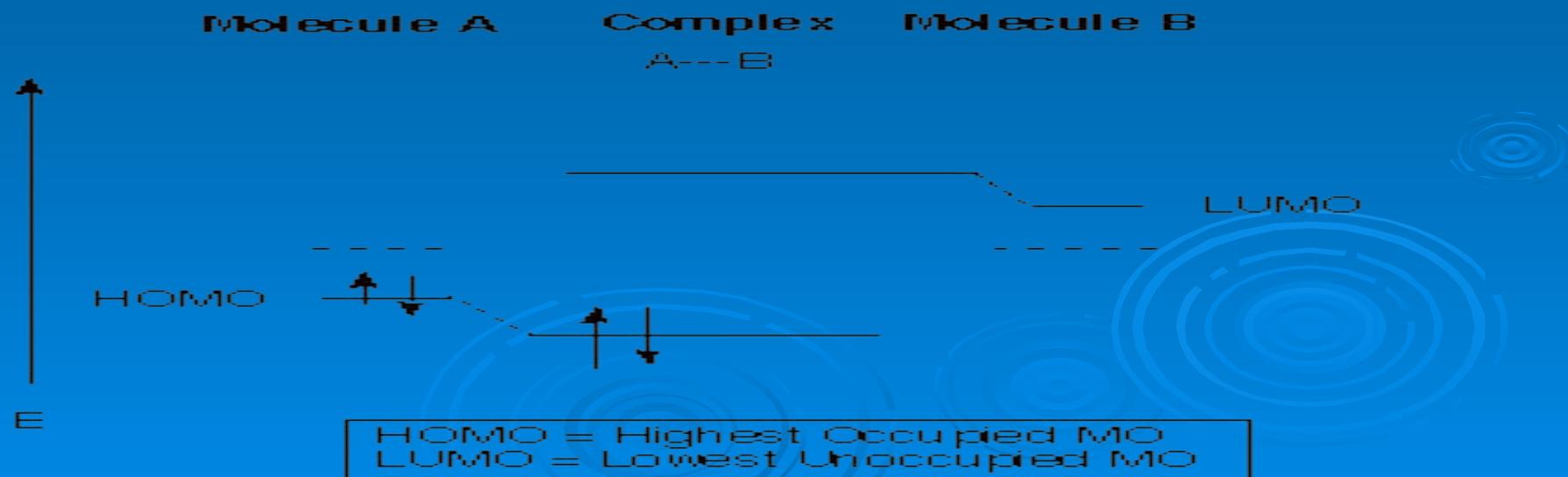
$$E = h\nu$$

Евращ =  $(v_1 + \frac{1}{2}) h\nu$  mit  $v = 0, 1, 2, \dots$

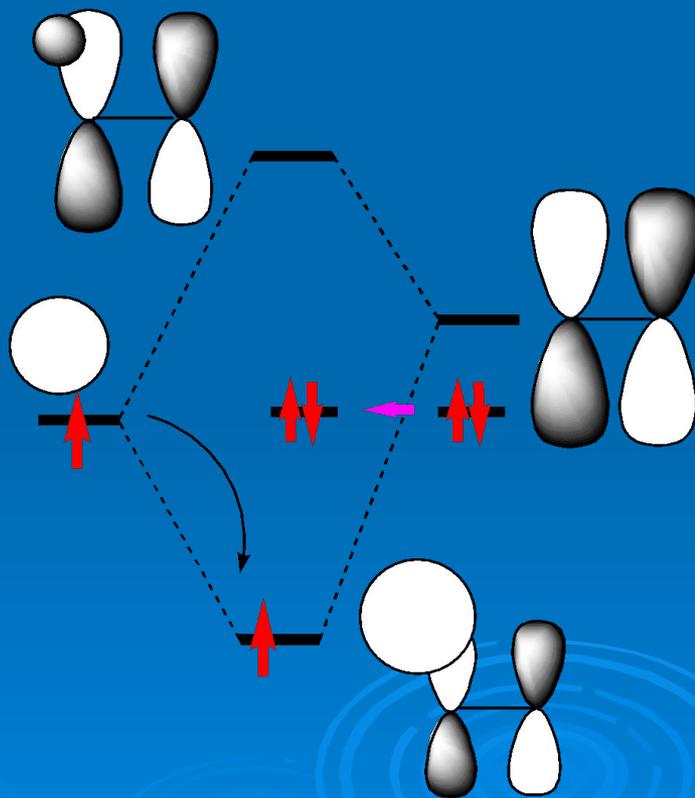
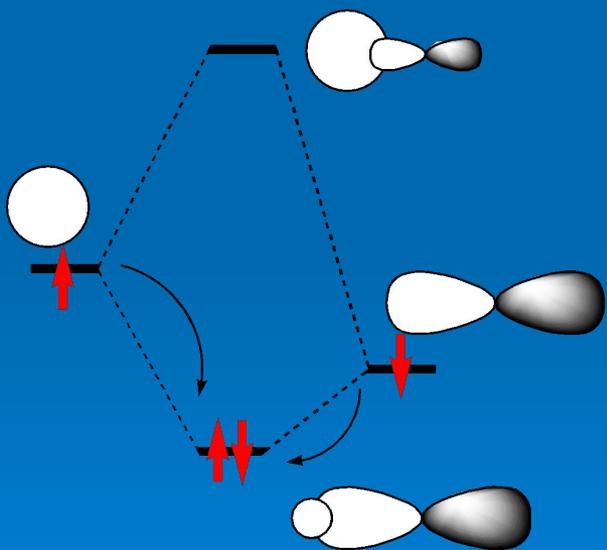
Еколеб =  $(v_2 + \frac{1}{2}) h\nu$  mit  $v = 0, 1, 2, \dots$



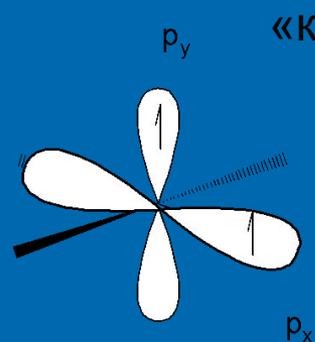
**Filled MO's** interact with **vacant MO's** to give complex MO's in which the stabilized complex MO has two electrons; consider as one example, the interaction of the highest energy filled MO of **A** with the lowest energy vacant MO of **B**:



# некоторые примеры протекания реакций без изменения структуры МО

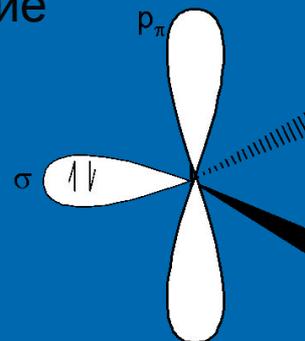
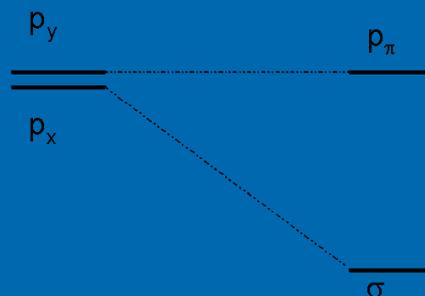


# Метилен (карбен) как реакционная частица



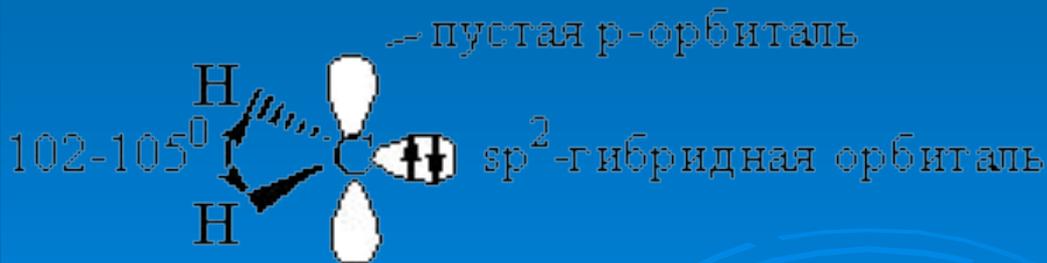
Triplet  
sp-hybridized

«классическое» представление

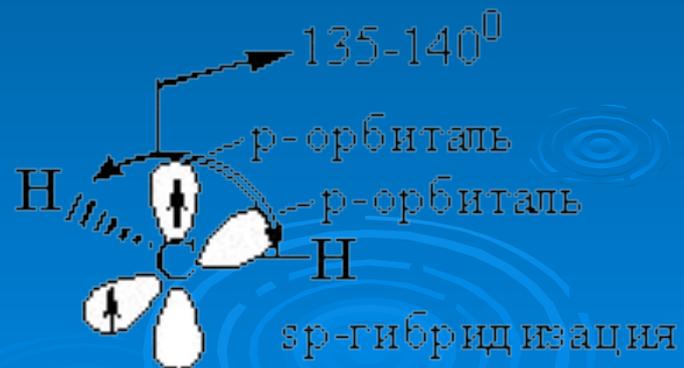


Singlet  
sp<sup>2</sup>-hybridized

экспериментальные данные

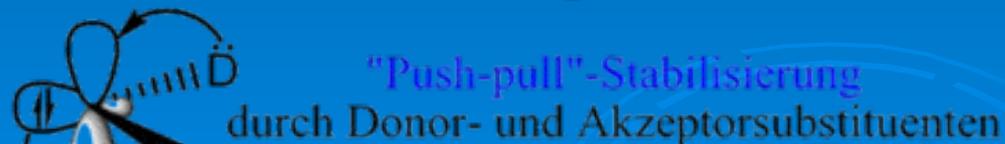
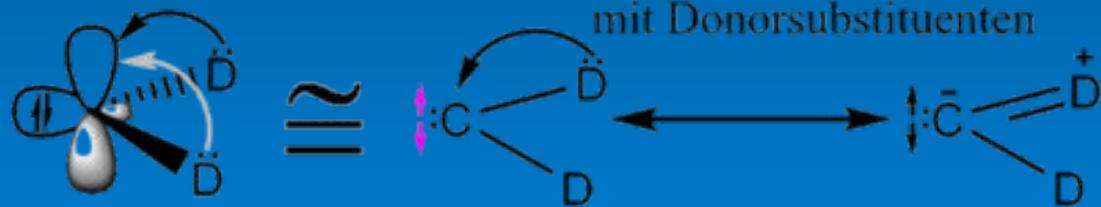
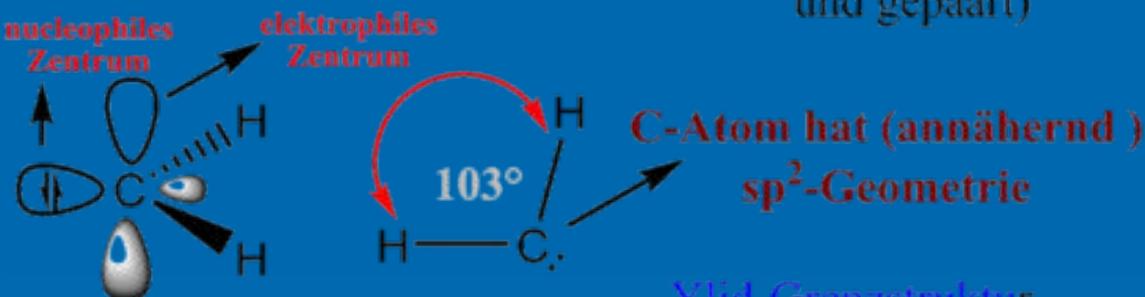
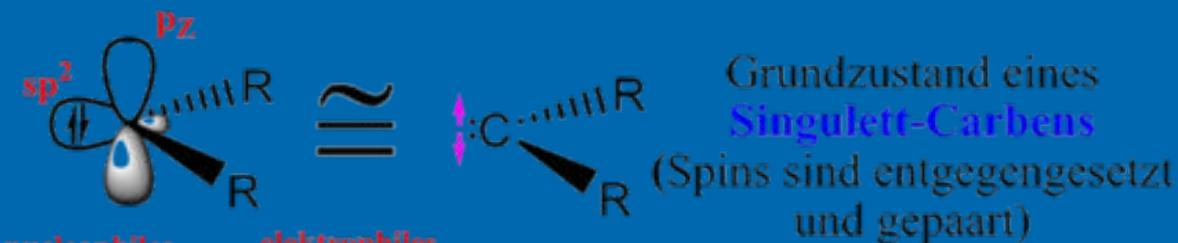


синглетный метилен  
(углерод sp<sup>2</sup>-гибриден)

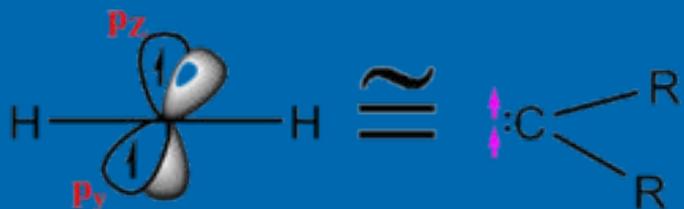
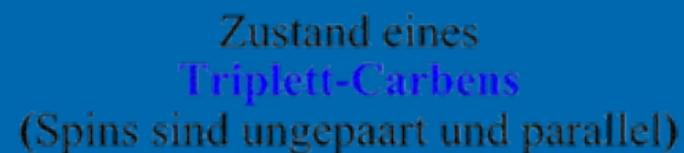


триплетный метилен  
(углерод sp-гибриден)

