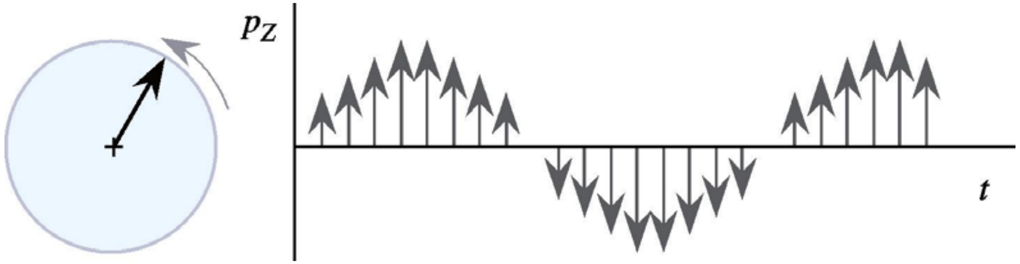
Molekulska spektroskopija
Rotacija molekula

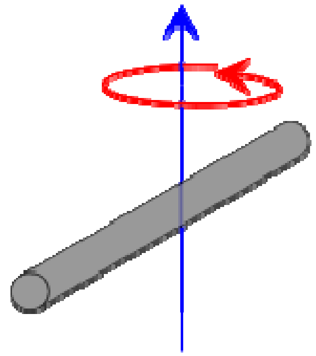


- mikrovalno područje, daleki IR (λ ≈ 1 mm – 100 μm)

- plinoviti uzorci

- model krutog rotora

Rotacija molekula



Moment inercije (tromosti): I

Osi inercije: a, b i c

Glavni momenti inercije $I_a \leq I_b \leq I_c$

Kinetička energija tijela koje rotira: $$T = \frac{1}{2}\sum_i I_i \omega_i^2$$

$$T = \frac{1}{2}\sum_i \frac{P^2}{I_i} \quad P = I\omega$$

$$T = \frac{1}{2} I_a \omega_a^2 + \frac{1}{2} I_b \omega_b^2 + \frac{1}{2} I_c \omega_c^2$$

$$T = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_c}$$

Kinetička energija –kruti rotor

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

$$I_x = \sum_i m_i x_i^2 \qquad I_y = \sum_i m_i y_i^2 \qquad I_z = \sum_i m_i z_i^2$$

$$E = E_x + E_y + E_z$$

$$E = \frac{1}{2}\sum_i m_i v_{x(i)}^2 + \frac{1}{2}\sum_i m_i v_{y(i)}^2 + \frac{1}{2}\sum_i m_i v_{z(i)}^2$$

$$= \frac{1}{2}\sum_i m_i x_i^2 \omega_x^2 + \frac{1}{2}\sum_i m_i y_i^2 \omega_y^2 + \frac{1}{2}\sum_i m_i z_i^2 \omega_z^2$$

