Rotationspektrometri

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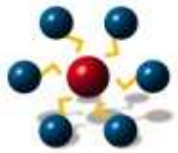


Tröghetsmoment

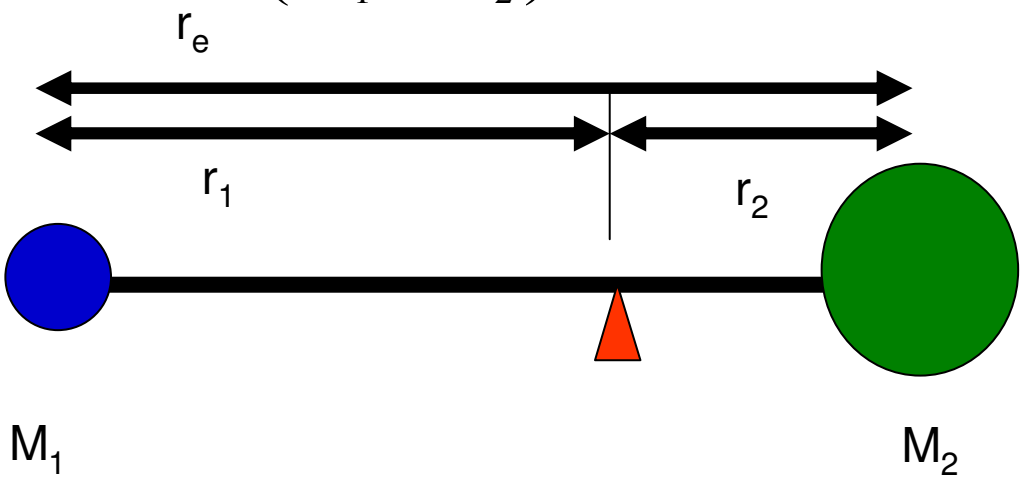
Tröghetsmoment I

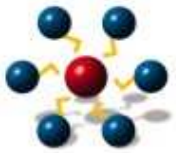
$$I = \sum_k M_k r_k^2$$

För en tvåatomig molekyl

$$I = \left(\frac{M_1 M_2}{M_1 + M_2} \right) r_e^2 = \mu r_e^2$$

μ=reducerad massa





Rotationsrörelse

Impulsmoment (för roterande molekyl)

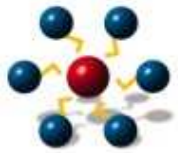
$$J = I\omega$$ Jfr. p = mv

Kinetisk energi

$$T = \frac{1}{2} I\omega^2 = \frac{1}{2I} J^2$$ Jfr. $T=p^2/2m$

I sfäriska koordinater och enligt kvantmekaniken

$$\hat{T} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\right)\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin\phi}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]$$



Rotationsrörelse

Schrödingers ekvation

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\right)\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin\phi}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]Y_J^m(\theta,\phi)=E_J Y_J^m(\theta,\phi)$$

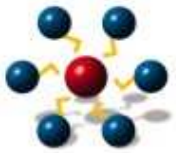
(Tryckfel i kompendiet)

Lösningarna

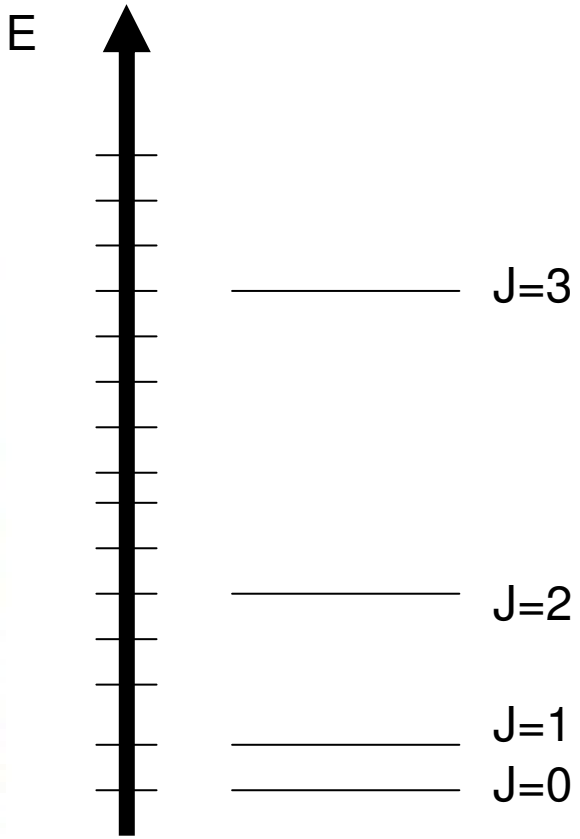
$Y_J^m(\theta,\phi)$ Vågfunktion = ytklotfunktion

$$E_J = BJ(J+1) \quad B=\frac{\hbar^2}{2I}=\frac{\hbar^2}{2\mu r_e^2}$$

B = Rotationskonstant

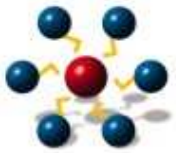


Energinivåerna



CO: B = 1.93 cm^{-1}

E_0 = 0 cm^{-1}
E_1 = 3.86 cm^{-1}
E_2 = 11.58 cm^{-1}
E_3 = 23.16 cm^{-1}
E_4 = 38.60 cm^{-1}



Övergångsenergier

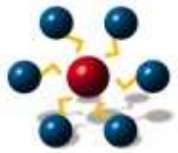
Energinivåerna

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

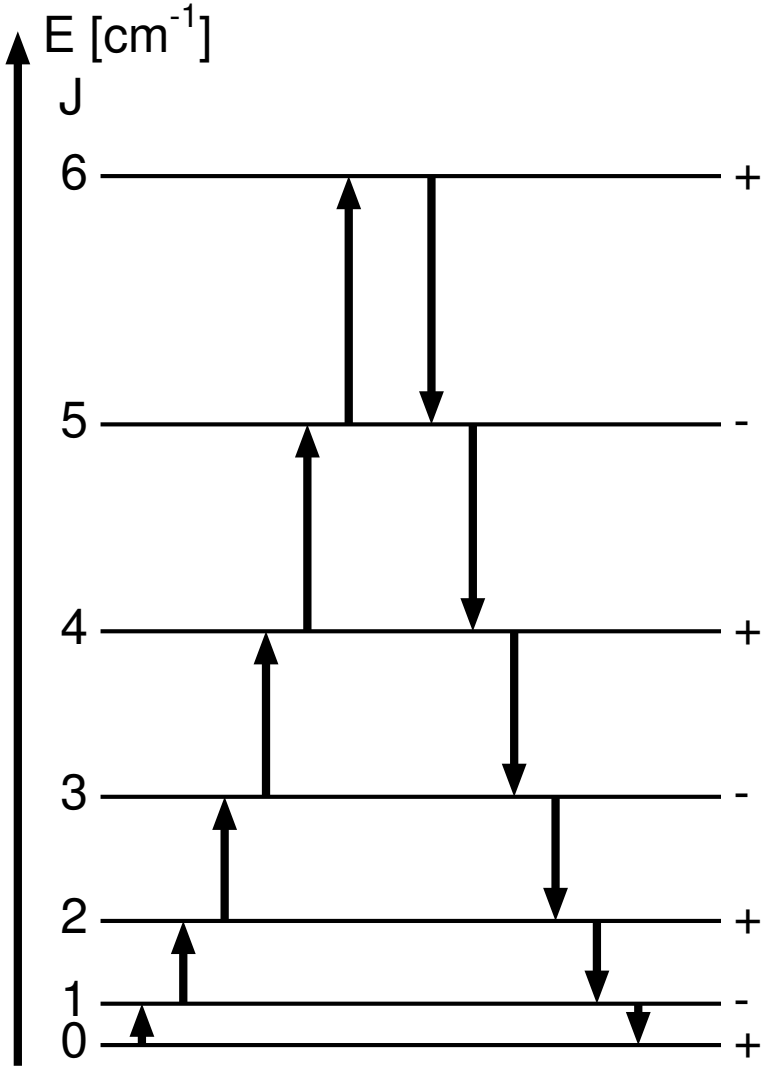
Urvalsregel: $\Delta J = \pm 1$ (för tvåatomiga molekyler)

