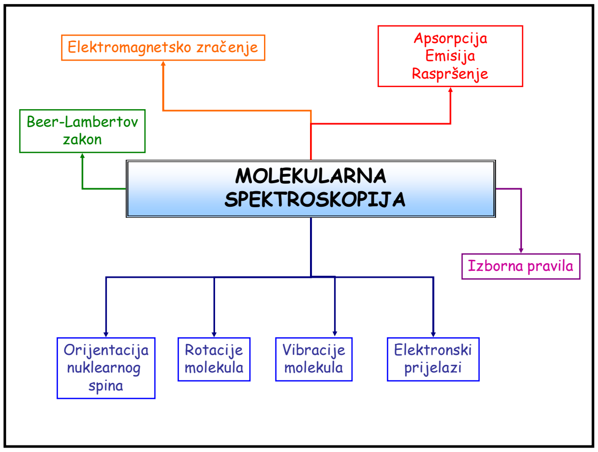
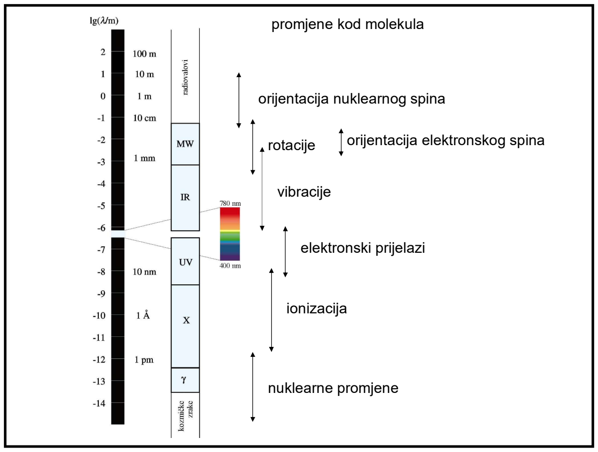


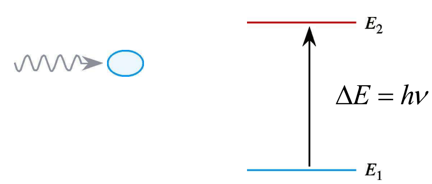


$$\lambda = \frac{c}{\nu} \qquad \tilde{\nu} = \frac{1}{\lambda} \qquad \nu = c\tilde{\nu}$$

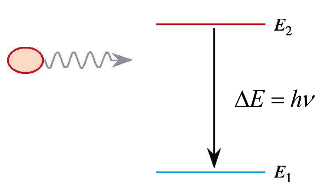
-Interakcija EMZ s materijom

-refleksija, transmisija, apsorpcija

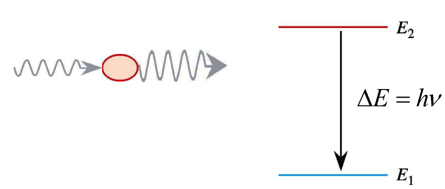
Apsorpcija



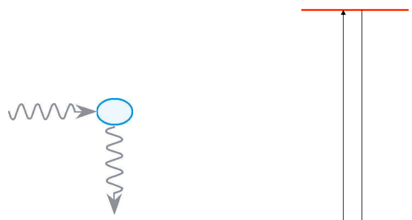
Spontana emisija



Inducirana (stimulirana) emisija



Raspršenje



Interakcija EMZ s materijom

$$I_0 = I_{\text{refl}} + I_{\text{aps}} + I_{\text{trans}}$$

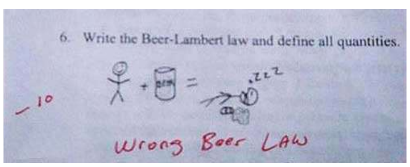
$\rho = I_{\text{refl}} / I_0$ reflektancija

$\alpha = I_{\text{abs}} / I_0$ apsorptancija

$\tau = I_{\text{trans}} / I_0$ transmitancija

$$\rho + \alpha + \tau = 1 \qquad \alpha + \tau = 1$$

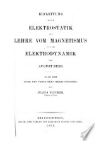
Lambert- Beerov zakon



Lambert- Beerov zakon

Johann Heinrich Lambert (1728–1777)