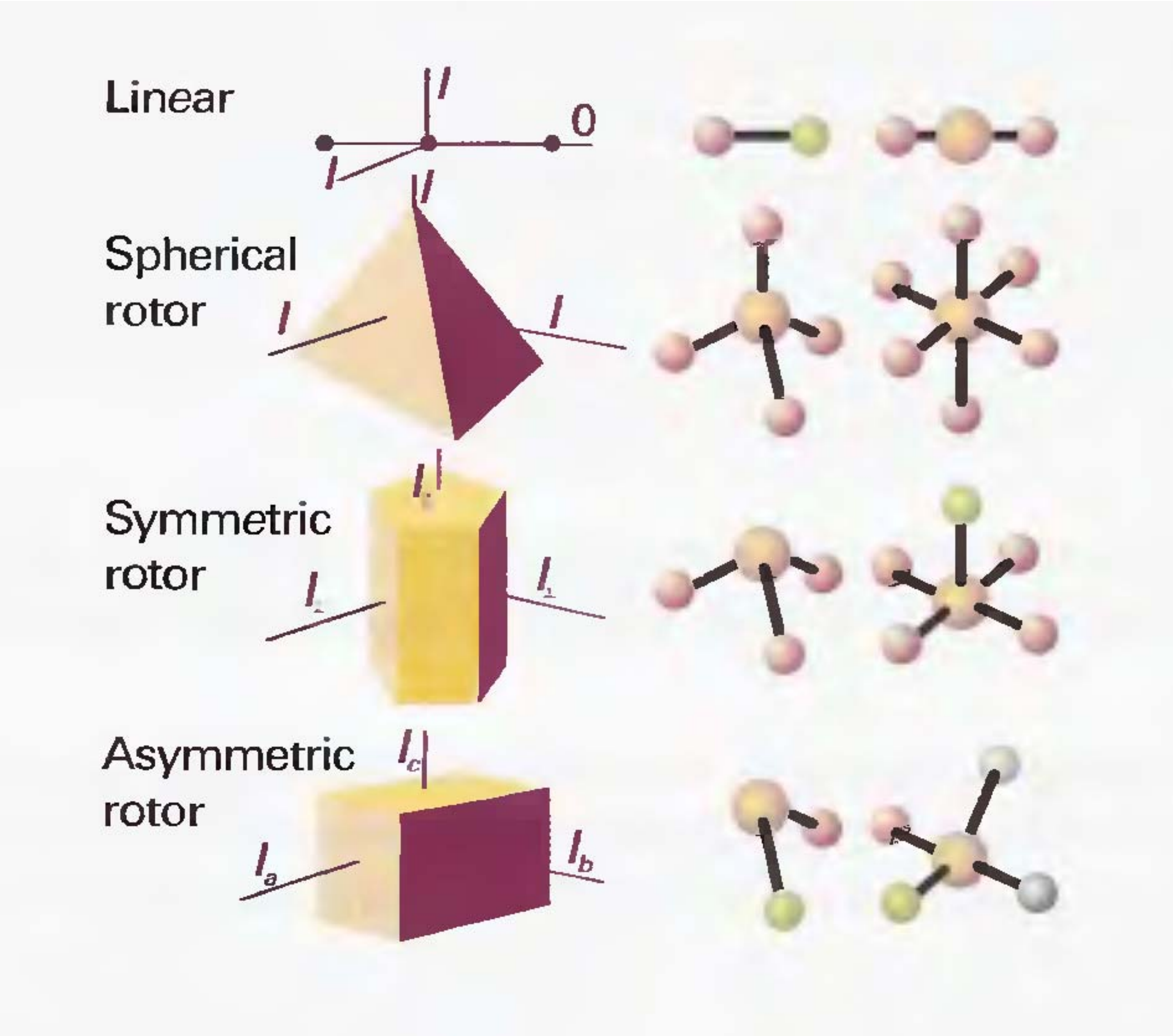
$$= \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2$$

