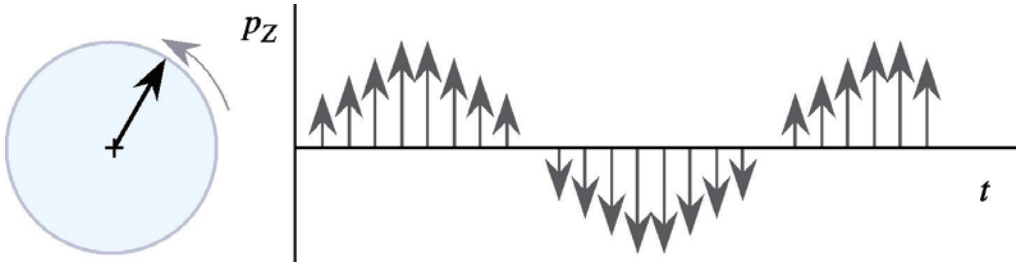
Molekulska spektroskopija
Rotacija molekula



- mikrovalno područje, daleki IR ($\lambda \approx 1$ mm – 100 μm)

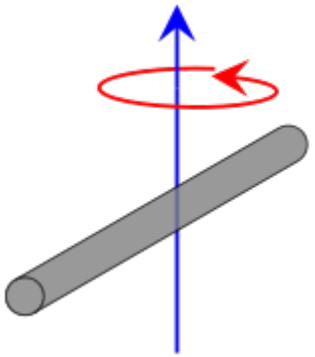
- plinoviti uzorci

- model krutog rotora

Kinetička energija –kruti rotor

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

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



$$E = E_x + E_y + E_z$$

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

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

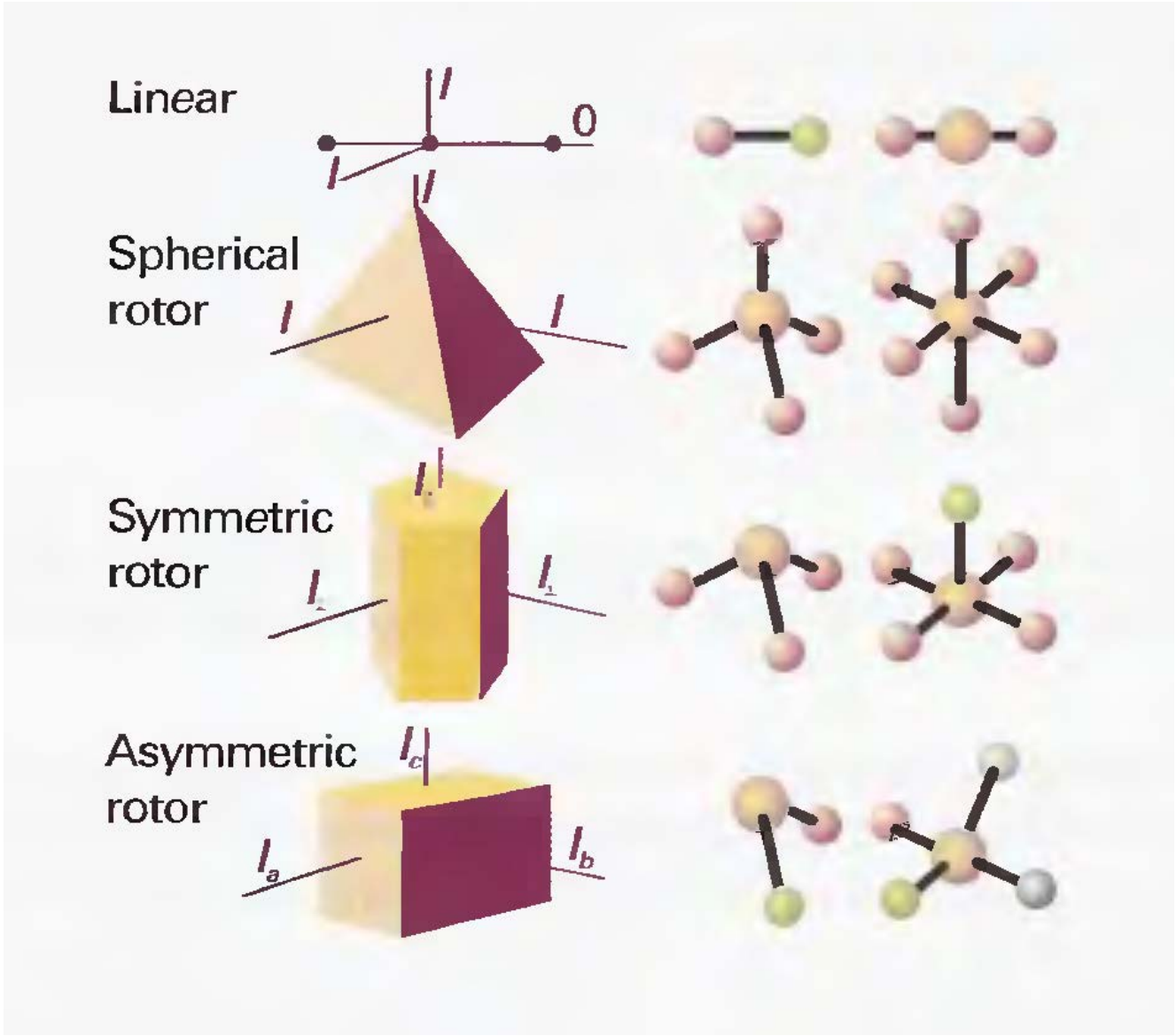
$$= \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2$$