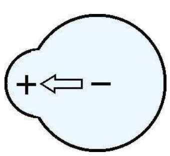
Jean-Henri Lambert



August Beer (1825 –1863)

$$A = \varepsilon\, b\, c$$

Električni dipolni moment

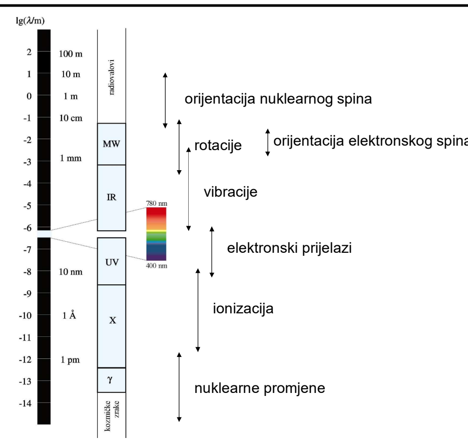


HCl

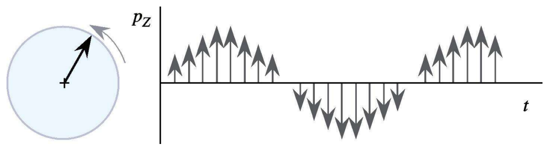
polarna molekula

$$\vec{p} = \sum_i Q_i \vec{r}_i$$

dipolni moment

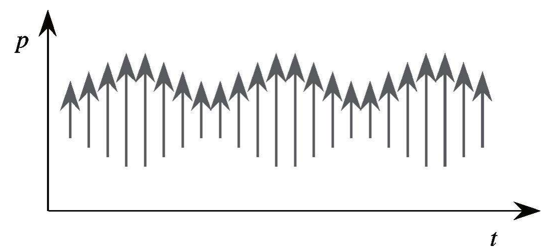


Rotacija molekula

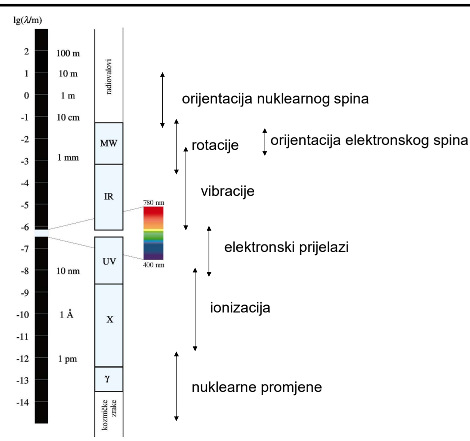


- kod molekule koja ima stalni dipolni moment vrtnjom dipola mijenjaju se prostorne komponente dipolnog momenta s vremenom

Vibracija molekula



- vibracija uzrokuje periodičnu promjenu dipolnog momenta



Molekularna spektroskopija
Rotacija molekula

-mikrovalno područje, daleki IR
 (λ ≈ 1 mm – 100 μm)

- plinoviti uzorci

- model krutog rotora

Molekularna spektroskopija
Rotacija molekula

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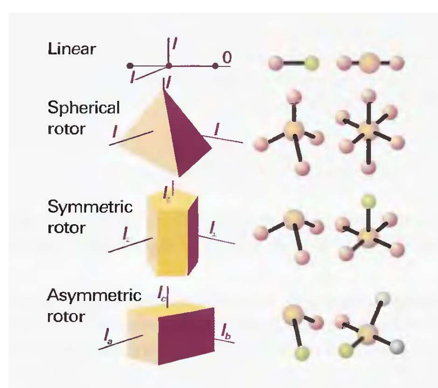


$I_b = I_c; \quad I_a = 0$

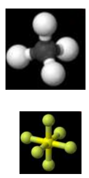
$I_a = I_b = I_c$

$I_a = I_b < I_c$

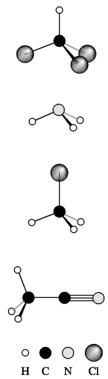
$I_a < I_b = I_c$

$I_a < I_b < I_c$

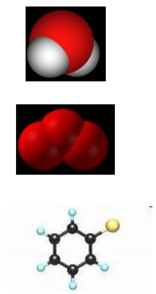
Sferni rotori



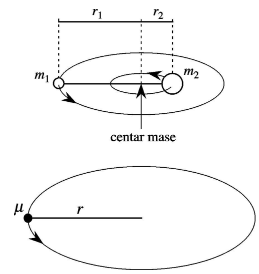
Simerični rotori



Asimerični rotori



Rotacija dvoatomne molekule



Stvarna vrtnja
oko centra mase

Ekvivalentna vrtnja

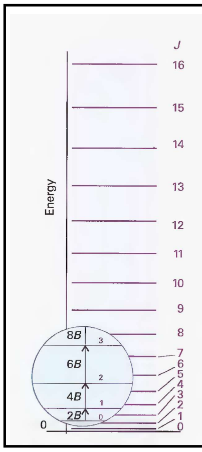
Linearne molekule

$$I=\sum_i m_i r_i^2$$

I. Klasični hamiltonijan $$H=\frac{P_b^2}{2I_b}+\frac{P_c^2}{2I_c}=\frac{P^2}{2I_b}$$

II. Kvantnomehanički hamiltonijan $$\hat{H}=\frac{\hat{P}^2}{2I_b}$$

III. Schrödingerova jednadžba $$\frac{1}{2I_b}\hat{P}^2\Psi_r=E_r\Psi_r$$



Rješenje Schrödingerove jednadžbe:

