

Teorie Molekulových Orbitalů (MO)

Kombinace **atomových** orbitalů na **všech atomech** v molekule

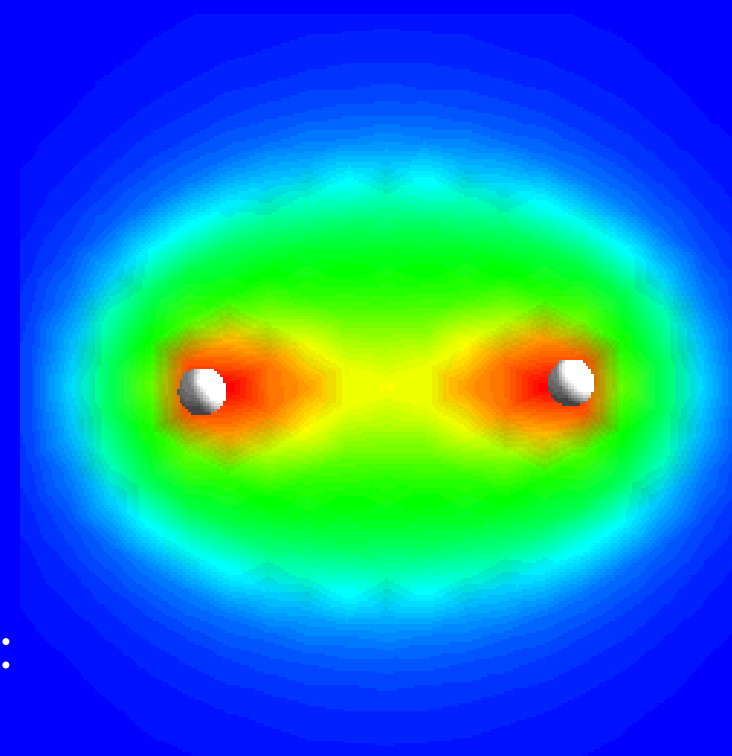
- Vhodná symetrie
- Vhodná (podobná) energie

Z n AO vytvoříme n MO

Pro začátek dvouatomové molekuly:

H_2 , F_2 , CO ,....

Stejně i pro víceatomové: BF_3 , CH_4 ,....



Vazebný MO v molekule H_2

Born-Oppenheimerova aproximace

The Hamiltonian operator consists of five terms:

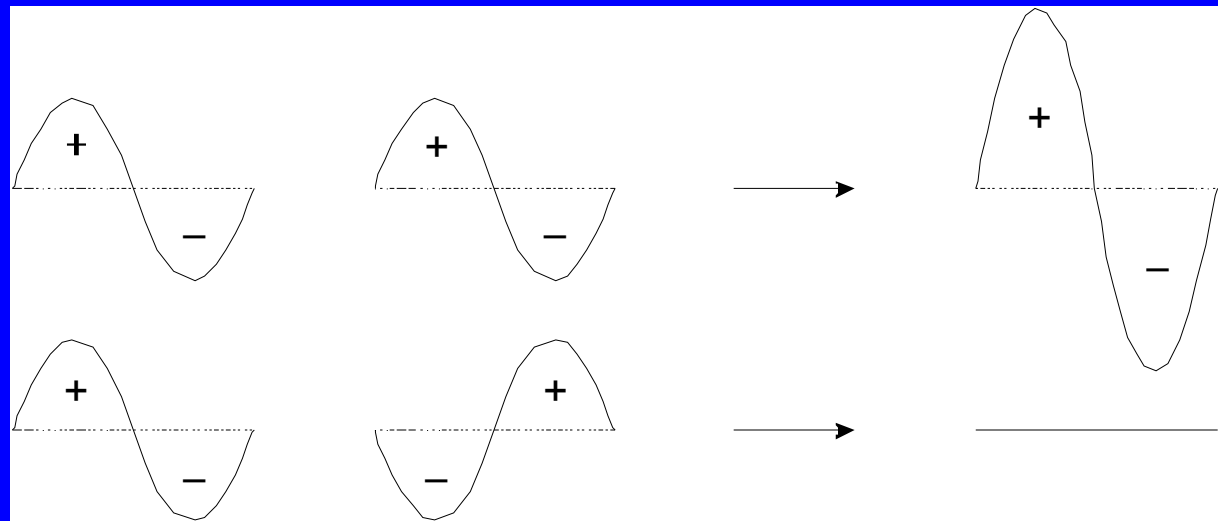
$$H = T_e + T_n + V_{ee} + V_{en} + V_{nn} \quad (2.3)$$

where T_e and T_n are operators of the kinetic energy of electrons and nuclei, respectively; V_{ee} , V_{en} and V_{nn} are operators of the potential energy, including electrostatic interactions electron-electron, electron-nucleus and nucleus-nucleus, respectively. The Born-Oppenheimer approximation neglects the term T_n (coordinates of nuclei are included as parameters) and instead of the Hamiltonian operator H uses the electronic Hamiltonian operator H_e , defined by this equation:

$$H_e = T_e + V_{ee} + V_{en} + V_{nn} \quad (2.4)$$

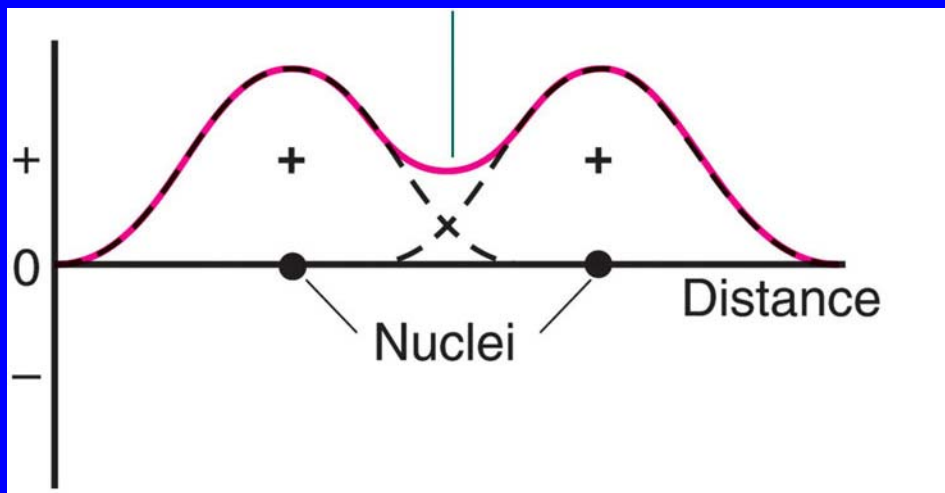
Interference vlnových funkcí

Konstruktivní



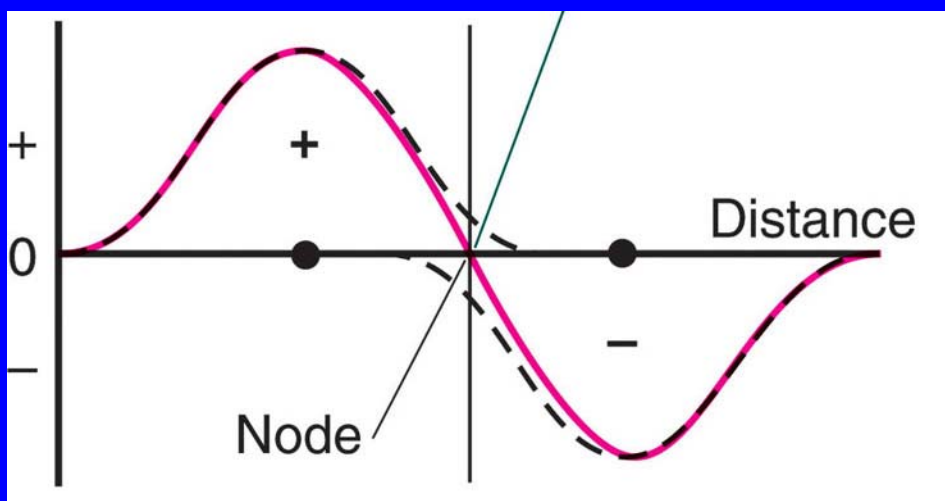
Destruktivní

LCAO = Lineární kombinace atomových orbitalů



Kombinace dvou vlnových funkcí (orbitalů) se stejným znaménkem

$$\Psi = c_1 \Psi_A + c_2 \Psi_B$$
$$\Psi^* = c_3 \Psi_A - c_4 \Psi_B$$



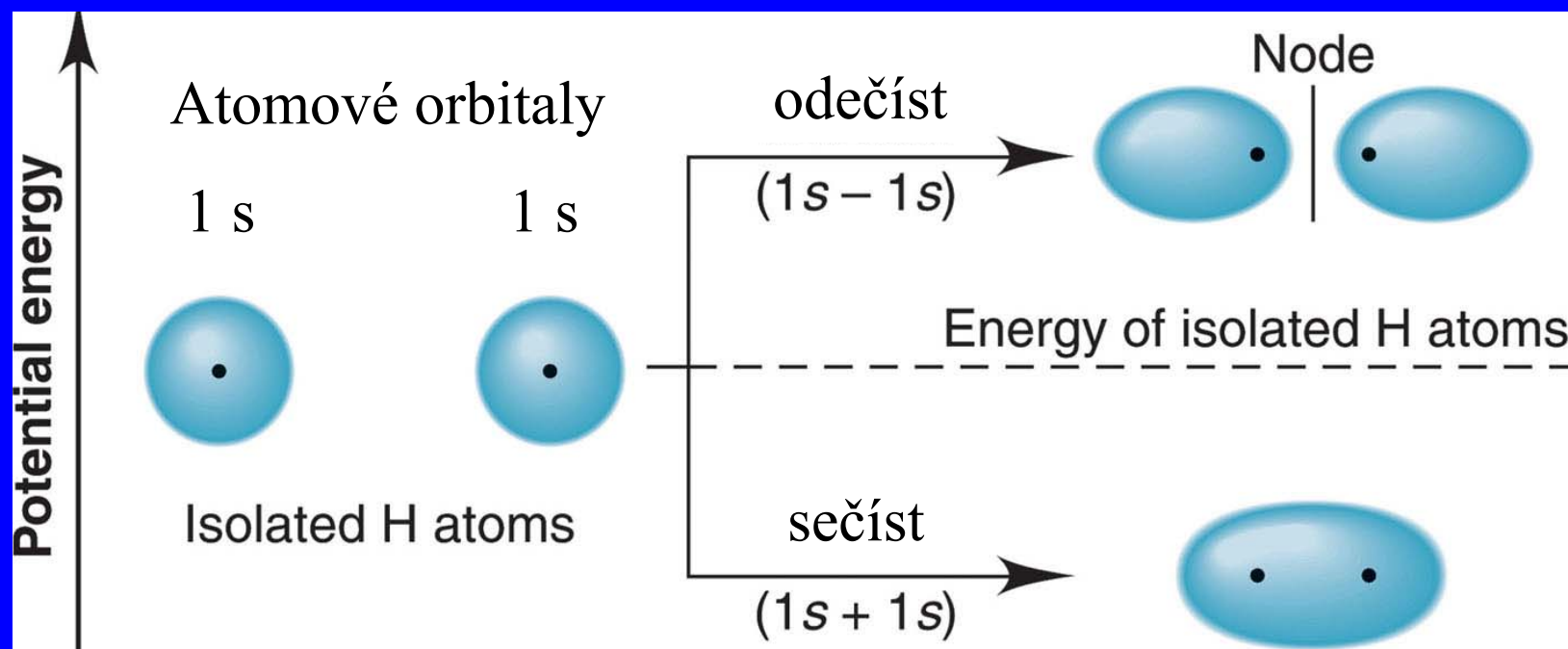
Kombinace dvou vlnových funkcí (orbitalů) s opačným znaménkem

LCAO = Lineární kombinace atomových orbitalů

$$\Psi = c_1 \Psi_A + c_2 \Psi_B$$

$$\Psi^* = c_3 \Psi_A - c_4 \Psi_B$$

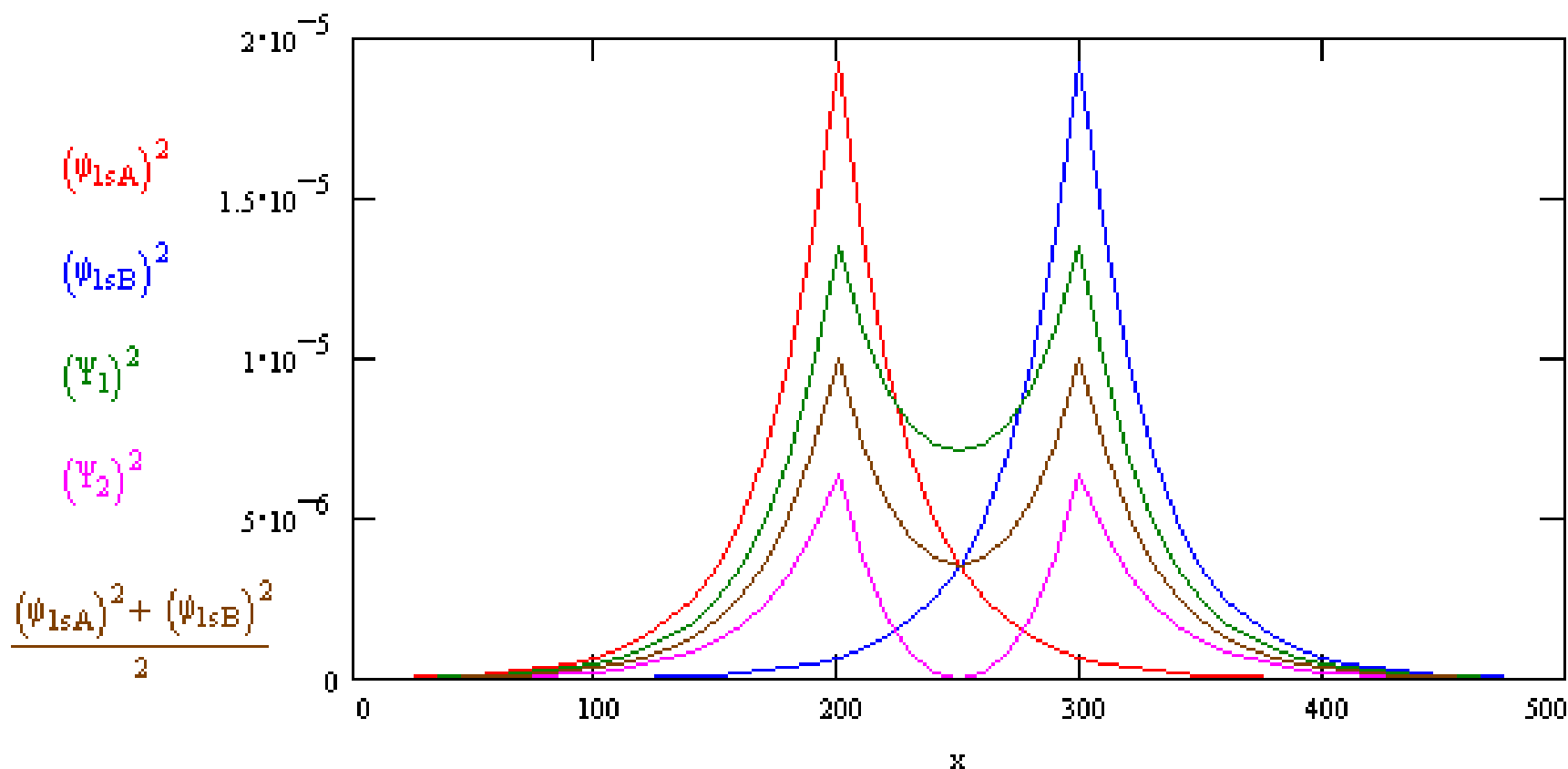
Ψ^* Protivazebný MO



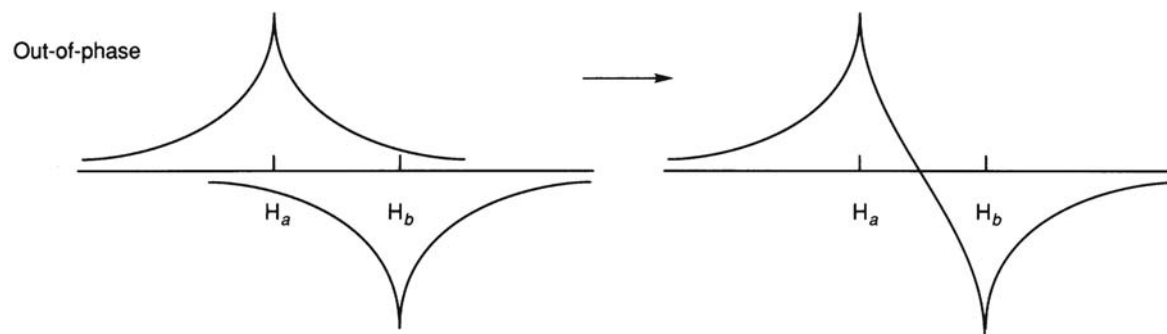
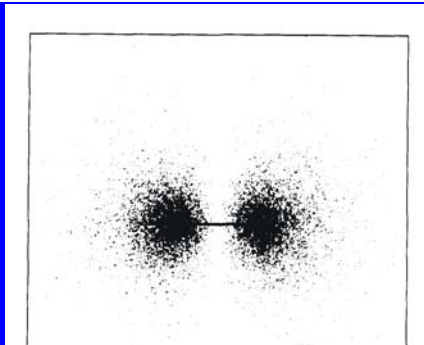
Ψ Vazebný MO

Počet MO = počet AO

LCAO = Lineární kombinace atomových orbitalů

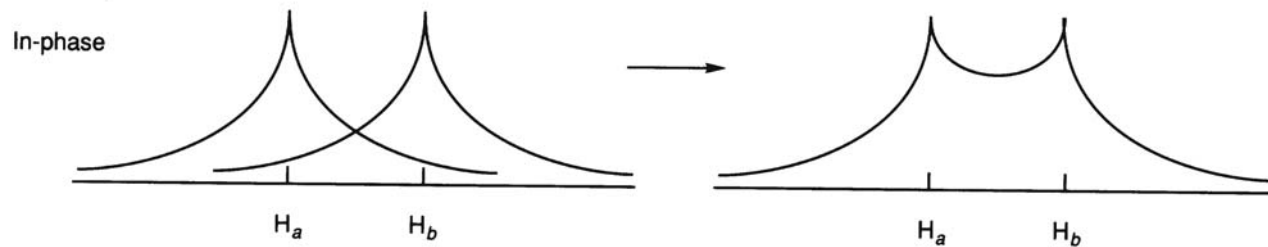
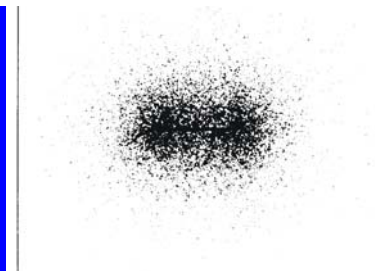


Ψ^* Protivazebný MO



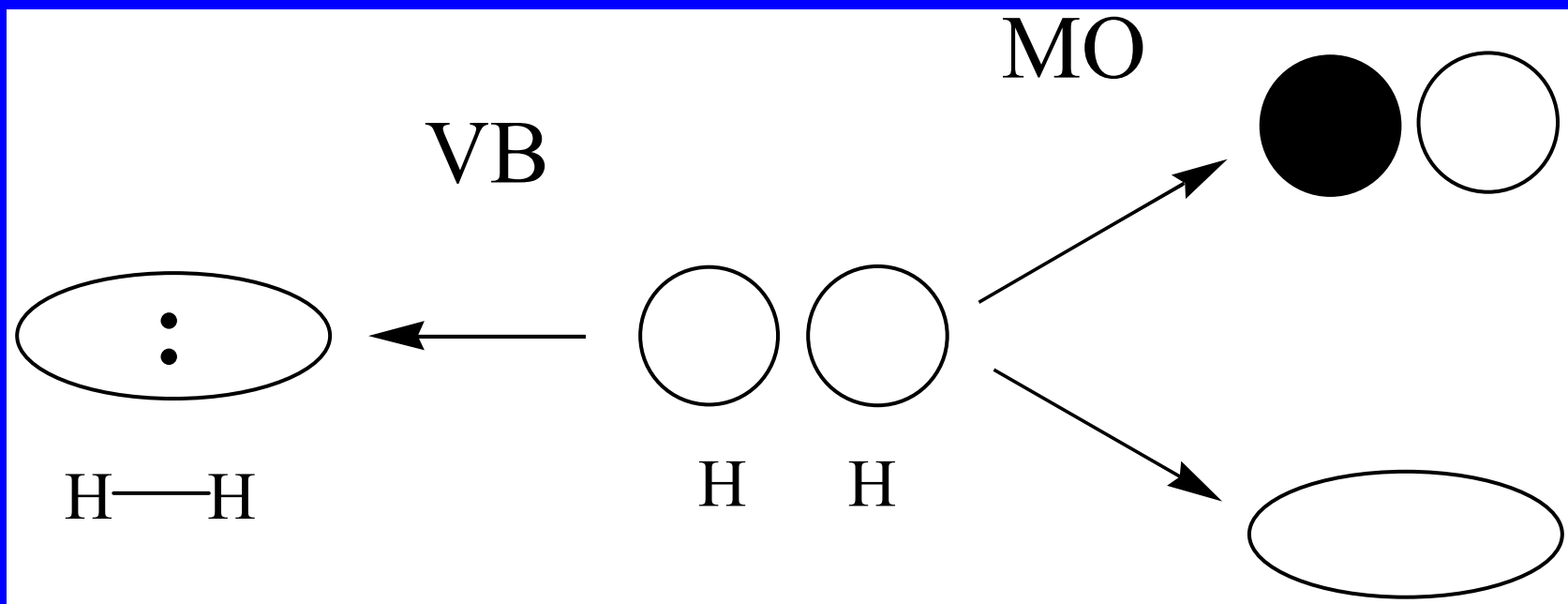
Destructive interference of the waves from two hydrogen 1s orbitals on adjacent atoms (the 'out-of-phase' combination).

Ψ Vazebný MO



Reinforcement of the waves from two hydrogen 1s orbitals on adjacent atoms (the 'in-phase' combination).

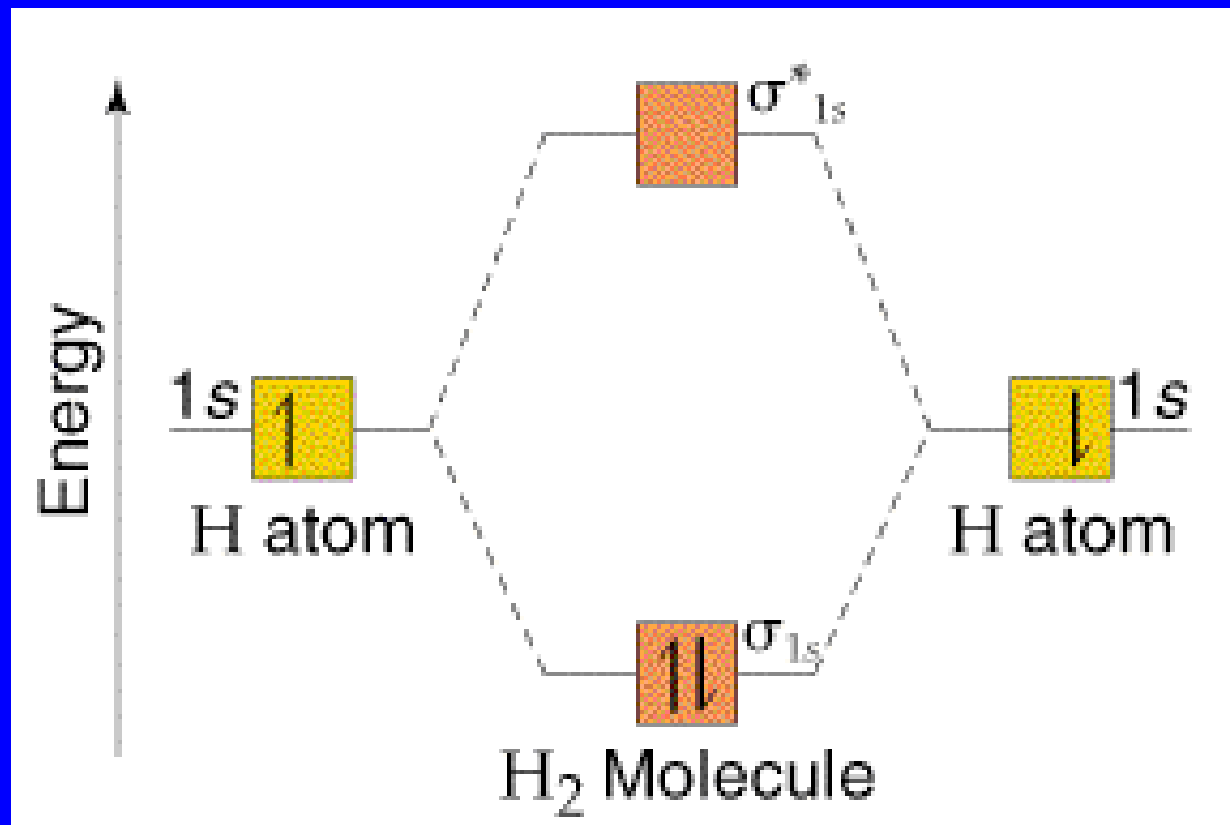
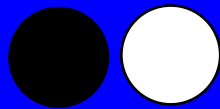
Rozdíl mezi VB a MO