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

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

$$P_x = I_x \omega_x$$

Podjela molekula prema odnosima glavnih momenta tromosti



$I_b = I_c; \quad I_a = 0$

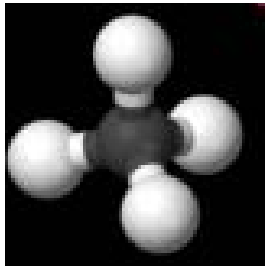
$I_a = I_b = I_c$

$I_a = I_b < I_c$

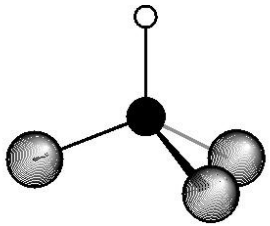
$I_a < I_b = I_c$

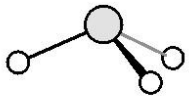
$I_a < I_b < I_c$

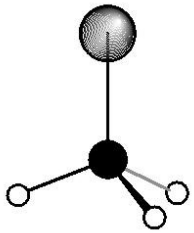
Sferni rotori

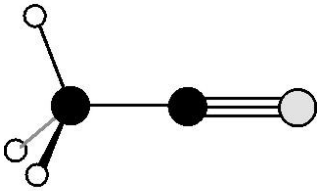


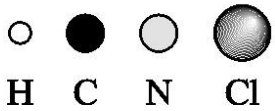
Simerični rotori



