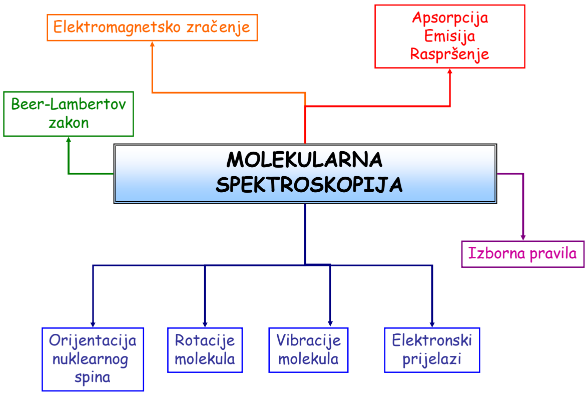
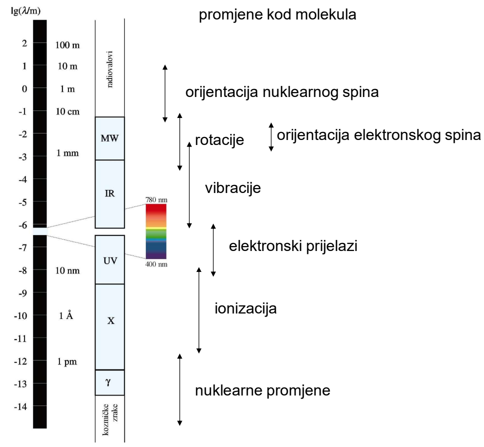


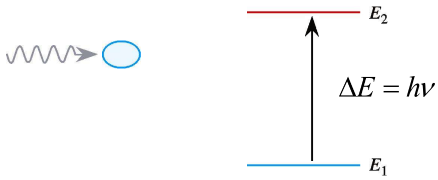


$$\lambda = \frac{c}{\nu} \qquad \tilde{\nu} = \frac{1}{\lambda} \qquad \nu = c\tilde{\nu}$$

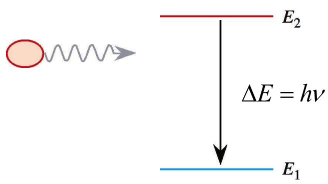
-Interakcija EMZ s materijom

-refleksija, transmisija, apsorpcija

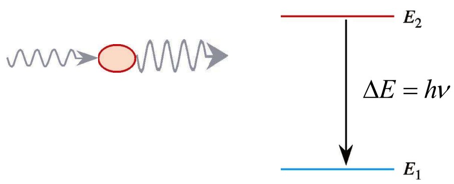
Apsorpcija



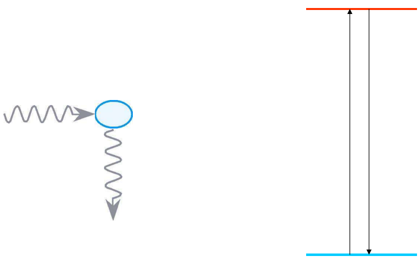
Spontana emisija



Inducirana (stimulirana) emisija



Raspršenje



Interakcija EMZ s materijom

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

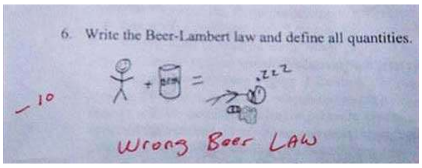
$\rho = I_{\text{refl}} / I_0$ reflektancija

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

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

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

Lambert- Beerov zakon



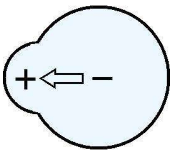
Lambert- Beerov zakon

Johann Heinrich Lambert (1728-1777)
Jean-Henri Lambert

August Beer (1825 -1863)