Lokalizované vazby

Delokalizované vazby

Ψ^* Protivazebný MO



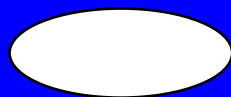
Energetická

destabilizace

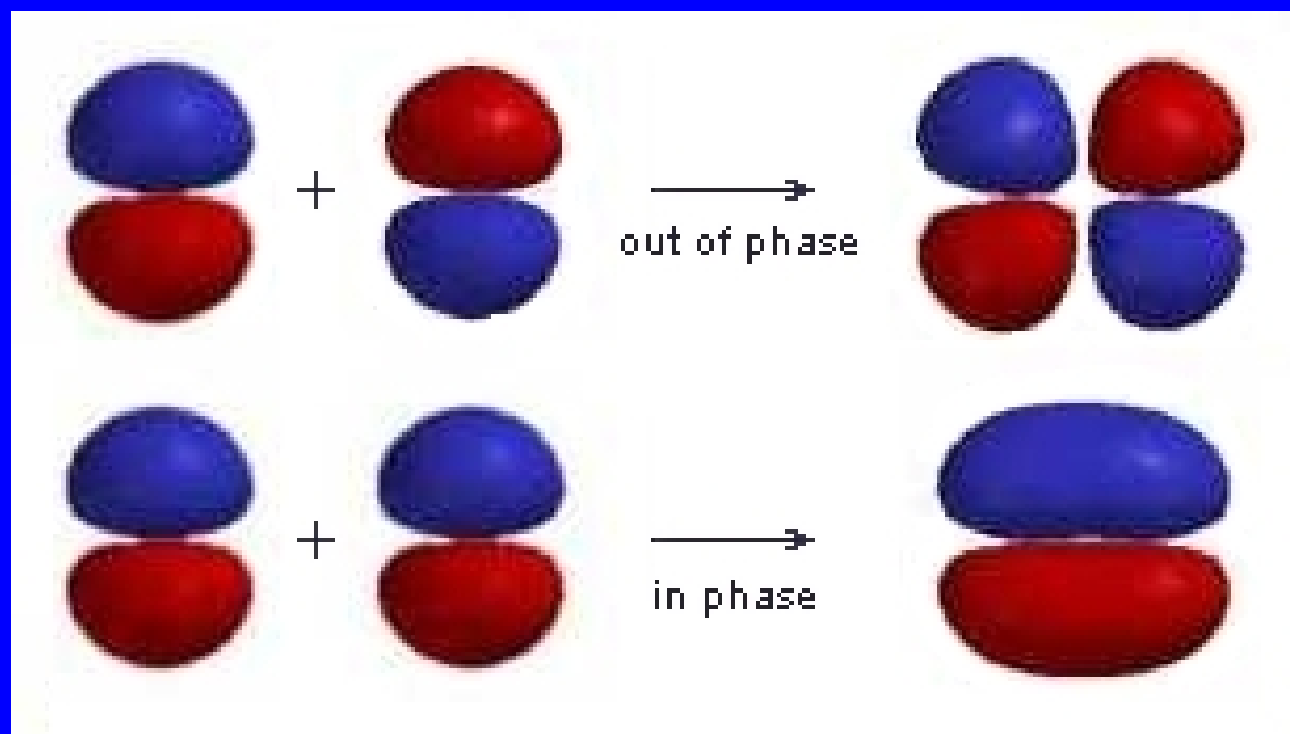
stabilizace

ve srovnání s
volnými atomy

Ψ Vazebný MO



π MO vzniklé kombinací p AO

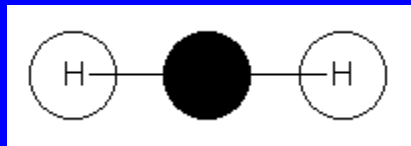


Protivazebný π MO

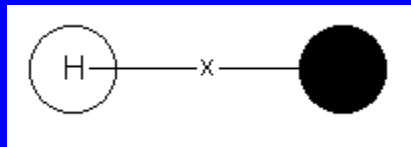
Vazebný π MO



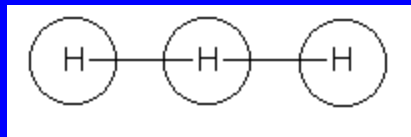
Vzrůstá energie, klesá stabilita



Protivazebný MO

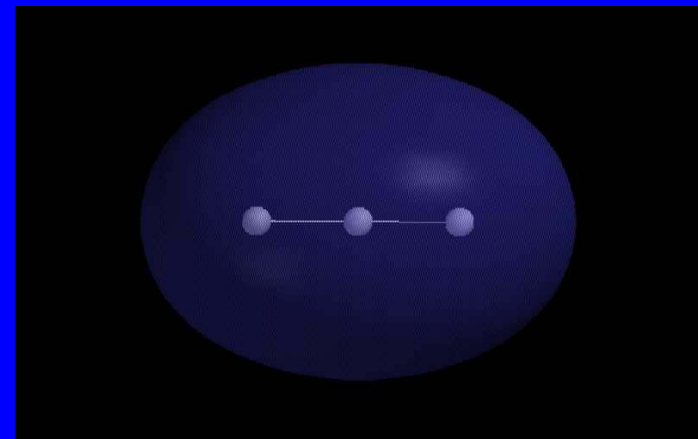
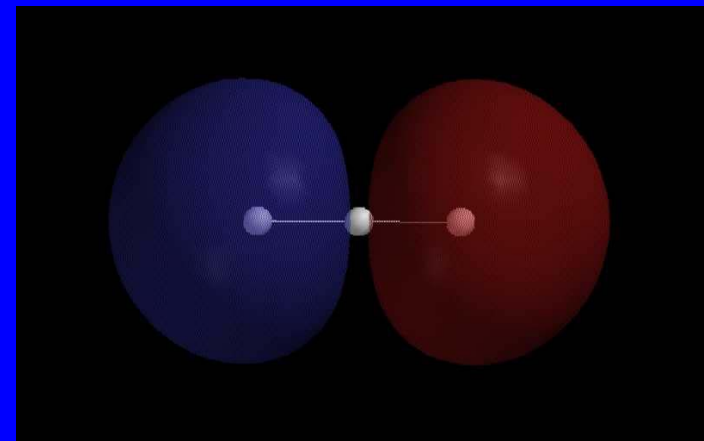
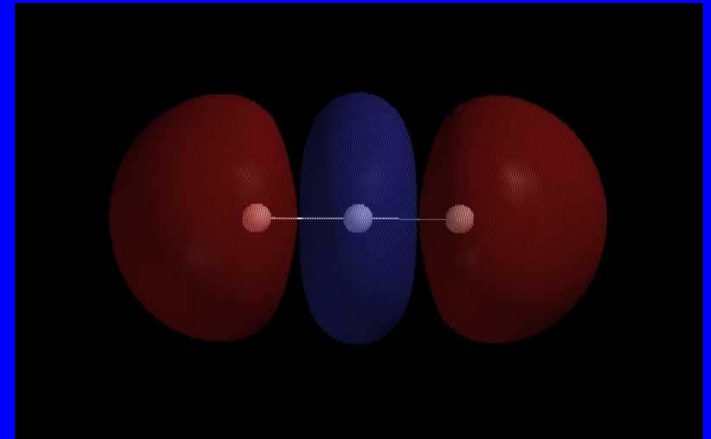


Nevazebný MO



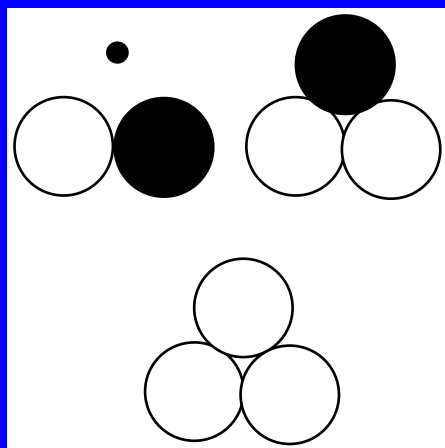
Vazebný MO

Vzrůstá počet uzlových rovin

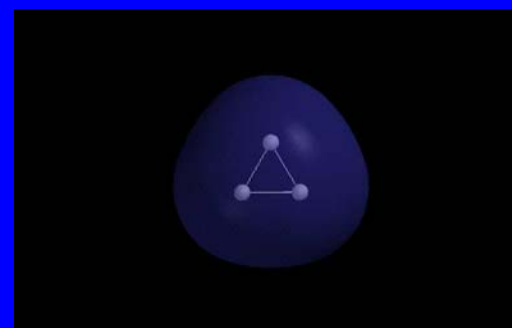
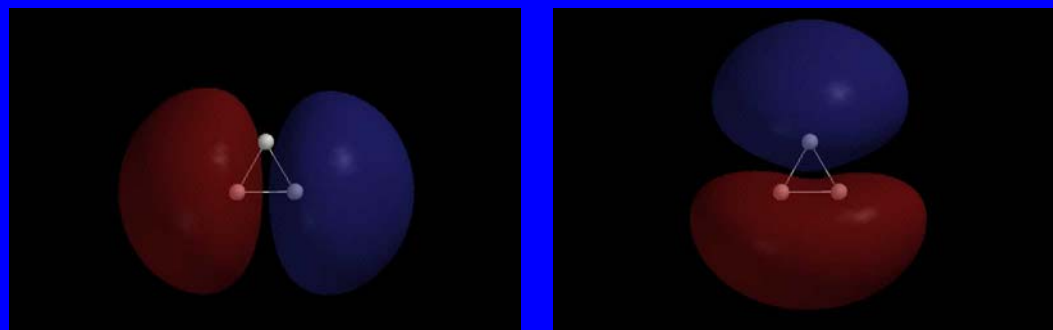




Vzrůstá energie,
klesá stabilita



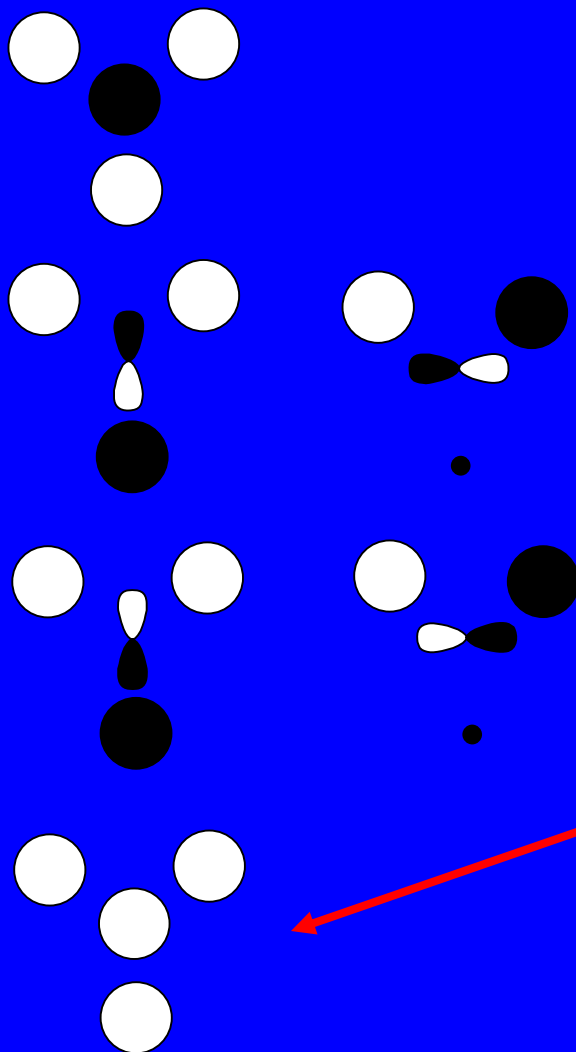
Protivazebné MO



Vazebný MO

Vzrůstá počet uzlových rovin

LCAO = Lineární kombinace AO



LCAO

obecně pro n atomů a m orbitalů

$$\Psi_i = c_1 \Psi_1 + c_2 \Psi_2 + c_3 \Psi_3 + \dots + c_n \Psi_n$$

Ze 6 AO ($s+2p+3s$) vznikne 6 MO

MO s nejnižší energií, nemá žádnou uzlovou rovinu, nejvíce vazebný, kombinace po jednom AO z každého atomu, všechny se stejným znaménkem

Zaplňování MO elektrony

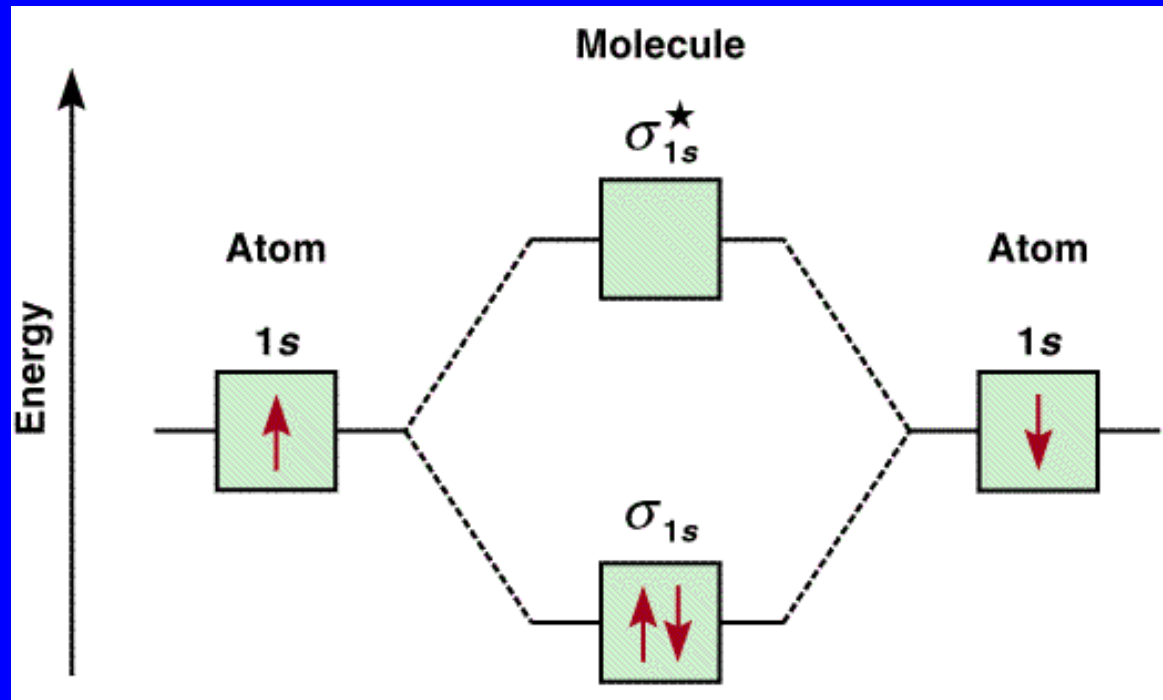
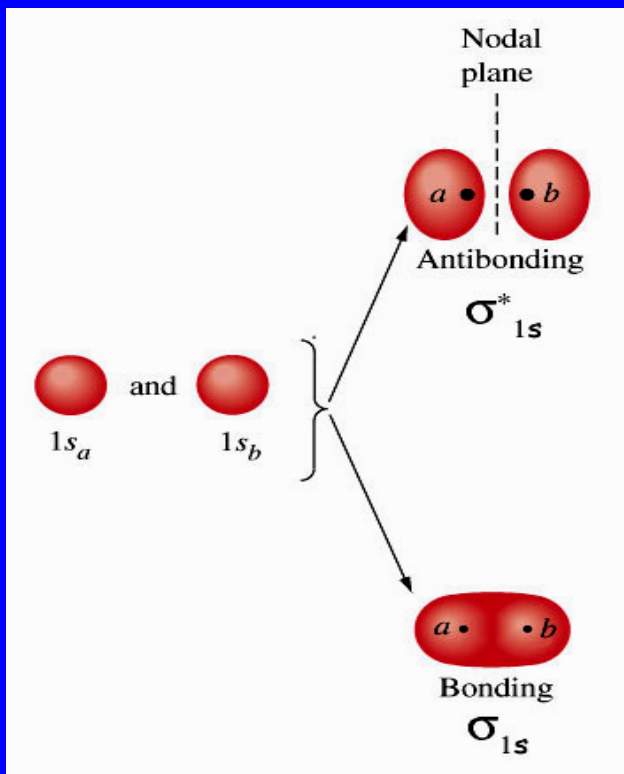
Aufbau

Hund

Pauli

Pravidla pro zaplňování MO elektrony

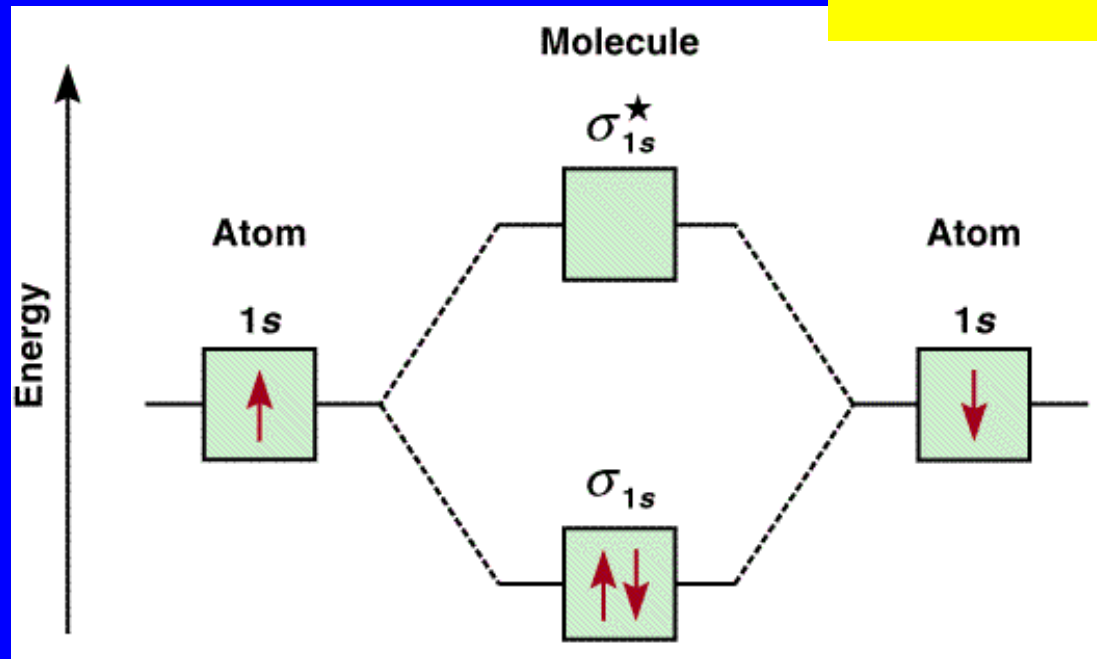
Protivazebný MO



Vazebný MO

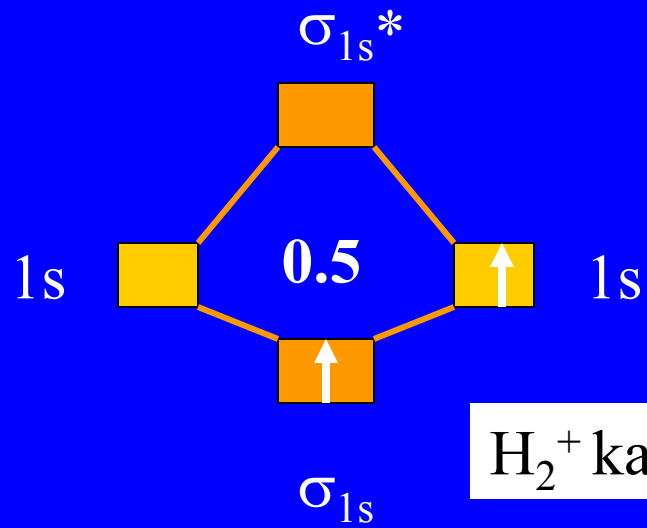
Řád vazby

$$\text{Řád} = \frac{eMO - eMO^*}{2}$$

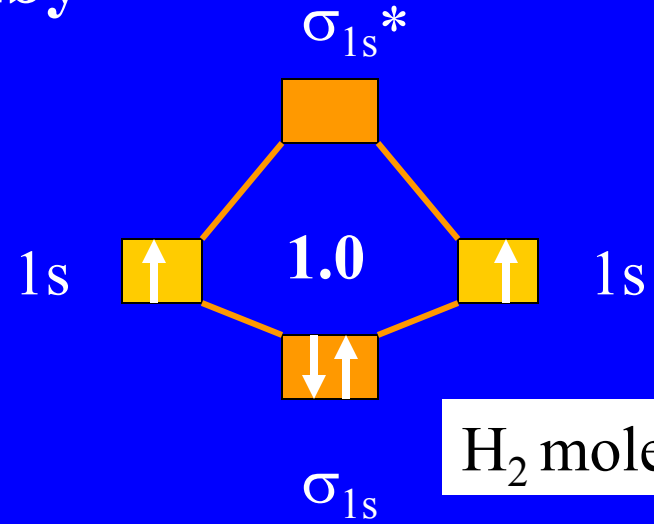


Řád vazby = $\frac{1}{2}$ (počet vazebných e – počet protivazebných e)

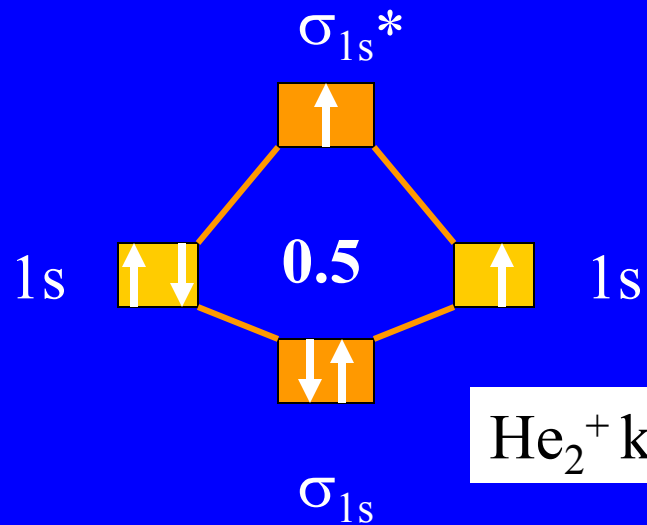
Řád vazby



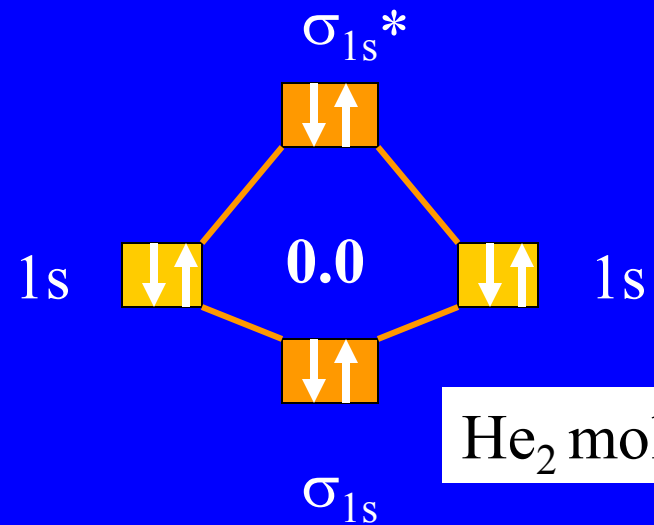
H_2^+ kation



H_2 molekula



He_2^+ kation

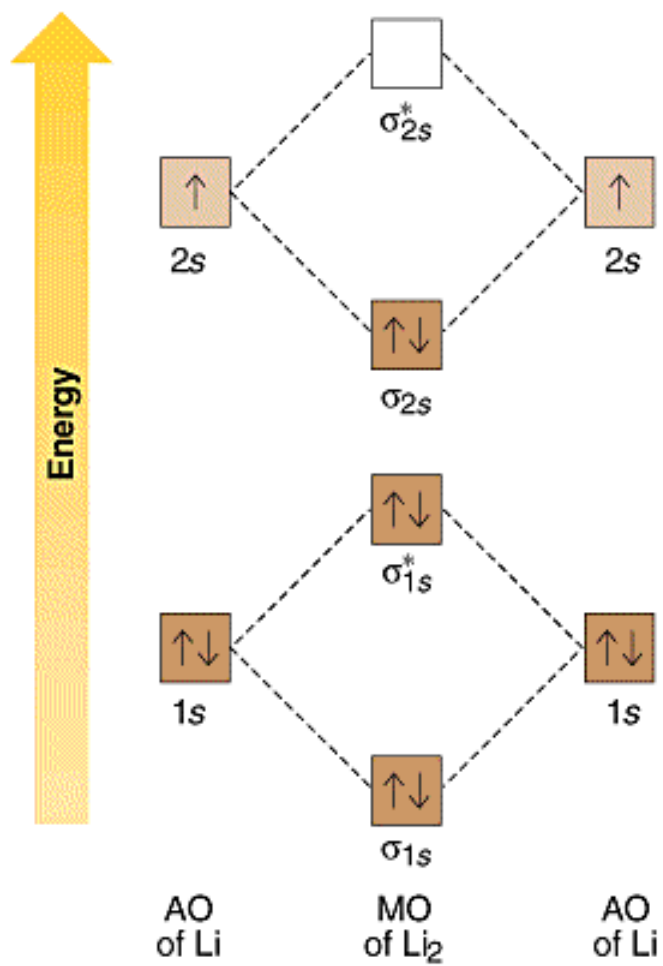


He_2 molekula

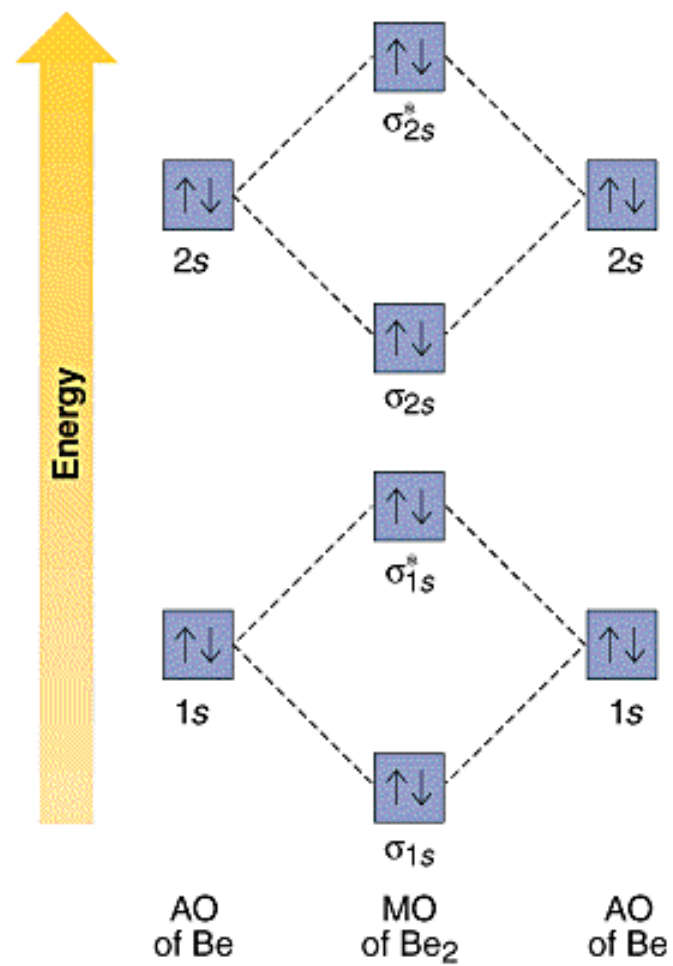
Řád vazby

Molekula	Vazebné elektrony	Protivaz. elektrony	Řád vazby	Délka vazby, Å	Vazebná energie, kJ mol ⁻¹
H ₂ ⁺	1	0	0.5	1.06	255
H ₂	2	0	1	0.74	432
He ₂ ⁺	2	1	0.5	1.08	230
He ₂	2	2	0	---	0

1 elektronová vazba: 1 vazebný e⁻ tvoří silnější vazbu než 2 vazebné a 1 protivazebný e⁻

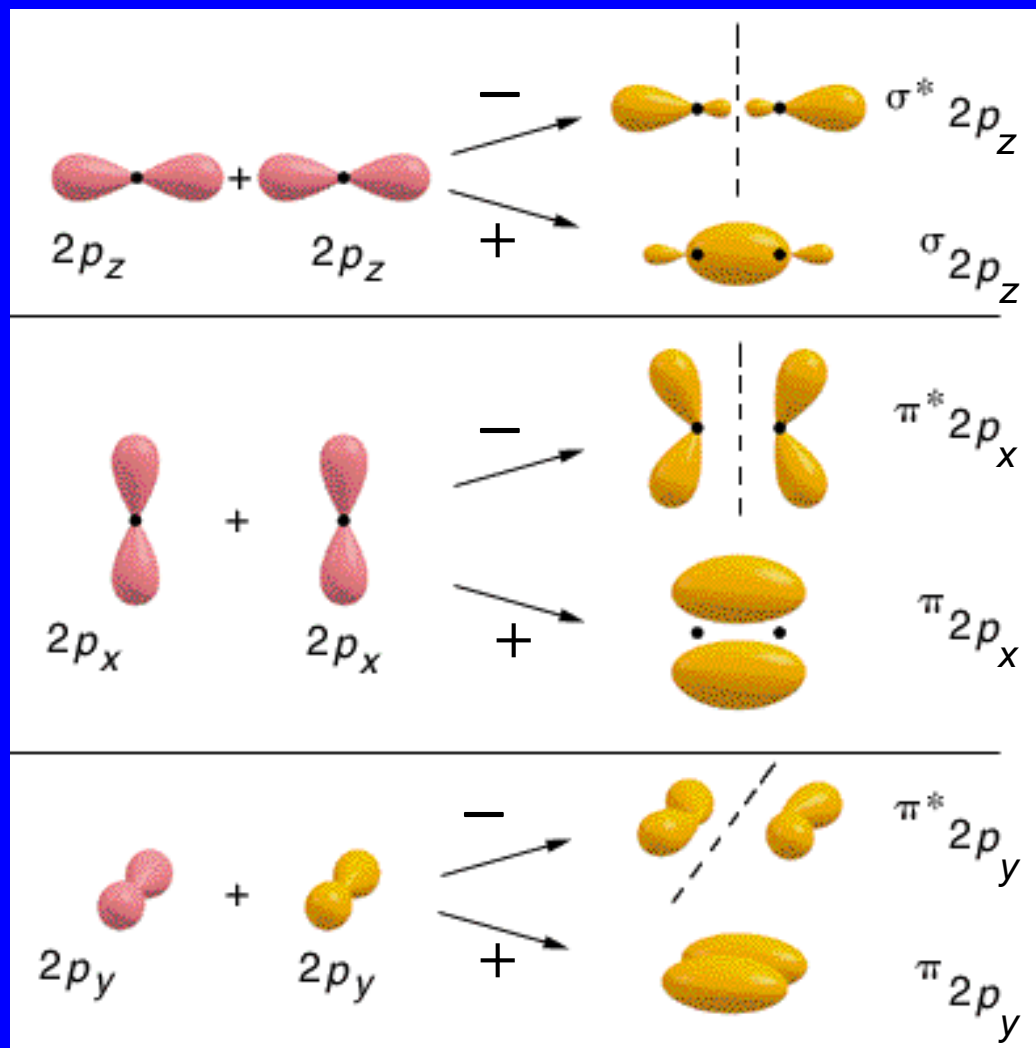


A Li₂ bond order = 1



B Be₂ bond order = 0

MO vzniklé kombinací p AO



MO vzniklé kombinací p AO

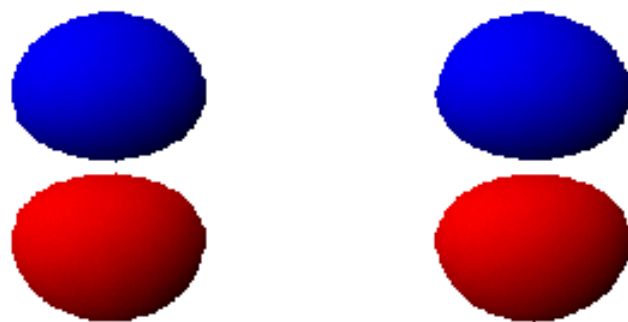
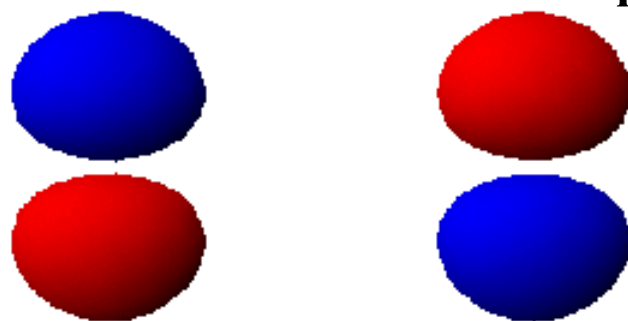
Protivazebný MO σ_{2pz}^*