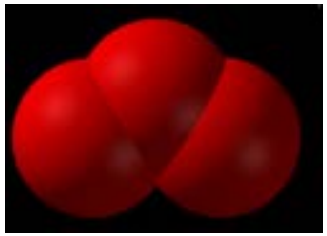


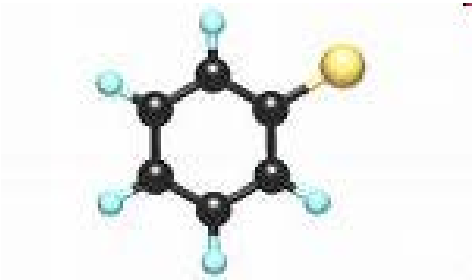




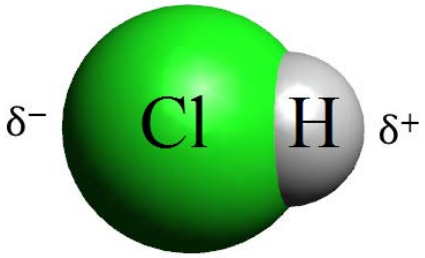


Asimerični rotori





Linearne molekule



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

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

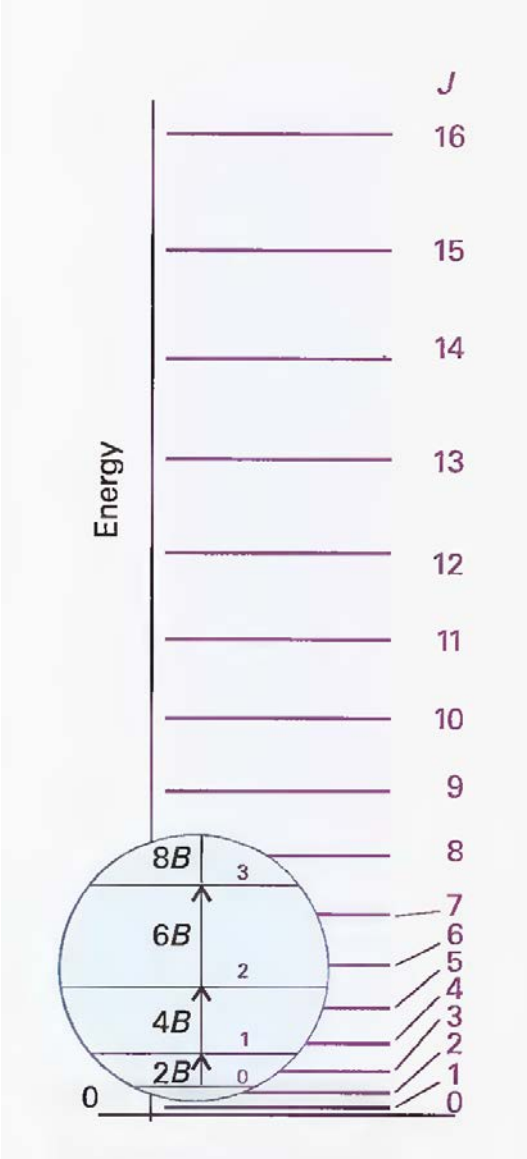
(linearne molekule, dvoatomne molekule)

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

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

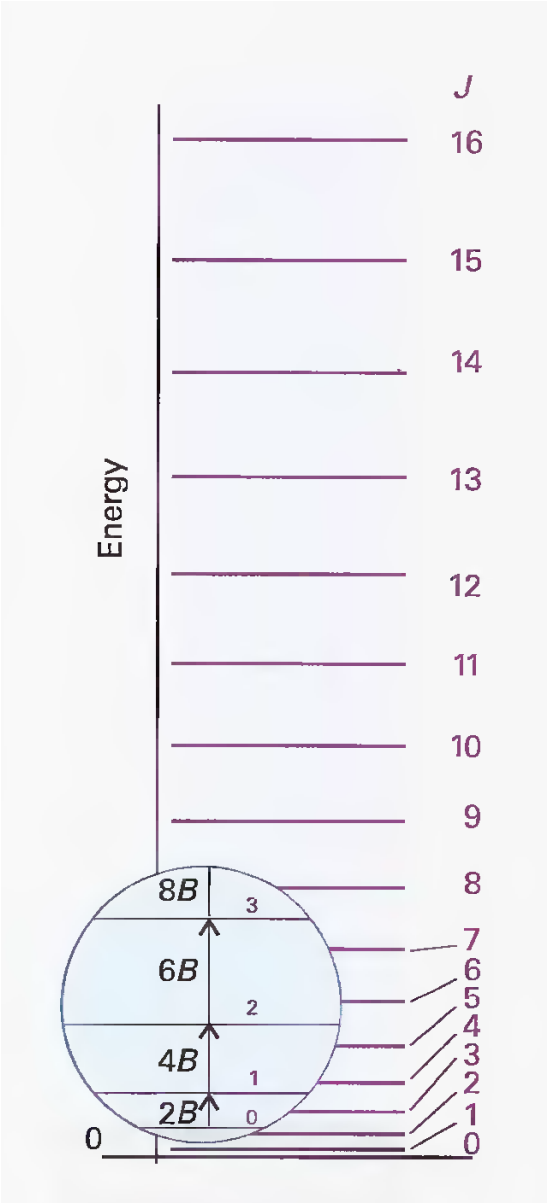
IV. Rješenje $$\frac{\hbar^2 J(J+1)}{2I}\Psi_r = E_r\Psi_r \quad J=0,1,2,3$$