Övergångsenergi för övergången J+1←J

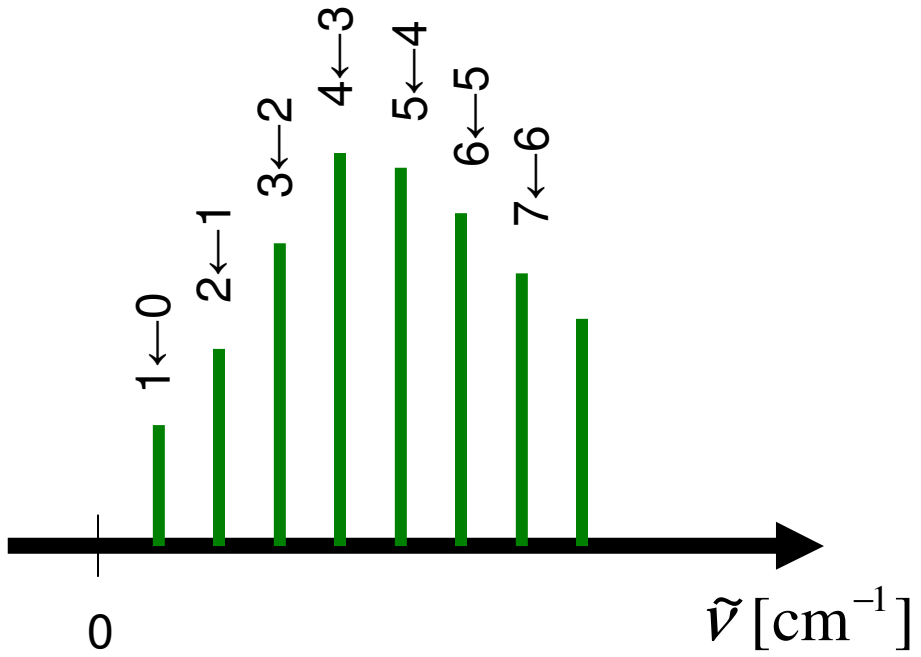
$$\Delta E(J+1 \leftarrow J) = E_{J+1} - E_J = 2B(J+1)$$