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

Električni dipolni moment

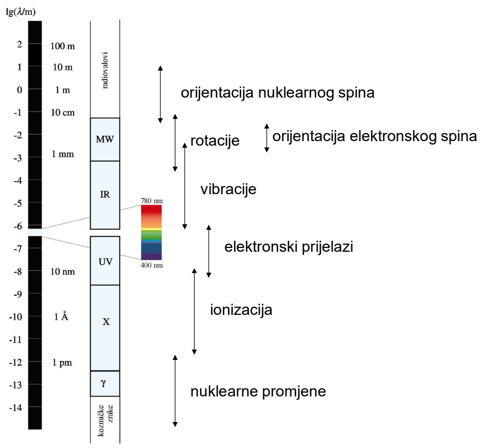


HCl

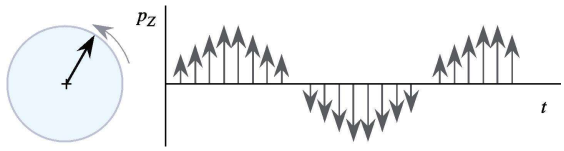
polarna molekula

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

dipolni moment

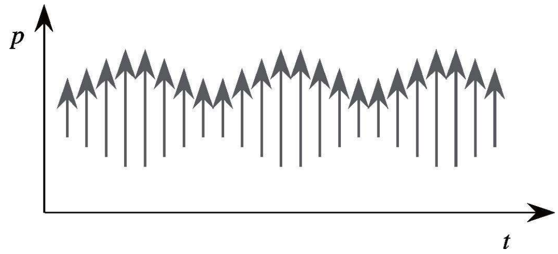


Rotacija molekula

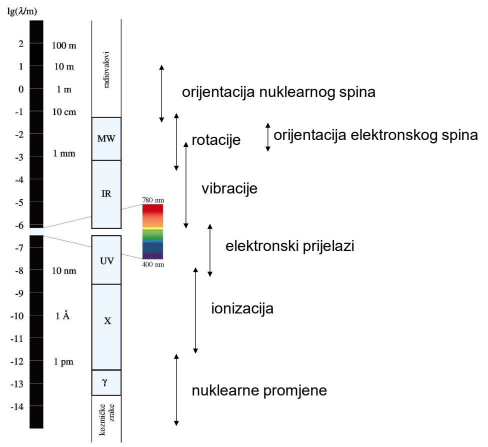


- kod molekule koja ima stalni dipolni moment vrtnjom dipola mijenjaju se prostorne komponente dipolnog momenta s vremenom

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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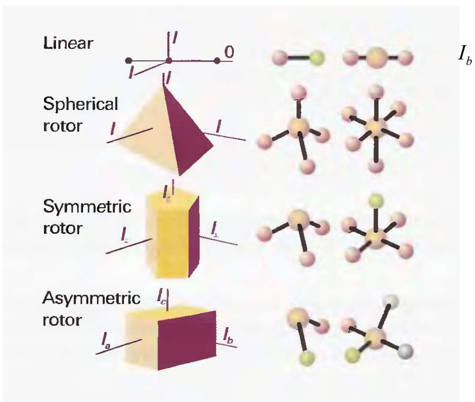