# Метилен (карбен) как реакционная частица

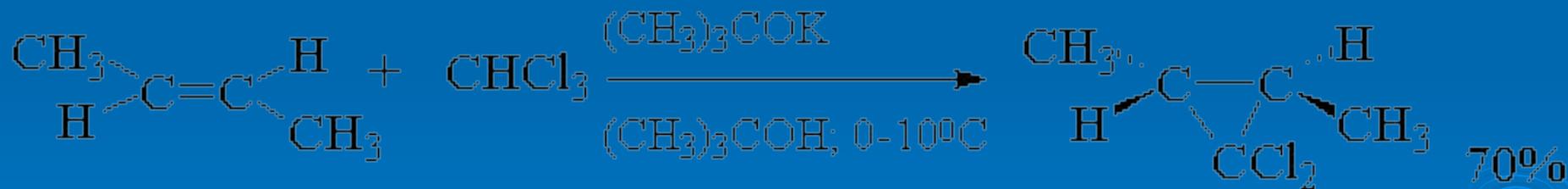
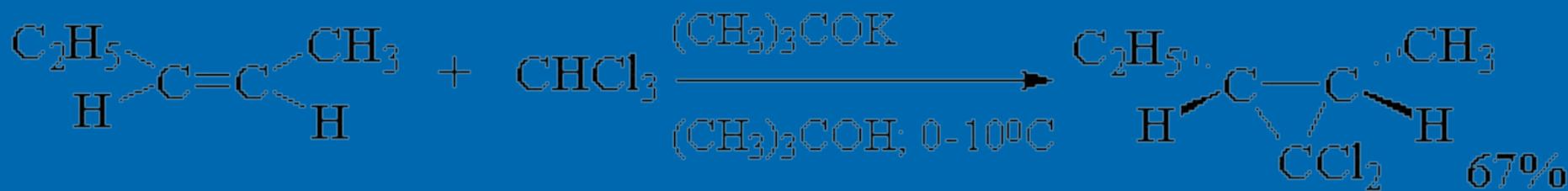


**Merke:**  
Die Addition von Singulett-Carbene verläuft konzertiert und stereospezifisch!

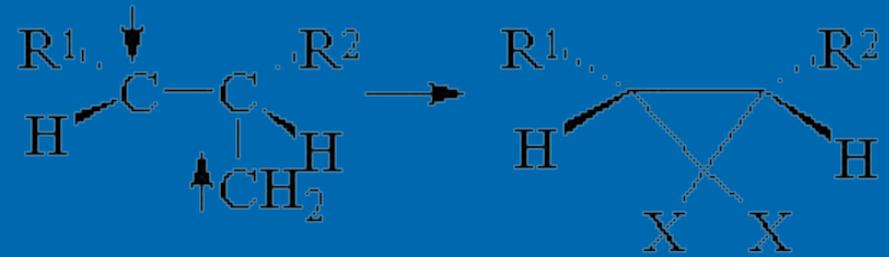
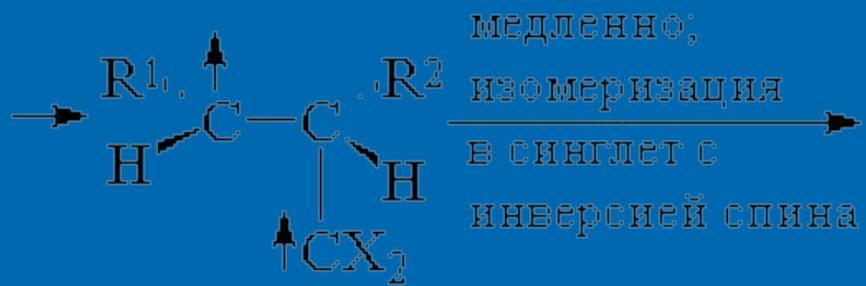
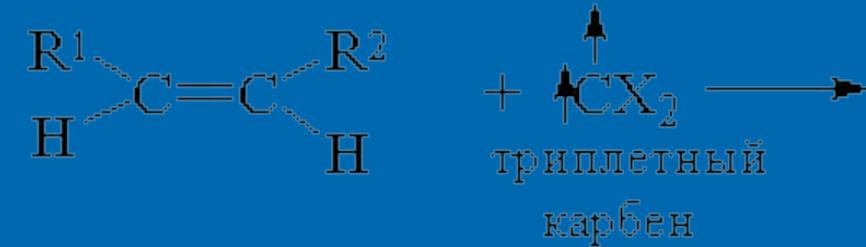


**Merke:**  
Die Addition von Triplet-Carbene verläuft nicht konzertiert (sondern stufenweise) und ist nicht stereospezifisch!

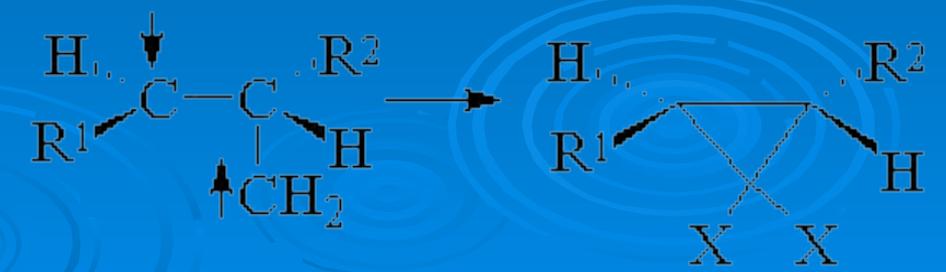
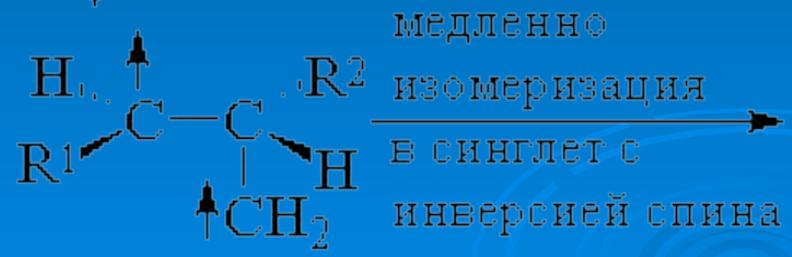
**Присоединение синглетной формы карбена по двойной связи происходит, строго стереоспецифично.**

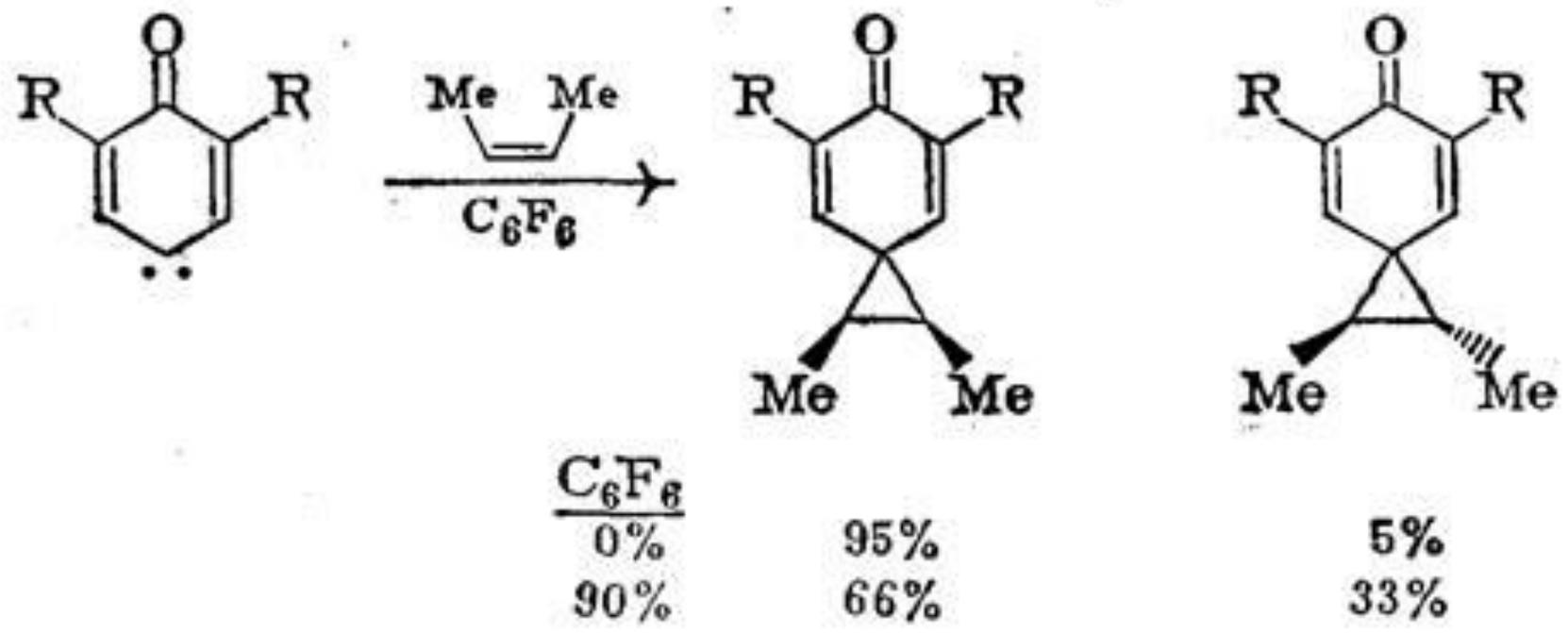
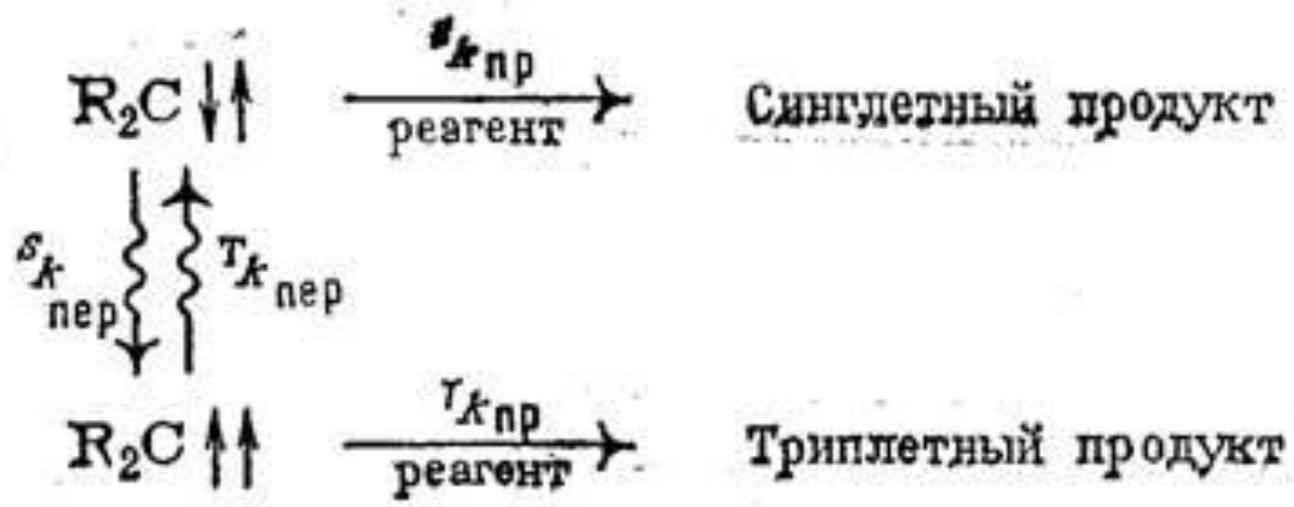