Vazebný MO σ_{2pz}

MO vzniklé kombinací p AO

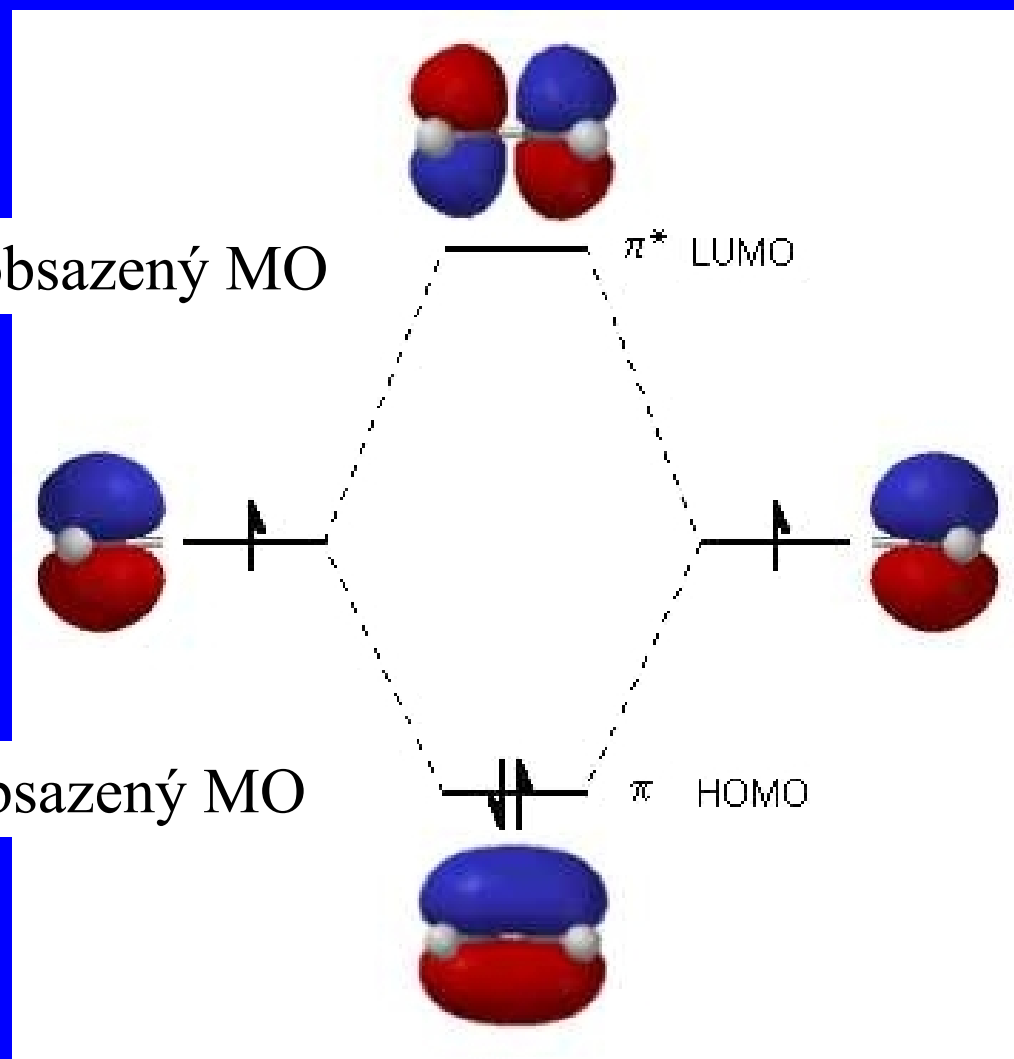
Protivazebný MO π_{2px}^*



Vazebný MO π_{2px}

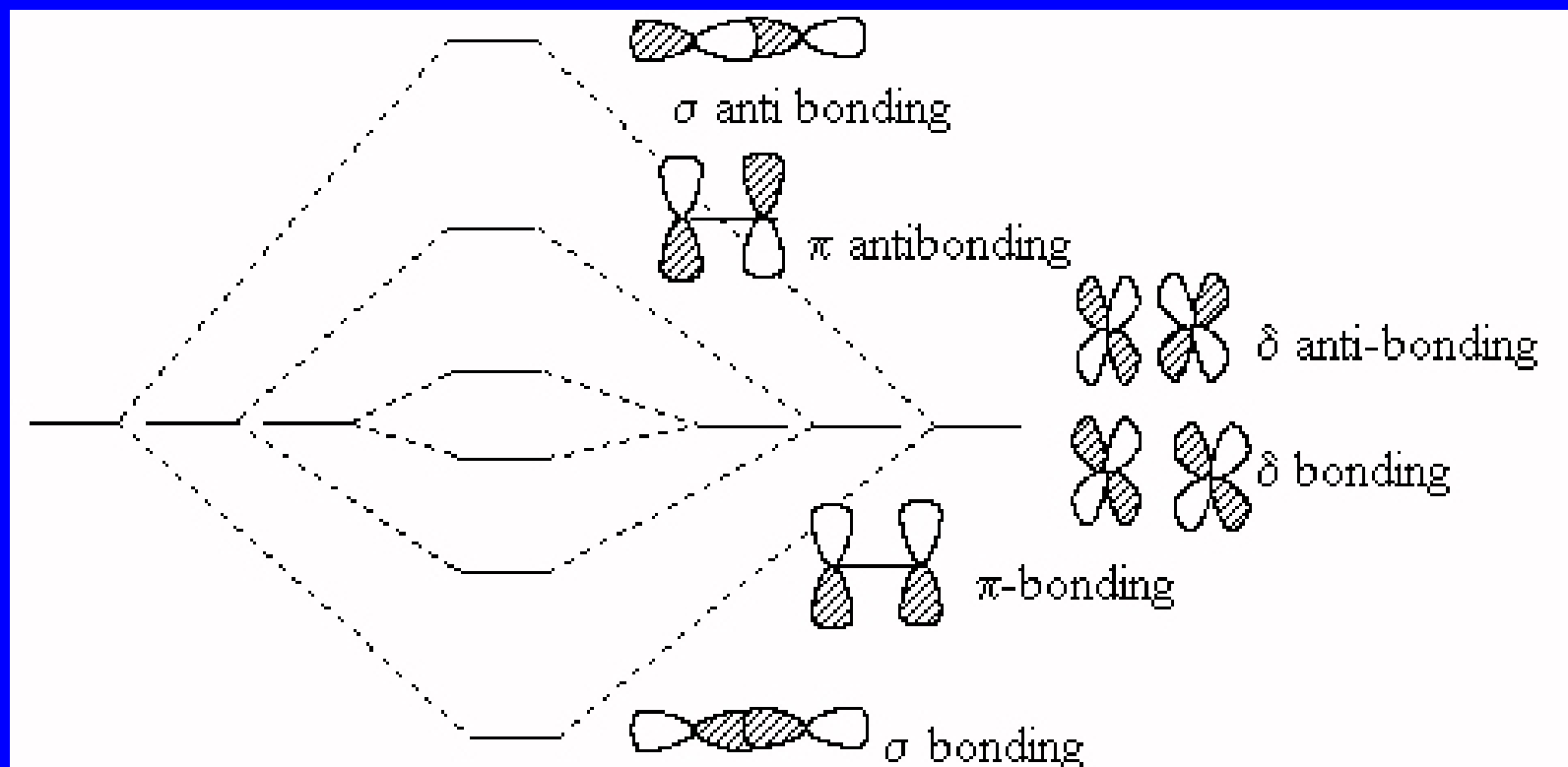
Pi vazba v ethenu pomocí MO

LUMO = nejnižší neobsazený MO



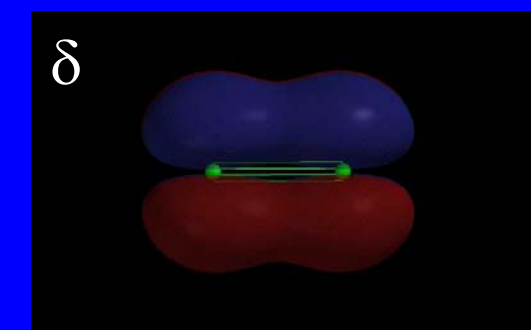
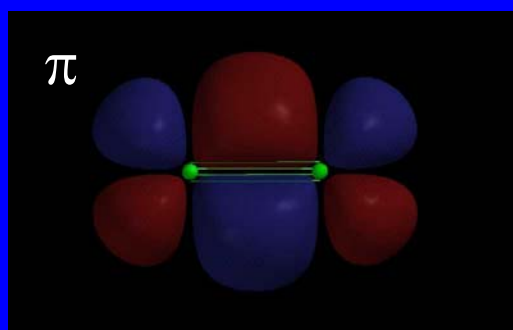
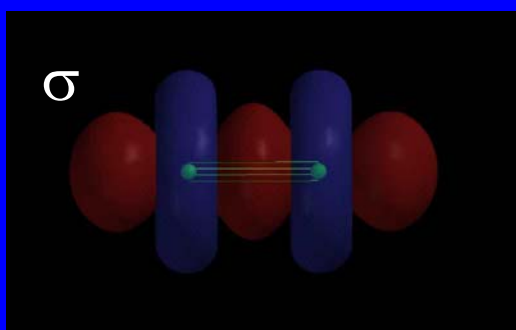
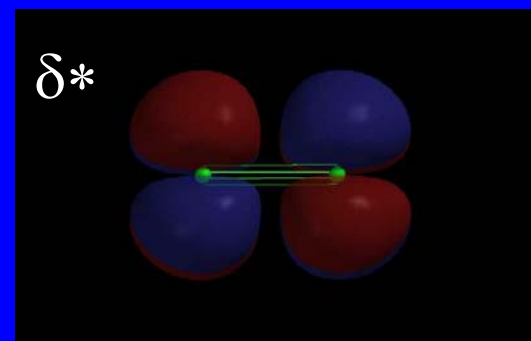
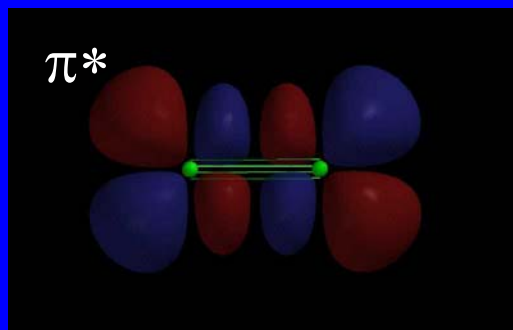
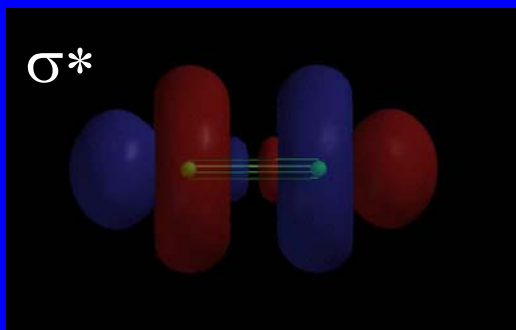
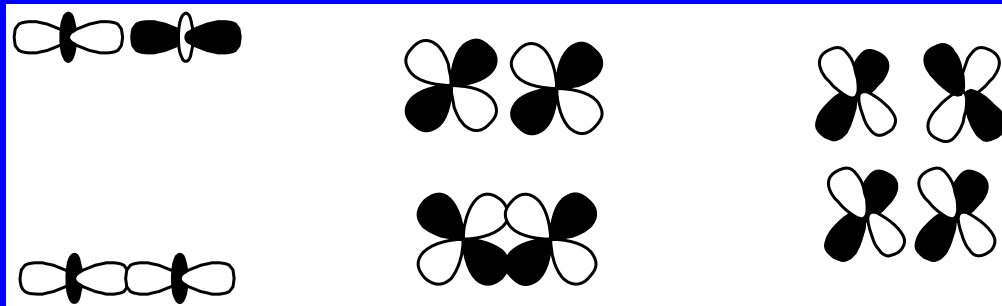
HOMO = nejvyšší obsazený MO

Typy molekulových orbitalů



Lepší překryv snižuje energii vazebného MO a zvyšuje energii protivazebného MO: $\sigma > \pi > \delta$