$$= \frac{P_x^2}{2I_x} + \frac{P_y^2}{2I_y} + \frac{P_z^2}{2I_z}$$

$$v_{x(i)} = \omega_x x_i; \quad (v = \omega r)$$

$$P_x = I_x \omega_x$$

Podjela molekula prema odnosima glavnih momenta tromosti



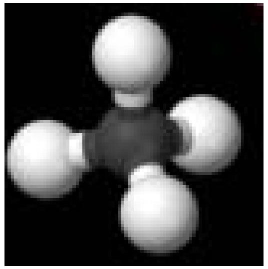
$$I_b = I_c; \quad I_a = 0$$

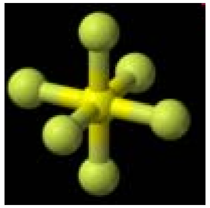
$$I_a = I_b = I_c$$

$$I_a = I_b < I_c$$
$$I_a < I_b = I_c$$

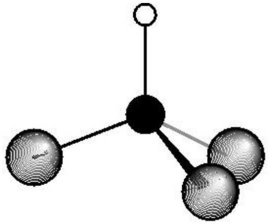
$$I_a < I_b < I_c$$

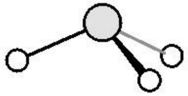
Sferni rotori

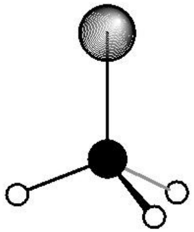


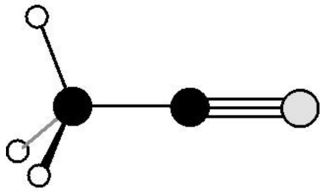


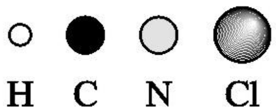
Simerični rotori



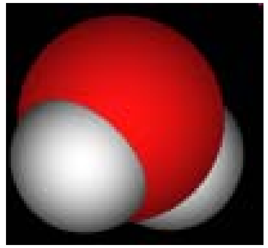


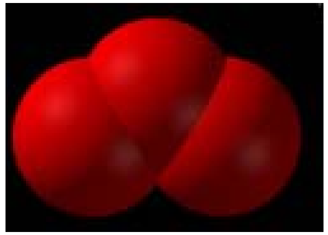


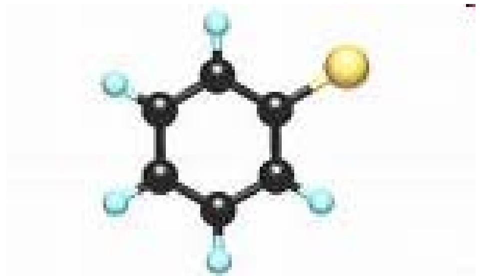




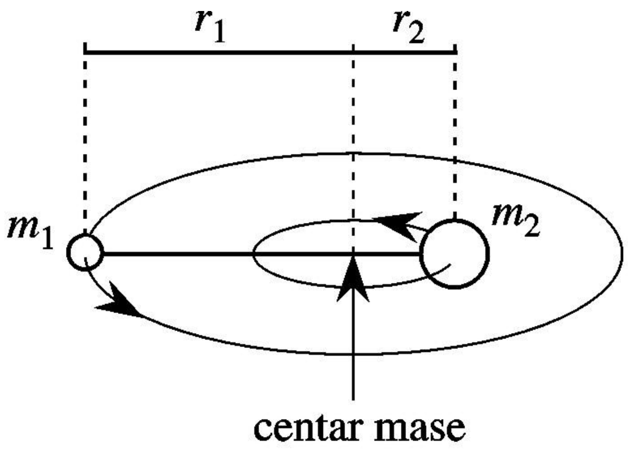
Asimerični rotori



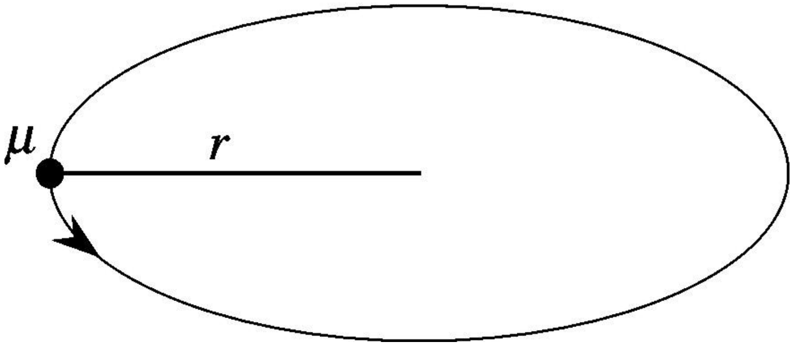




Linearne molekule
(dvoatomne)