# Присоединение триплетной формы карбена по двойной связи происходит, не стереоспецифично.

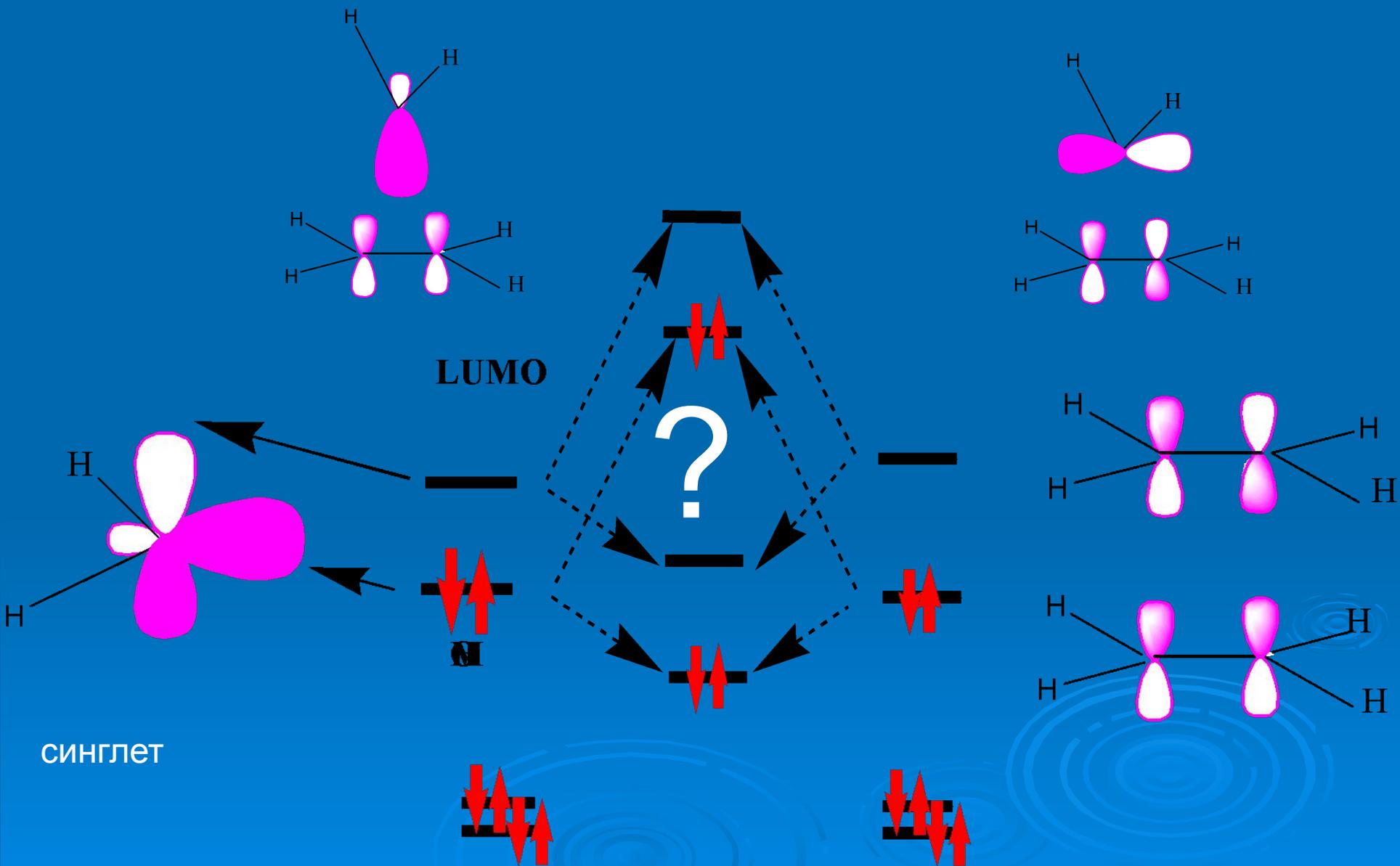


быстро;  
поворот вокруг  
C-C-связи

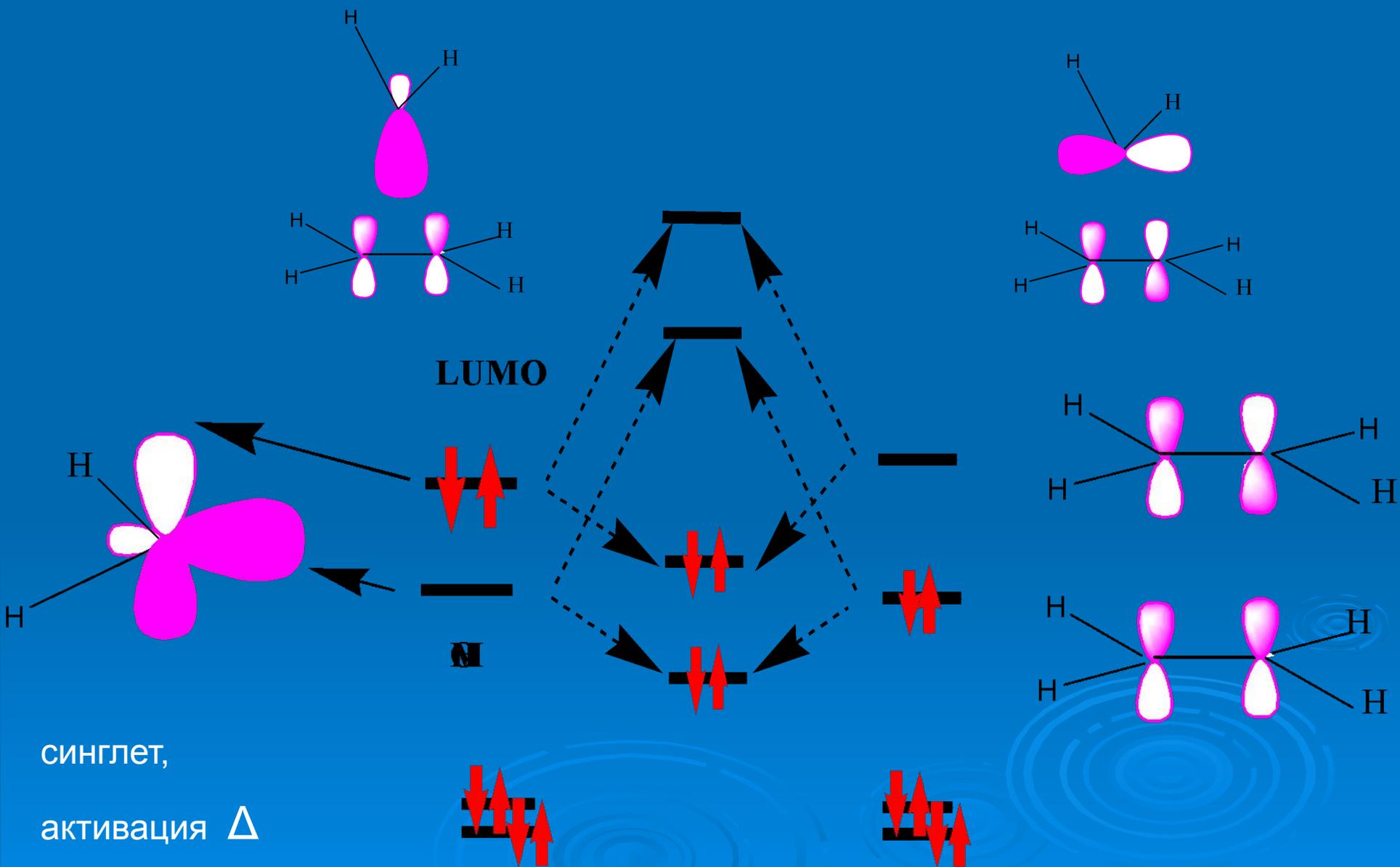




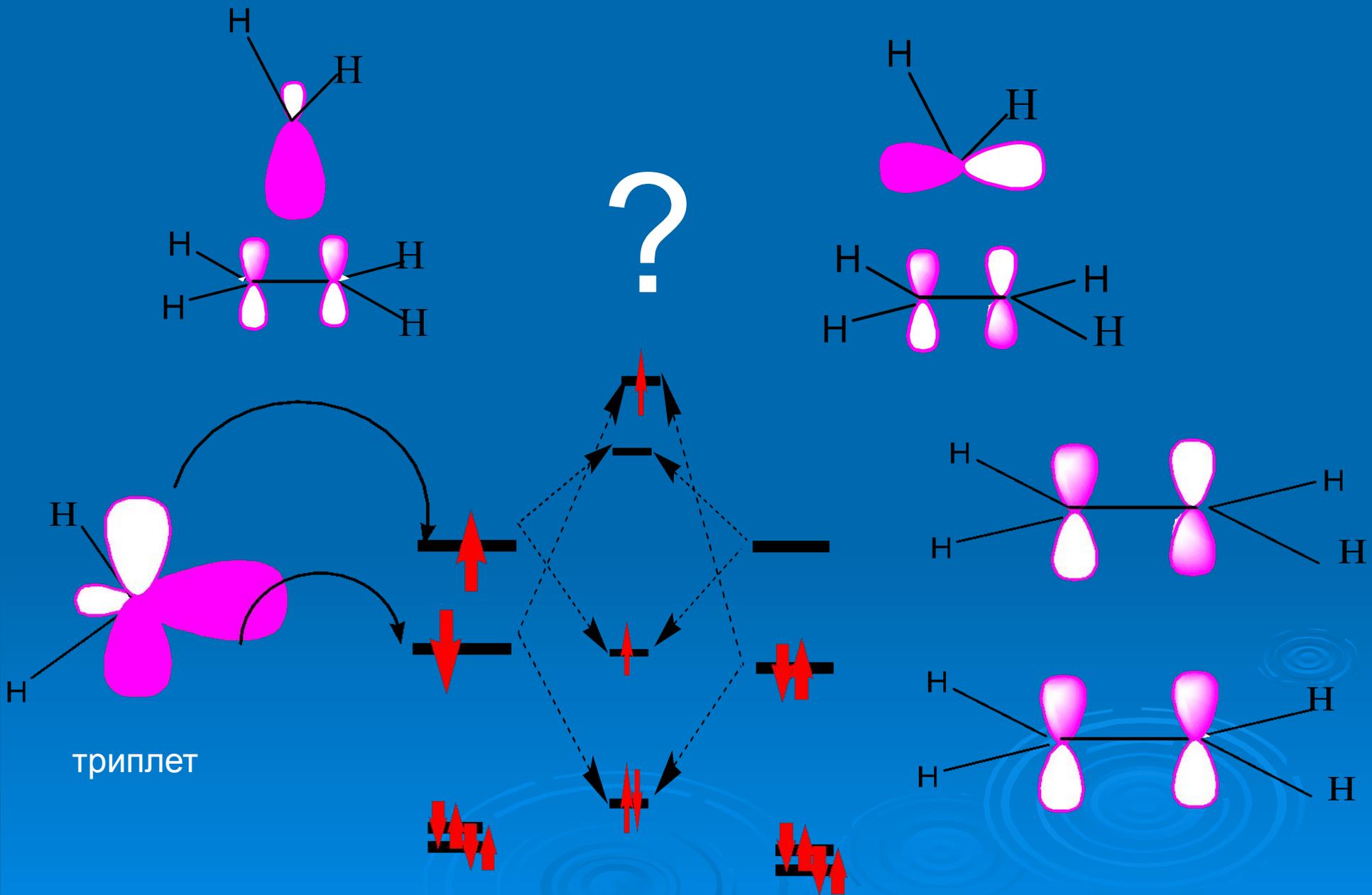
# Взаимодействие этилена с метиленом (карбеном)

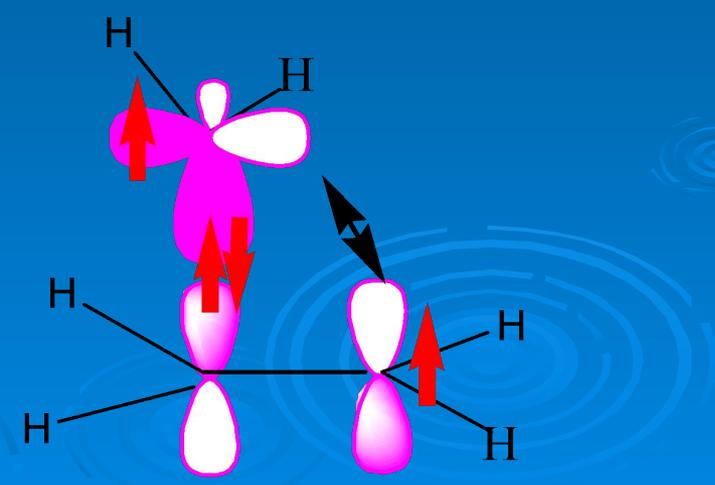
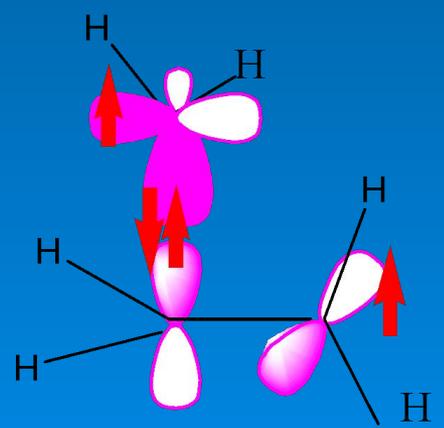
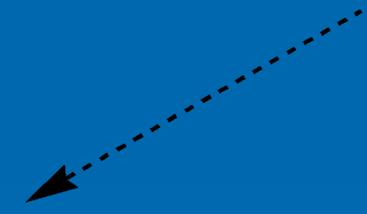
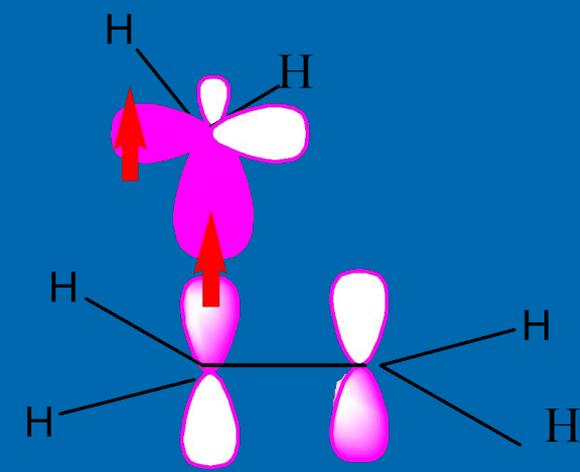
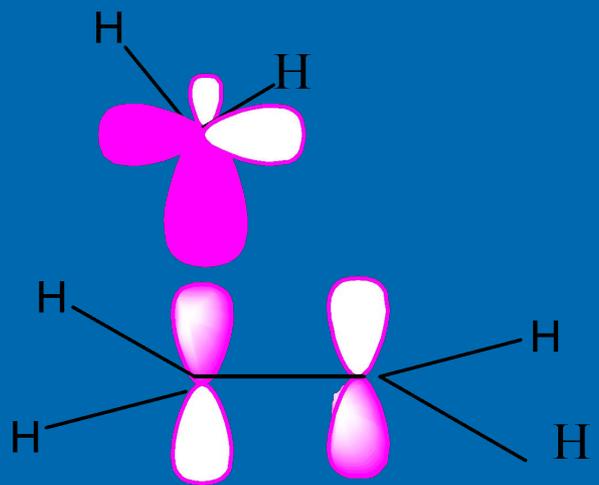