Tvorba MO z d orbitalů



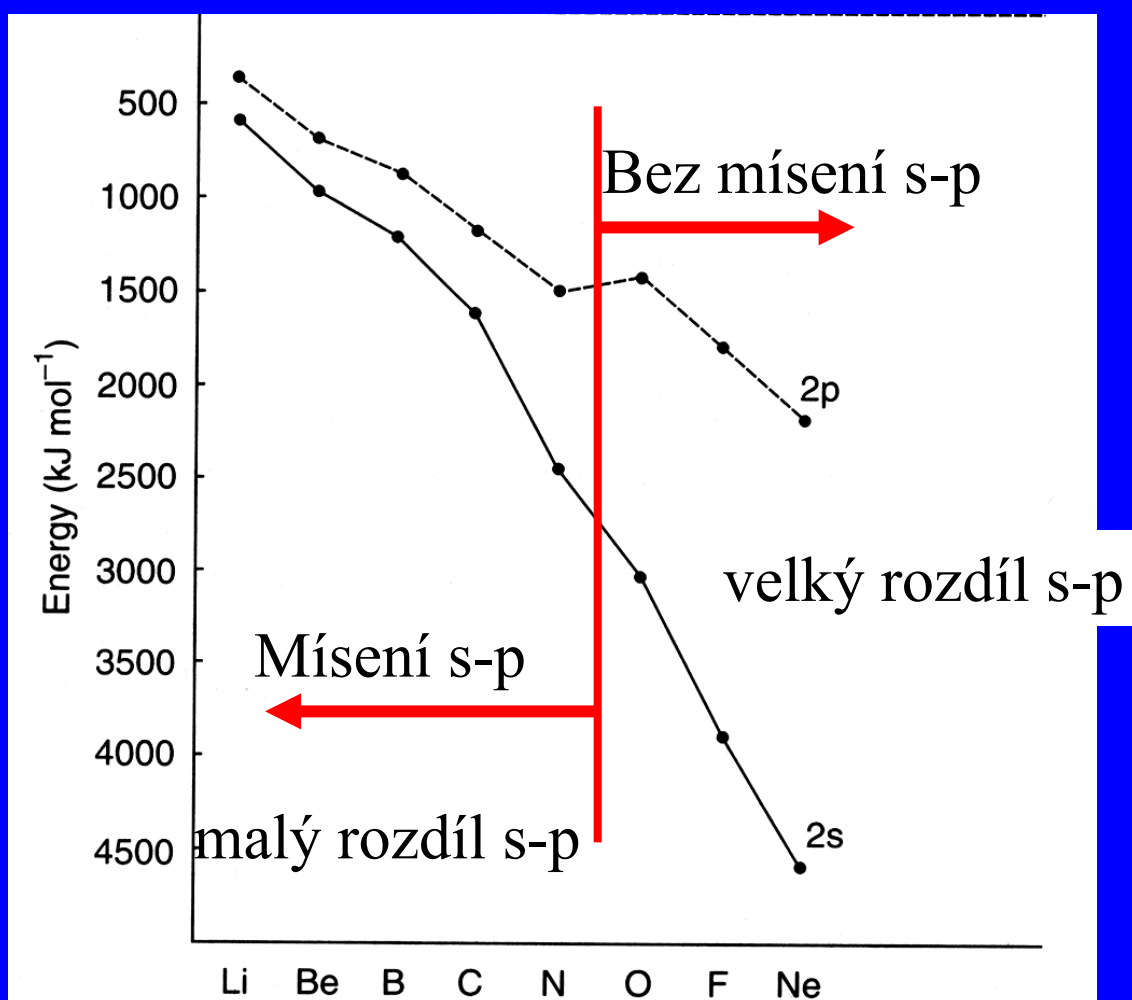
$d(z^2) d(z^2)$

$d(xz) d(xz)$
 $d(yz) d(yz)$

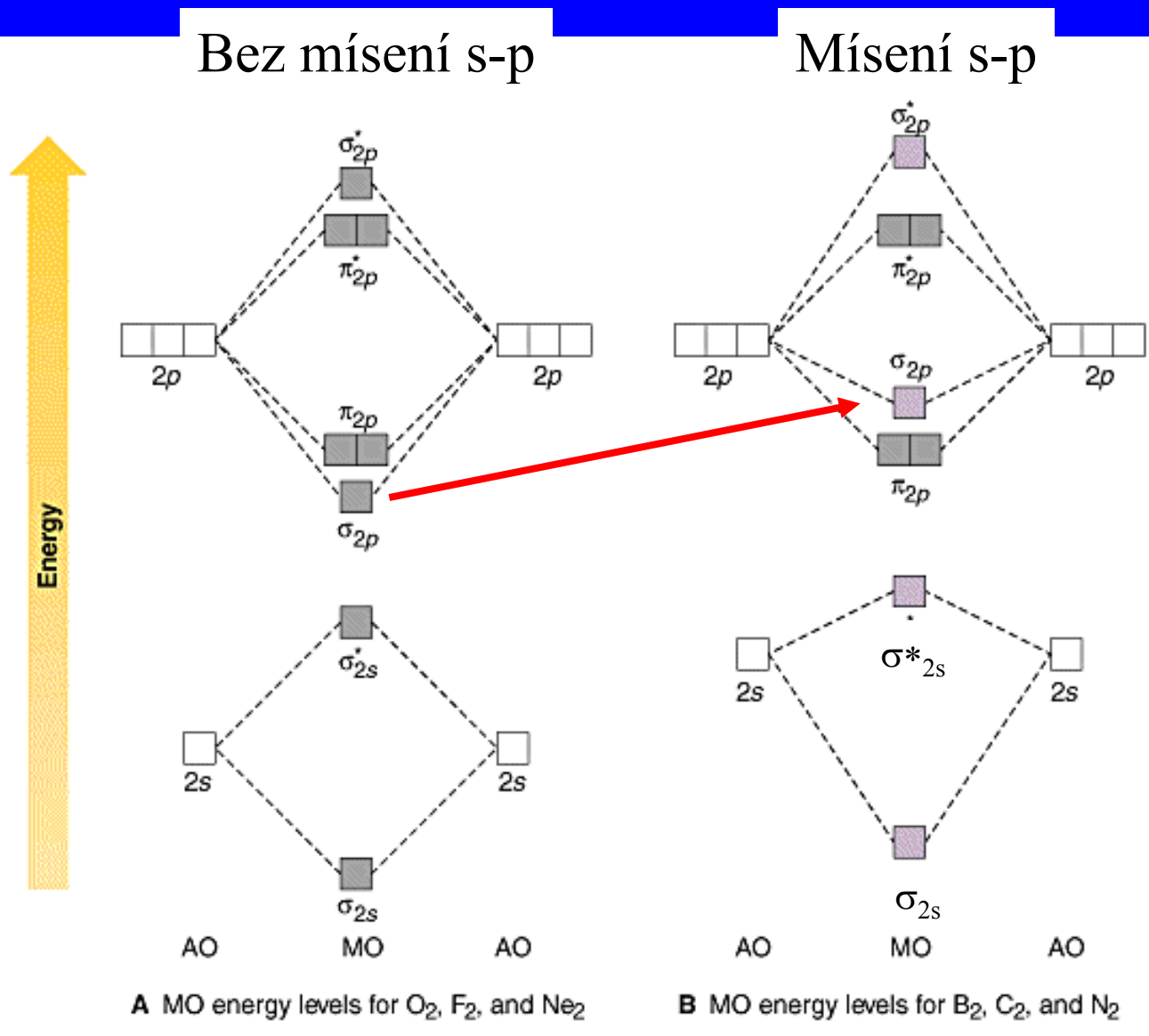
$d(x^2-y^2) d(x^2-y^2)$
 $d(xy) d(xy)$

Mísení s-p orbitalů

Energeticky blízké orbitály na stejném atomu se mohou smíchat



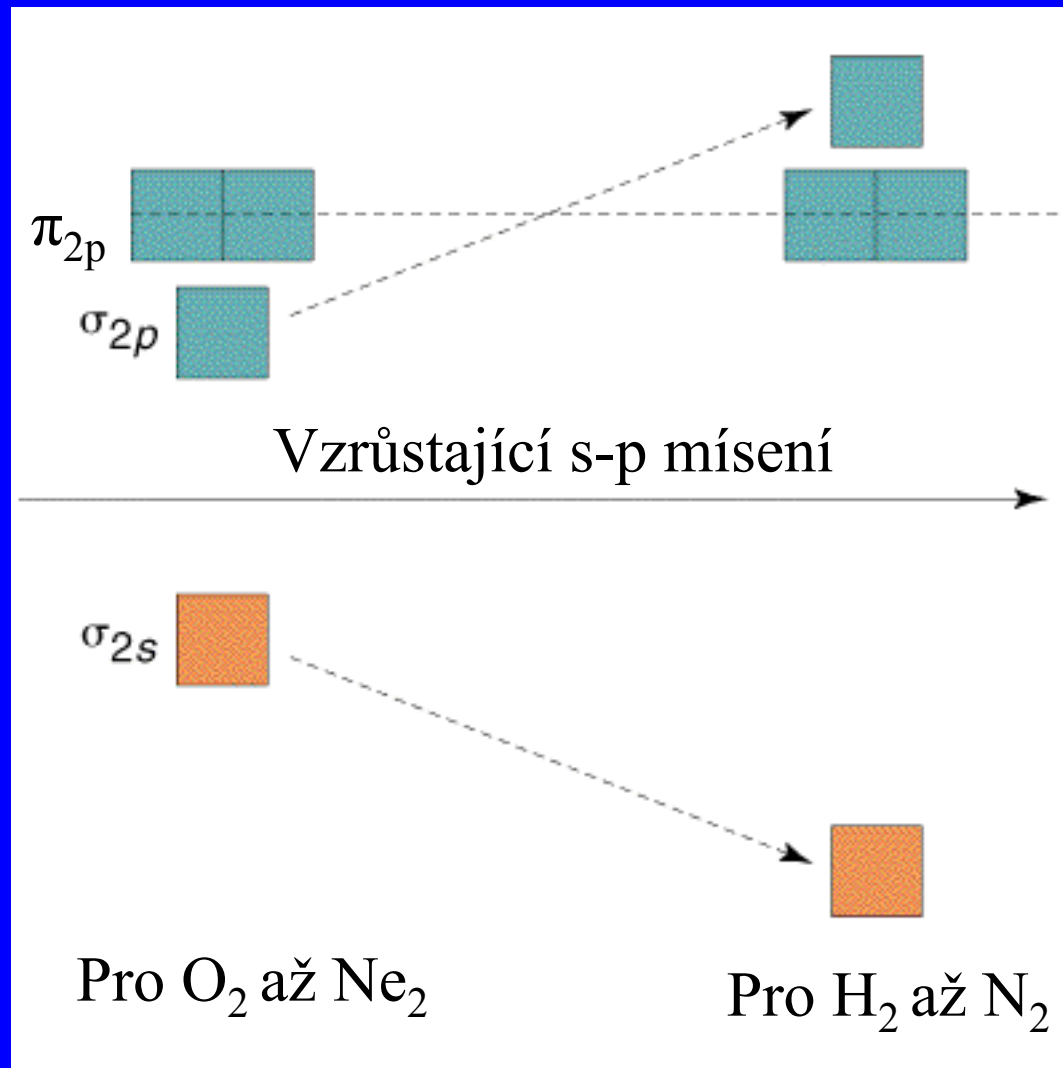
Energie



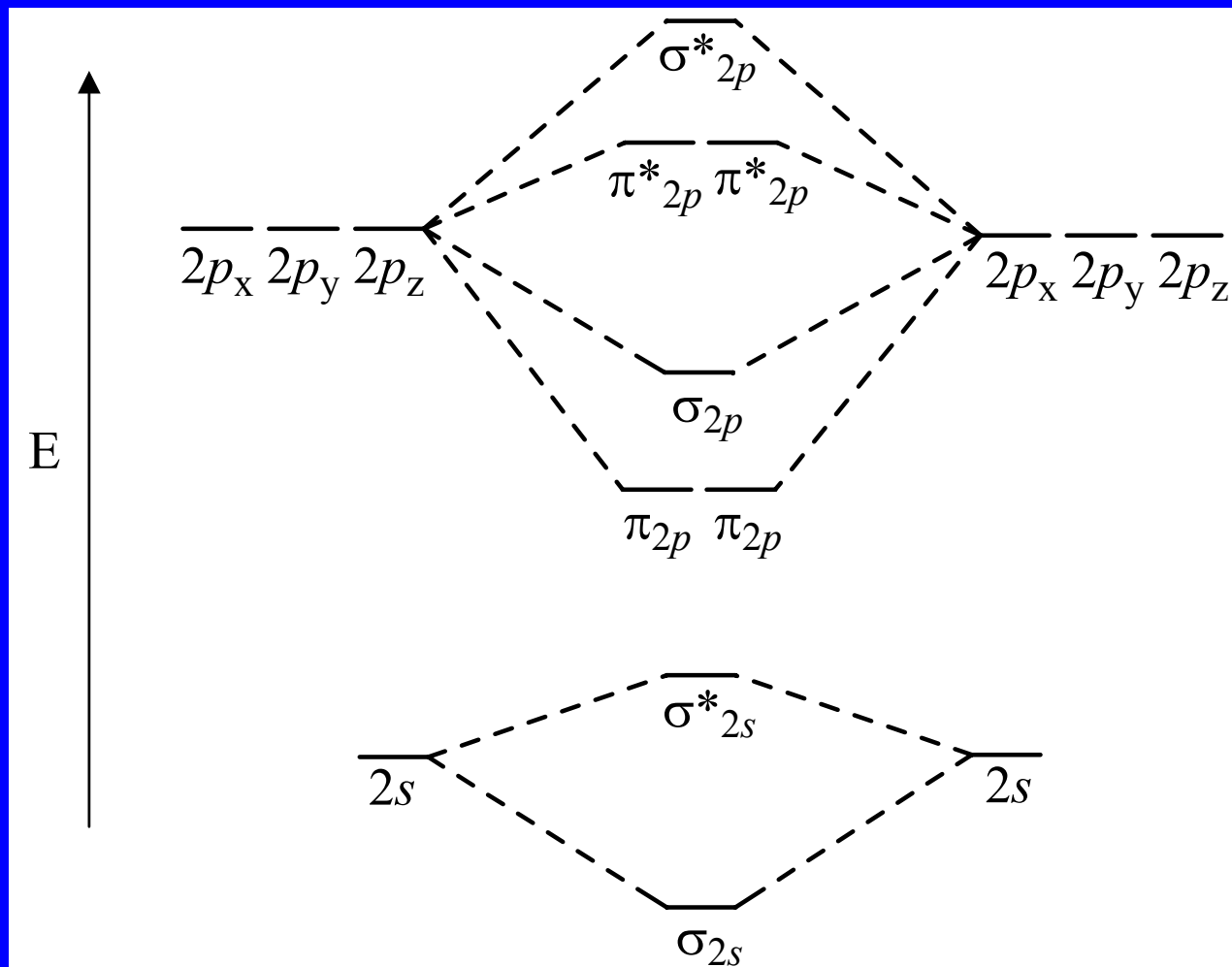
Pro O_2 až Ne_2

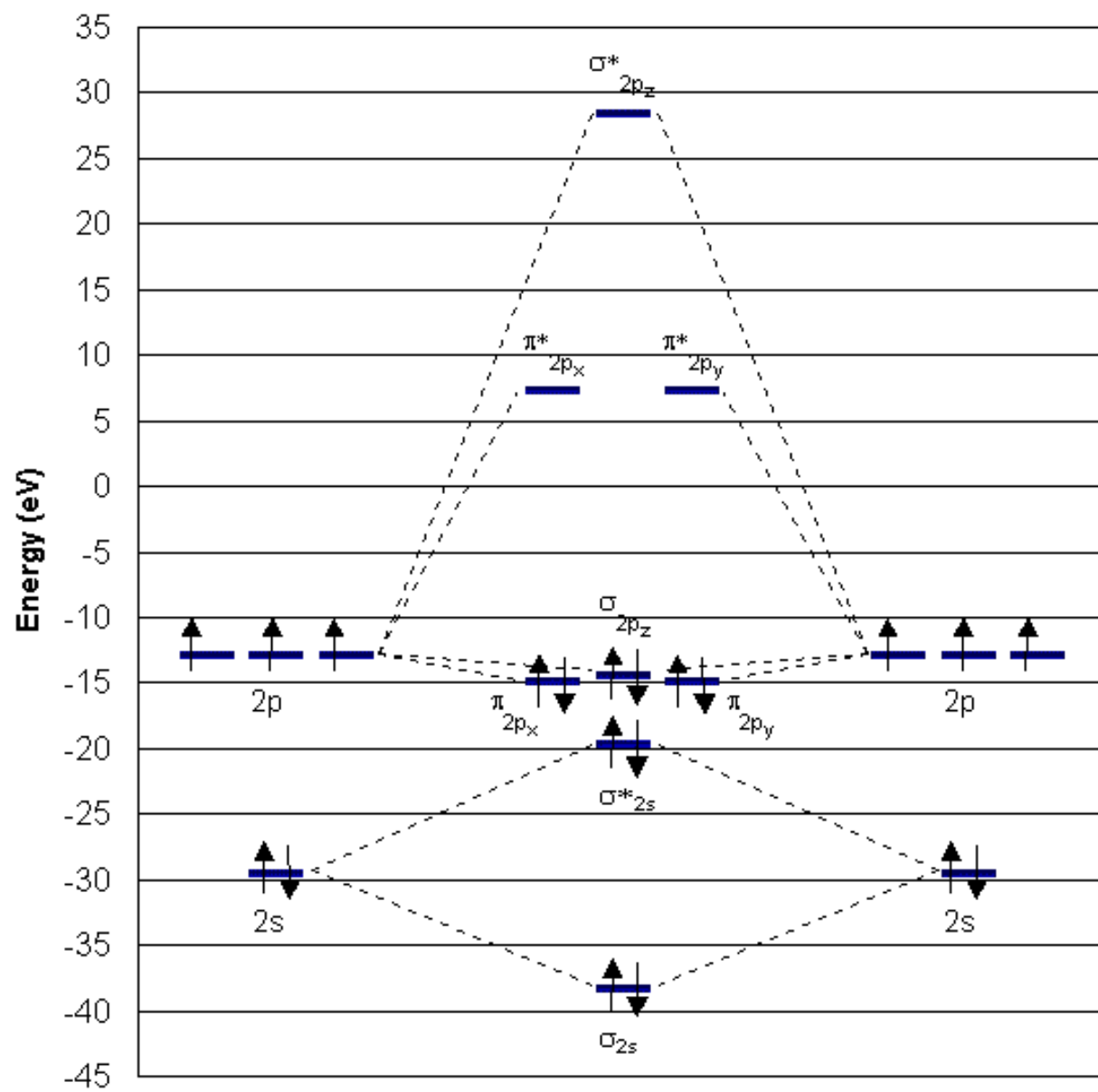
Pro H_2 až N_2

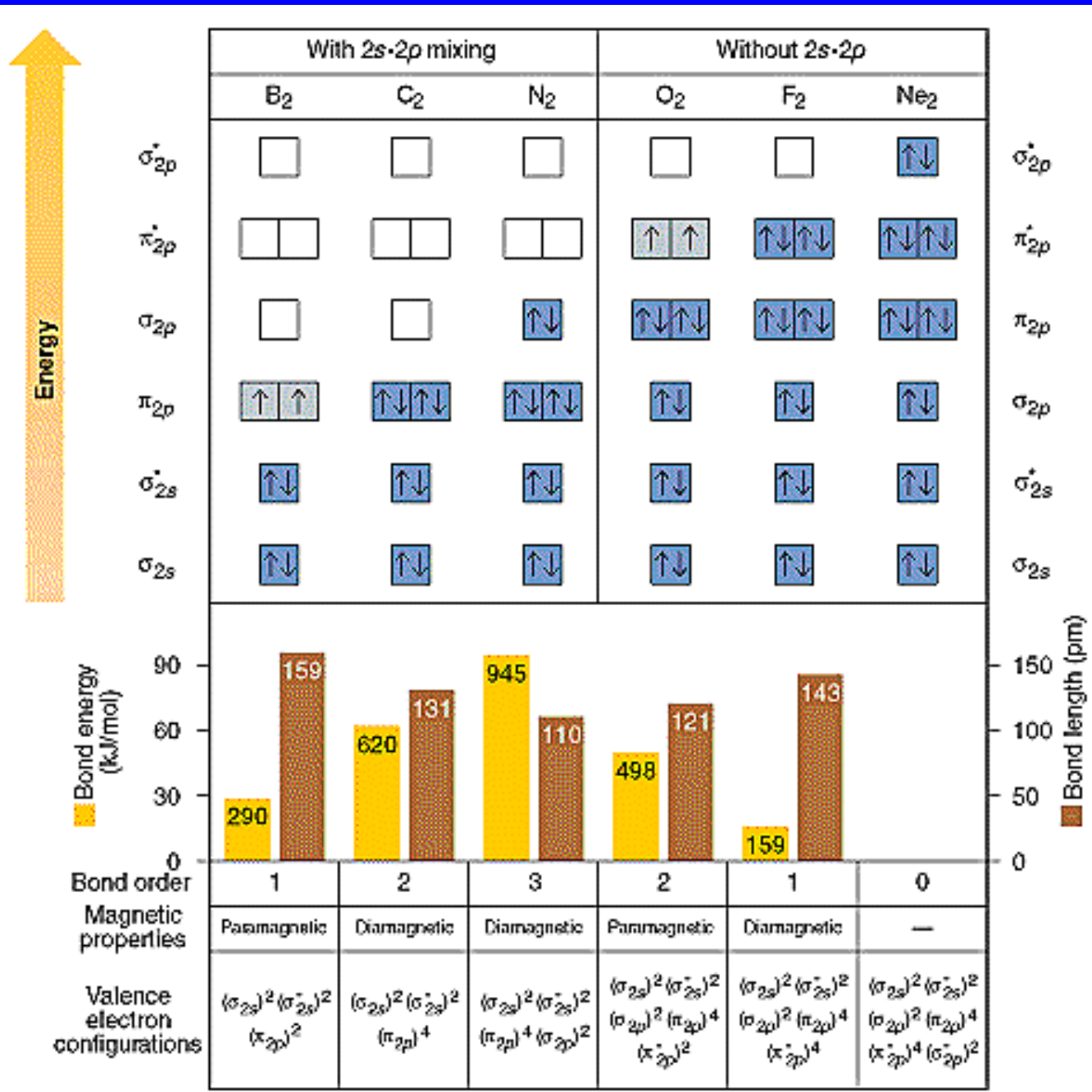
Diatomické molekuly



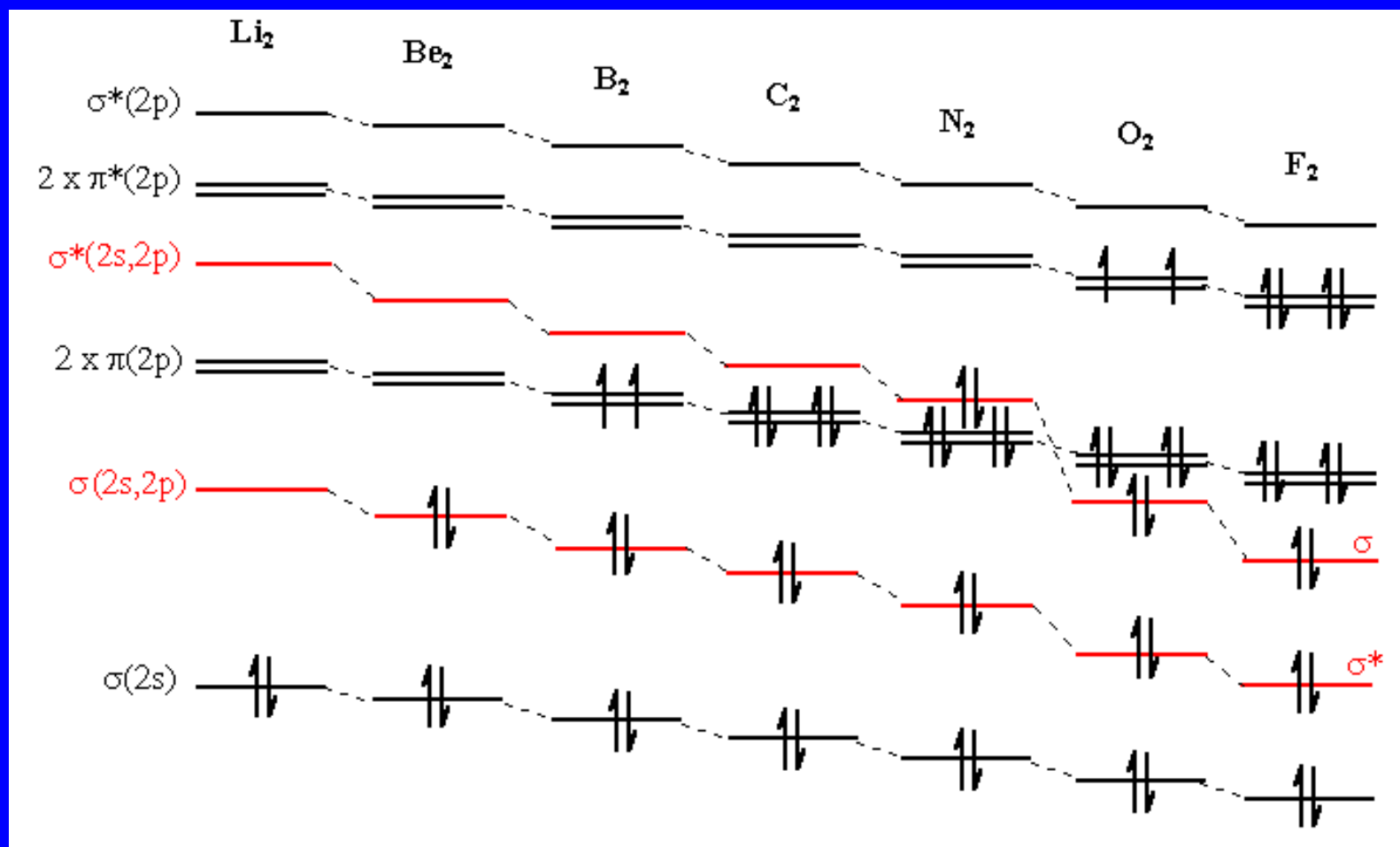
Interakční diagram pro Li_2 až N_2





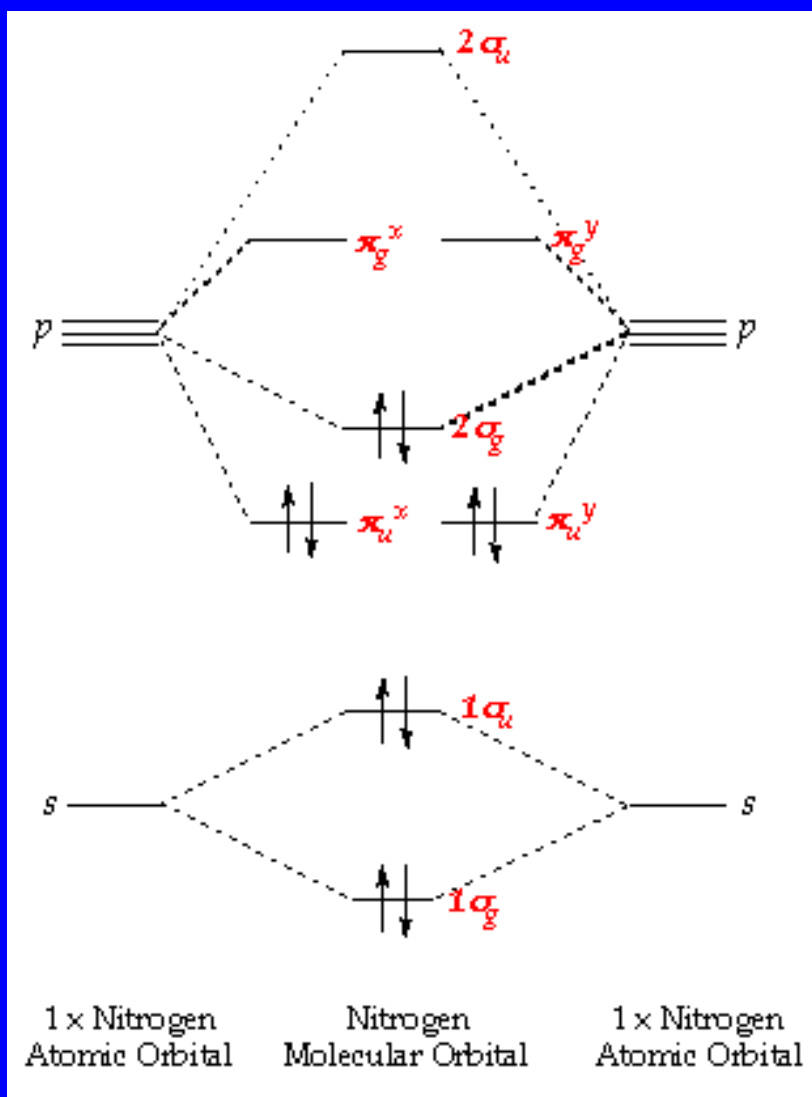


Diatomické molekuly

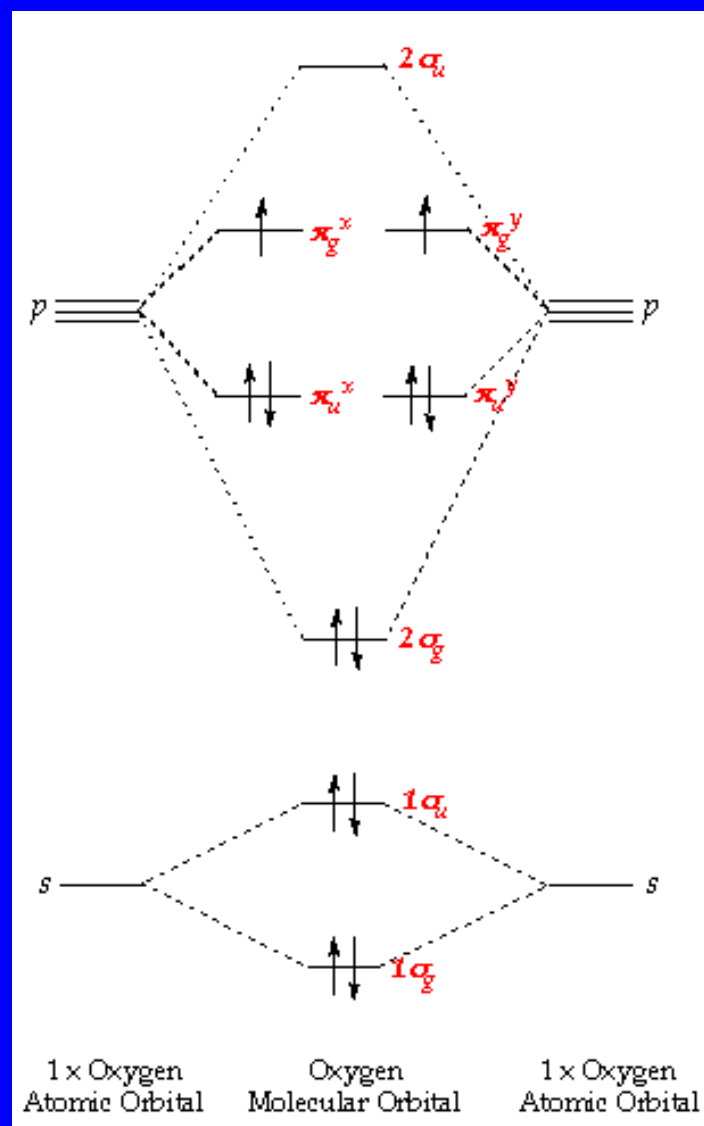


Diatomické molekuly v plynné fázi

		Délka (pm)	E_{vaz} (kJ mol ⁻¹)
Li-Li	σ_{2s}^2	267	110
Be...Be	$\sigma_{2s}^2 \sigma_{2s}^{*2}$?	?
B-B	$\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^2$	159	290
C=C	$\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4$	124	602
N≡N	$\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^2$	110	942
O=O	$\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*2}$	121	494
F-F	$\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*4}$	142	155



N_2 trojná vazba



O_2 paramagnetická molekula

Kyslík a jeho molekulové ionty

	O_2^+	O_2	O_2^-	O_2^{2-}
Počet valenčních elektronů	11	12	13	14
Obsazení HOMO π_x^* a π_y^*	↑	↑ ↑	↑↓ ↑	↑↓ ↑↓
Řád vazby	2.5	2.0	1.5	1.0
Délka vazby, pm	112	121	126	149

Multiplicita

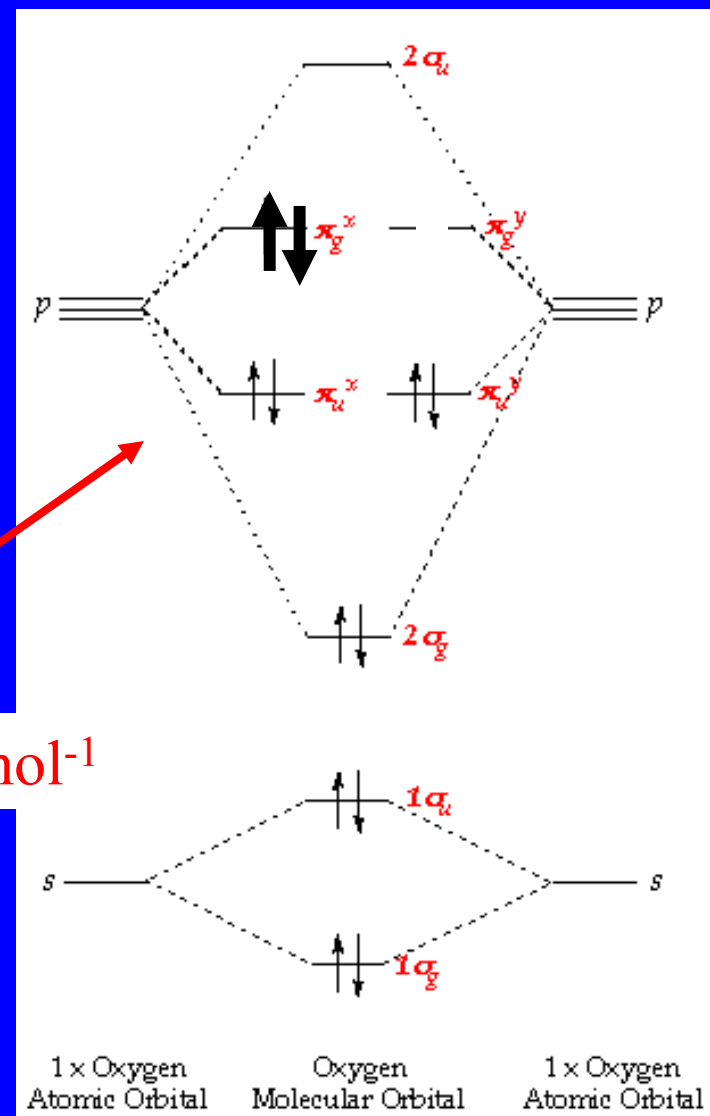
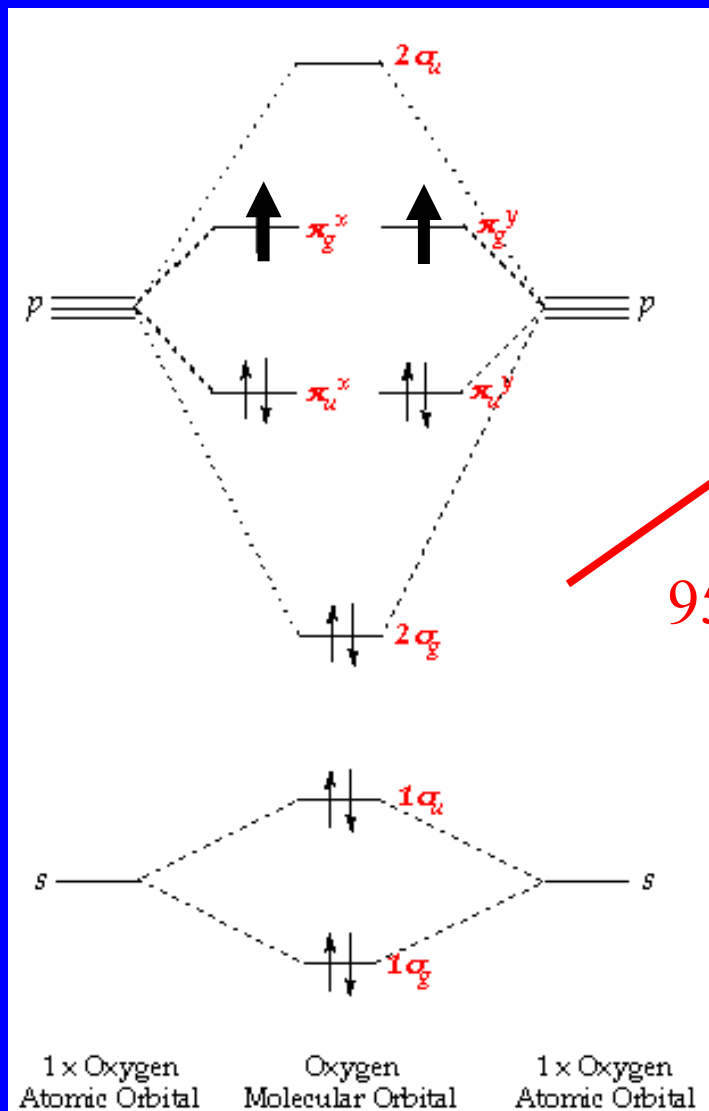
$$M = 2S + 1$$

S = součet nepárových spinů ($\frac{1}{2}$) v atomu nebo molekule

M	název	S	
1	singlet	0	↑↓
2	dublet	$\frac{1}{2}$	↑
3	triplet	1	↑↑
4	kvartet	$1\frac{1}{2}$	↑↑↑
5	kvintet	2	↑↑↑↑
6	sextet	$2\frac{1}{2}$	↑↑↑↑↑

Singletový kyslík $^1\Delta$

Tripletový kyslík $^3\Sigma$



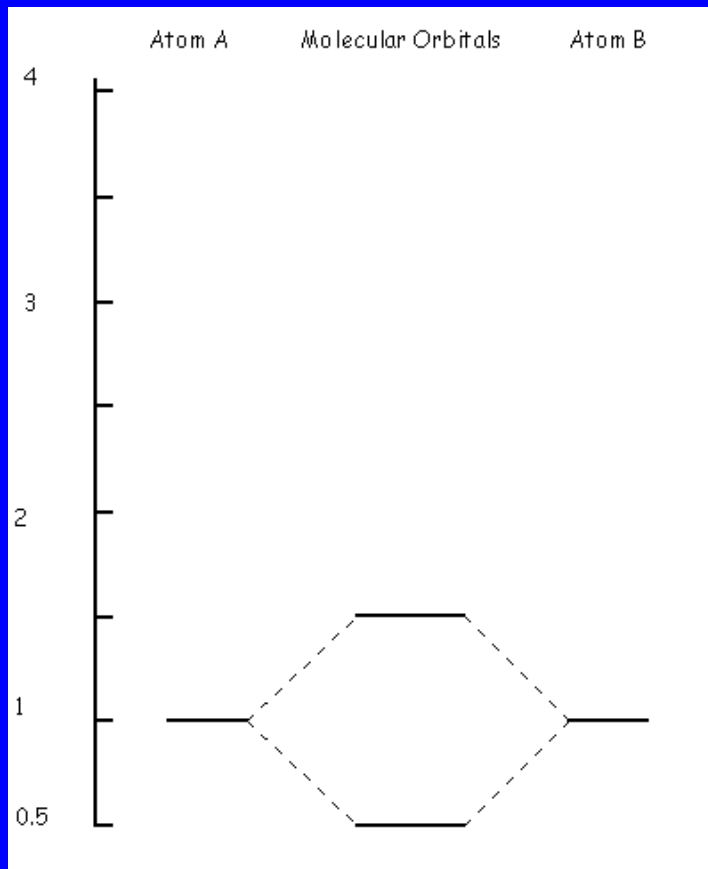
95 kJ mol⁻¹

Izoelektronové sloučeniny

Počet val. elektr.	Příklady diatomických částic
9	BO, CN, CP, CO ⁺
10	N ₂ , CO, CN ⁻ , BF, NO ⁺ , TiO, SiO
11	O ₂ ⁺ , ·NO, SO ⁺
12	O ₂ , SO
13	O ₂ ⁻ , Cl ₂ ⁺ , ·ClO
14	F ₂ , O ₂ ²⁻ , ClO ⁻

MO v polárních molekulách

$$\Psi^* = c_3 \Psi_A - c_4 \Psi_B$$



$$\Psi = c_1 \Psi_A + c_2 \Psi_B$$

$\chi(A) \ll \chi(B)$ iontová vazba

$c_1 \rightarrow 0$ vazebný MO = Ψ_B

$c_4 \rightarrow 0$ protivazebný MO = Ψ_A

$\chi(A) < \chi(B)$ polární vazba

$c_1 < c_2$ vazebný MO má větší příspěvek od B

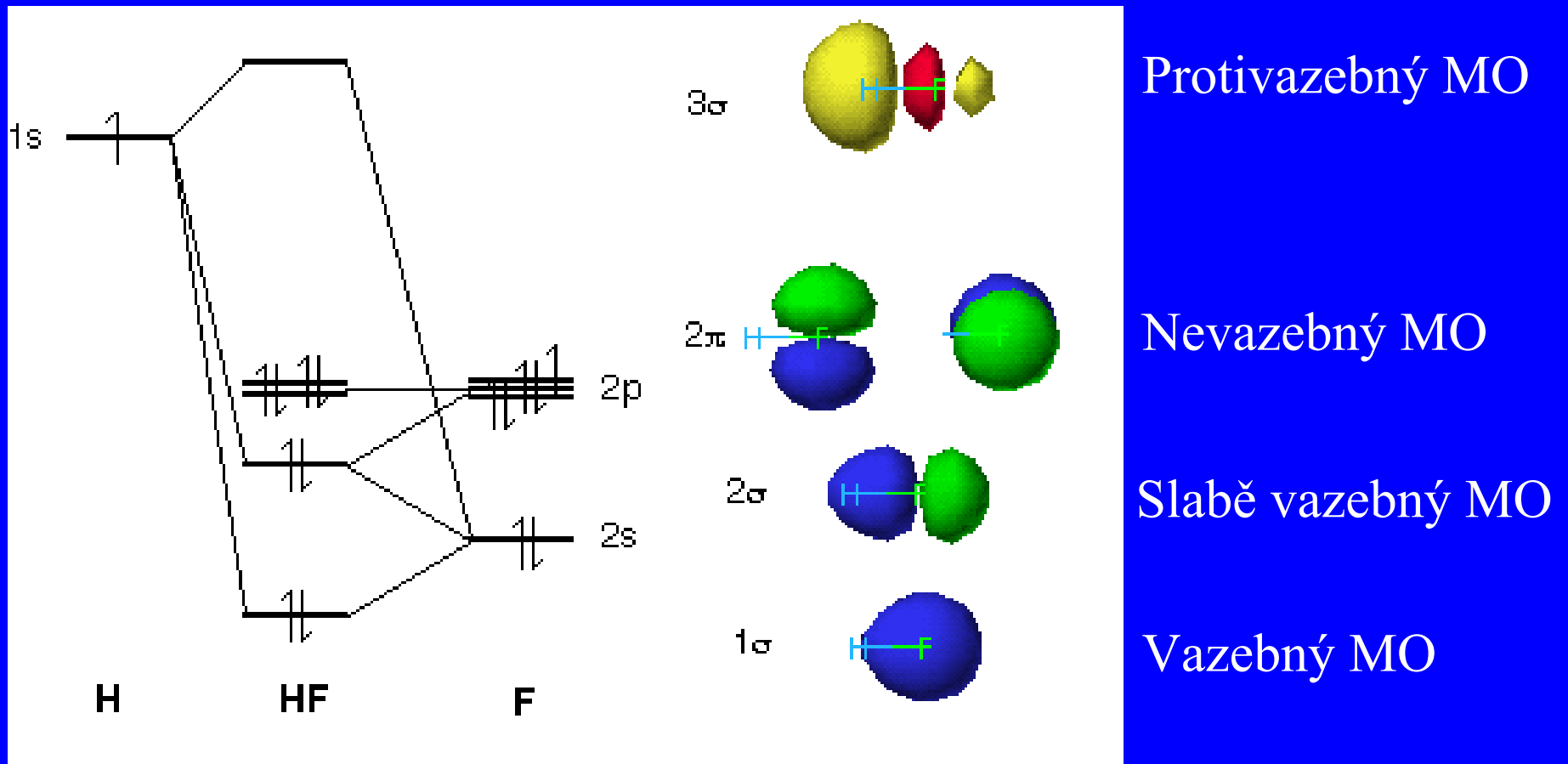
$c_3 > c_4$ protivazebný MO má větší příspěvek od A