Övergångar

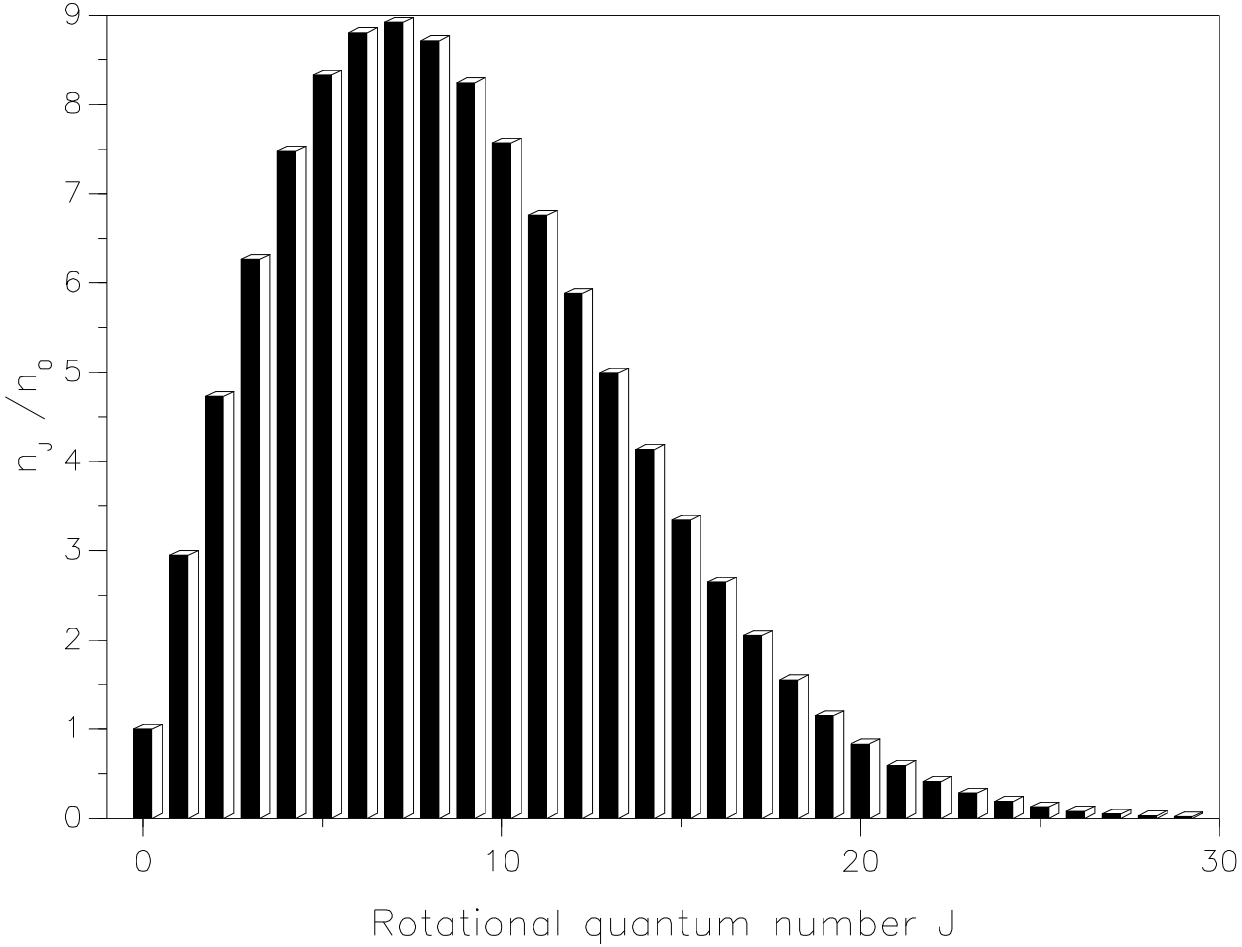


Rotationspektrum



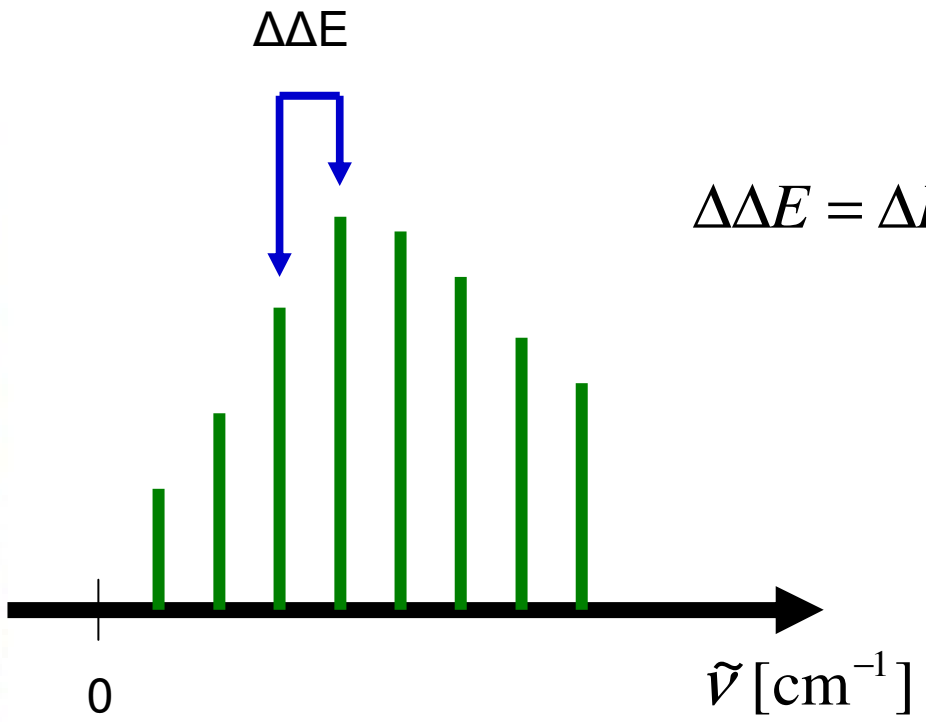
Populationer

- Boltzmannfördelning

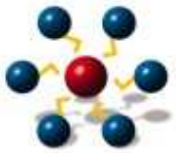


Avståndet mellan linjerna

Konstant avstånd mellan spektrallinjerna oberoende av J

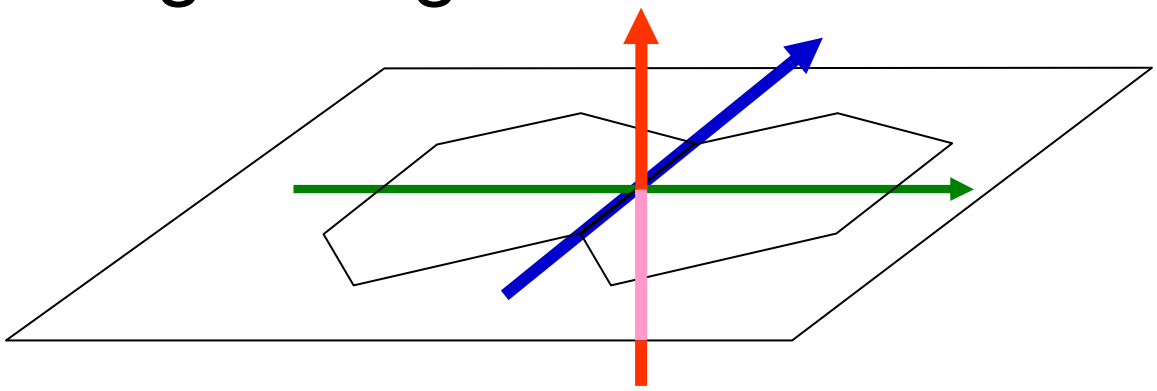


$$\Delta\Delta E = \Delta E_{J+2\leftarrow J+1} - \Delta E_{J+1\leftarrow J} = 2B$$

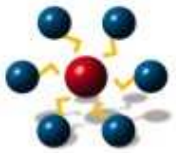


Fleratomiga molekyler

- Tre olika rotationsaxlar: A, B och C
- Rotationerna genom de tre axlarna är oberoende av varandra => Energibidragen är additiva



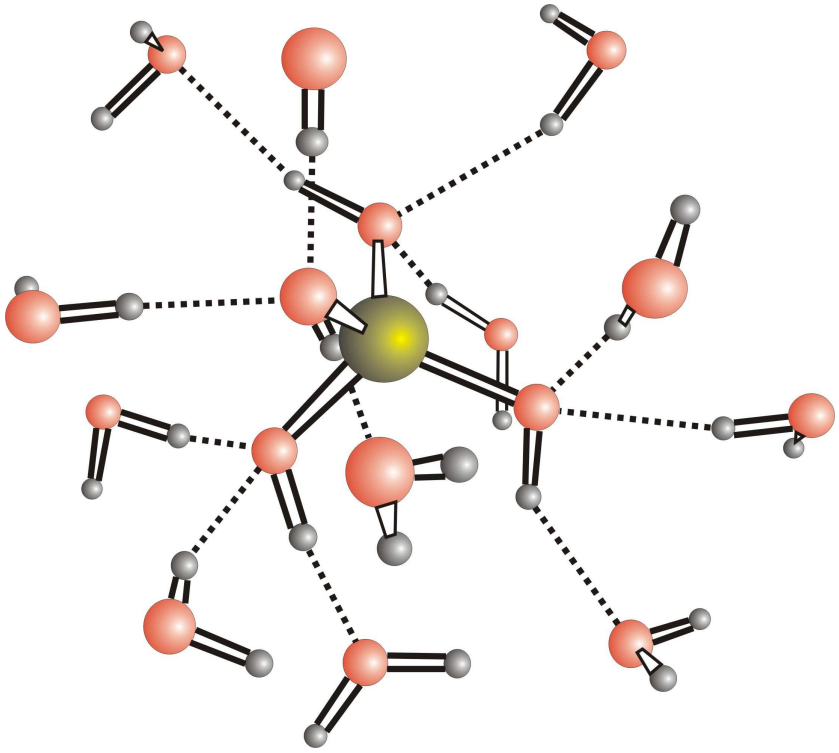
$\hat{H} = B\hat{J}^2$ Per rotationsaxel