Stvarna vrtnja
oko centra mase



Ekvivalentna vrtnja

$$I = \sum_i m_i r_i^2 \xrightarrow{\text{IZVOD}} I = \mu r^2$$

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

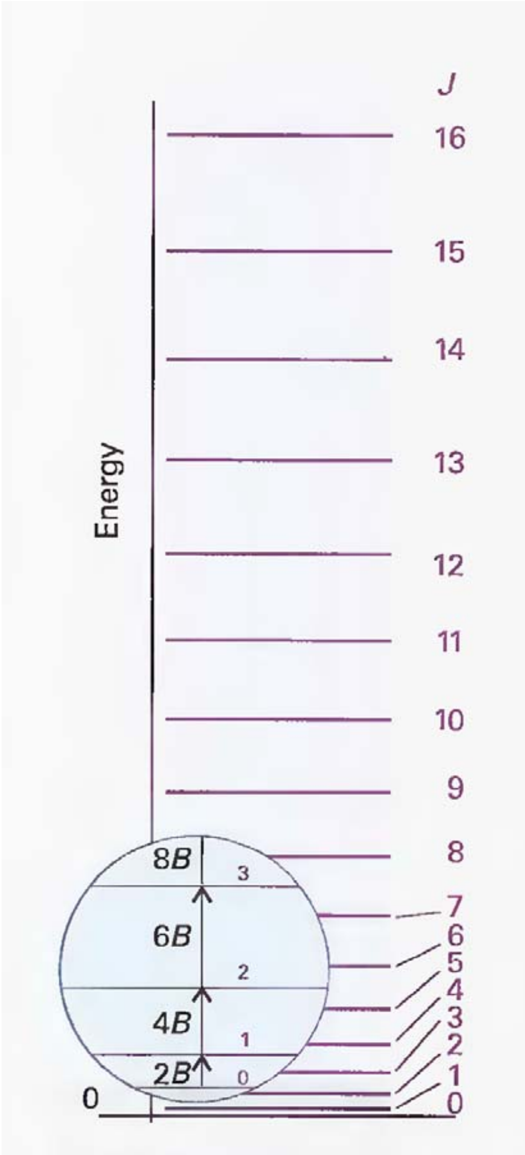
$$\hat{H} = \frac{\hat{P}^2}{2I_b}$$

III. Schrödingerova jednadžba

$$\frac{1}{2I_b}\hat{P}^2\Psi_r = E_r\Psi_r$$

Linearne molekule

Rotacijske energije

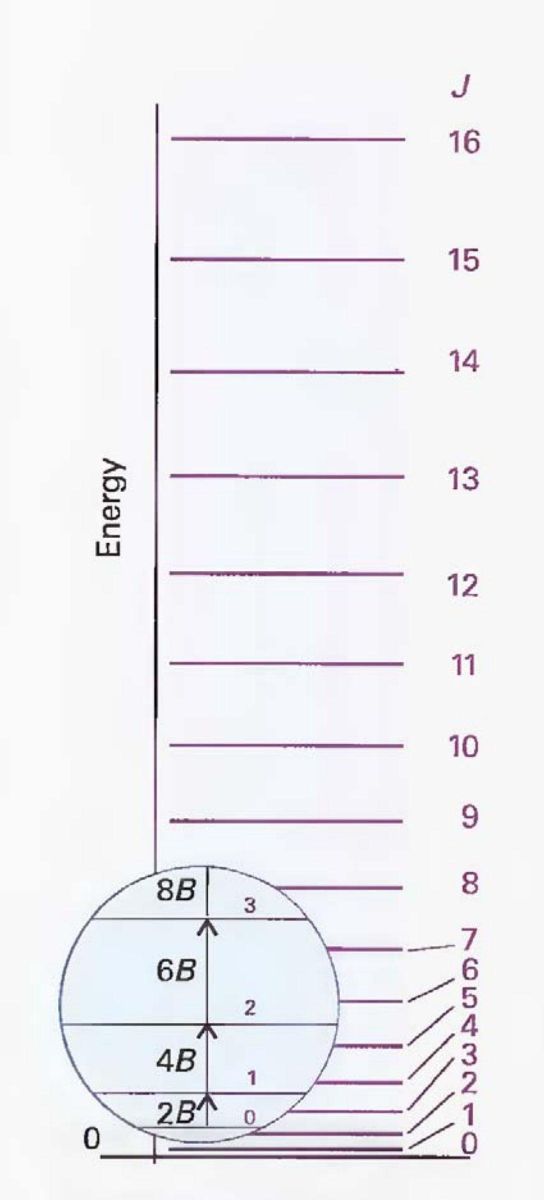