Rotacijske energije



$$E_r = \frac{\hbar^2}{2I} J(J+1) = \frac{h^2}{8\pi^2 I} J(J+1)$$

Rotacijski termovi



Term *T*

$$T = \frac{E}{hc}$$

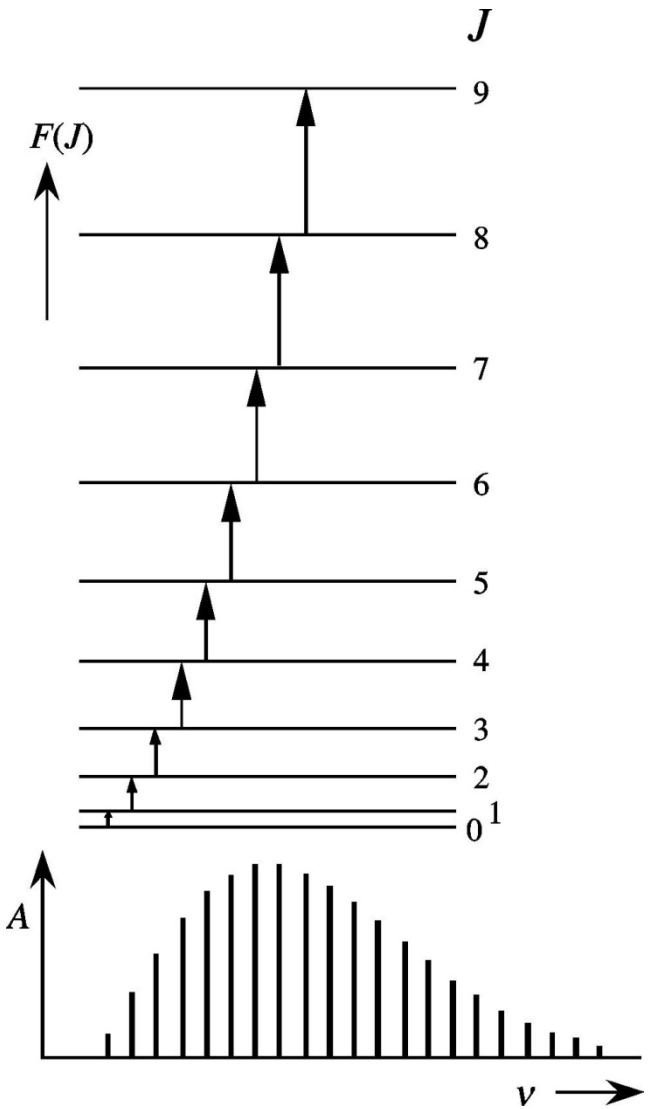
Rotacijski term *F*

$$\frac{E_r}{hc} = F = \frac{h^2}{8\pi^2 I\, hc} J(J+1)$$

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

$$F(J) = BJ(J+1)$$

Rotacijski spektri



Izborno pravilo:
(dopušteni prjelazi)