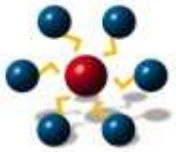


Fleratomiga molekyler

- Hamiltons operator i det allmänna fallet

$$\hat{H} = A\hat{J}_A^2 + B\hat{J}_B^2 + C\hat{J}_C^2$$

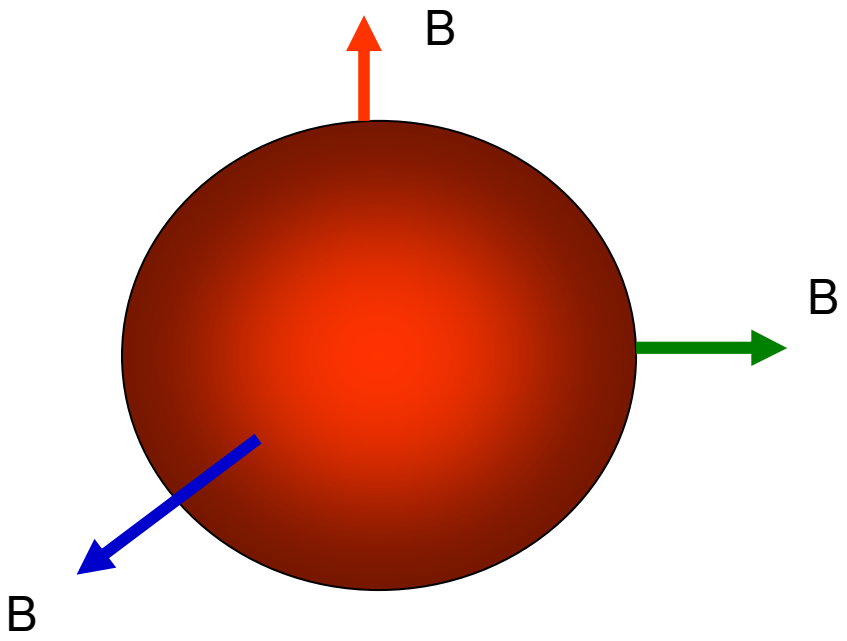


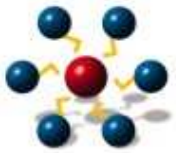


Sfärisk molekyl

Alla tre rotationsaxlar är likvärda

$$\hat{H} = B\hat{J}^2 \qquad E_J = BJ(J+1)$$

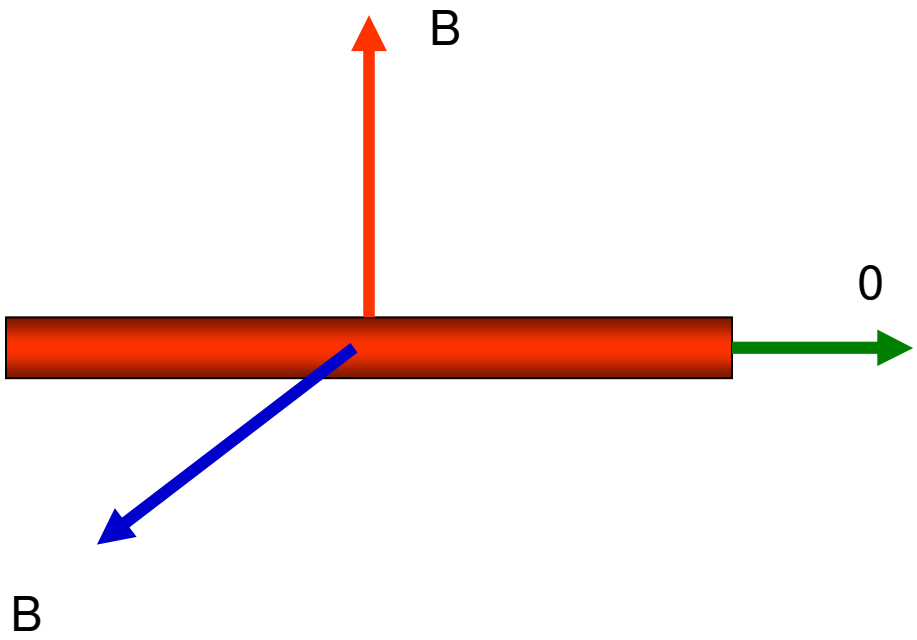


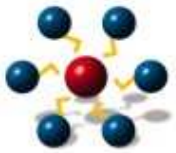


Lineär molekyl

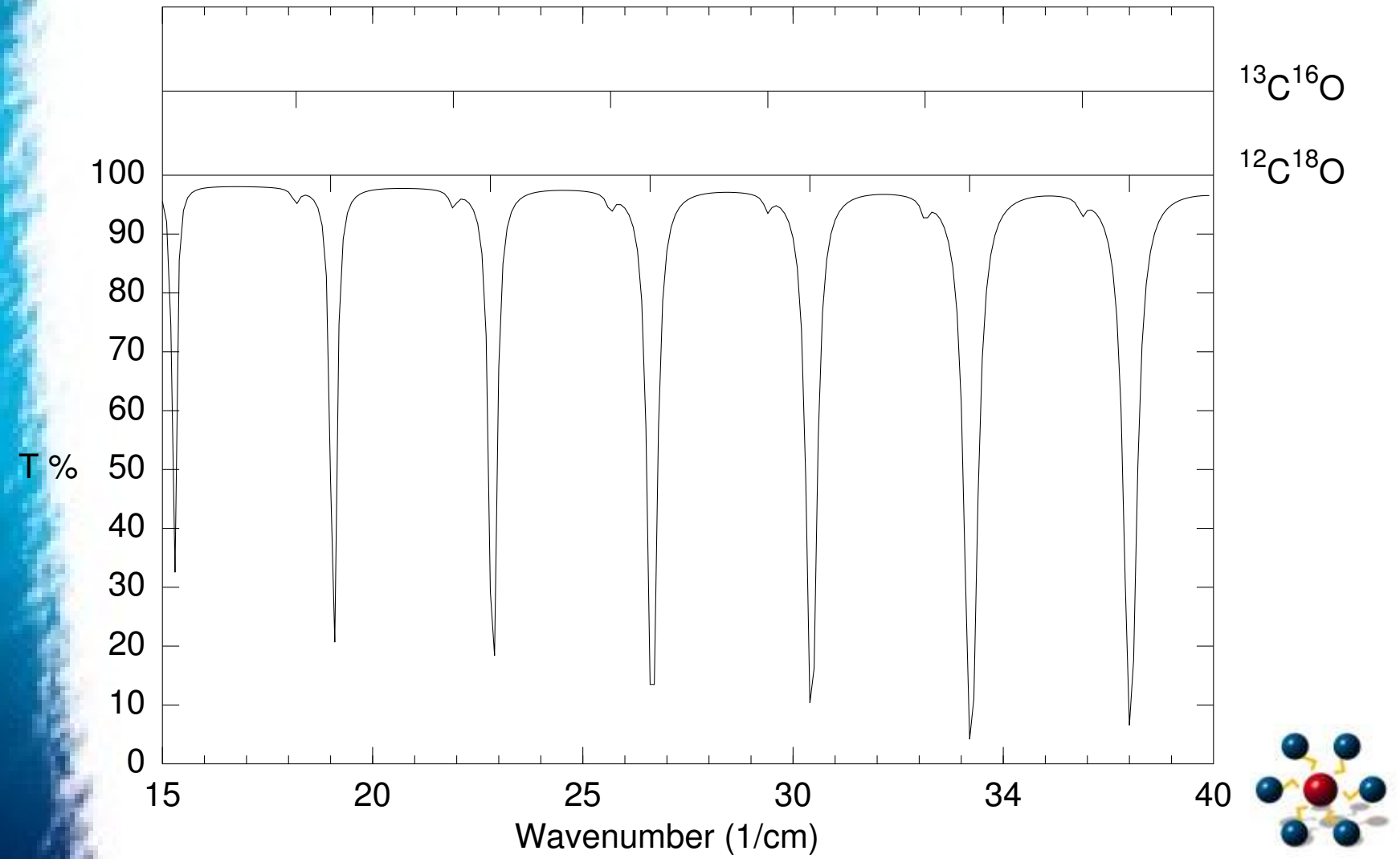
Två likvärda rotationsaxlar, en som är noll