$$E_r = \frac{\hbar^2}{2I_b} J(J+1)$$

Rotacijski termovi

Linearne molekule

$$E_{\mathrm{r}} = \frac{\hbar^2}{2I_b} J(J+1)$$



Term *T*

$$T = \frac{E}{h} \qquad \tilde{T} = \frac{E}{hc}$$

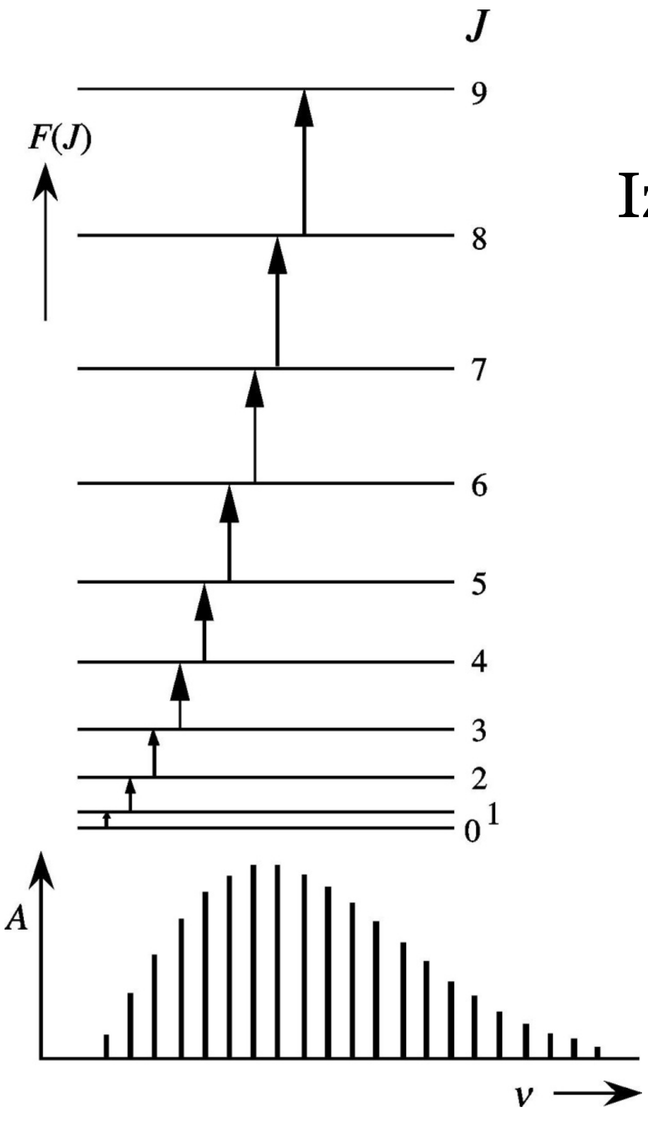
Rotacijski term *F*

$$F = \frac{E_{\mathrm{r}}}{h} \qquad \tilde{F} = \frac{E_{\mathrm{r}}}{hc}$$

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

$$F(J) = BJ(J+1) \qquad \tilde{F}(J) = \tilde{B}J(J+1)$$