# Взаимодействие этилена с метиленом (карбеном)

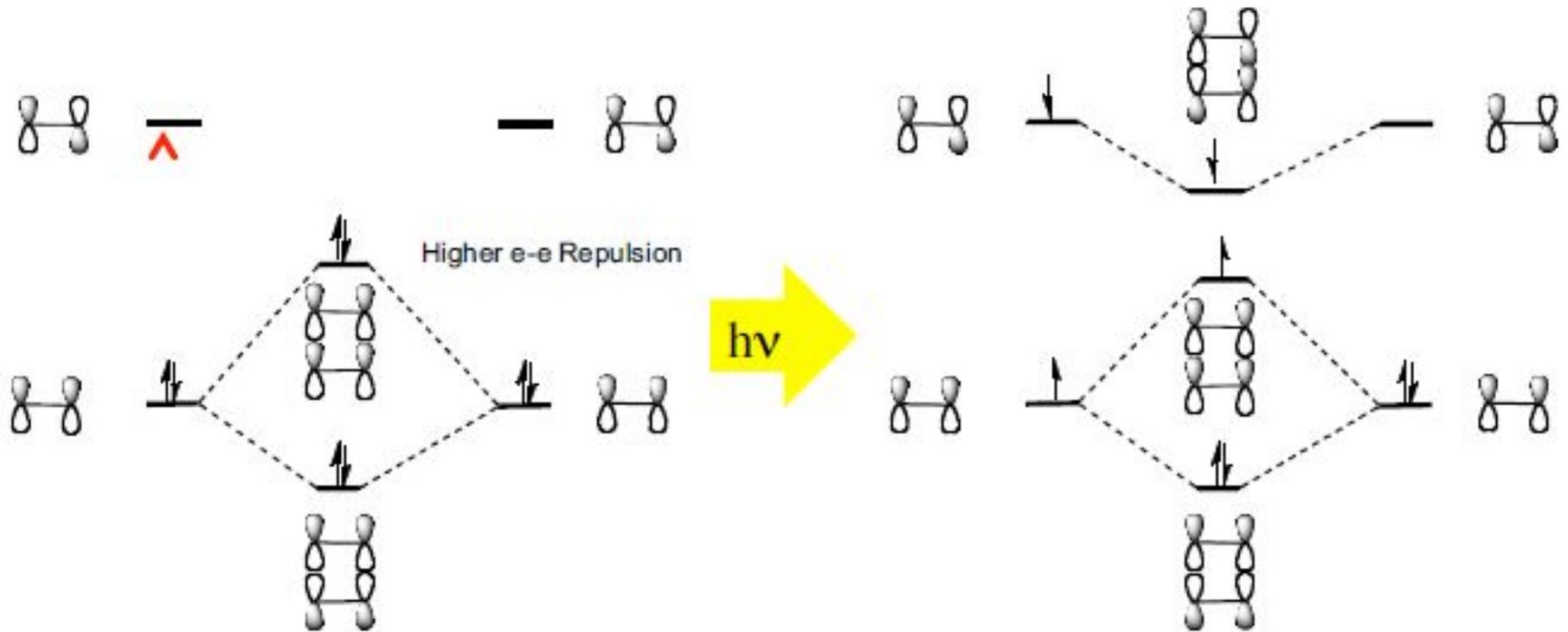


# Взаимодействие этилена с метиленом (карбеном)

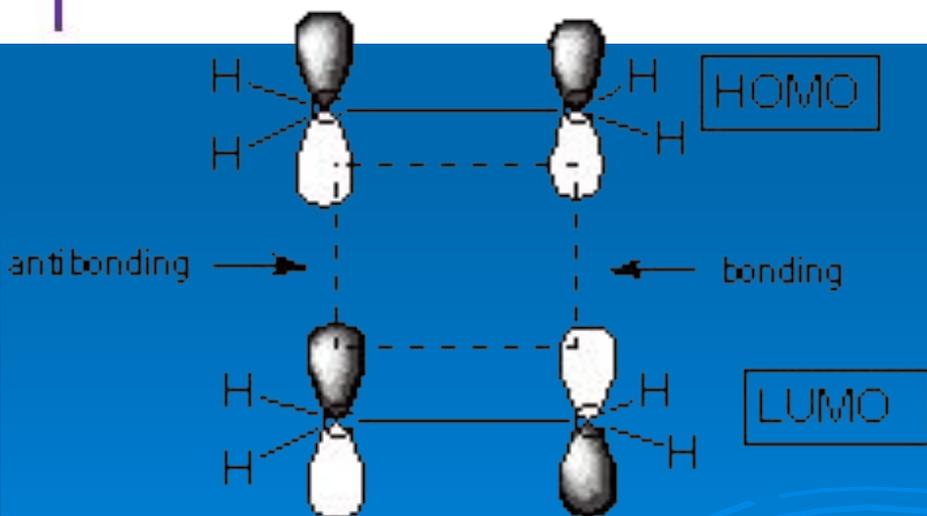
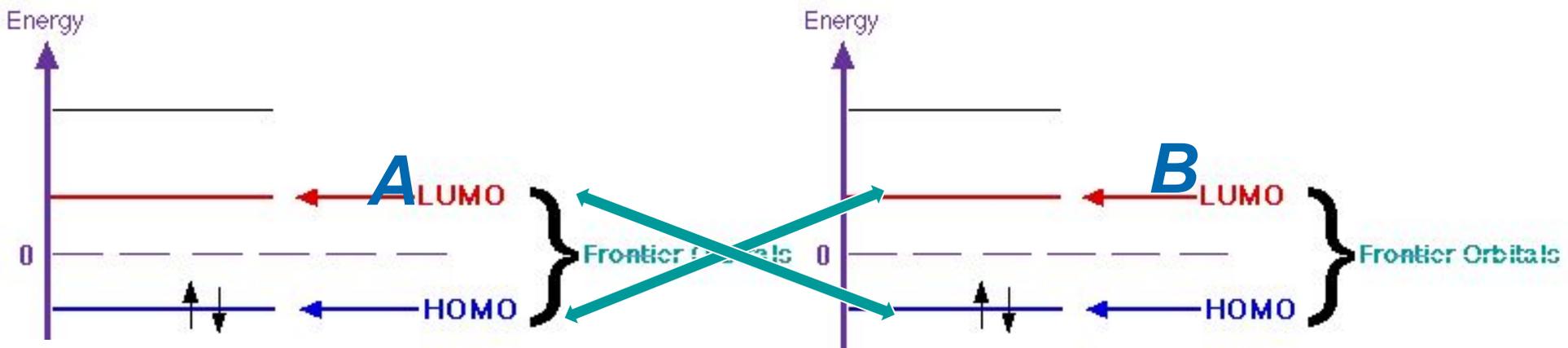




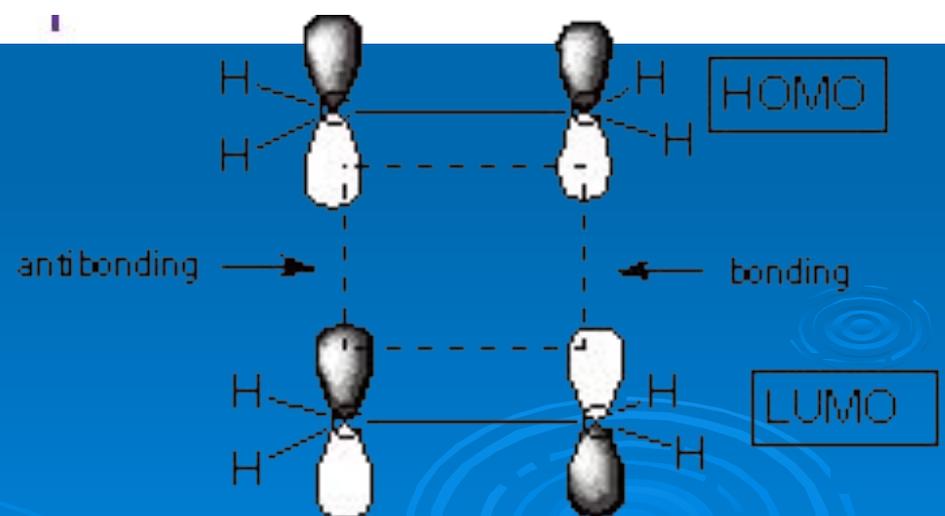
# Dimerization of Ethylene



# Димеризация этилена

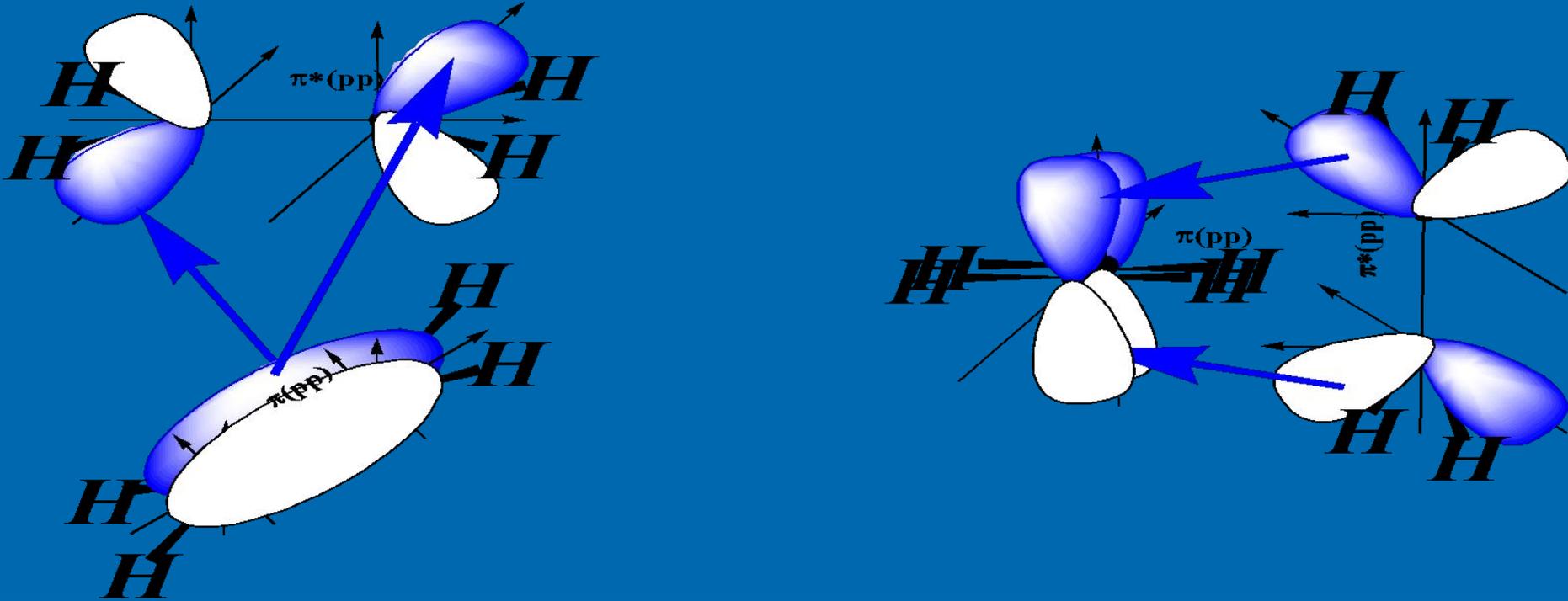


Result: Zero net bonding!

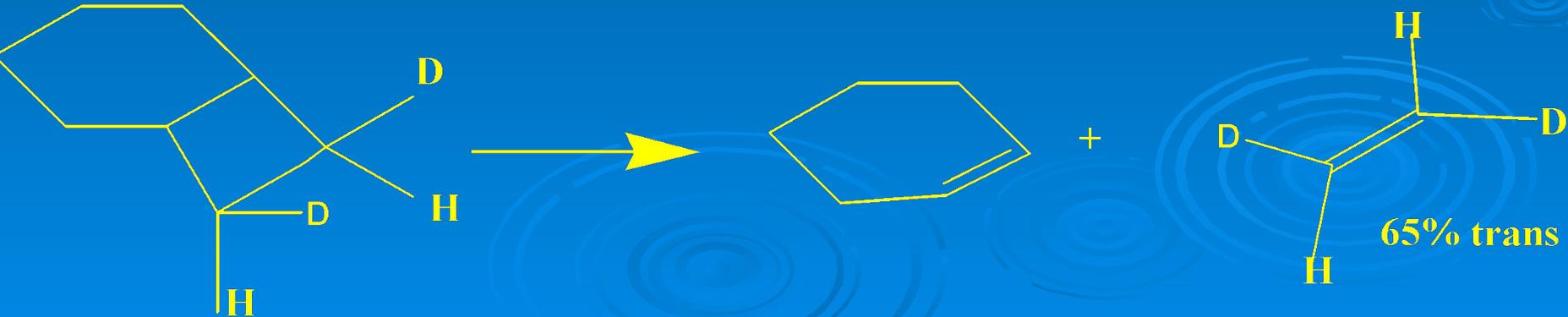


Result: Zero net bonding!

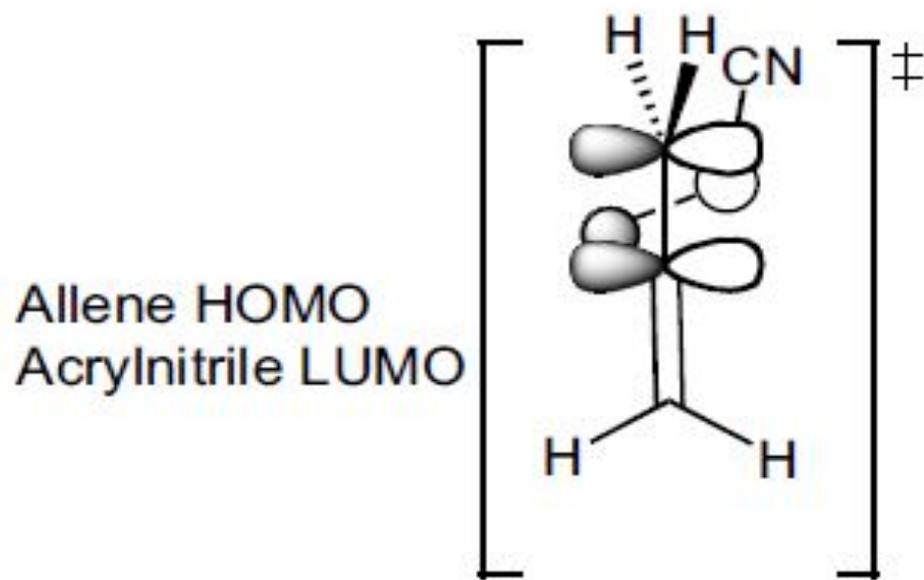
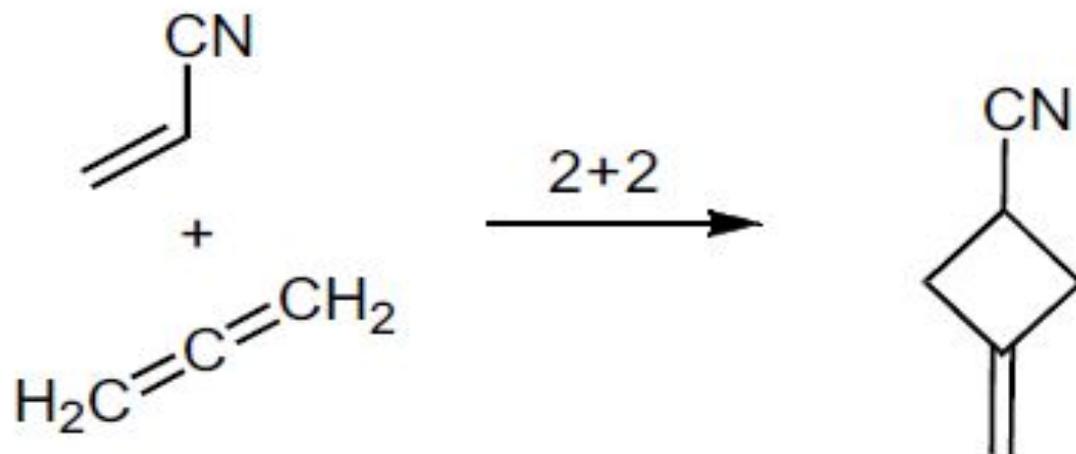
The rate of the thermal reaction of ethylene to form cyclobutane has been measured over the temperature range 723°–786°K and at pressures between 300 and 1300 torr.