Energije krutih linearnih molekula

$$E_r=\frac{\hbar^2}{2I_b}J(J+1)$$

$$\tilde{F}(J)=\frac{E_r}{hc}=\frac{h}{8\pi^2 I_b c}J(J+1)=\tilde{B}J(J+1)$$

rotacijski term

$$F(J)=\frac{E_r}{h}=\frac{h}{8\pi^2 I_b}J(J+1)=BJ(J+1)$$

Rješenje Schrödingerove jednadžbe:

valne funkcije

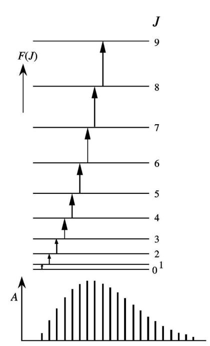
kugline funkcije koje ovise o dva kuta ϑ i φ a označuju se kvantnim brojevima J i m

Izborna pravila:
$\Delta J = +1$
$\Delta m = 0$

kvadrat valne funkcije opisuje orijentaciju molekule u prostoru

$$\tilde{\nu}=F(J')-F(J'')=B(J+1)(J+2)-BJ(J+1)$$

Rotacijski spektri



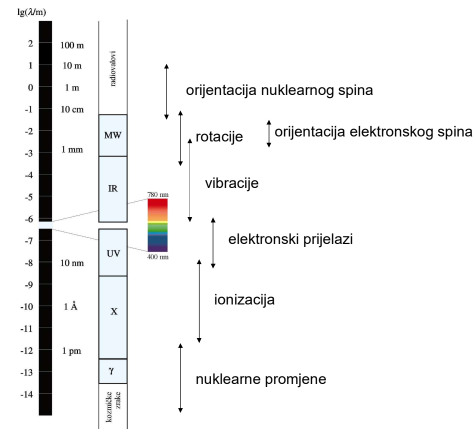
Razlika između energetskih nivoa
→
valni brojevi linija u spektru

$$\tilde{\upsilon}=2B(J+1)$$

Intenziteti linija

- ovisi o dipolnom momentu molekule
- ovisi o napućenosti energetskih nivoa

$$N_J \propto (2J+1)\exp\left[\frac{-hc}{kT}\tilde{B}J(J+1)\right]$$



Molekularna spektroskopija
Vibracije molekula

- uslijed vibriranja dolazi do periodičke promjene dipolnog momenta

- IR – područje elektromagnetskog zračenja (≈ 300 cm^{-1} – 3000 cm^{-1})

- Nelinearne molekule: 3N-6 načina vibriranja
- Linearne molekule: 3N-5 načina vibriranja

Vibracije dvoatomnih molekula

Harmonijski oscilator

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \qquad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

Gibanje dviju čestica mase m_1 i m_2 može se svesti na gibanje jedne čestice reducirane mase μ

$$V(x) = \tfrac{1}{2}kx^2$$

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\Psi_v}{\mathrm{d}x^2} + \frac{kx^2}{2}\Psi_v = E_v\Psi_v$$

Schrödingerova jednadžba

IV. Rješenje Schrödingerove jednadžbe – Harmonijski oscilator

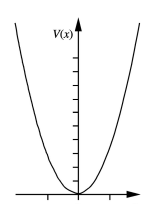
Energija $E_v = h\nu_e\left(v + \frac{1}{2}\right) \qquad v = 0, 1, 2, \ldots$

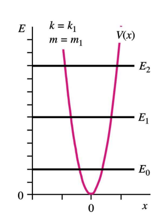
Klasična frekvencija titrala $\nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Klasični valni broj HO $\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

Vibracijski term $G(v) = \frac{E_v}{hc} = \omega_e\left(v + \frac{1}{2}\right) \qquad v = 0,1,2,\ldots$

Vibracije dvoatomnih molekula





Harmonijski oscilator – izborno pravilo:

$\Delta v = 1$

Harmonijski oscilator – valni broj apsorbiranog zračenja:

$$\tilde{v} = G(v+1) - G(v) = \omega_e$$

Anharmonijski oscilator

Morseov potencijal

$$V(x) = hcD_e\left\{1 - e^{-\beta(r-r_e)}\right\}^2$$

Vibracijski term

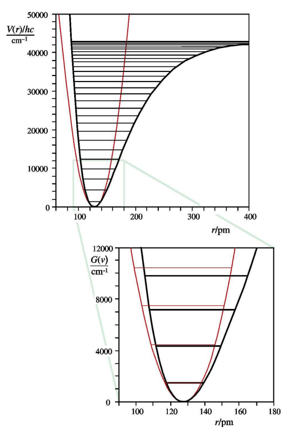
$$G(v) = \frac{E_v}{hc} = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2 \qquad v = 0, 1, 2, \ldots$$