Rotacijski spektri



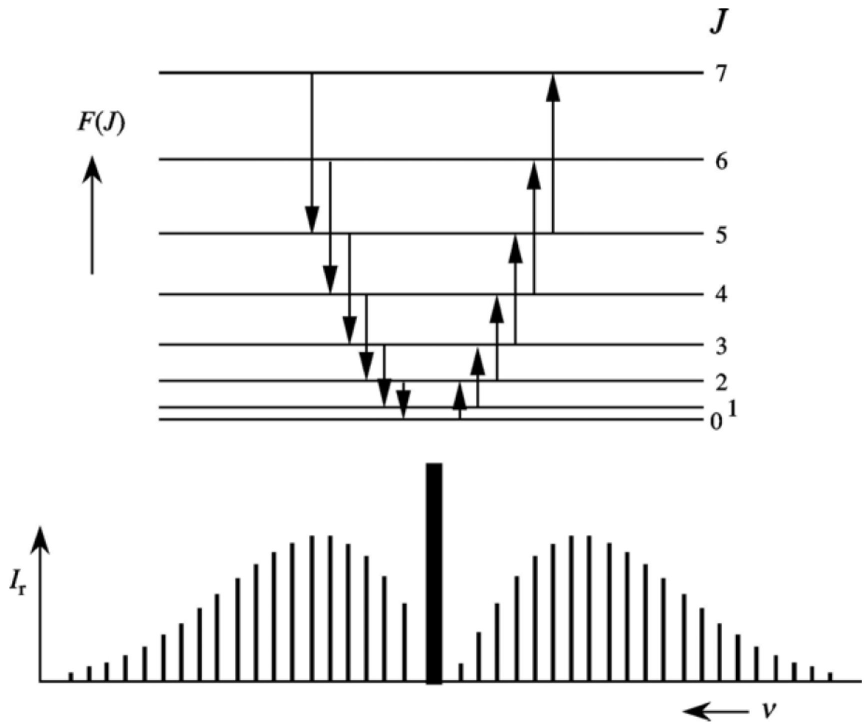
Izborno pravilo: $\Delta J = +1$

$$\nu = \Delta F \qquad \tilde{\upsilon} = \Delta \tilde{F}$$

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

Rotacijski Ramanovi spektri

Linearne molekule



$$\Delta J = +2$$

$$\tilde{\nu} = \tilde{\nu}_{\mathrm{exc}} - [F(J+2) - F(J)] = \tilde{\nu}_{\mathrm{exc}} - 4B(J + \tfrac{3}{2})$$