$I_b = I_c; \quad I_a = 0$

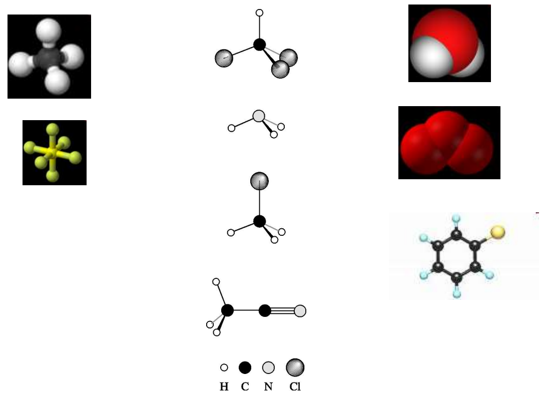
$I_a = I_b = I_c$

$I_a = I_b < I_c$

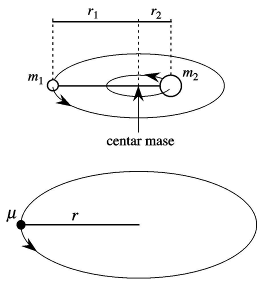
$I_a < I_b = I_c$

$I_a < I_b < I_c$

Sferni rotori | Simerični rotori | Asimerični rotori



Rotacija dvoatomne molekule



Stvarna vrtnja
oko centra mase

Ekvivalentna vrtnja

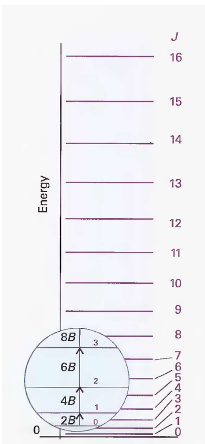
Linearne molekule

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

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

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

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



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

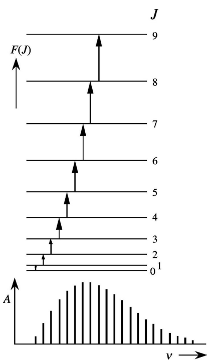
kugline funkcije koje
ovise o dva kuta ϑ i φ
a označuju se kvantnim
brojevima J i m

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



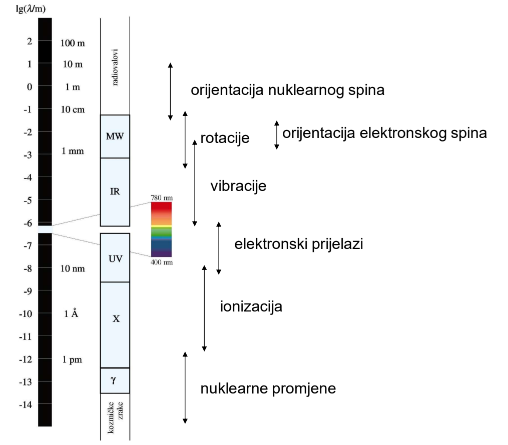
Razlika između energetskih nivoa
→
valni brojevi linija u spektru

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

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

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

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

Schrödingerova jednadžba

IV. Rješenje Schrödingerove jednadžbe – Harmonijski oscilator

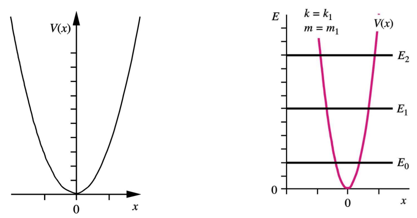
Energija $E_v = h\nu_e\left(v + \frac{1}{2}\right) \qquad v = 0, 1, 2, \ldots$

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:

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

Anharmonijski oscilator

Morseov potencijal

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

Vibracijski term

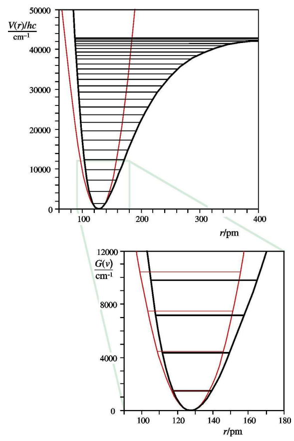
$$G(v) = \frac{E_v}{hc} = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e \left(v+\frac{1}{2}\right)^2 \qquad v = 0,1,2,\ldots$$

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:

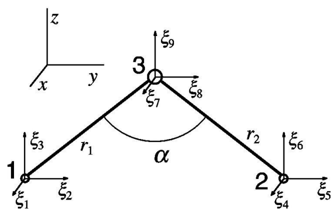
$\Delta v = 1, 2, \ldots$

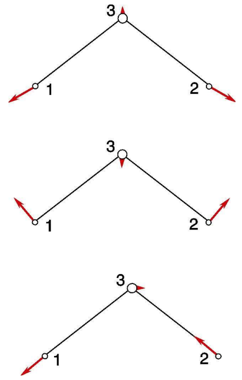
osnovni prijelazi

gornji ili viši tonovi

vruće vrpce

Vibracije višeatomnih molekula





simetrija

a_1	ν_1	simetrično istezanje	3000 cm^{-1}
a_1	ν_2	deformacija kuta	
b_2	ν_3	antisimetrično istezanje