Razlika susjednih termova

$$\Delta G(v) = G(v+1) - G(v) = \omega_e - 2\omega_e x_e(v+1)$$

Druga razlika susjednih termova

$$\Delta G(v+1) - \Delta G(v) = -2\omega_e x_e$$



Energija disocijacije

$$\Delta G(v) = G(v+1) - G(v) = \omega_e - 2\omega_e x_e(v+1) = 0$$

$$v_{max} = \frac{1}{2x_e} - 1$$

$$G(v_{max}) = D_e$$

Anharmonički oscilator – izborno pravilo:

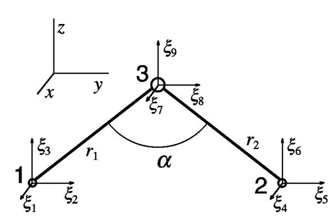
$\Delta v = 1, 2, \ldots$

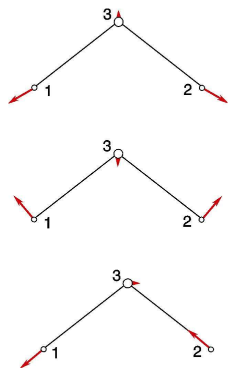
osnovni prijelazi

gornji ili viši tonovi

vruće vrpce

Vibracije višeatomnih molekula





simetrija

a_1 ν_1 3000 cm^{-1}

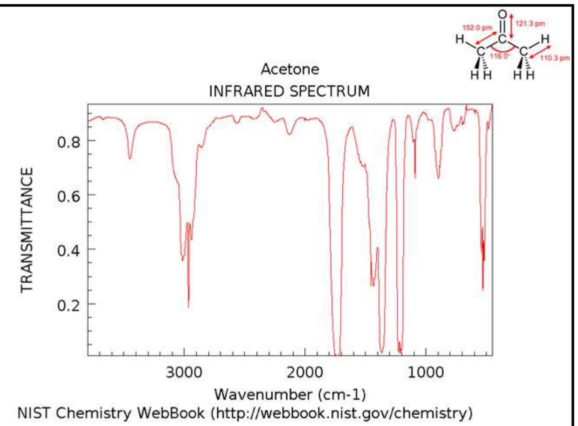
simetrično istezanje

a_1 ν_2

deformacija kuta

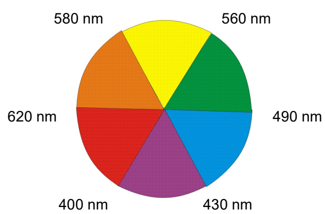
b_2 ν_3

antisimetrično istezanje



Elektronski prijelazi
Elektronski spektri

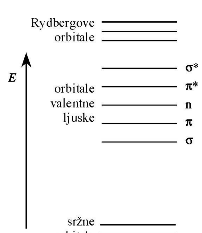
- interakcija sa zračenjem u vidljivom i ultraljubičastom dijelu spektra



Elektronski prijelazi

- osnovno elektronsko stanje neke molekule okarakterizirano je nekom elektronskom konfiguracijom
- apsorpcijom zračena u vidljivom ili ultraljubičastom dijelu spektra molekule mogu prijeći u pobuđena elektronska stanja – drugačija elektronska konfiguracija

Vrste orbitala u molekuli



tipovi orbitala kod molekula i kvalitativni odnosi pripadnih energija

$$\tilde{\upsilon} = \frac{E_i}{hc} - \frac{R}{(n-\delta)^2}$$

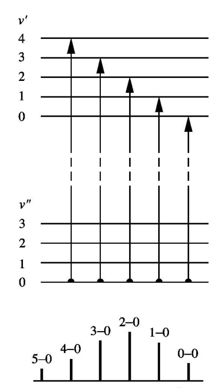
Prijelazi:
- prema tipu orbitala čija se napučenost mijenja
- prema multiplicitetu elektronskih stanja

vibronski prijelazi – promjena i elektronske i vibracijske energije

rovibronske linije

PROGRESIJE

- vibronske vrpce koje nastaju prijelazima iz zajedničke početne razine redom na sve više razine drugog elektronskog stanja



$$\Delta\tilde{\upsilon} = \omega'_e$$

Informacije dobivene analizom elektronskih spektara

1. Elektronska struktura molekula

2. Rovibronska struktura vrpci daje informacije koje se mogu dobiti i iz vibracijskih i rotacijskih spektara

3. Tip veze

4. Kvalitativna analiza

5. Kvantitativna analiza