доказательство

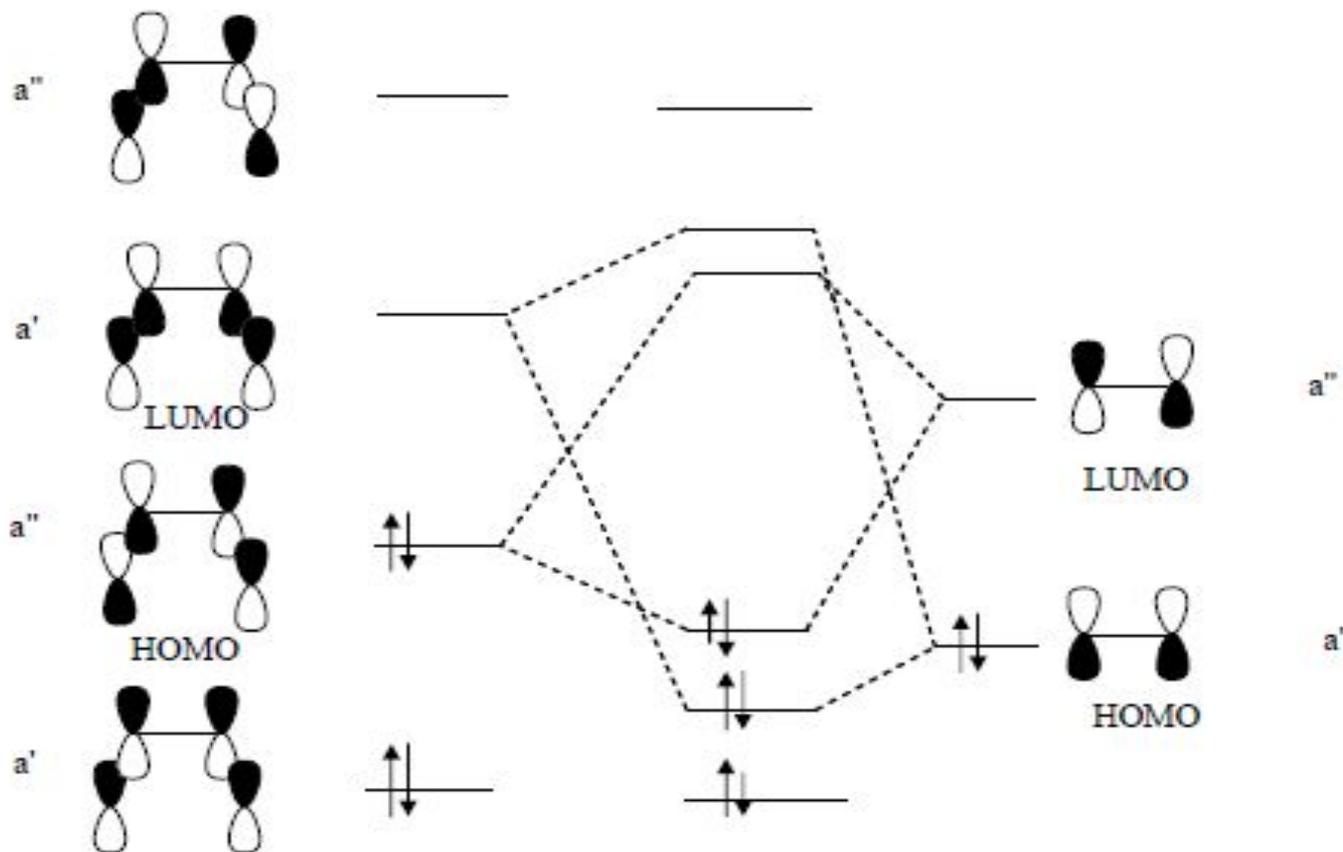


# Example of a Thermally Allowed 2+2



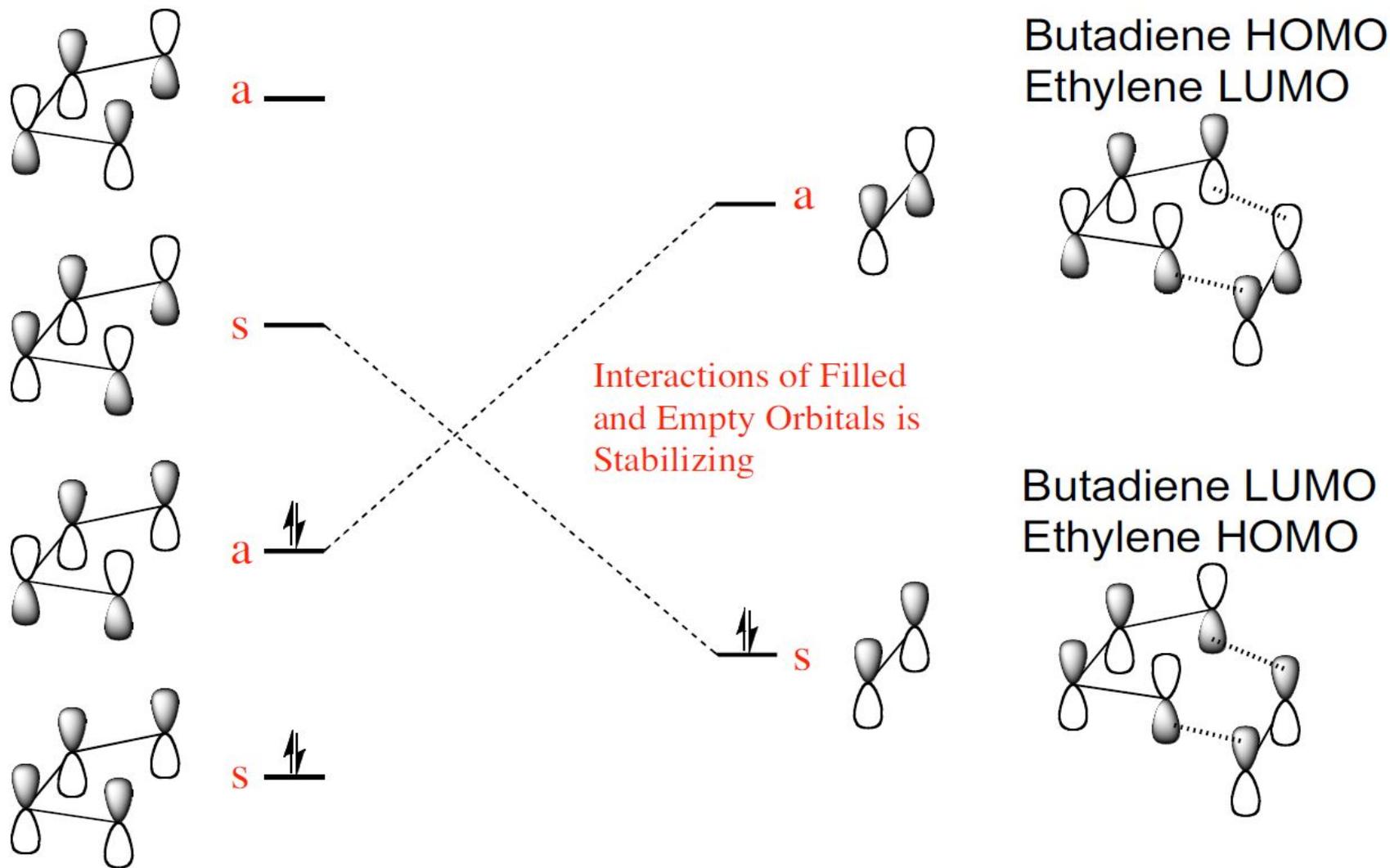
Bonding in the  
Transition State

# Цикдоприсоединение этилена к бутадиену

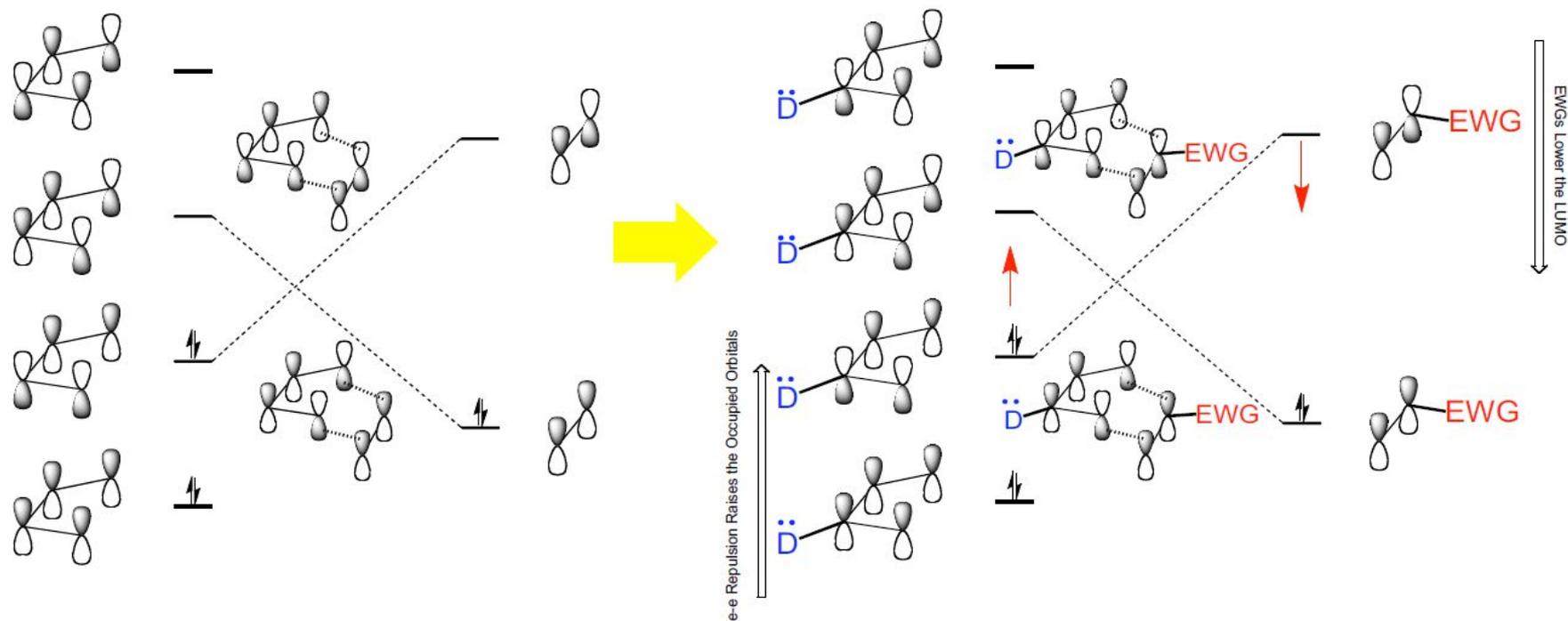


Reaction will proceed thermally.

# 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

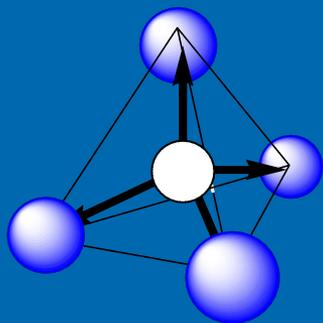


Arousal  
leads to  
reactivity?