$\chi(A) = \chi(B)$ nepolární vazba

$c_1 = c_2$ $c_3 = c_4$

stejný příspěvek od obou atomů 38

MO v polárních molekulách, HF



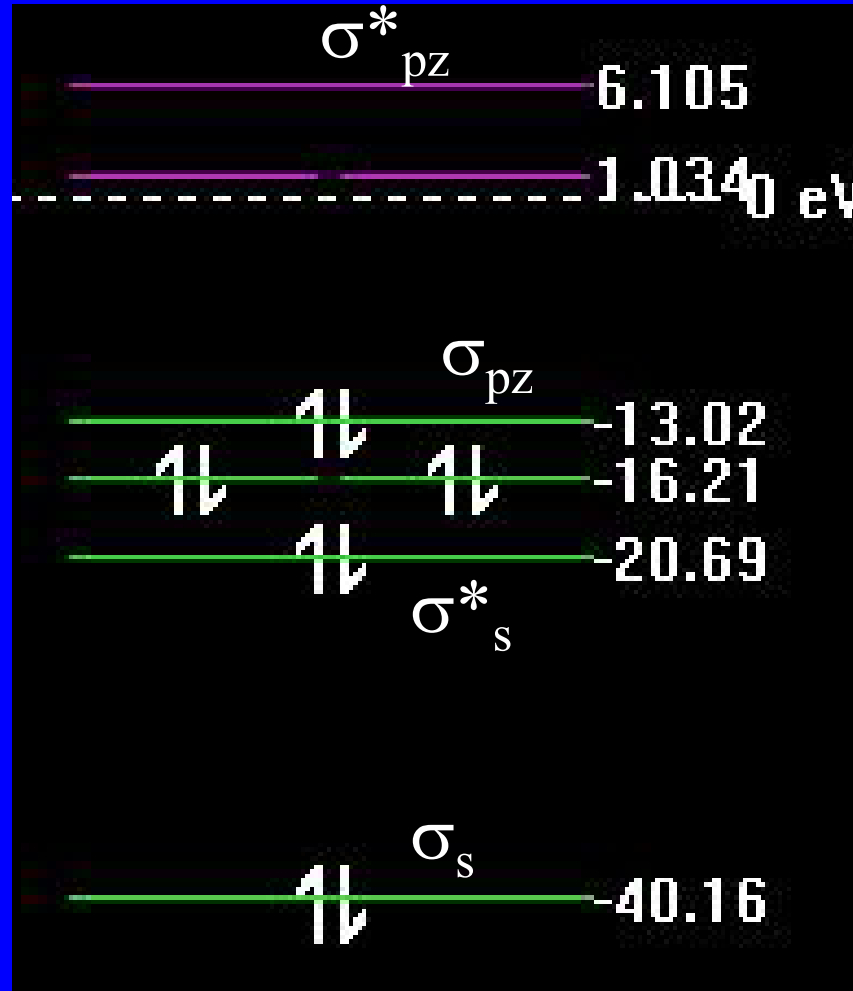
Vazebný MO koncentrován na atomu s vyšší elektronegativitou - F

Protivazebný MO koncentrován na atomu s nižší elektronegativitou - H

MO v CO

LUMO

HOMO

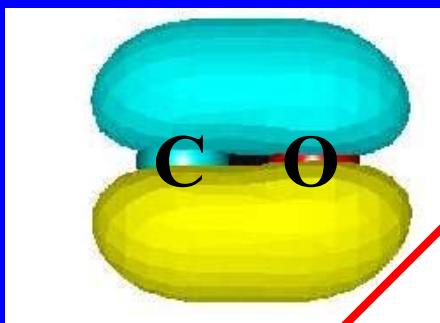
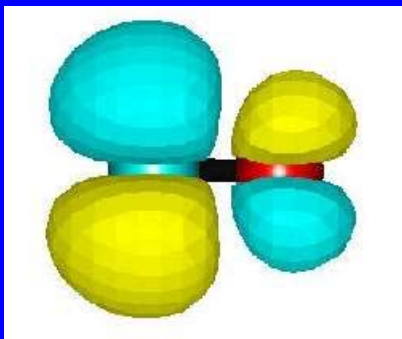


$\pi^*_{px, y}$

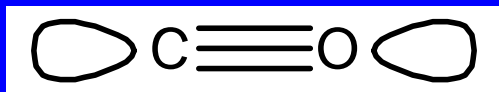
$\pi_{px, y}$

C + O
10 elektronů

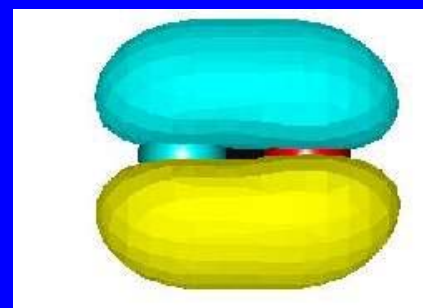
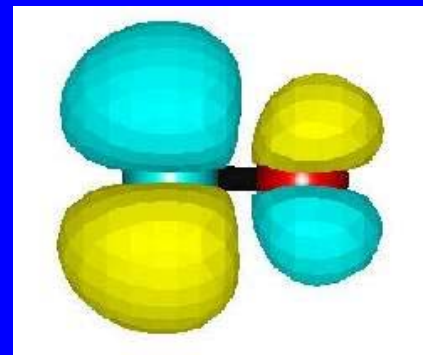
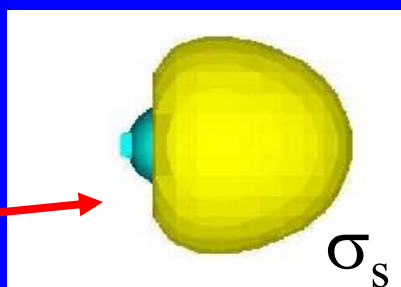
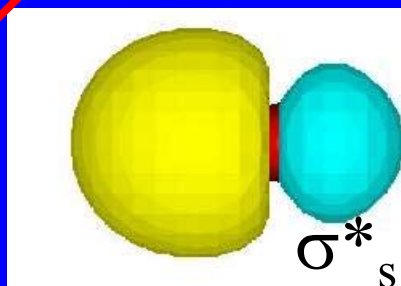
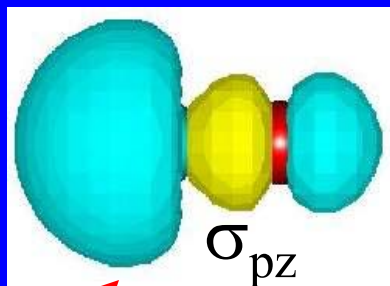
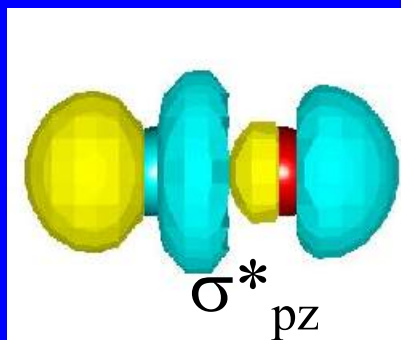
LUMO



Volný e pár na C
HOMO

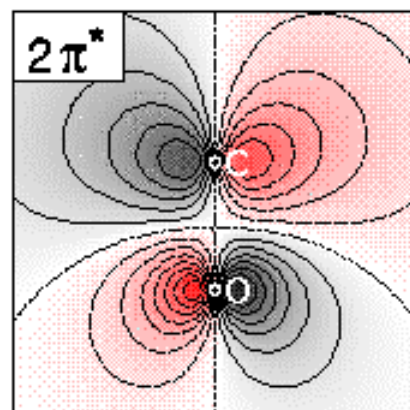
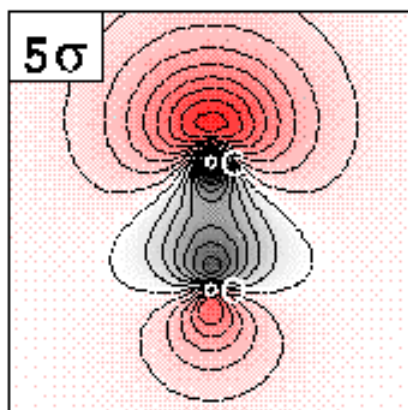
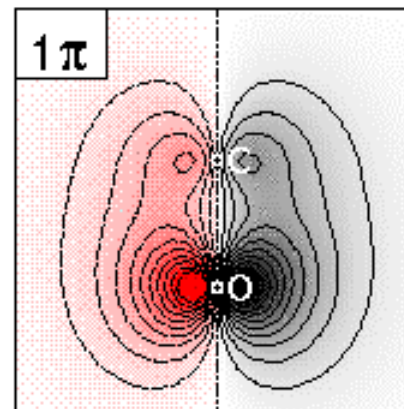
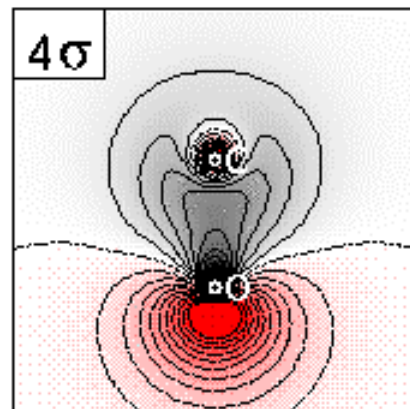
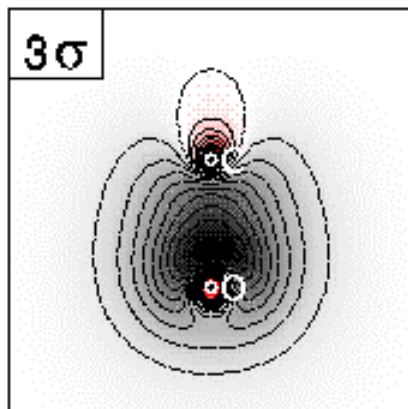


Volný e pár na O

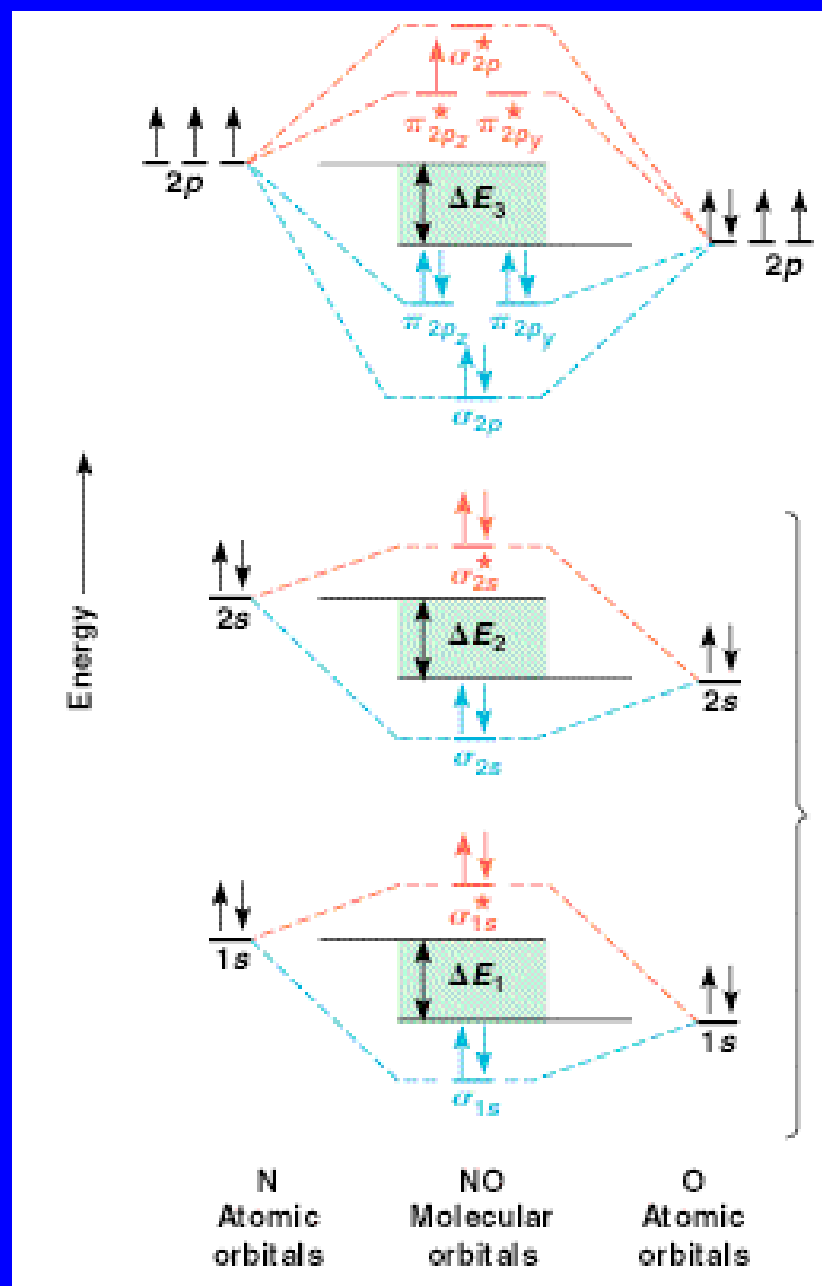


$\pi^*_{px,y}$

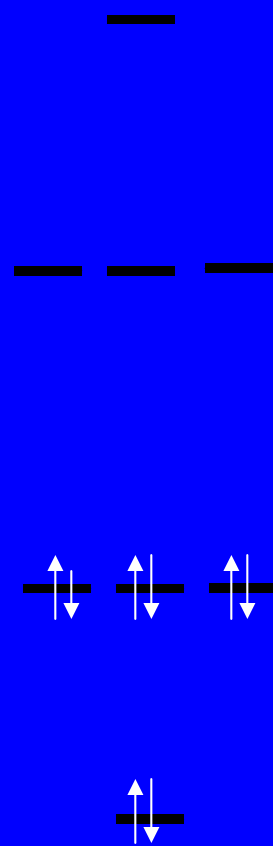
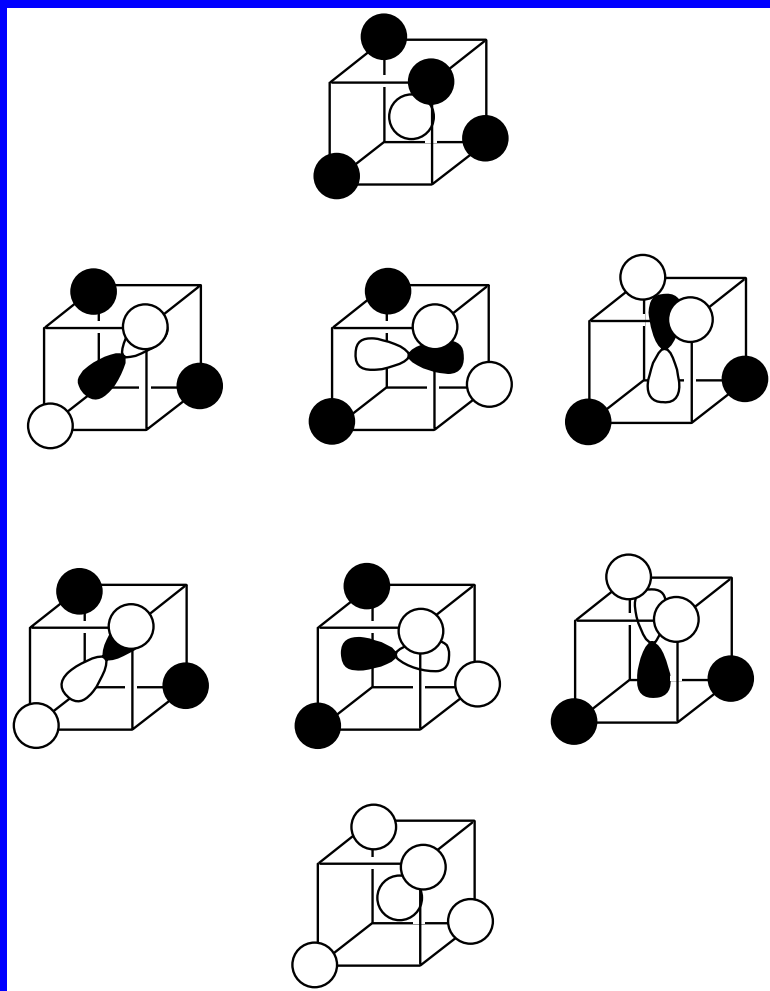
$\pi_{px,y}$



Free CO molecular orbitals



Molekulové orbitály CH₄

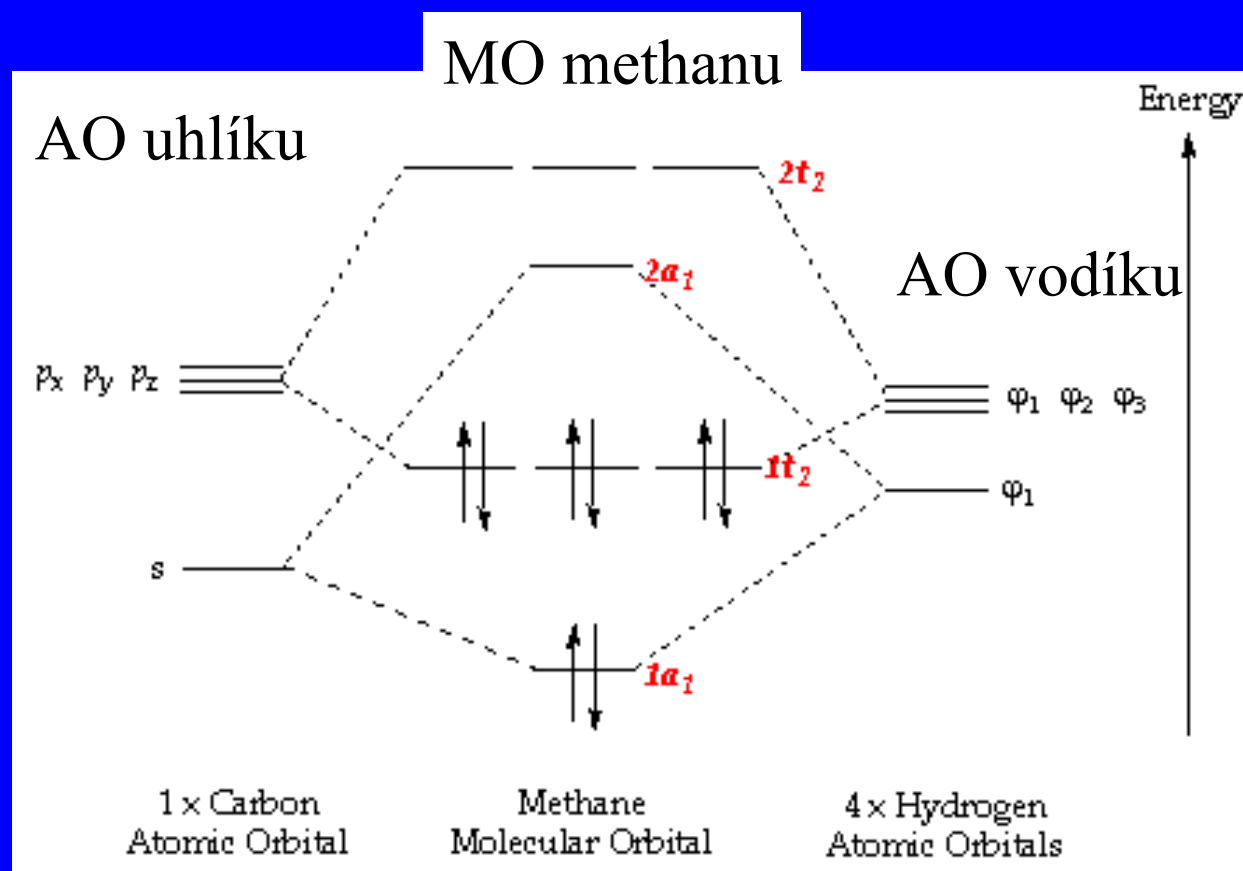


Použité
atomové orbitály

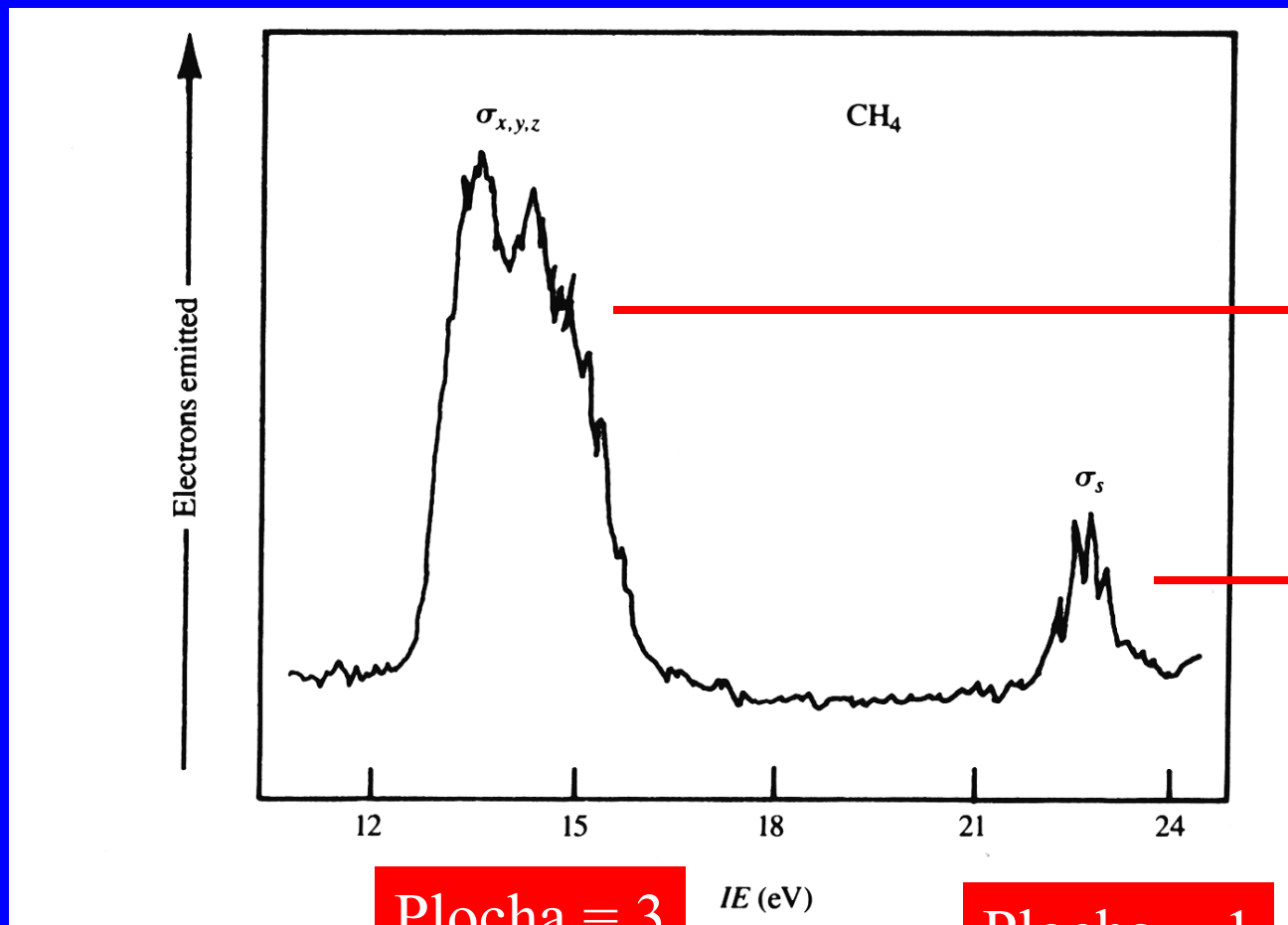
C $s + 3 \times p$
4H $4 \times s$

C + 4H
8 elektronů

Molekulové orbitály CH₄

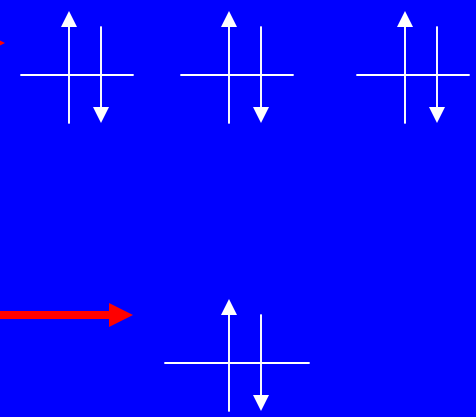


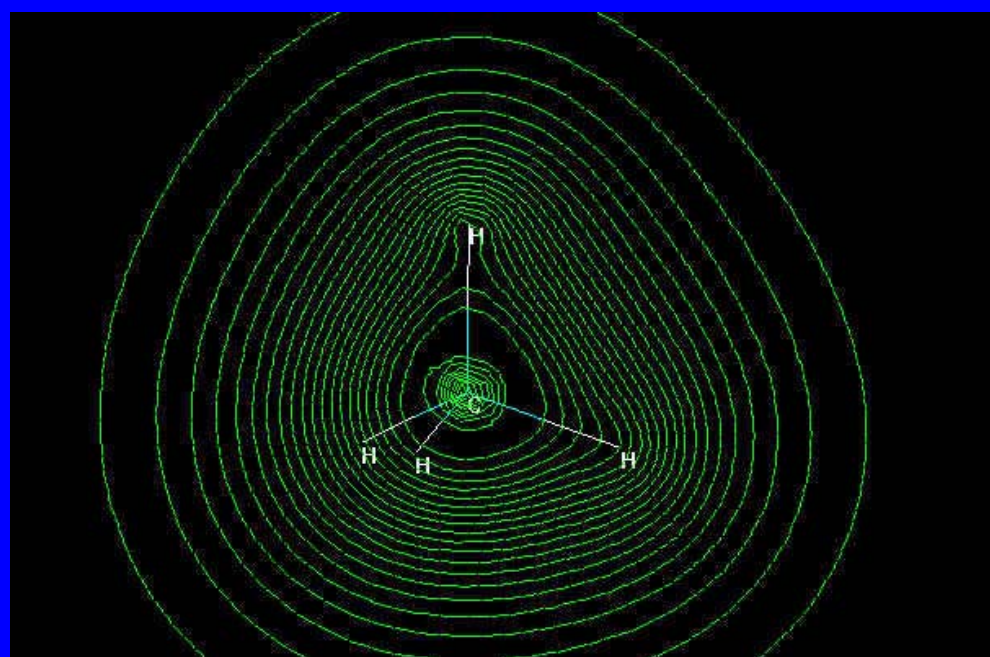
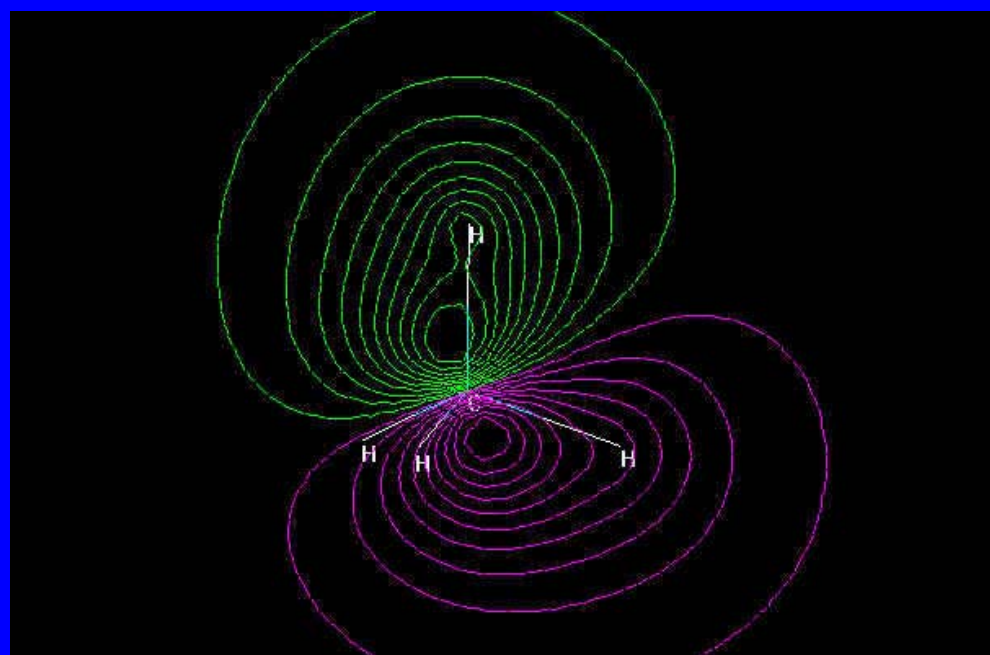
PES methanu souhlasí s modelem MO