$$\hat{H} = B\hat{J}^2 \qquad E_J = BJ(J+1)$$





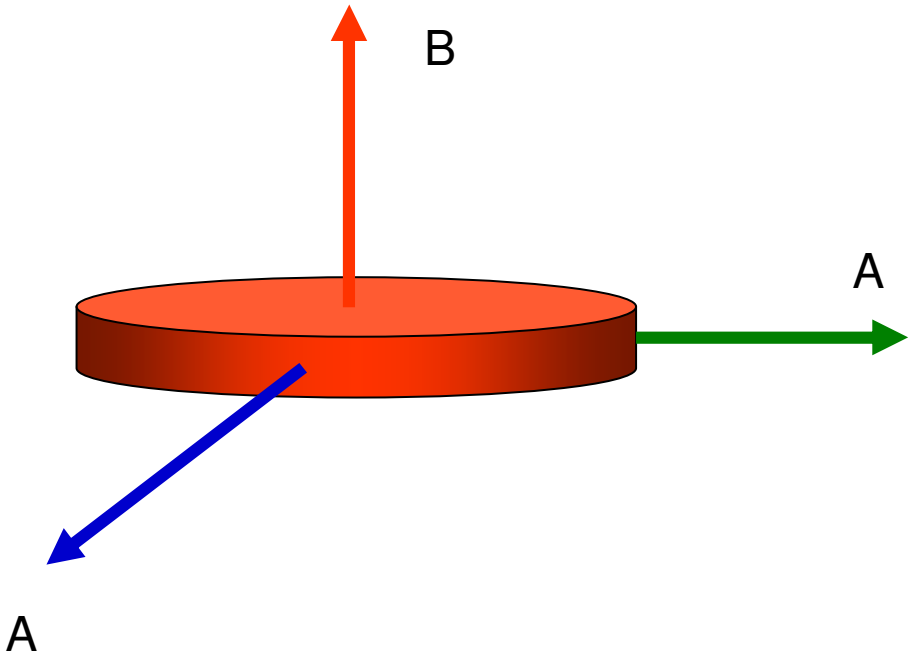
Koldioxids spektrum

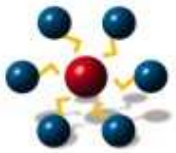


Symmetrisk molekyl

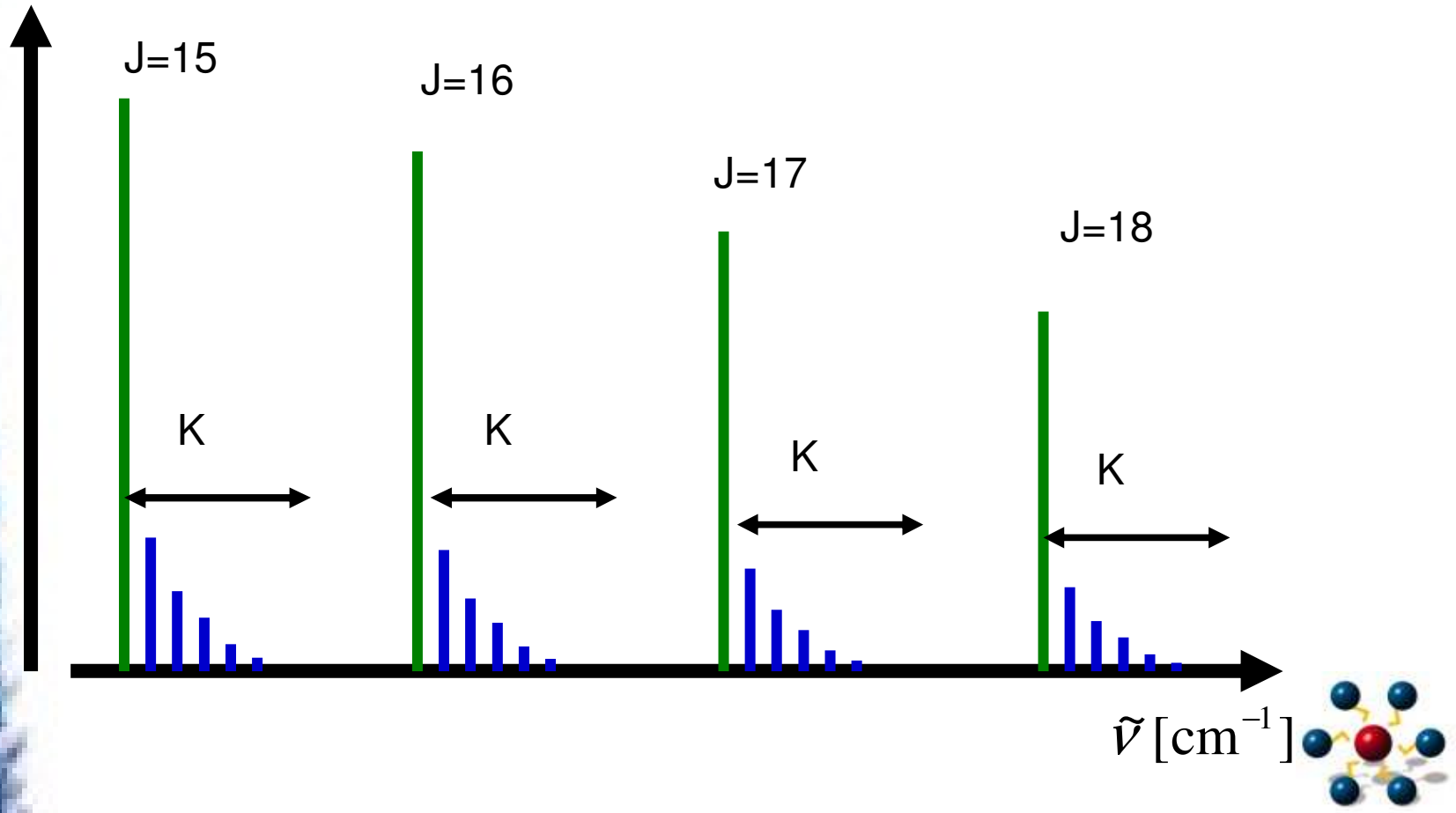
Två av tre rotationsaxlar är likvärda