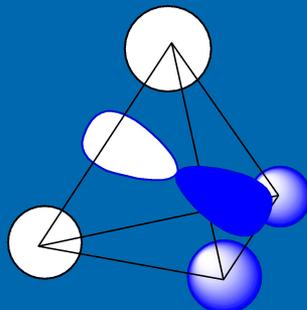
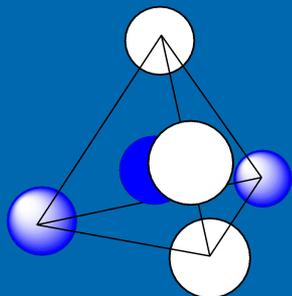
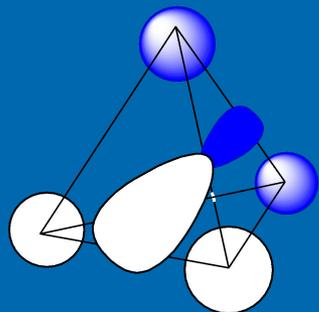
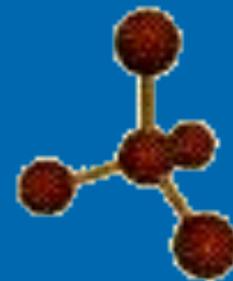
некоторые примеры протекания  
реакций с изменением структуры  
МО



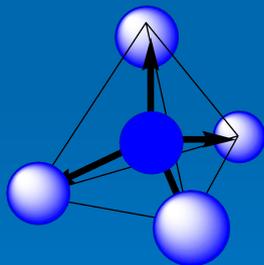
# Реакционная способность метана



*LUMO*

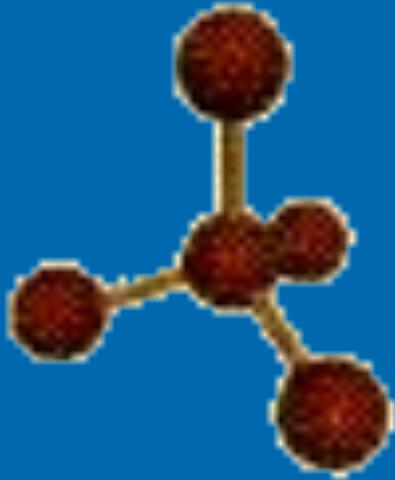


*HOMO*

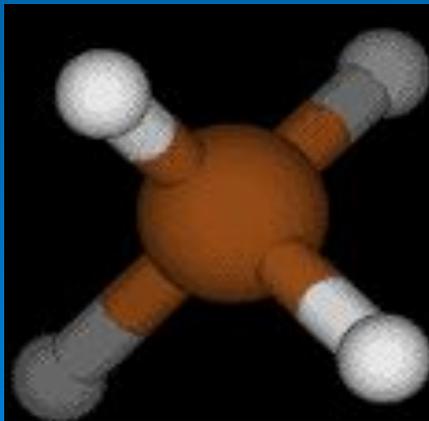


«фронтальные» («граничные») орбитали слишком диффузны, поэтому перекрывание их с локализованными орбиталями реагента слишком мало, т.е. мал выигрыш в энергии при образовании «активированного» комплекса, молекула в основном состоянии инертна.

# Реакционная способность метана



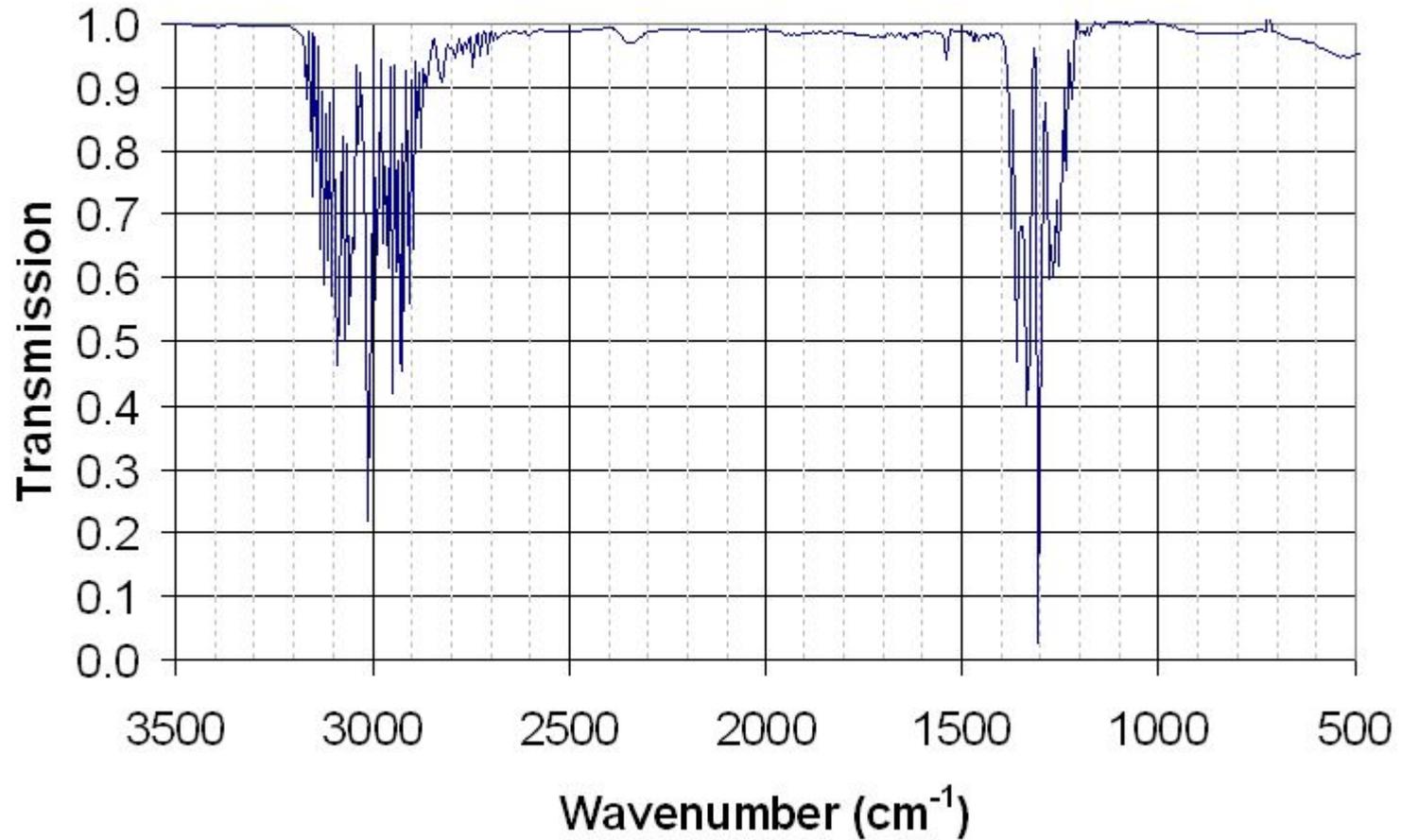
Вращение молекулы не может вызвать изменение геометрии орбиталей (в данном случае – изменение их диффузности)



Однако колебания частей молекулы должно приводить к изменению строения орбиталей

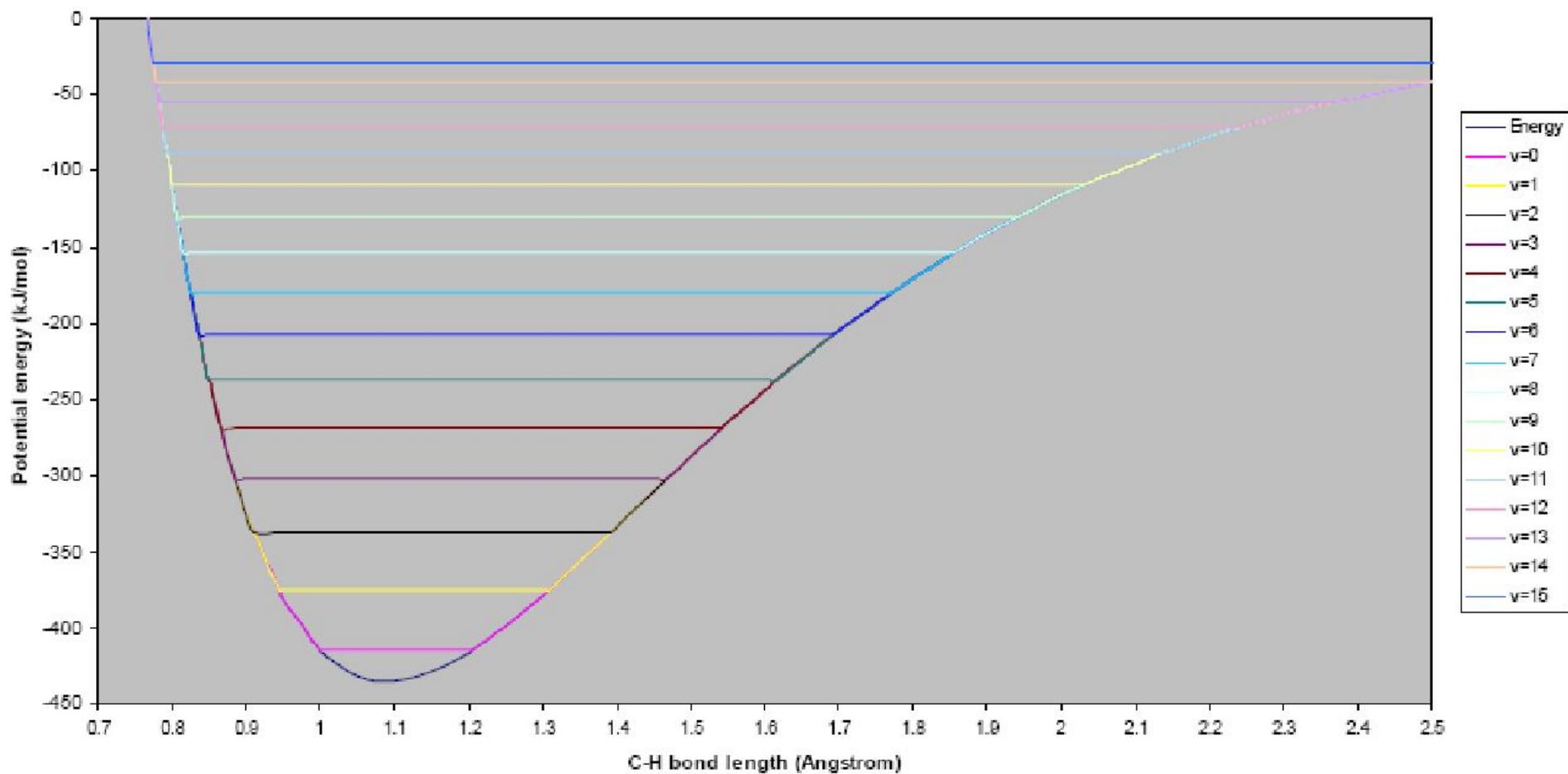
Энергию изменения геометрии орбиталей можно оценить по спектральным данным