$$\Delta J = +1$$

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

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

$$= B(J+1)(J+1+1) - BJ(J+1)$$

$$= B(J^2 + 2J + J + 2) - BJ(J+1)$$

$$= 2B(J+1)$$

$$\tilde{\upsilon}(0 \leftarrow 1) = 2B(0+1) = 2B$$

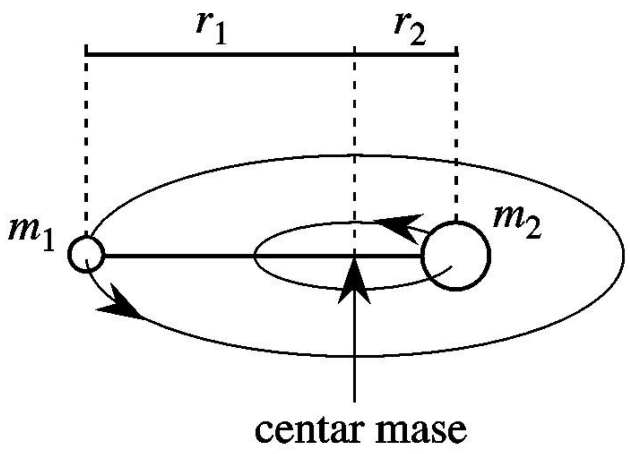
$$\tilde{\upsilon}(1 \leftarrow 2) = 2B(1+1) = 4B$$

$$\tilde{\upsilon}(2 \leftarrow 3) = 2B(2+1) = 6B$$

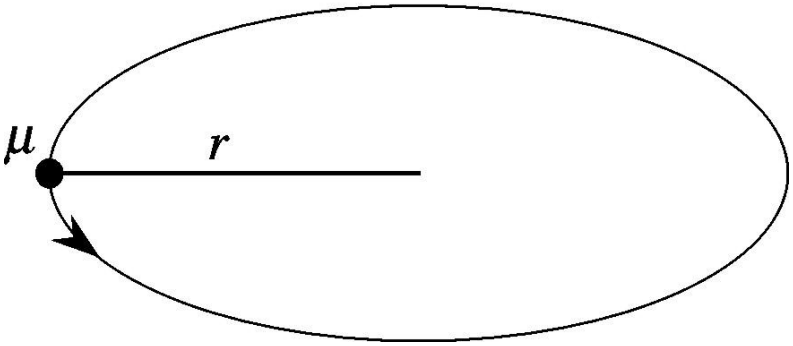
$$\tilde{\upsilon}(3 \leftarrow 4) = 2B(3+1) = 8B$$

Razmak između linija:
$2B$

Linearne molekule (dvoatomne)



Stvarna vrtnja
oko centra mase



Ekvivalentna vrtnja

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

(izvod -pogledati Bohrov model atoma)