$$\hat{H} = A\hat{J}_A^2 + B\hat{J}_B^2 \qquad E_{JK} = BJ(J+1) + (A-B)K^2$$





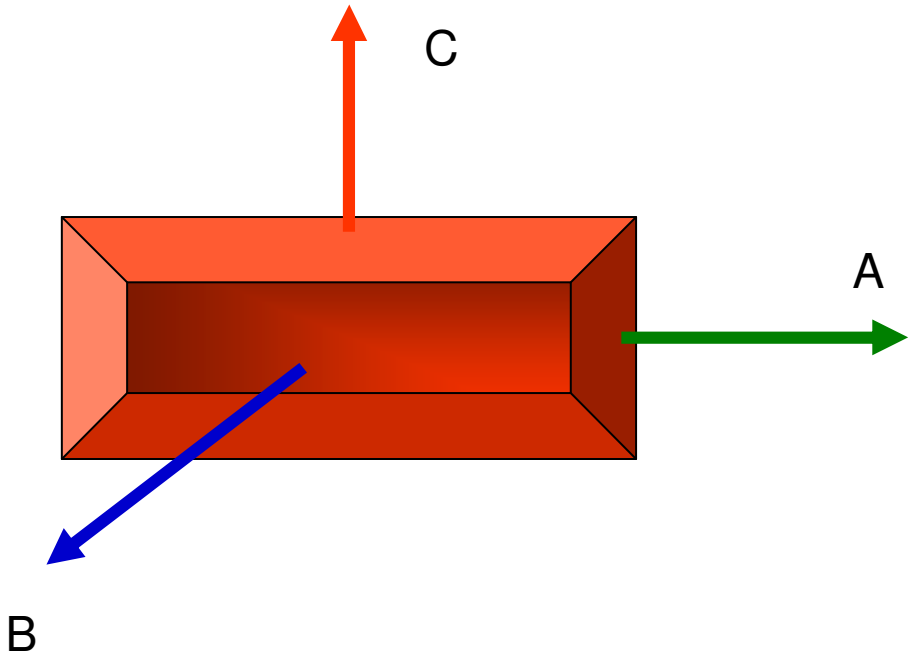
Symmetriska snurrans spektrum



Asymmetrisk molekyl

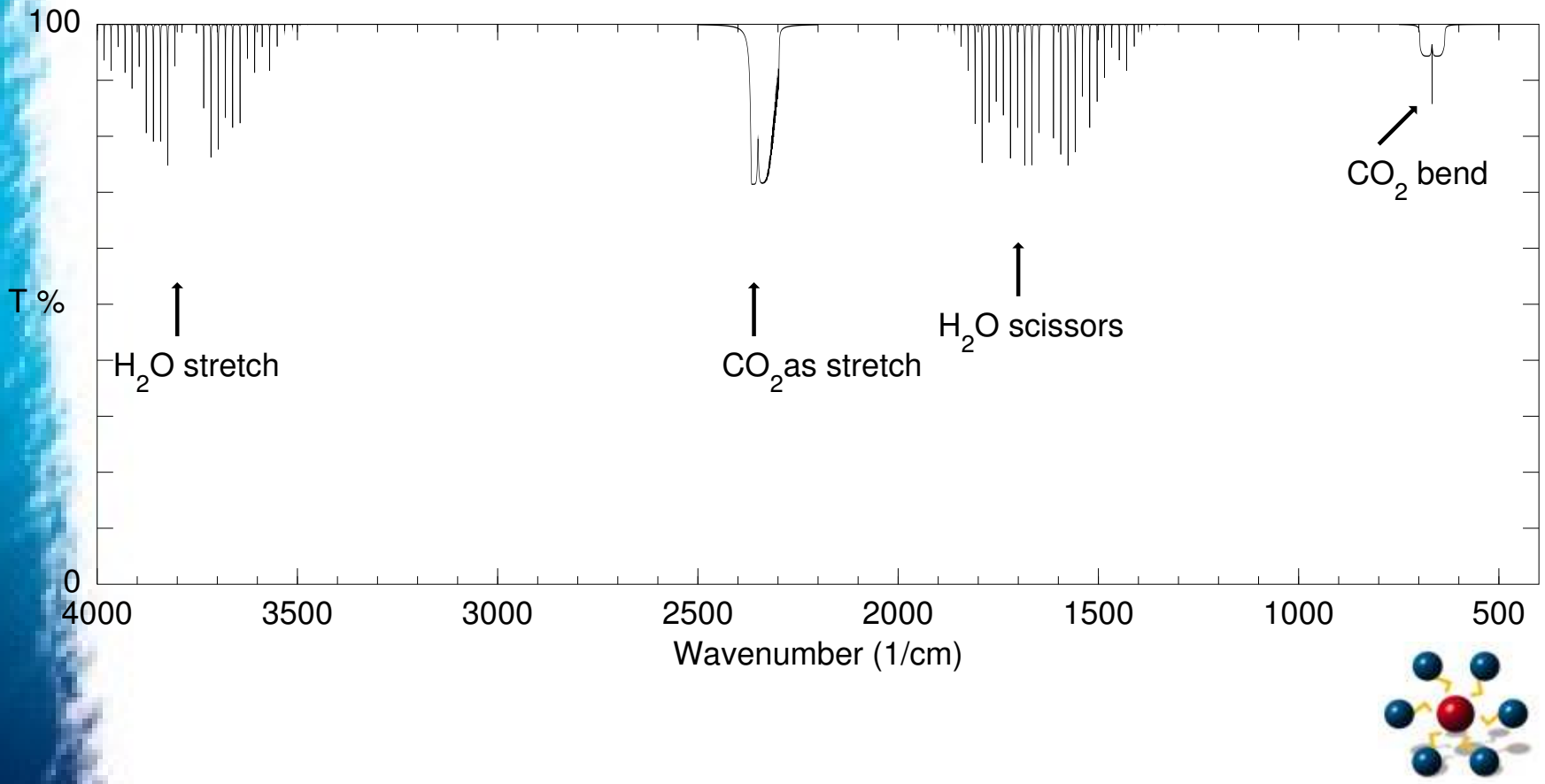
Alla tre rotationsaxlar är olika