## Methane



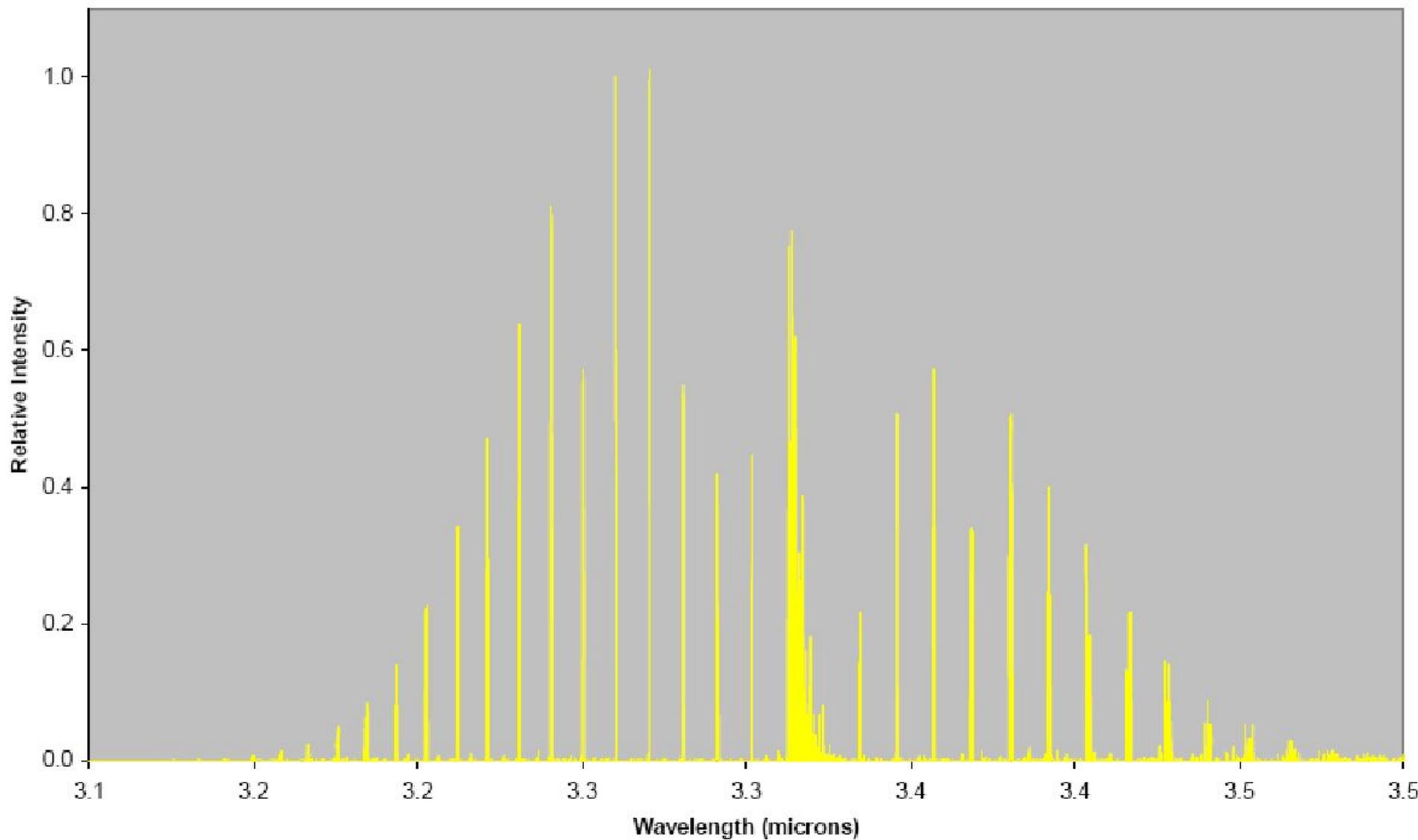
So 3000 cm<sup>-1</sup> => 3,3 microns

CH<sub>3</sub>-H potential energy diagram

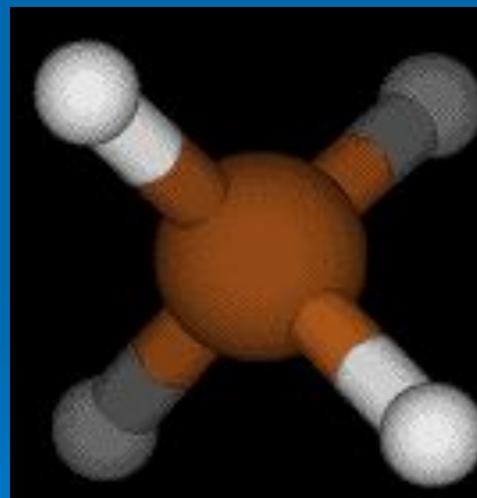
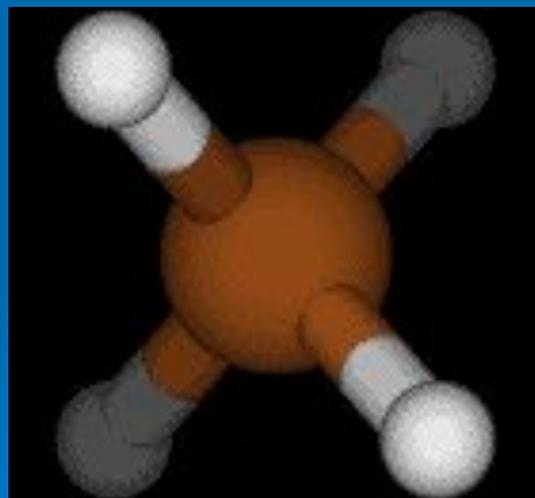
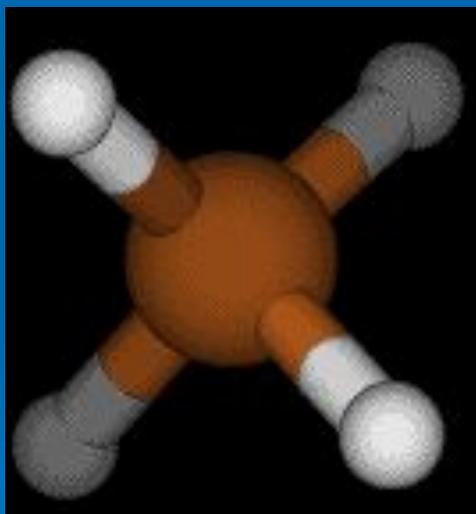
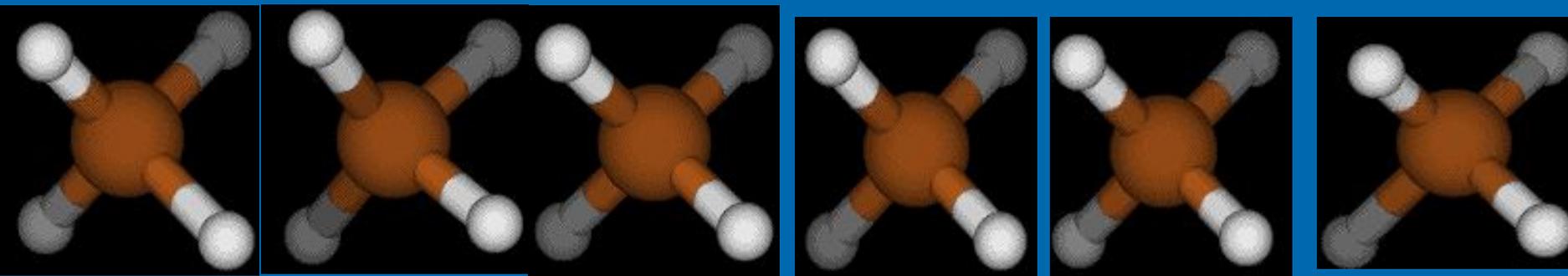


So  $3000\text{ cm}^{-1} \Rightarrow 3,3\text{ microns}$

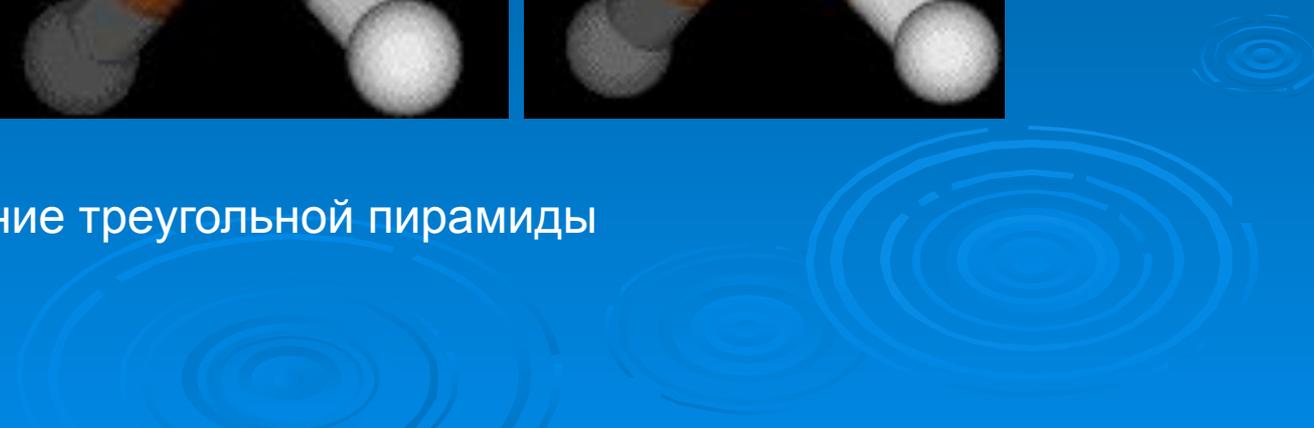
**Methane spectrum**

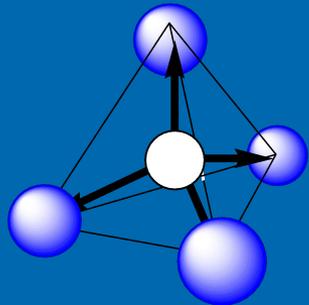


# Основные колебания в метане

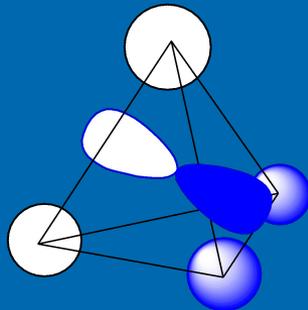
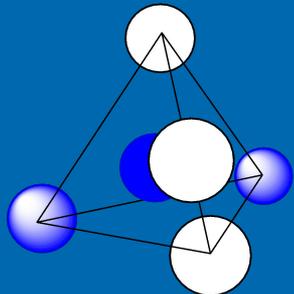
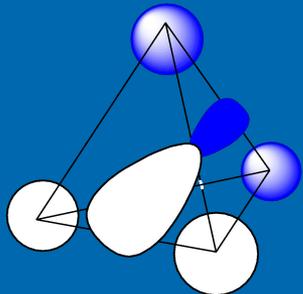


Образование треугольной пирамиды

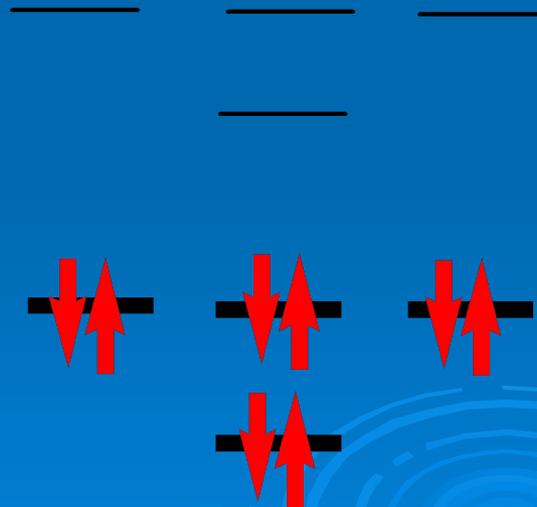
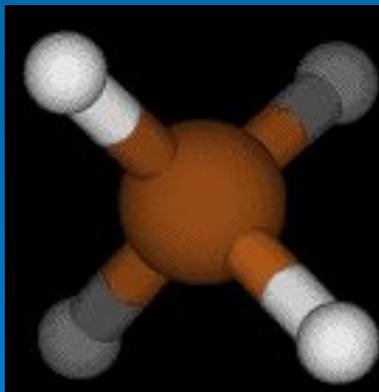
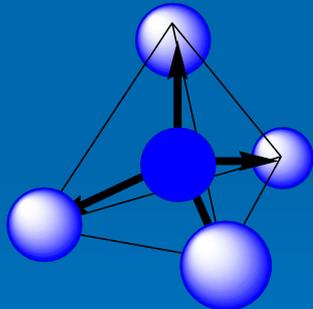




*LUMO*

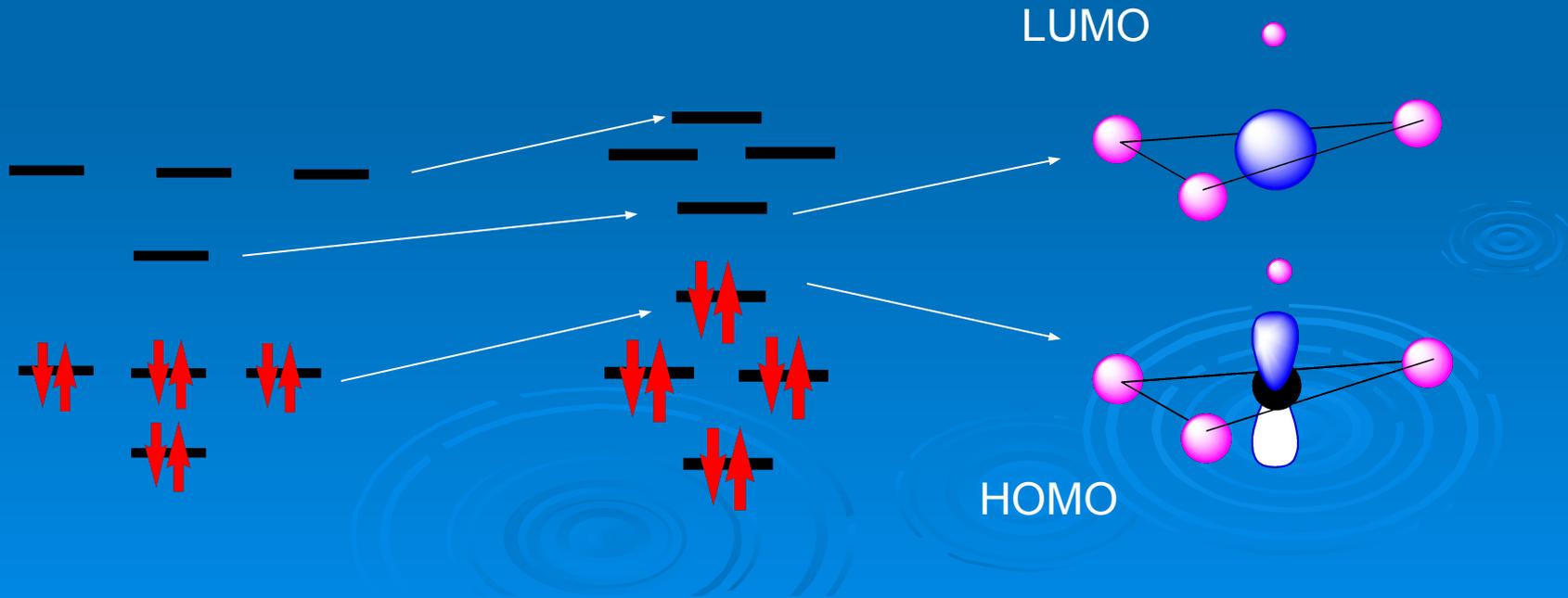
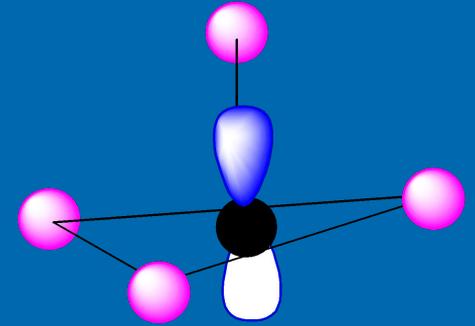
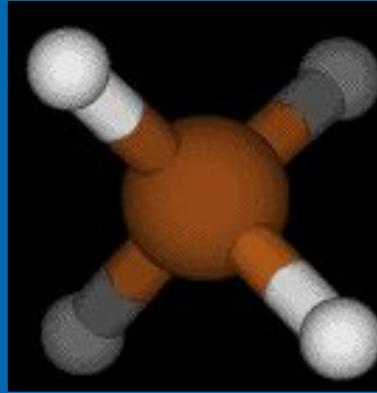
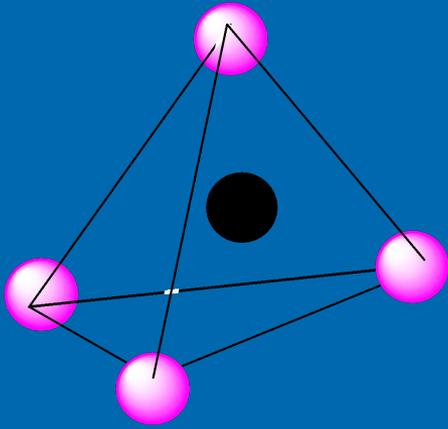