Intenziteti linija

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

$$\frac{N_i}{N_0} = \frac{g_J}{g_0} \; e^{-(\varepsilon_J - \varepsilon_0)/kT}$$

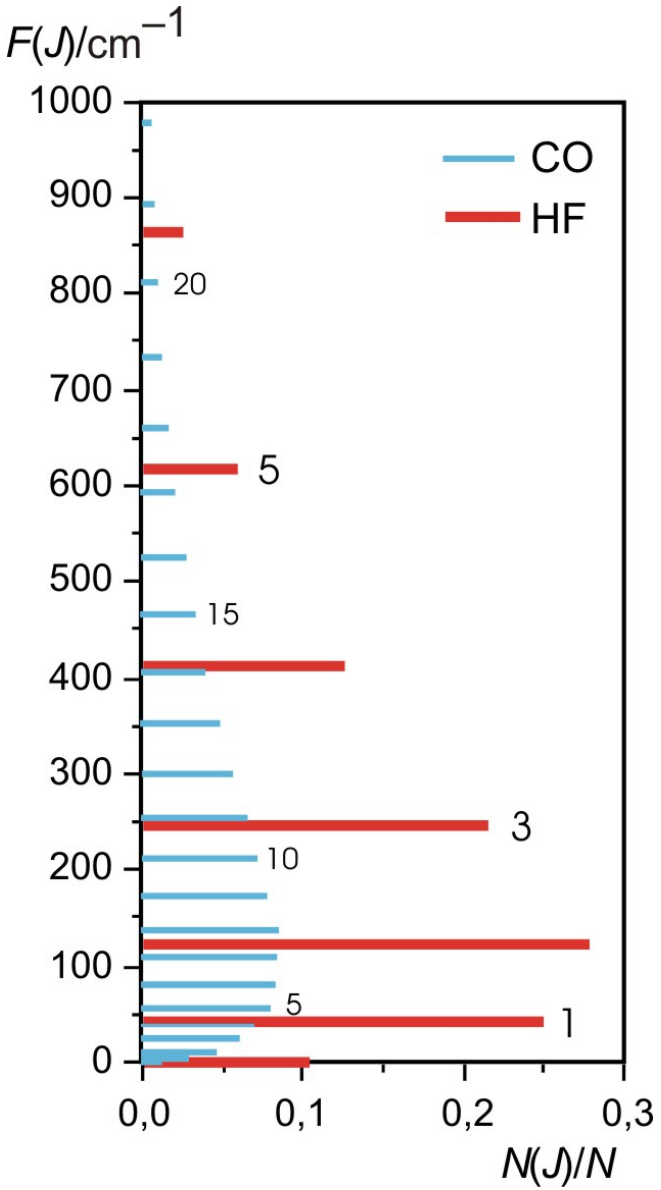
$$m_J = -J, ..0, ... + J$$

$$g_J = 2J + 1$$

$$\frac{N_i}{N_0} = (2J+1)\exp\left[\frac{-hc}{kT} BJ(J+1)\right]$$

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

NAPUČENOST (ROTACIJE)

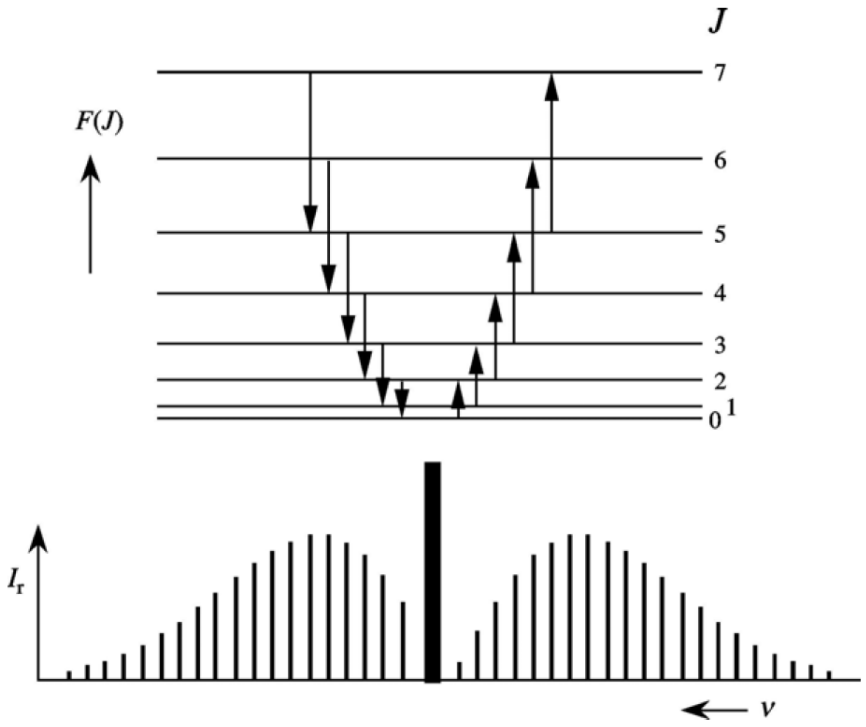


$$\frac{N_i}{N_j} = \frac{g_i}{g_j} \mathrm{e}^{-\Delta\varepsilon / kT}$$

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

Rotacijski Ramanovi spektri

Linearne molekule



$$\Delta J = +2$$

$$\tilde{\nu} = \tilde{\nu}_{\text{exc}} - [F(J+2) - F(J)] = \tilde{\nu}_{\text{exc}} - 4B(J+\tfrac{3}{2}) \qquad J = 0,1,2$$

$$\tilde{\nu} = \tilde{\nu}_{\text{exc}} + 4B(J+\tfrac{3}{2}) \qquad J = 0,1,2$$

(J – kvantni broj nižeg stanja)

Informacije koje se mogu dobiti iz rotacijskih spektara:

- geometrija molekule (duljina veze)

- 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.