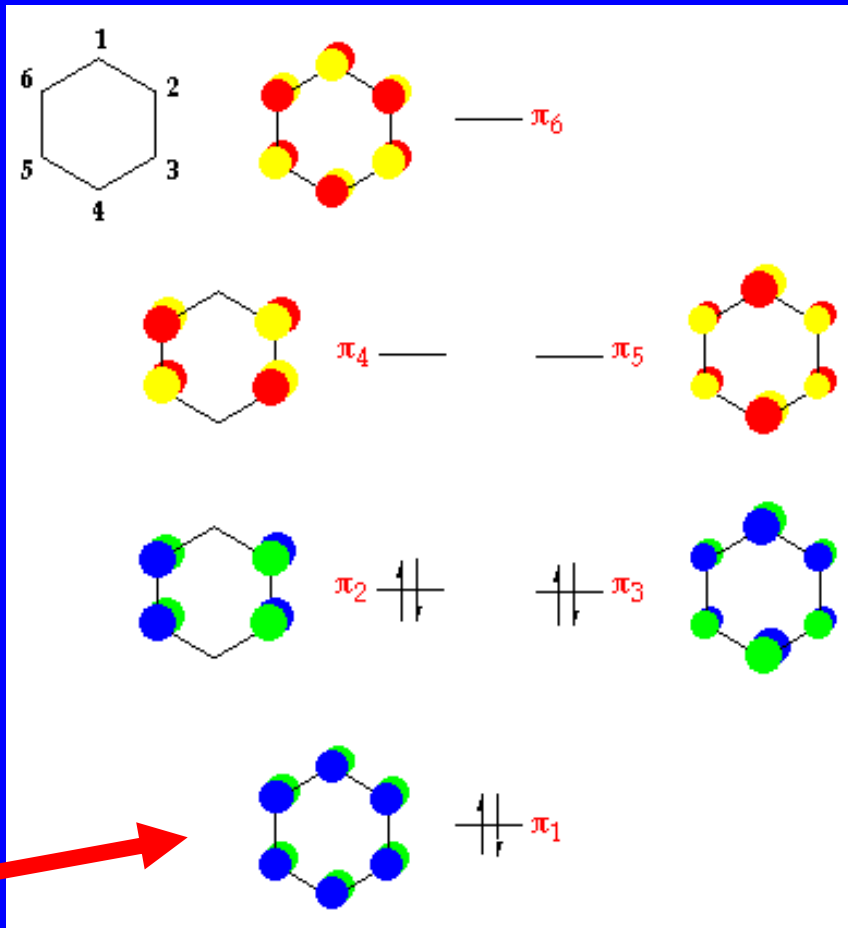
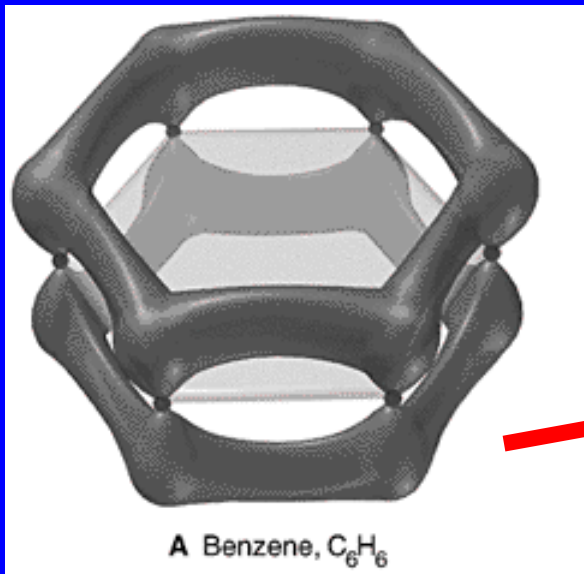
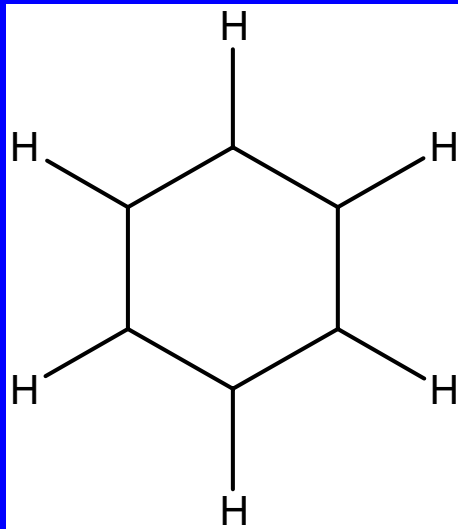
Plocha = 3

Plocha = 1



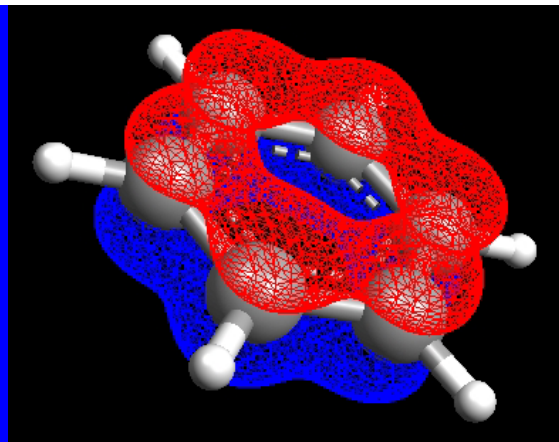
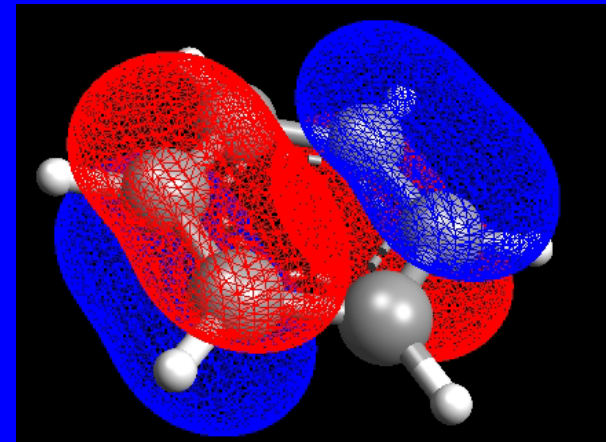
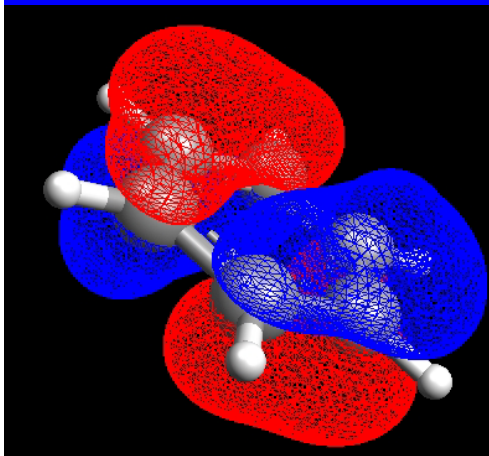
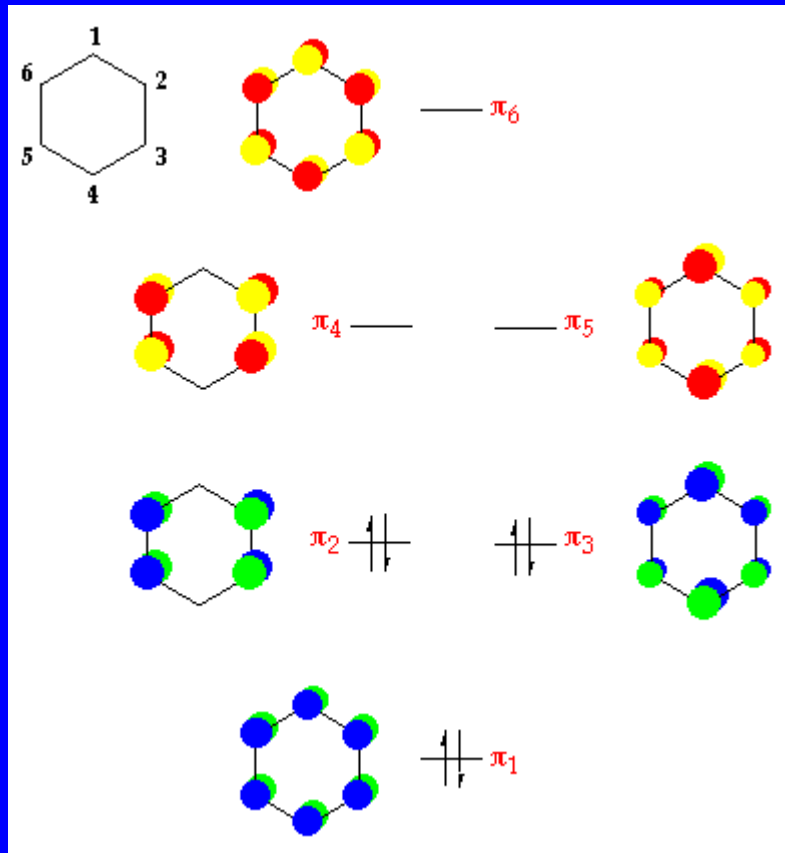


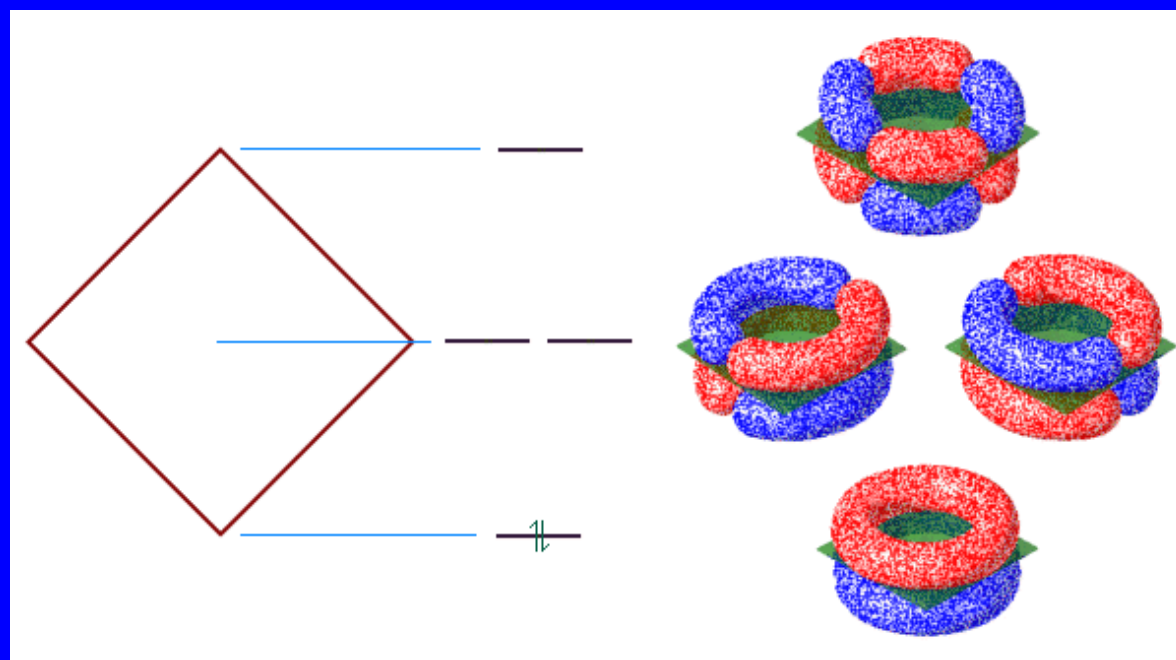
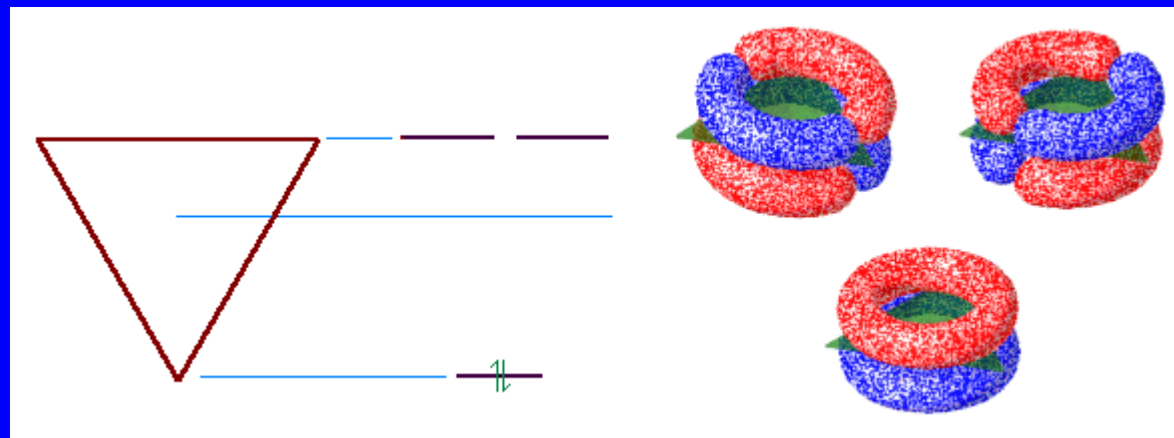
Benzen

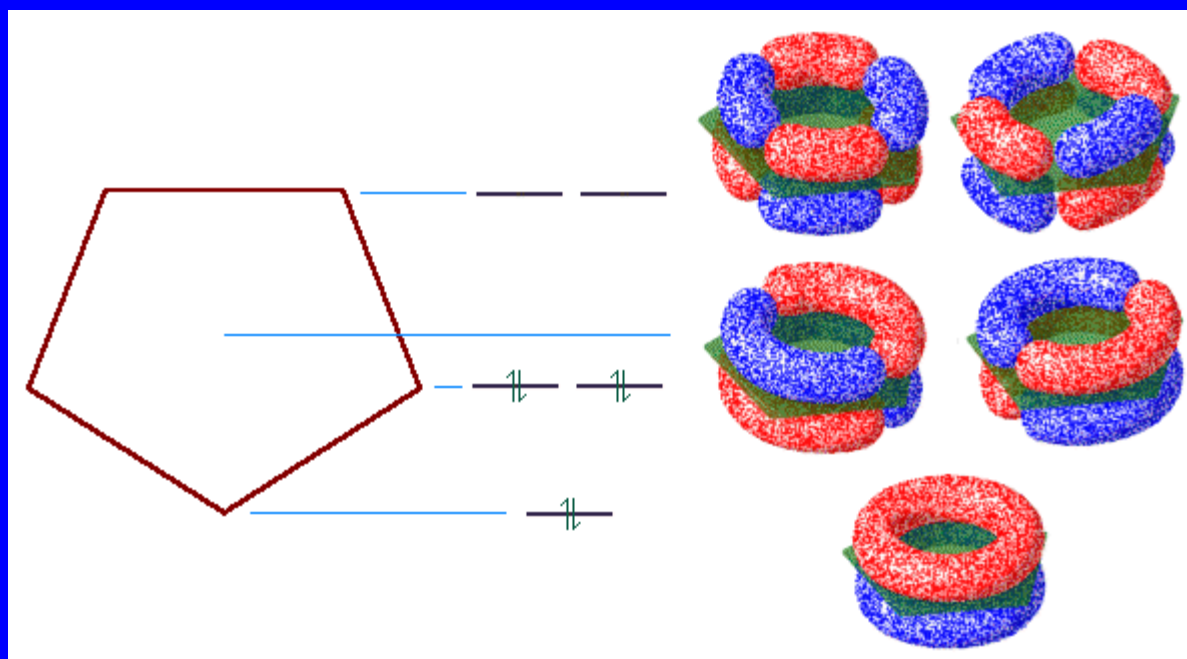


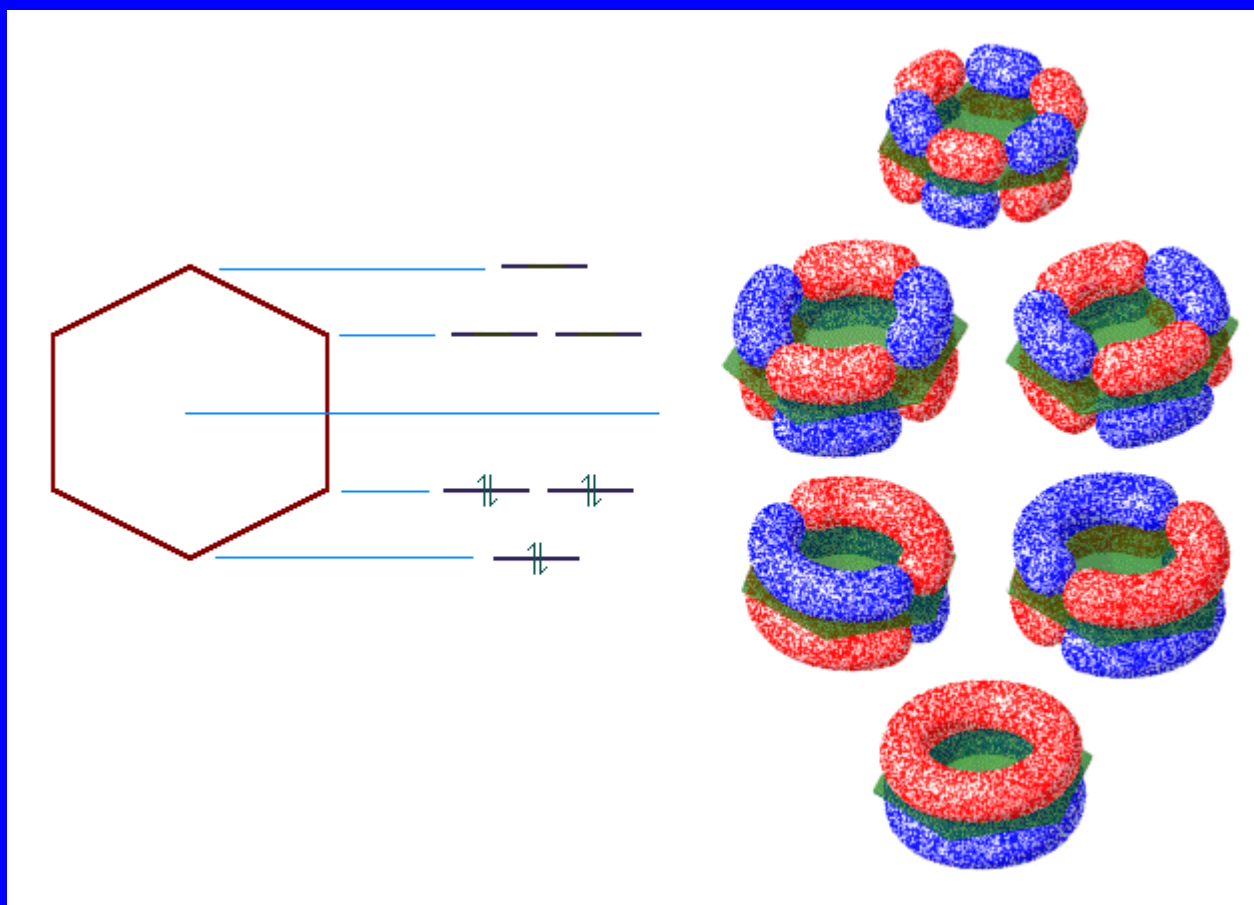
Oddělený pohled na sigma a pi systém

Vazebné MO v benzenu

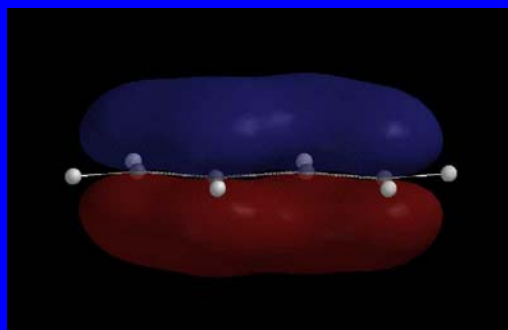
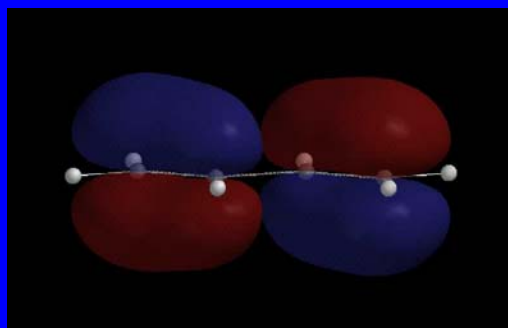
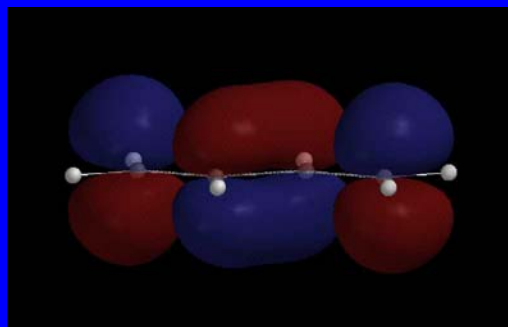
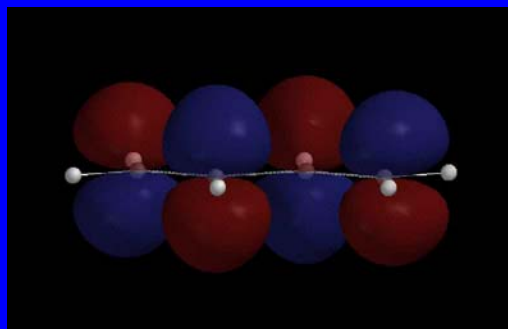
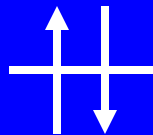
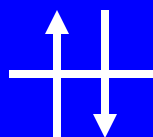
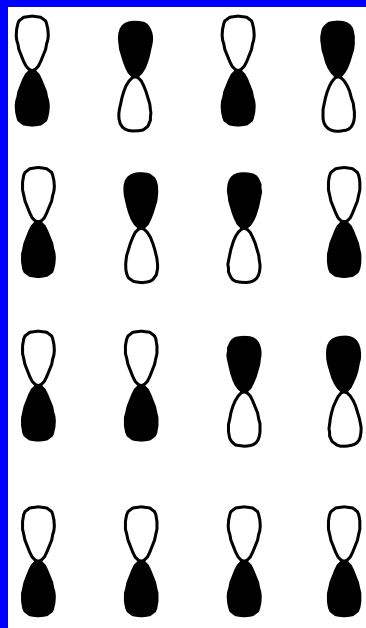
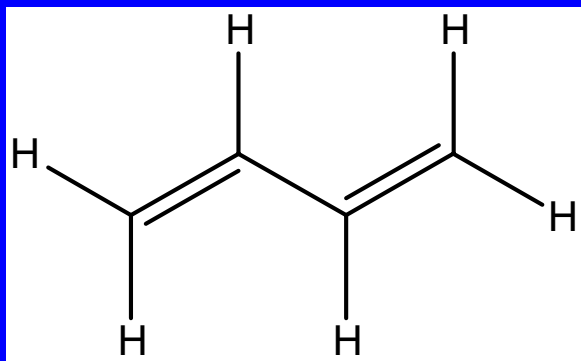








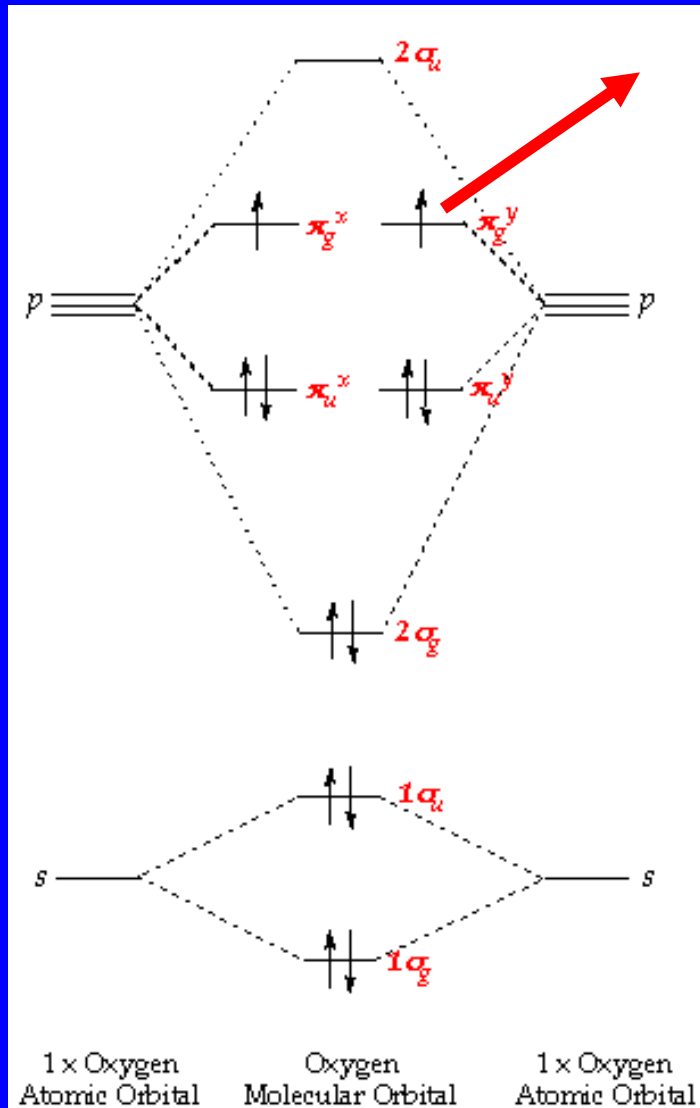
1,3-butadien



LUMO

HOMO

Molekulové ionty

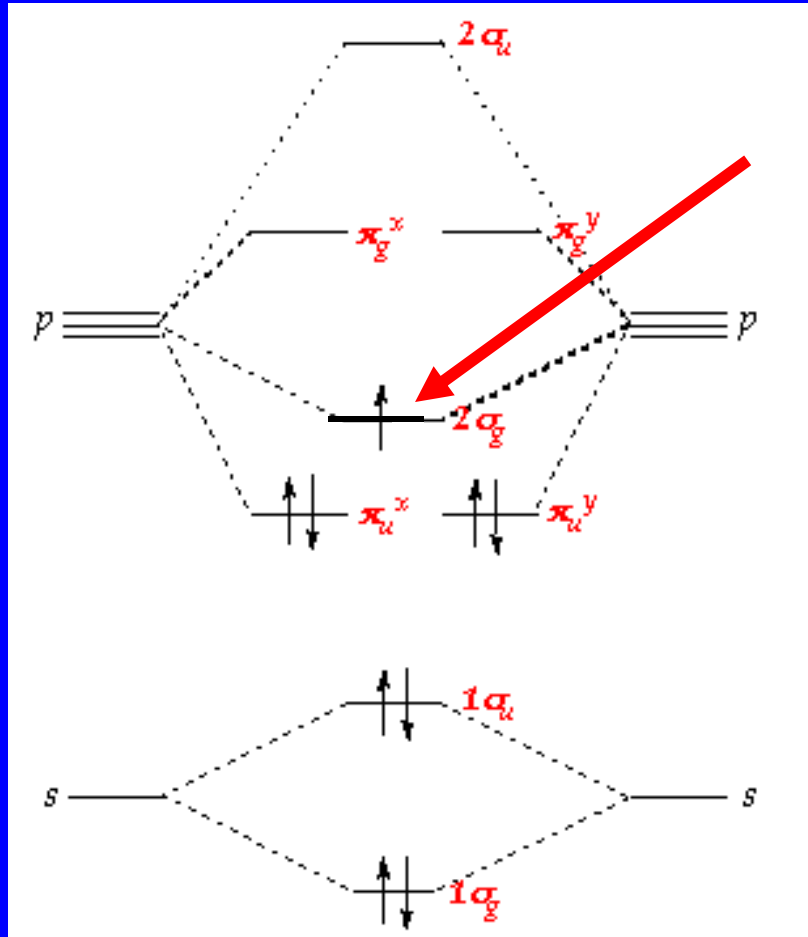


IE



Odtržení nejslaběji vázaného e
v HOMO

Molekulové ionty



Přidání e do HOMO

Excitace molekul

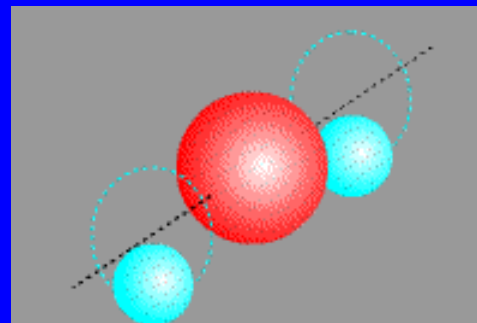
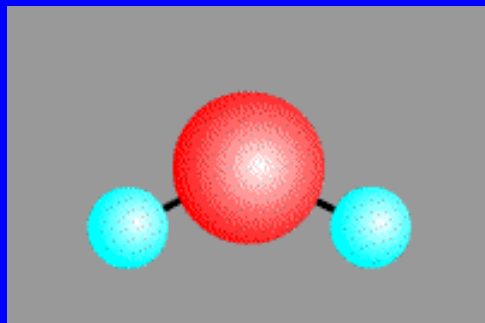
$$E_{\text{celk}} = E(\text{elektronová}) + E(\text{vibrační}) + E(\text{rotační}) + E_{\text{ost}}$$