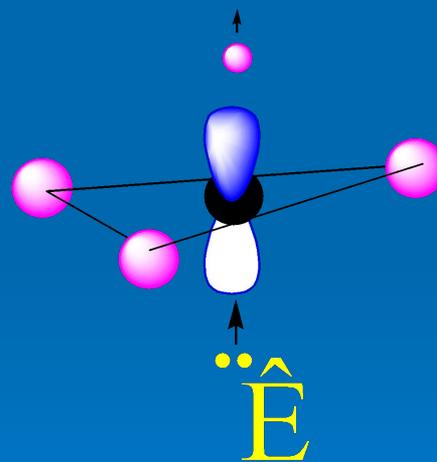
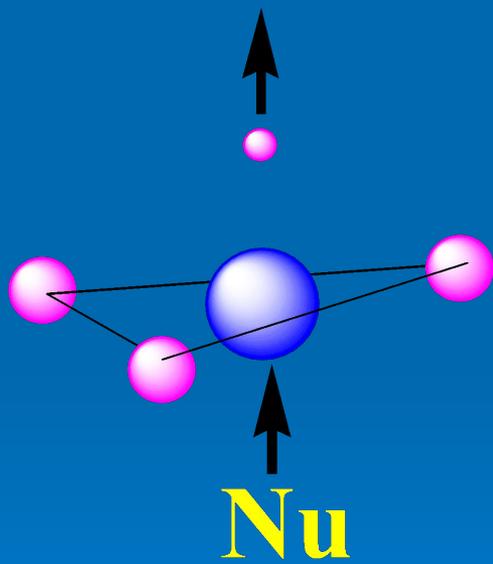
*HOMO*



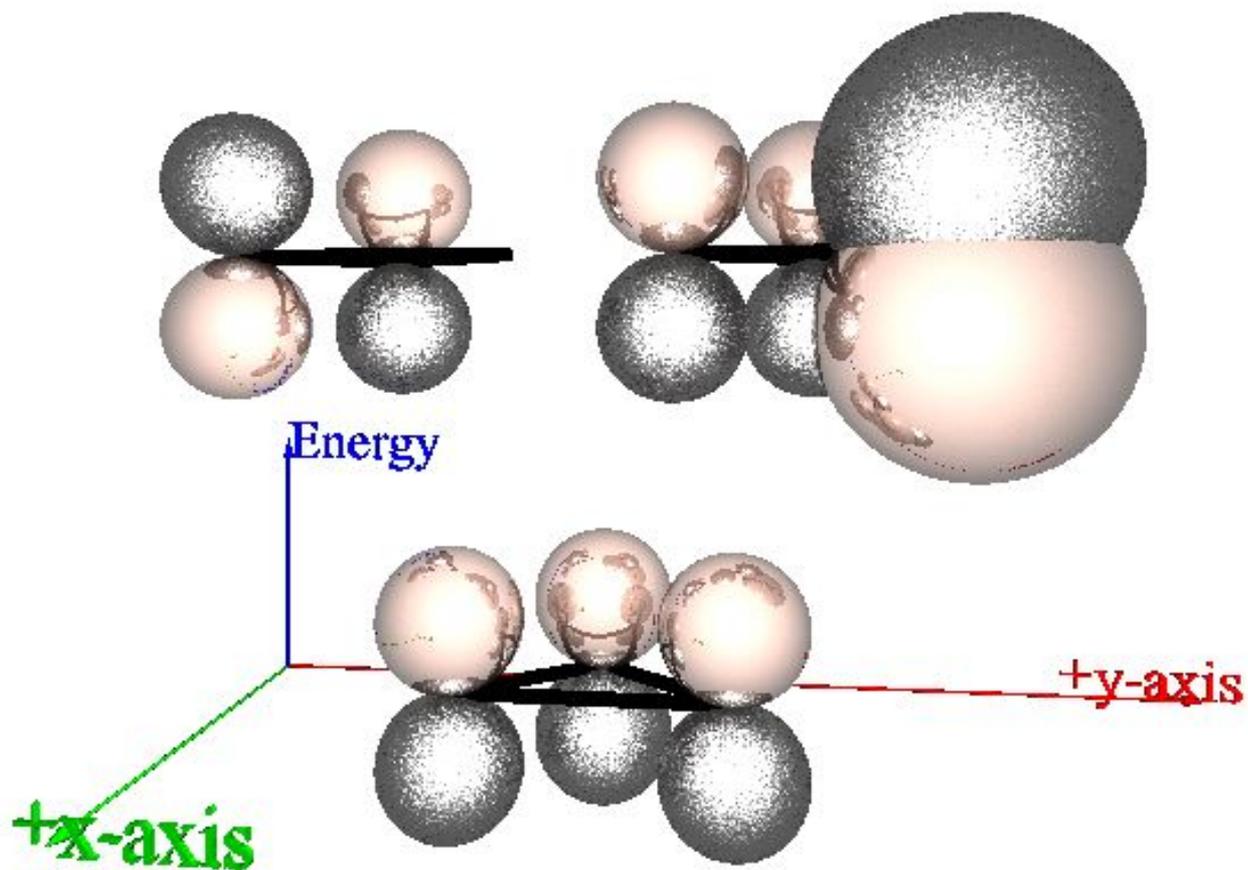
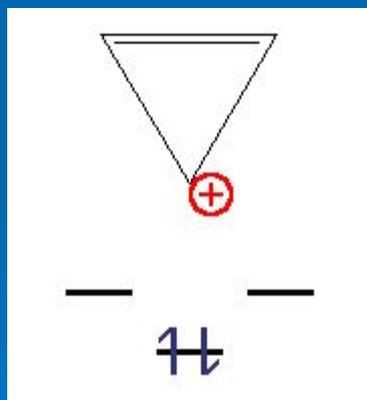
Что происходит с орбиталями?

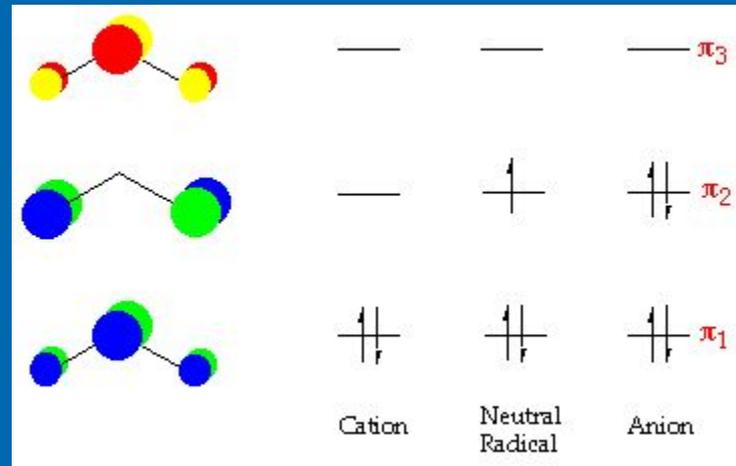
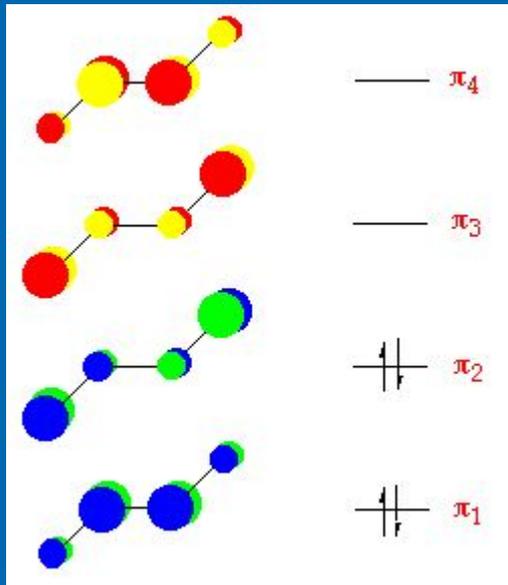
# Образование треугольной пирамиды

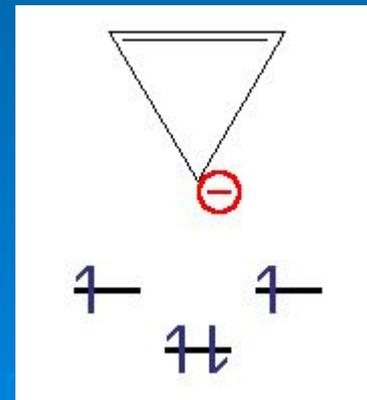
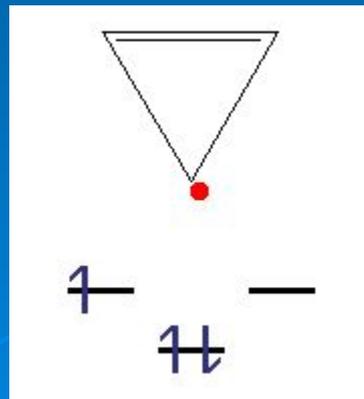
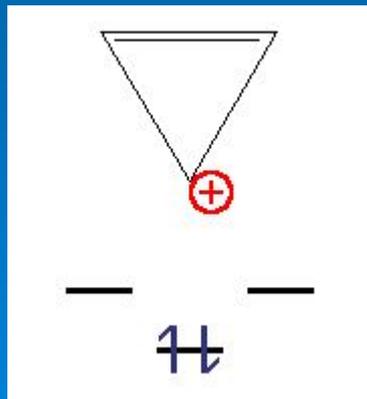
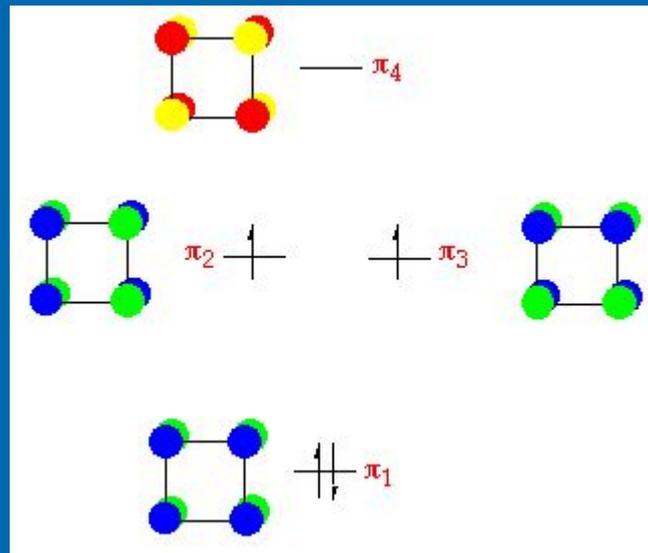


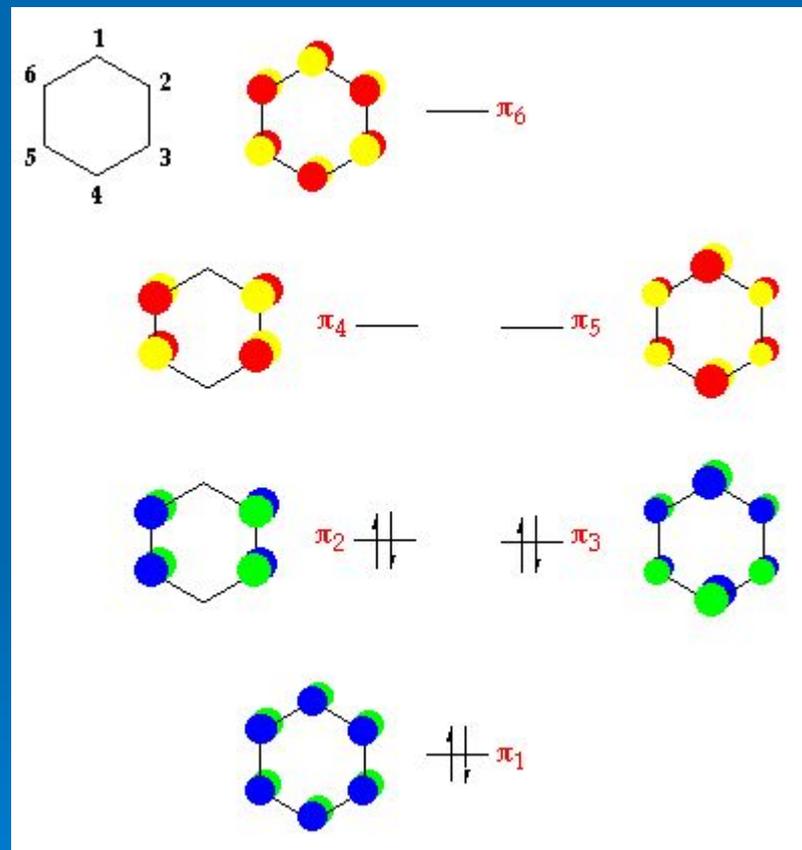
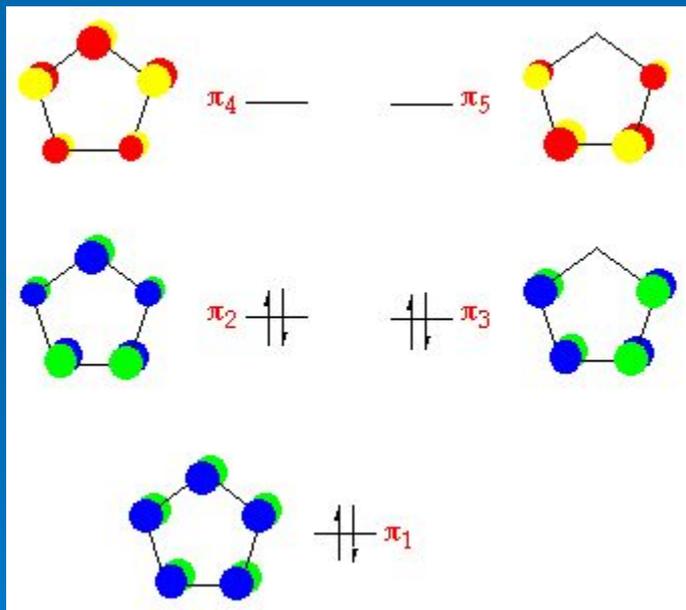


# Некоторые реакционные орбитали органических молекул











УДАЧИ

УДАЧИ

УДАЧИ