$$\hat{H} = A\hat{J}_A^2 + B\hat{J}_B^2 + C\hat{J}_C^2$$

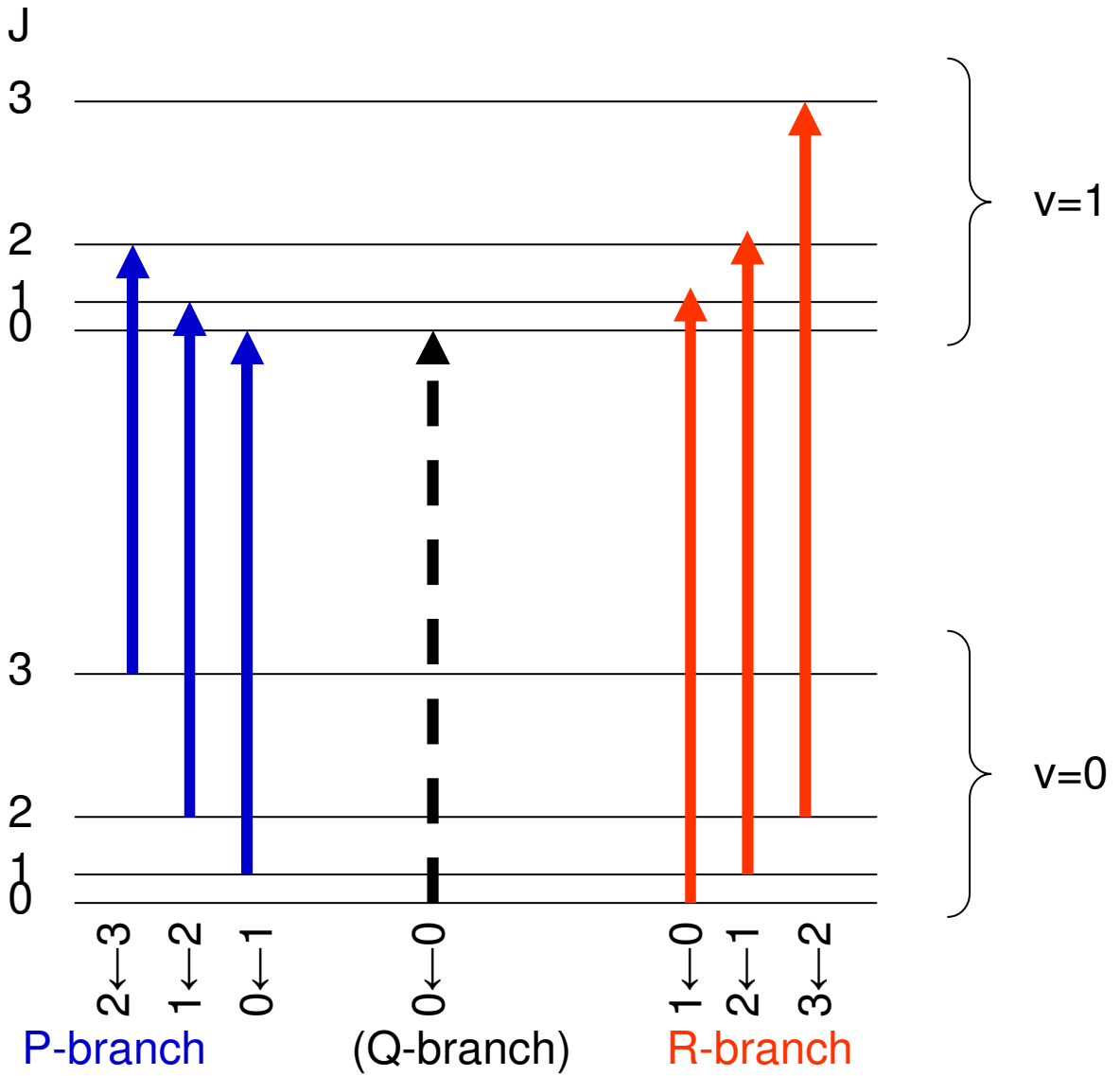


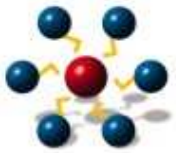
Spektrum

Vattens rotationspektrum

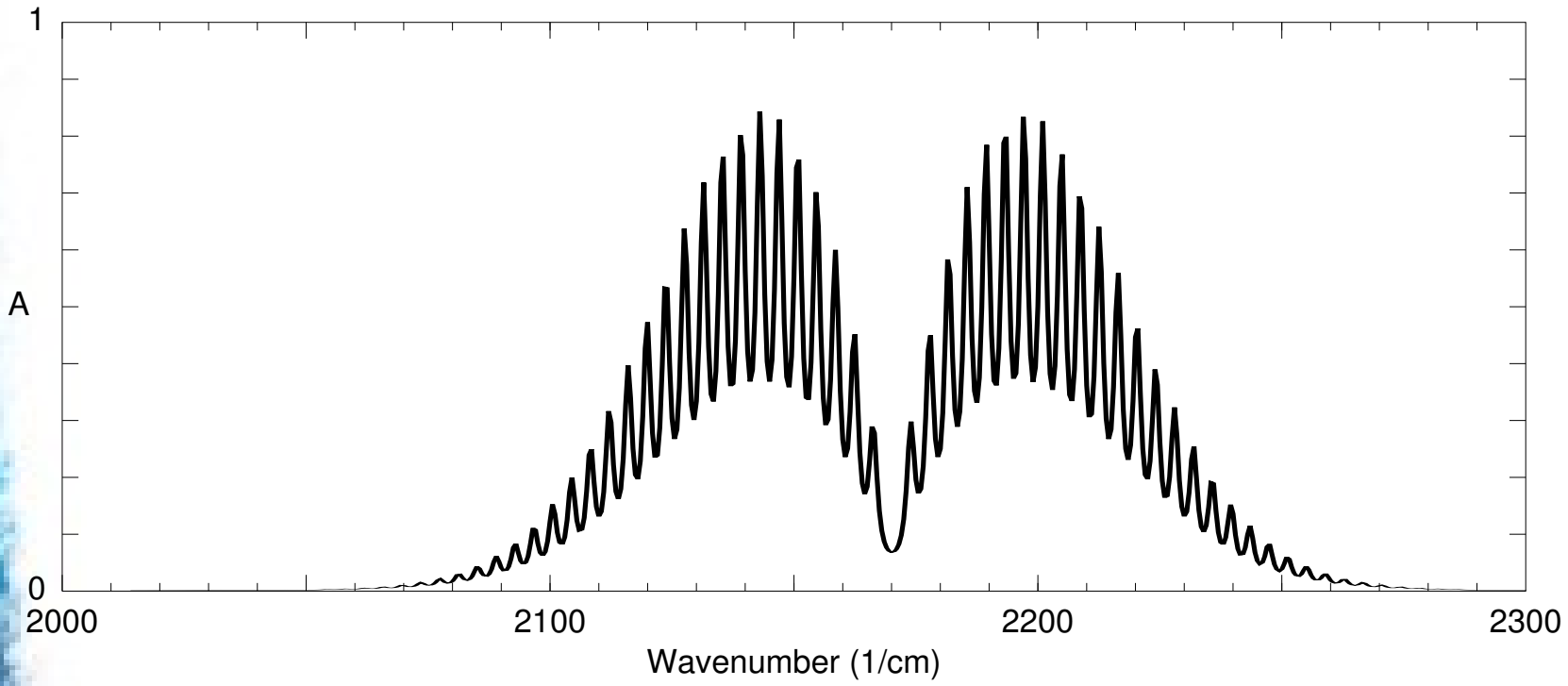


Rotationvibrationspektra