Jednotlivé složky E_{celk} jsou nezávislé – velmi rozdílné velikosti (Bornova-Oppenheimerova aproximace)

$E(\text{elektron})$ 100 kJ mol^{-1} UV a viditelná

$E(\text{vibrační})$ $1.5 - 50 \text{ kJ mol}^{-1}$ Infračervená

$E(\text{rotační})$ $0.1 - 1.5 \text{ kJ mol}^{-1}$ Mikrovlnná a daleká IČ



Rotační energie

Kvantování rotační energie

$$E(\text{rotační}) = (\hbar^2/2I) J(J + 1)$$

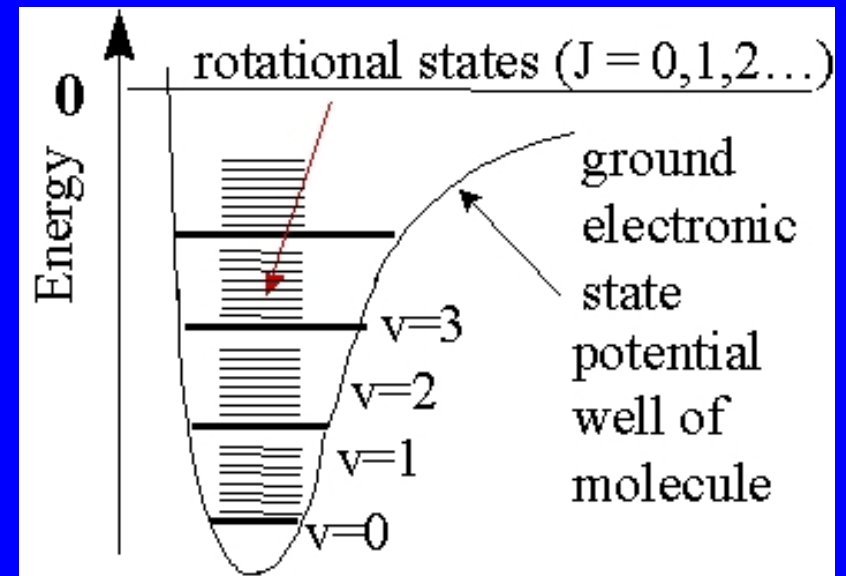
J = rotační kvantové číslo

I = moment setrvačnosti (μr^2)

$$\mu = m_1 m_2 / (m_1 + m_2)$$

Výběrové pravidlo $\Delta J = \pm 1$

Za normální teploty jsou molekuly v mnoha excitovaných rotačních stavech, rotační energie srovnatelná s tepelnou energií pohybu molekul



Mikrovlnná spektroskopie

Rotační spektra jen pro látky v plynné fázi

Lze získat velmi přesná data o vazebných délkách a úhlech

$I = \text{moment setrvačnosti} = \mu r^2$

Vazebná délka v H_2 0.74116 Å

Vibrační energie

Kvantování vibrační energie

$$E(\text{vibrační}) = k \hbar^2 (v + \frac{1}{2})$$

v = vibrační kvantové číslo

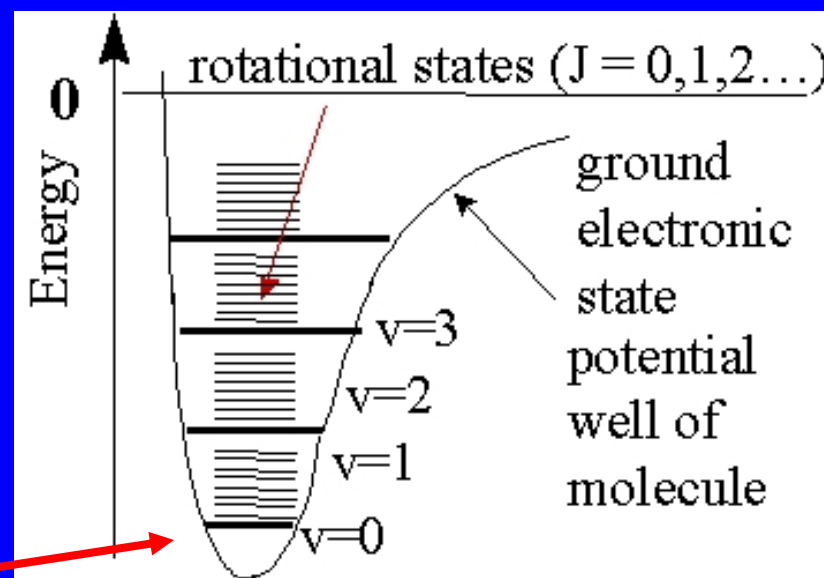
Výběrové pravidlo $\Delta v = \pm 1$

Energie nulového bodu:

$$\text{Pro } v = 0 \quad E(\text{vibrační}) = \frac{1}{2} k \hbar^2$$

$$\text{H}_2 \quad E(\text{disoc}) = 432 \text{ kJ mol}^{-1}$$

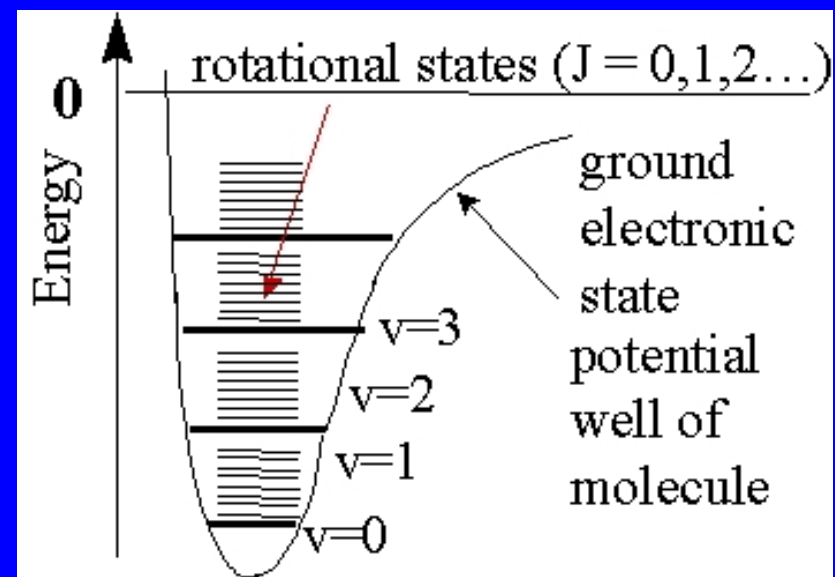
$$E(v = 0) = 25 \text{ kJ mol}^{-1}$$



Za normální teploty jsou molekuly v základním vibračním stavu $v = 0$

Vibrační energie

Molekula	Vibrační energie, cm^{-1}
H_2	4159.2
D_2	2990.3
H_2^+	2173



$$\tilde{\nu} = 1/2\pi (k/m)^{1/2}$$

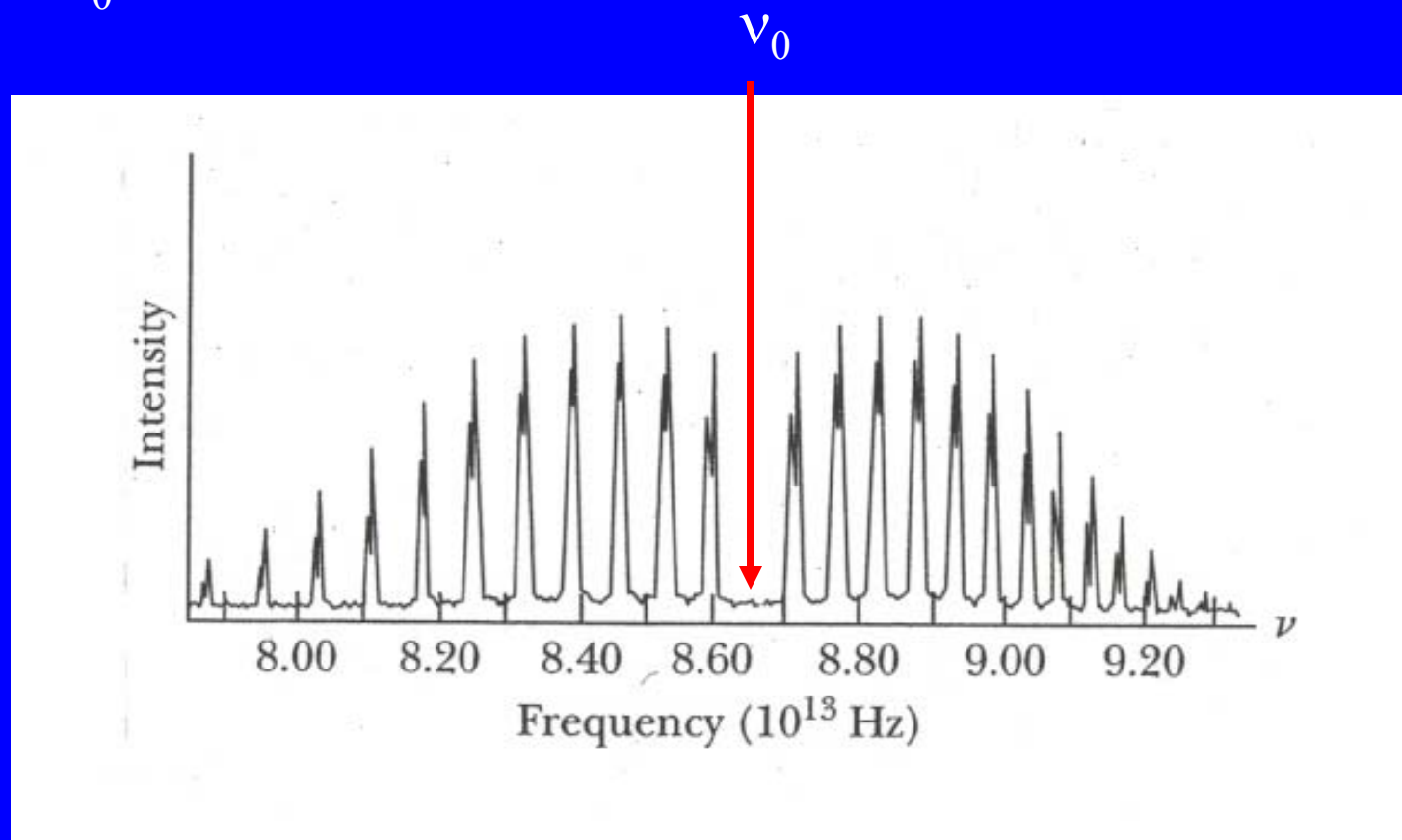
Rotačně – vibrační spektrum $\text{HCl}_{(g)}$

IČ oblast

$$\nu_0 = 2886 \text{ cm}^{-1}$$

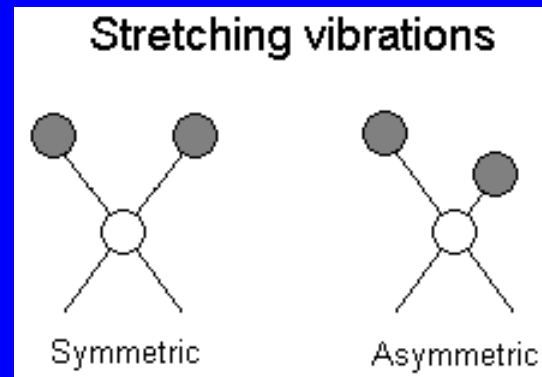
$$\Delta v = \pm 1$$

$$\Delta J = \pm 1$$

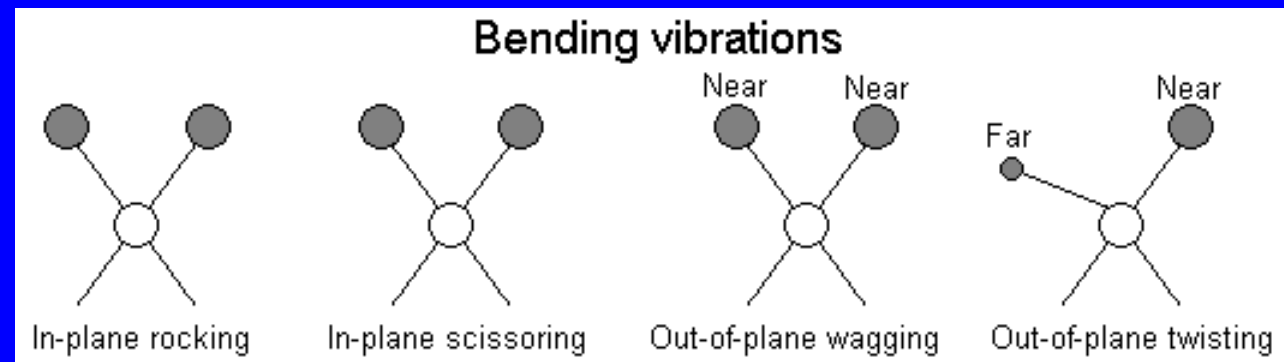


Typy vibrací

Valenční



Deformační



Vibrační spektroskopie

Oblast	λ (μm)	vlnočet (cm^{-1})
Blízká IČ	0.78 - 2.5	12800 - 4000
Střední IČ	2.5 - 50	4000 - 200
Daleká IČ	50 - 1000	200 - 10

Nejužitečnější oblast $4000 - 400 \text{ cm}^{-1}$ obsahuje vibrace většiny molekul

Infračervená a Ramanova spektroskopie

Infračervená spektroskopie

Vibrace musí měnit dipolový moment molekuly (HCl, H₂O)

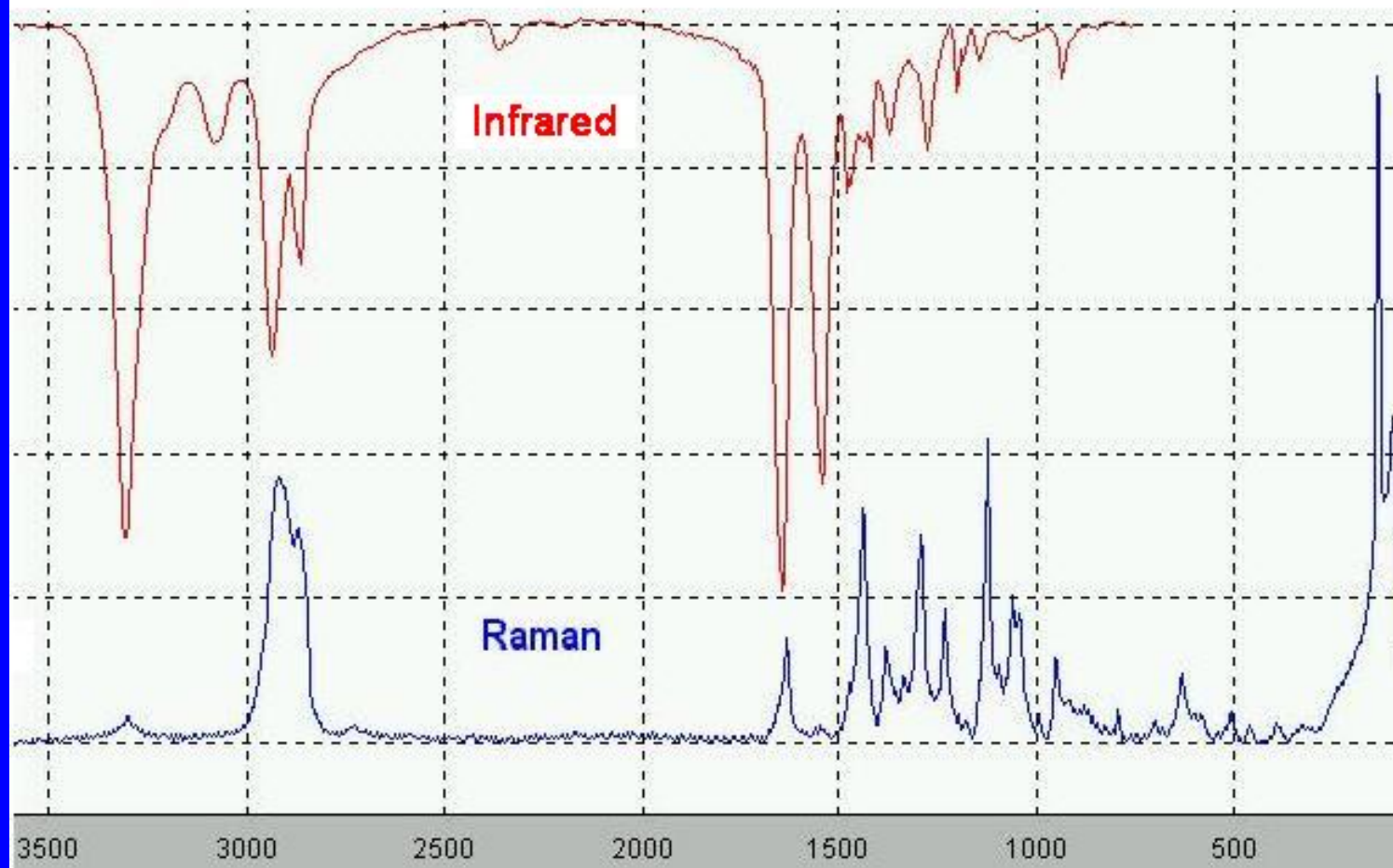
Průchod IČ záření přes vzorek, měříme absorbované množství

Ramanova spektroskopie

Vibrace musí měnit polarizaci molekuly (H₂)

Průchod viditelného záření (laser) přes vzorek, měříme rozptýlené množství

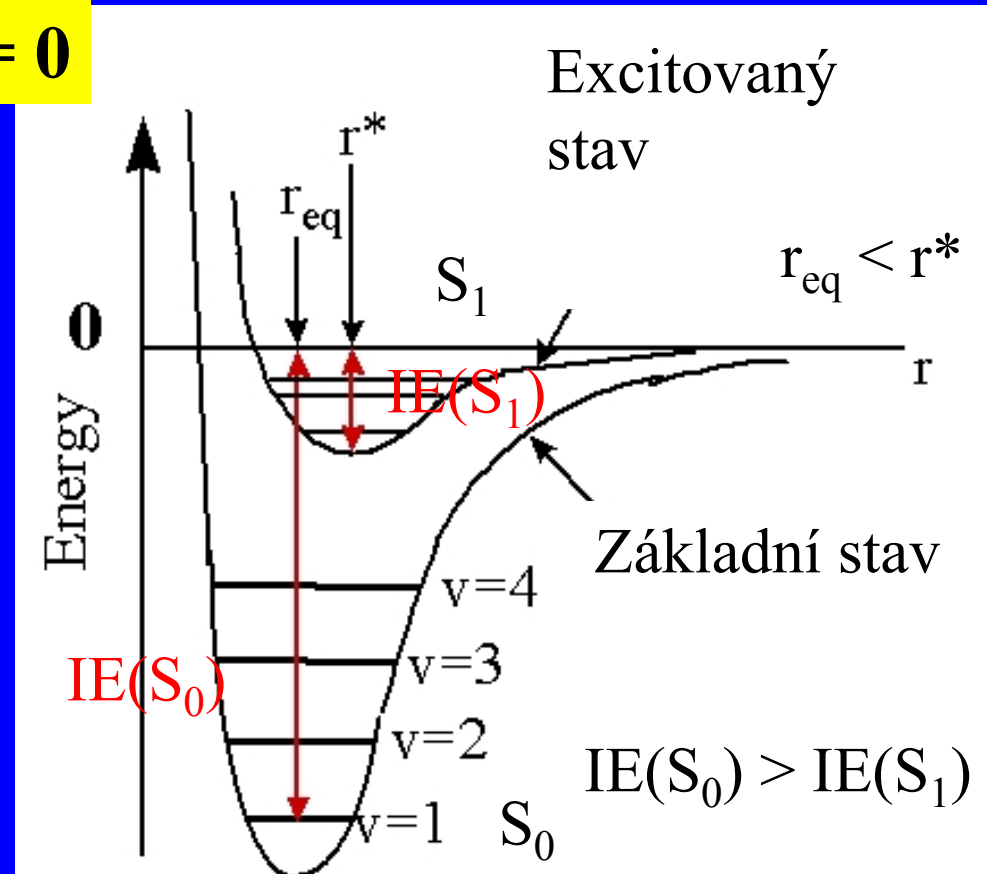
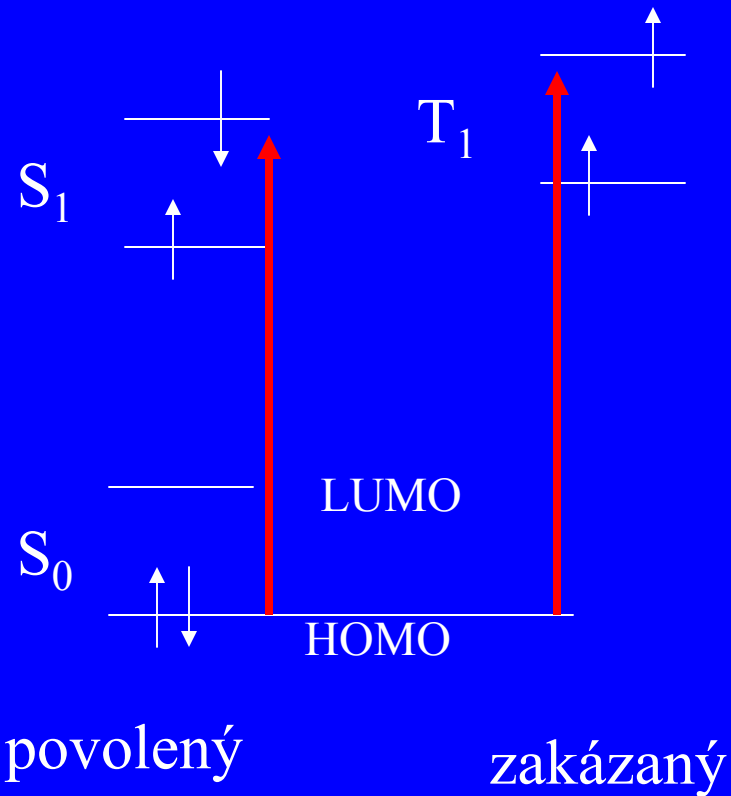
Infrared and Raman Spectra of Polyamide (Nylon 66)



$$\tilde{\nu} = 1/2\pi (k/m)^{1/2}$$

Elektronová energie

Výběrové pravidlo $\Delta S = 0$



Molekula H₂



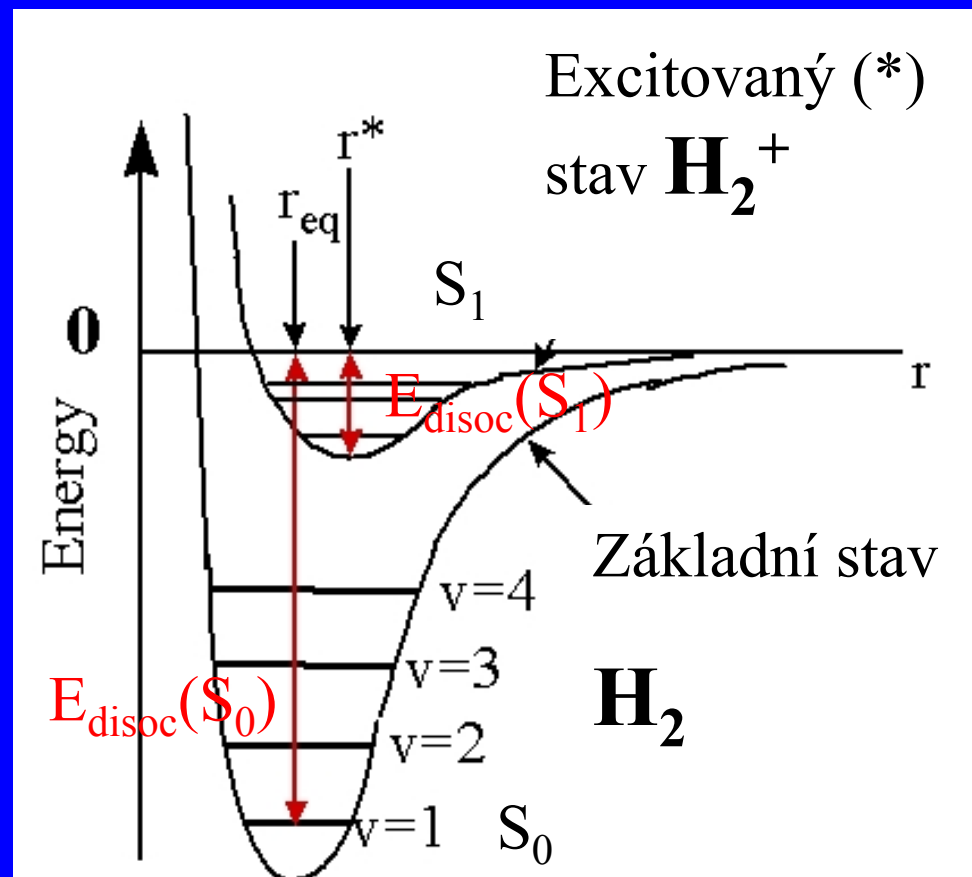
$$r_{\text{eq}}(\text{H}_2) = 0.74 \text{ \AA}$$