$$\tilde{\nu} = \tilde{\nu}_{\mathrm{exc}} + 4B(J + \tfrac{3}{2})$$

Intenziteti linija

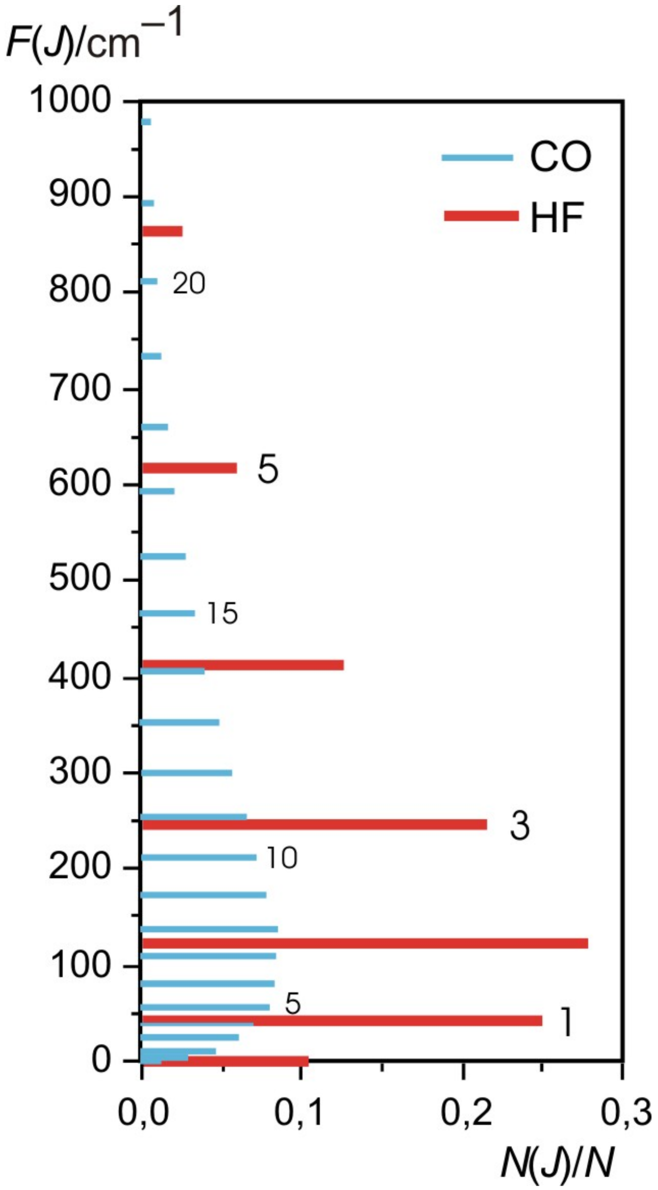
- ovisi o dipolnom momentu molekule
- ovisi o napučenosti energetskih nivoa

$$N_i \propto g_i \exp\left[-\frac{E_i}{kT}\right]$$

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

$$J_{\max} = \left(\frac{kT}{2hB}\right)^{1/2} - \frac{1}{2}$$

NAPUČENOST (ROTACIJE)



$$\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{-\Delta\varepsilon / kT}$$

$$\frac{N_i}{N_0} = (2J+1) e^{-\varepsilon_J / kT}$$

Degeneracija!

OVISNOST ROTACIJSKE KONSTANTE O VIBRACIJSKOM STANJU

$$B_v = B_e - \alpha_e^B (v + \tfrac{1}{2}) + \ldots$$

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$$F(J) = B_v\, J(J+1) - D_v\, J^2(J+1)^2$$

$$\tilde{\nu} = 2\, B_v\, (J+1) - 4\, D_v\, (J+1)^3$$

$$D_v = D_e + \beta_e\, (v + 1/2) + \ldots$$

Informacije koje se mogu dobiti iz rotacijskih spektara:

- geometrija molekule

- Izotopni efekt $\Delta\tilde{\upsilon} = \tilde{\upsilon}_1 - \tilde{\upsilon}_2$

$$\frac{\tilde{\upsilon}_1}{\tilde{\upsilon}_2} = \frac{\mu_2}{\mu_1}$$

Npr. pomak linija $^{1}H^{35}Cl$ u odnosu na $^{2}H^{35}Cl$.

Pitanja za ponavljanje

1. Što je moment tromosti?
2. Koji su uvjeti da bi došlo da apsorpcije u mikrovalnom području?
3. Kako se dijele molekule prema momentu tromosti?
4. Čemu su jednaki rotacijski termovi dvoatomnih molekula?
5. Koja su izborna pravila za apsorpciju i emisiju u mikrovalnom području?
6. Kako shematski izgleda apsorpcijski spektar linearne molekule?
7. O čemu ovisi intenzitet linija u rotacijskom spektru?
8. Čemu je jednak razmak linija u rotacijskom spektru linearne molekule?
9. Izvedite izraz za moment tromosti dvoatomne molekule.
10. Što je reducirana masa?
11. Pokažite da je: $m_1/2 \leq \mu \leq m_1$; ako je m_1 masa lakšeg atoma u molekuli.
12. Shematski prikažite rotacijske energetske nivoe dvoatomne molekule.