$$r^*(\text{H}_2^+) = 1.06 \text{ \AA}$$

$$E_{\text{disoc}}(\text{S}_0) = 432 \text{ kJ mol}^{-1}$$

$$E_{\text{disoc}}(\text{S}_1) = 255 \text{ kJ mol}^{-1}$$

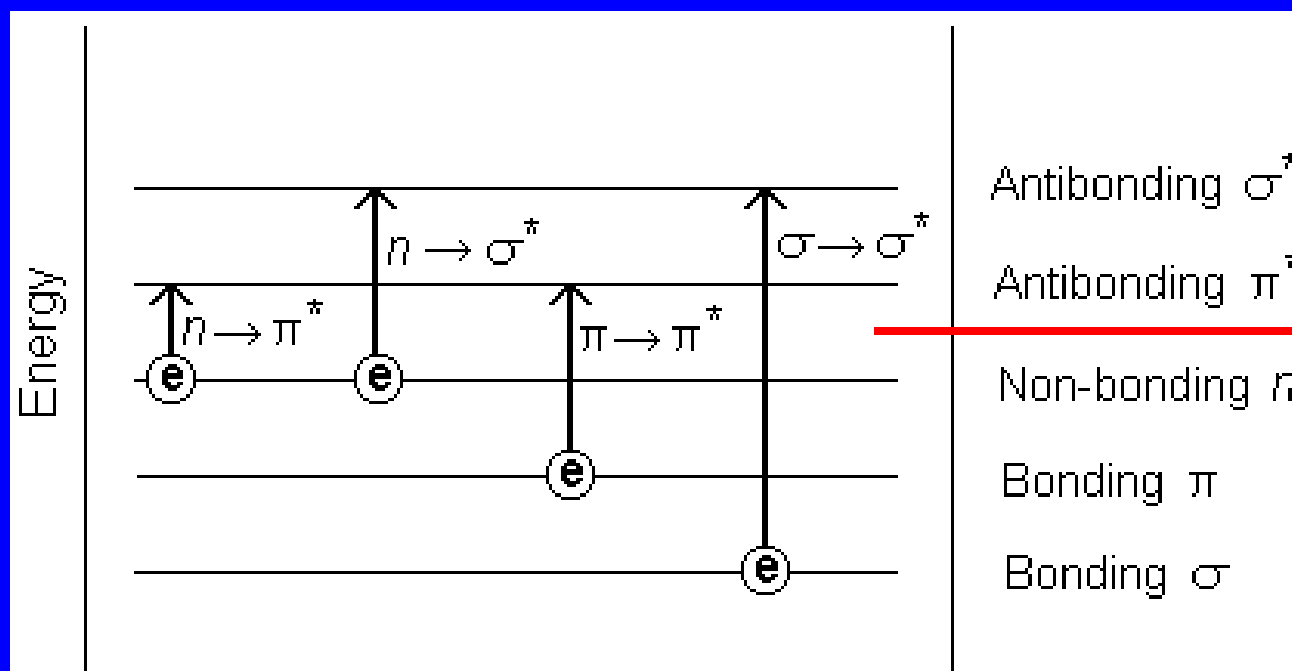
$$\text{IE}(\text{H}_2) = 1490 \text{ kJ mol}^{-1}$$



$$r_{\text{eq}} < r^*$$

$$E_{\text{disoc}}(\text{S}_0) > E_{\text{disoc}}(\text{S}_1) \quad 67$$

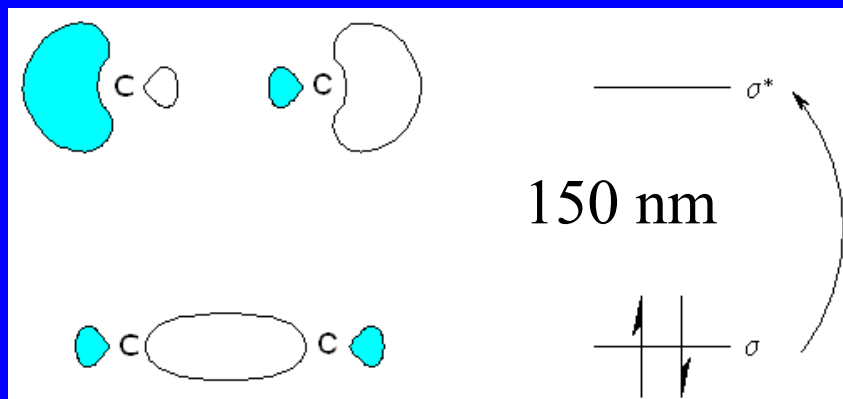
Elektronové přechody



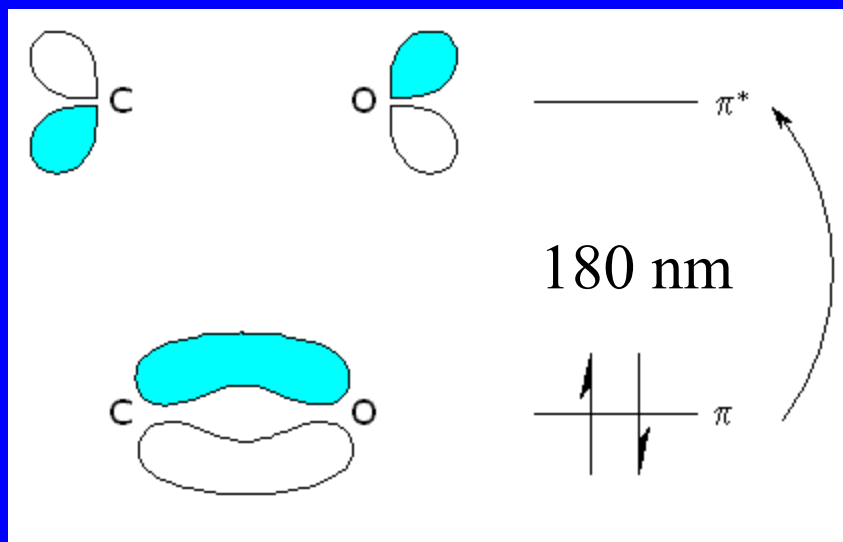
Prázdné

Zaplněno elektrony

Elektronové přechody

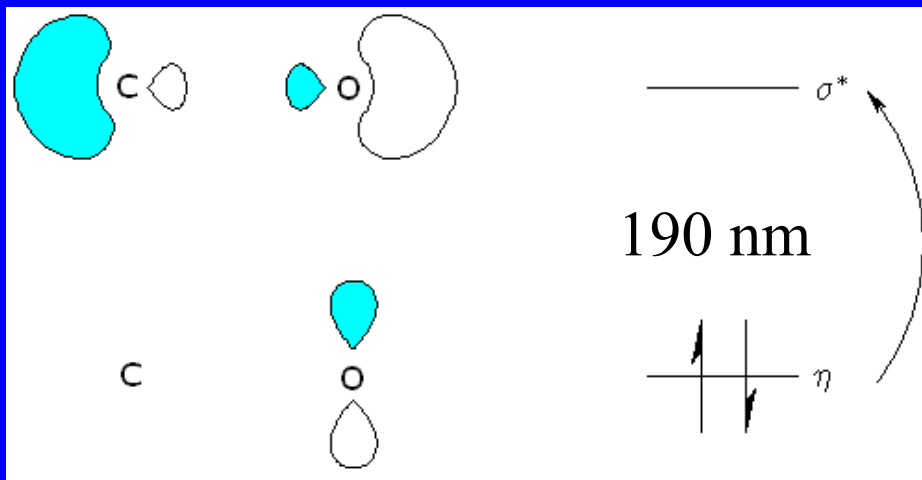


$\sigma\sigma^*$

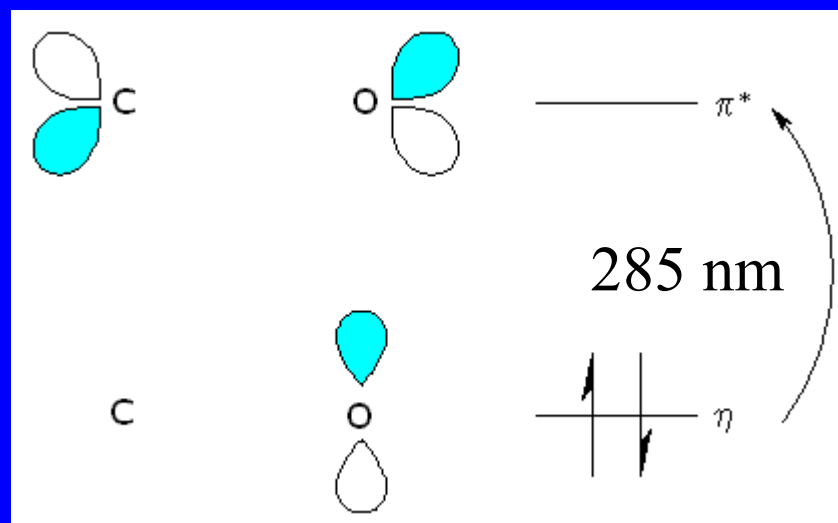


$\pi\pi^*$

Elektronové přechody

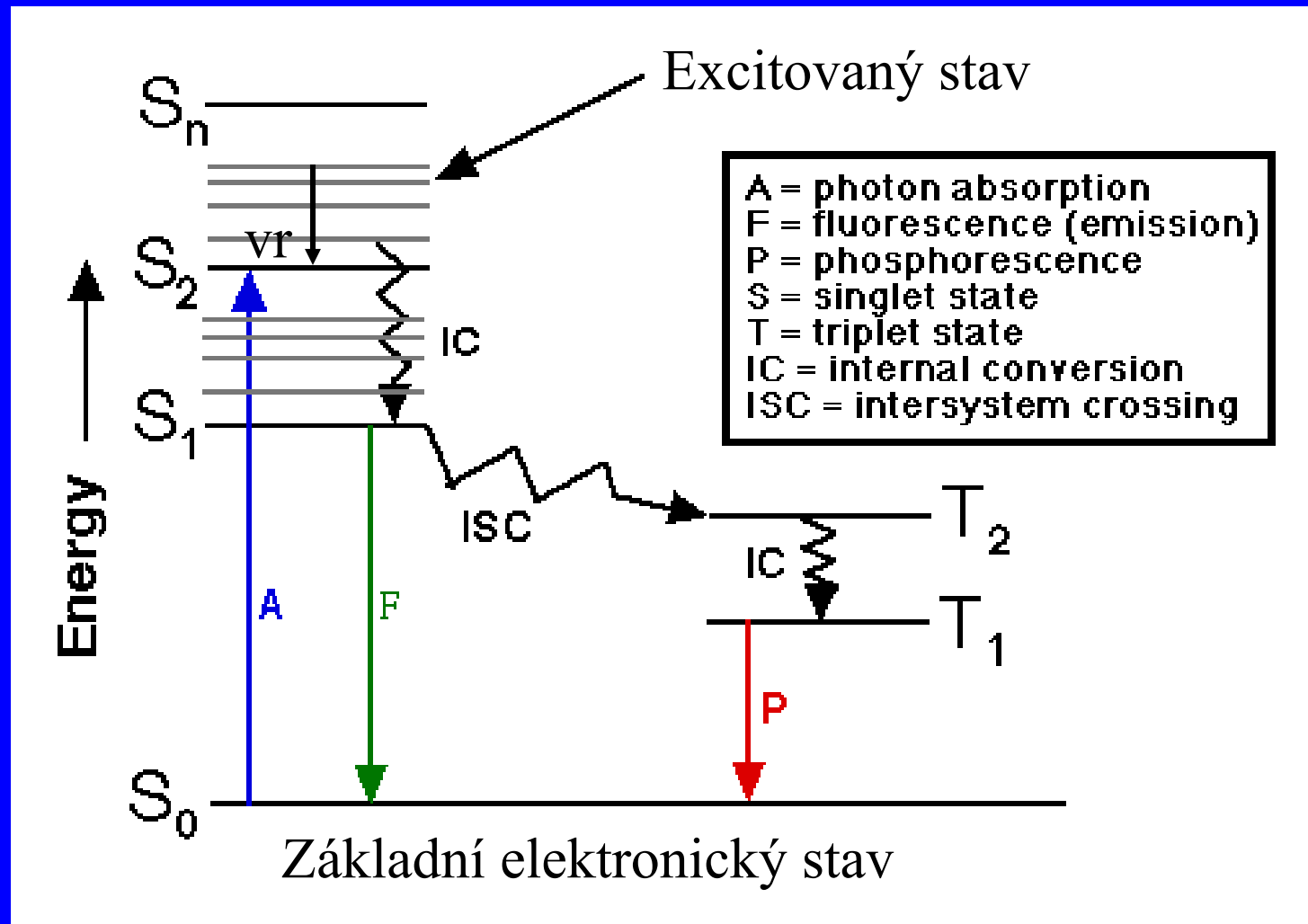


$n\sigma^*$

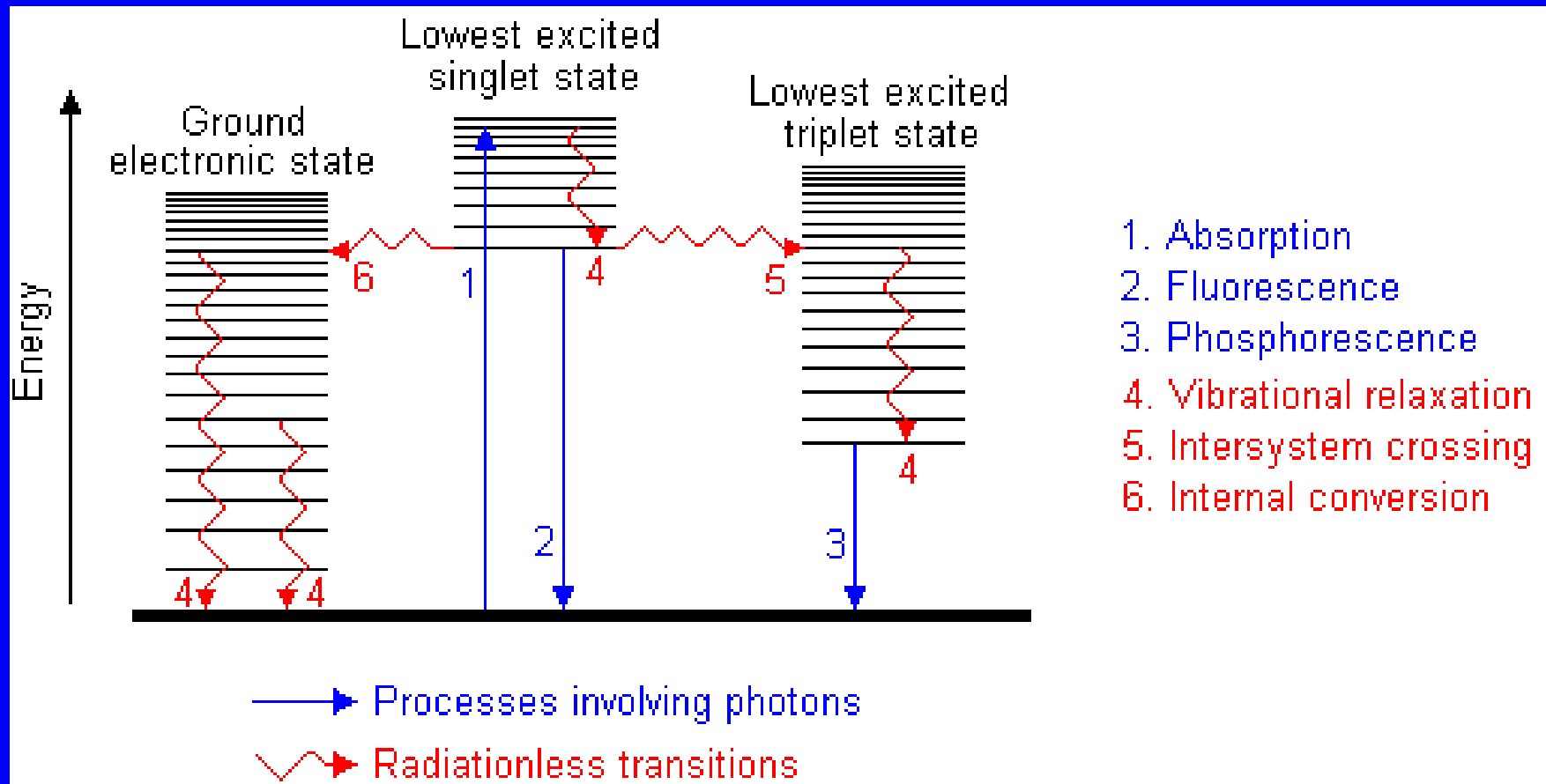


$n\pi^*$

Excitace - deexcitace



Excitace - deexcitace



Excitace - deexcitace

A = absorpce fotonu

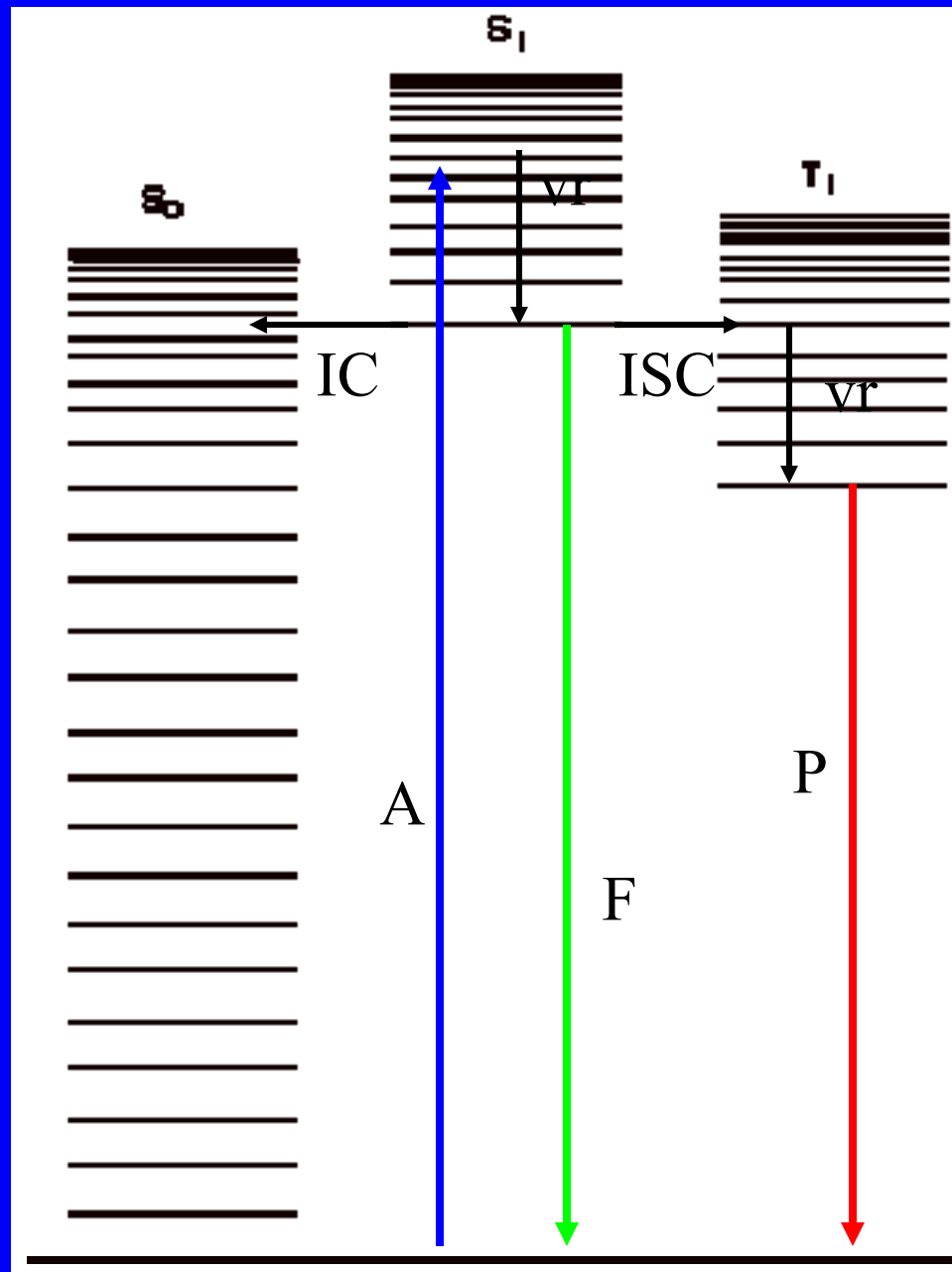
vr = vibrační relaxace, uvolnění tepla

IC = vnitřní přeměna, nezářivá, mezi stavy se stejnou multiplicitou, spinově povolená

ISC = mezisystémový přechod, nezářivá, mezi stavy se různou multiplicitou, spinově zakázaný

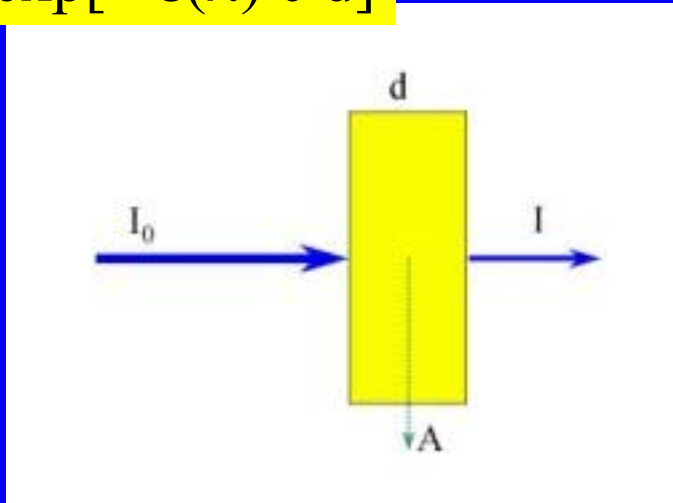
F = fluorescence, spinově povolená emise $S_1 \rightarrow S_0$, rychlá, vyzáření fotonu

P = fosforescence, spinově zakázaná emise $T_1 \rightarrow S_0$, pomalá, vyzáření fotonu



Lambert-Beerův zákon

$$I = I_0 \exp[-\epsilon(\lambda) c d]$$



$\epsilon(\lambda)$ = molární extinkční koeficient
 c = molární koncentrace (M)
 d = délka kyvety

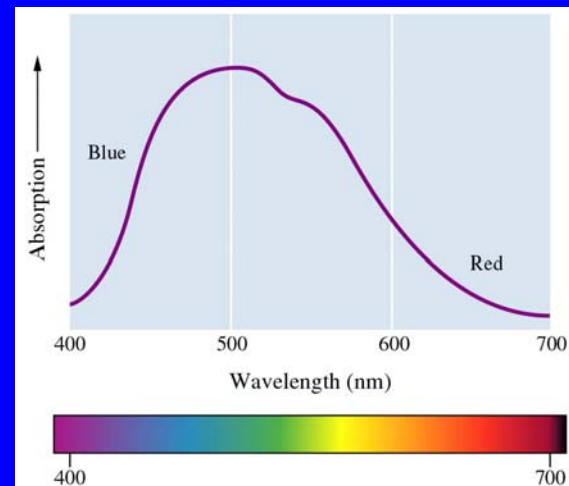
Platí pro určitou λ

Johann H. Lambert (1728-1777)

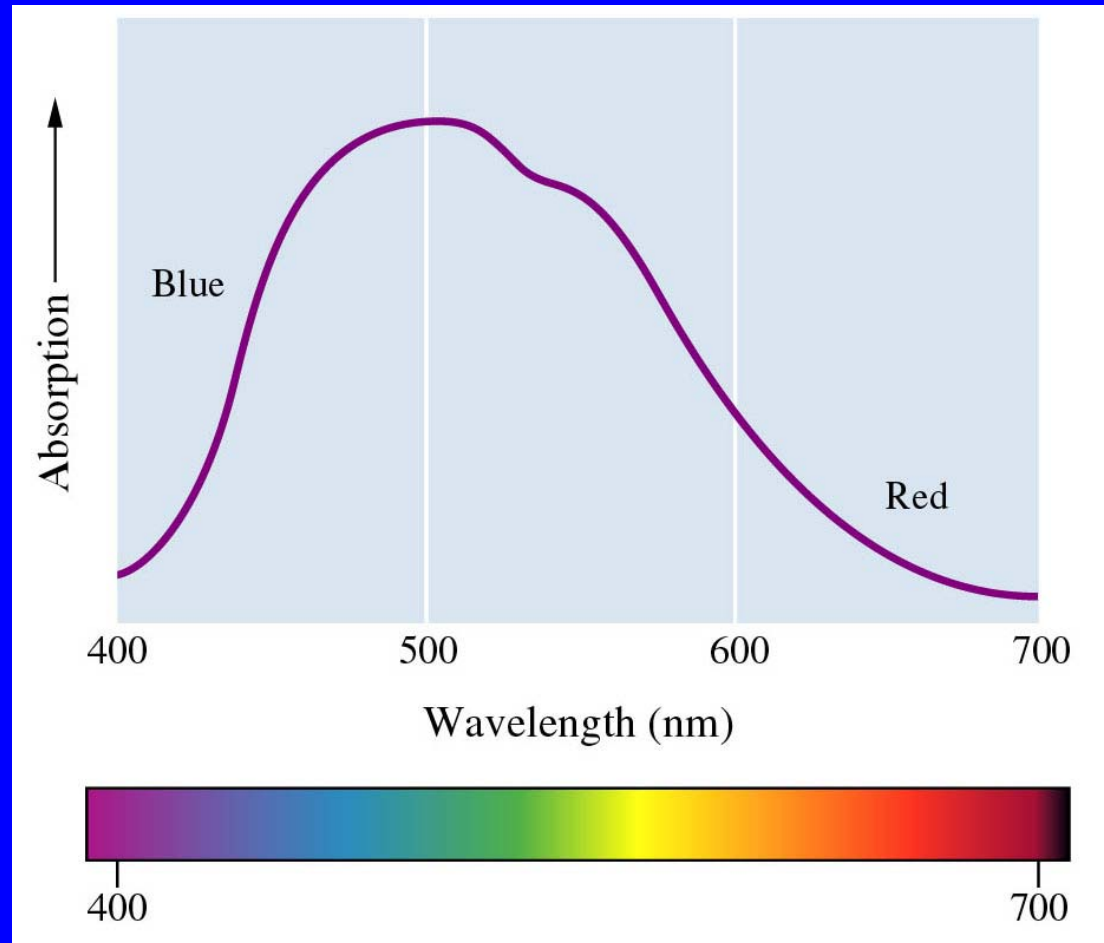
August Beer (1825-1863)

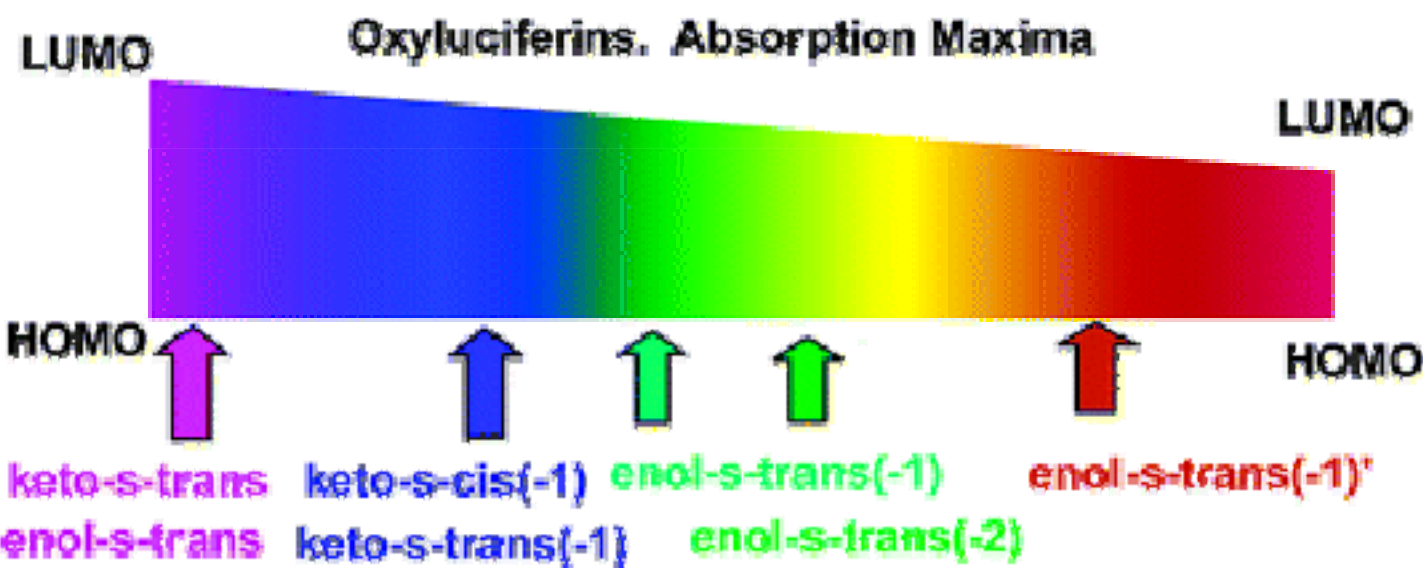
$$\% \text{ Transmittance} = (I / I_0) 100$$

$$\text{Absorbance} = -\log(I / I_0) = \epsilon(\lambda) c d$$



Absorpční spektrum





Mechanismy přetržení chemické vazby

Termální excitace

dodaná tepelná energie je napumpována do vibračních modů (valenčních vibrací), vazba se prodlužuje, zeslabuje, až se přeruší

relativně pomalé, 10^{-12} s

Elektronická excitace

energie dopadajícího záření (fotony, elektrony) je použita na excitaci vazebného elektronu do protivazebného orbitalu

okamžité, 10^{-15} s

Mechanismy přetržení chemické vazby

Smíšená vibračně elektronická excitace

energie (tepelná) několika vibrací (fononů) je spojena a napumpována do elektronického přechodu valenčního elektronu do protivazebného orbitalu