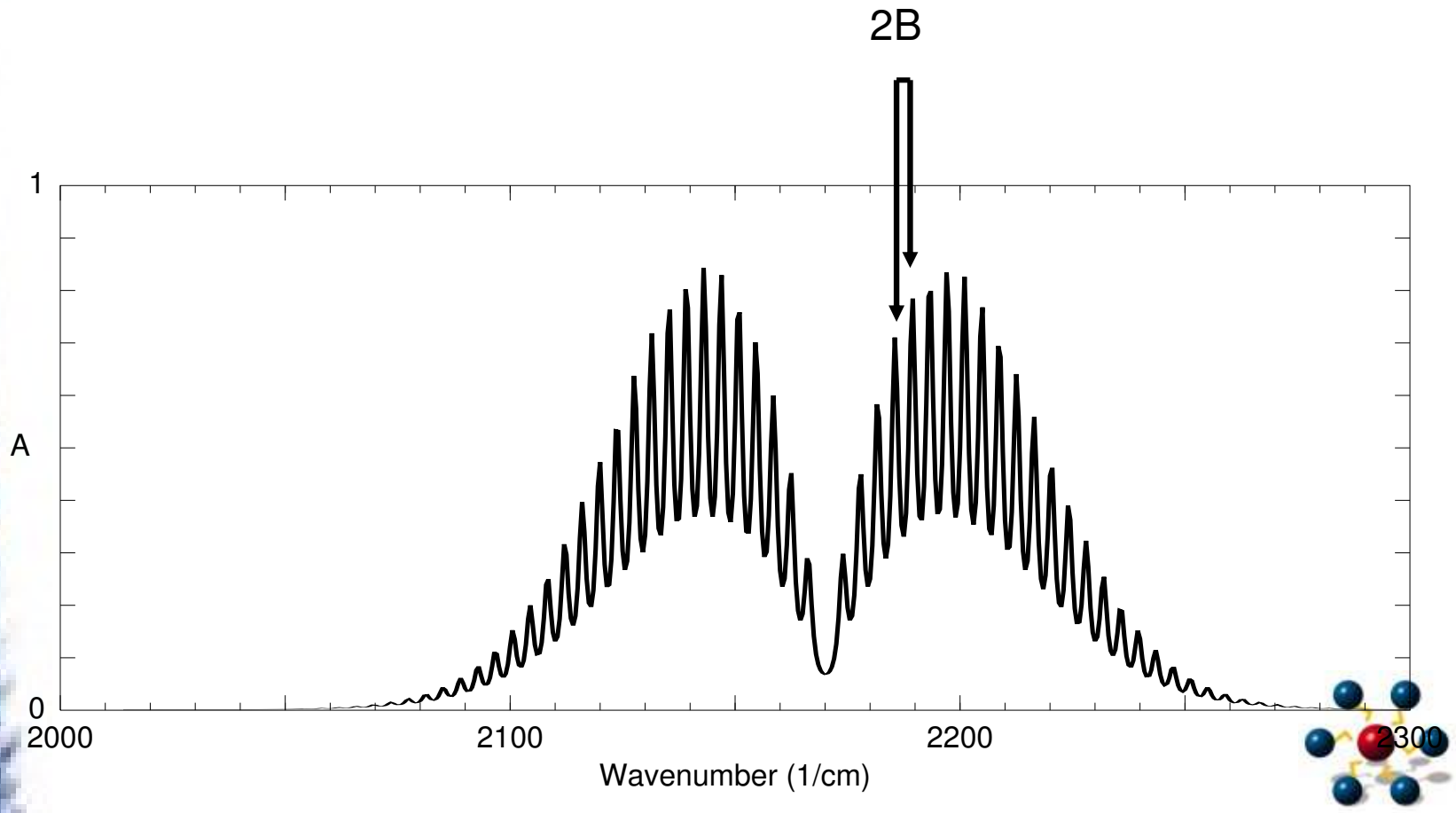




Spektrum: kolmonoxid



Bestäm rotationskonstanten



Bättre metod

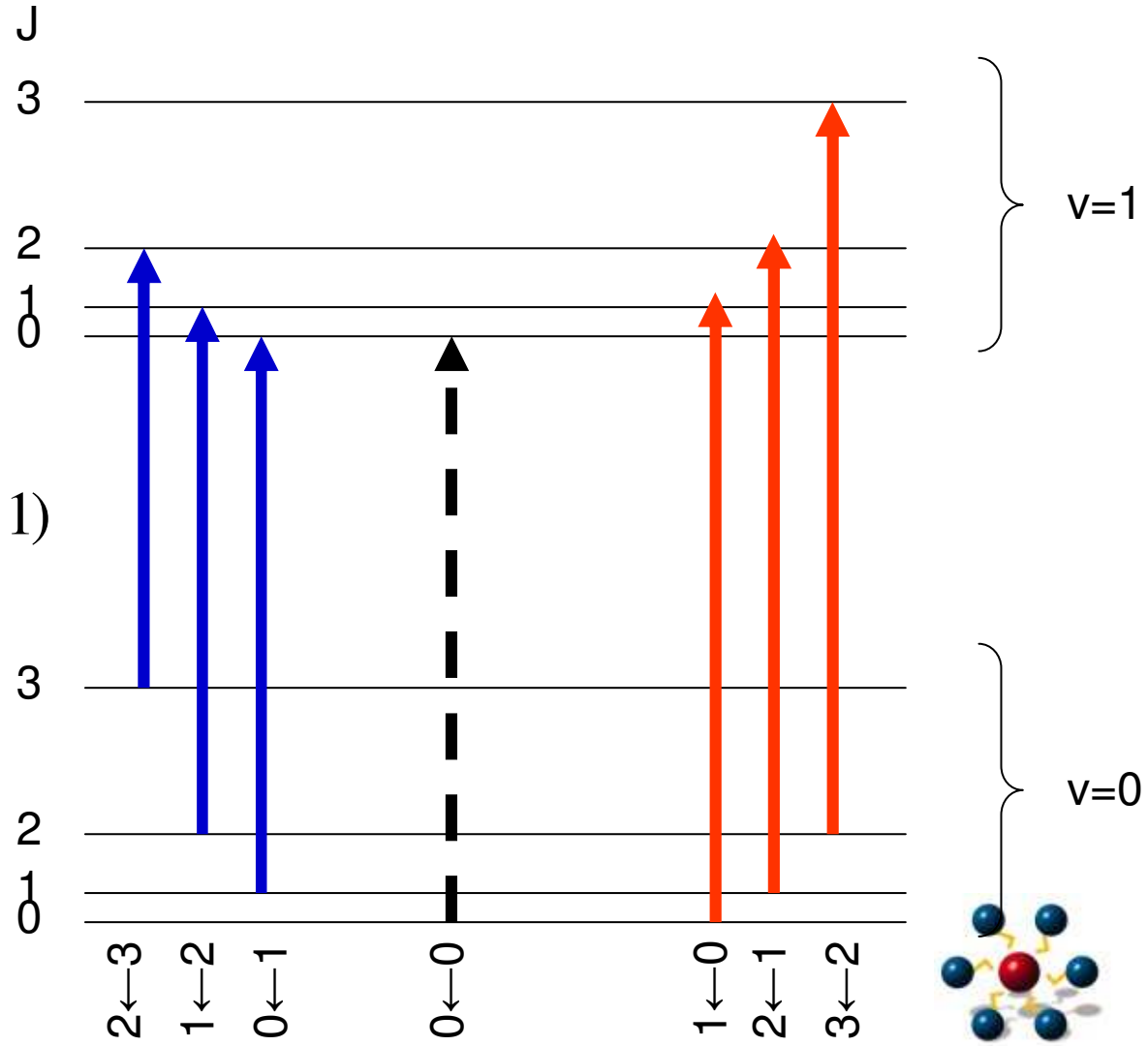
$$E_{J,v} = E_v + BJ(J+1)$$

$$\Delta E(P) = \Delta E_{vib,1\leftarrow 0} - 2BJ$$

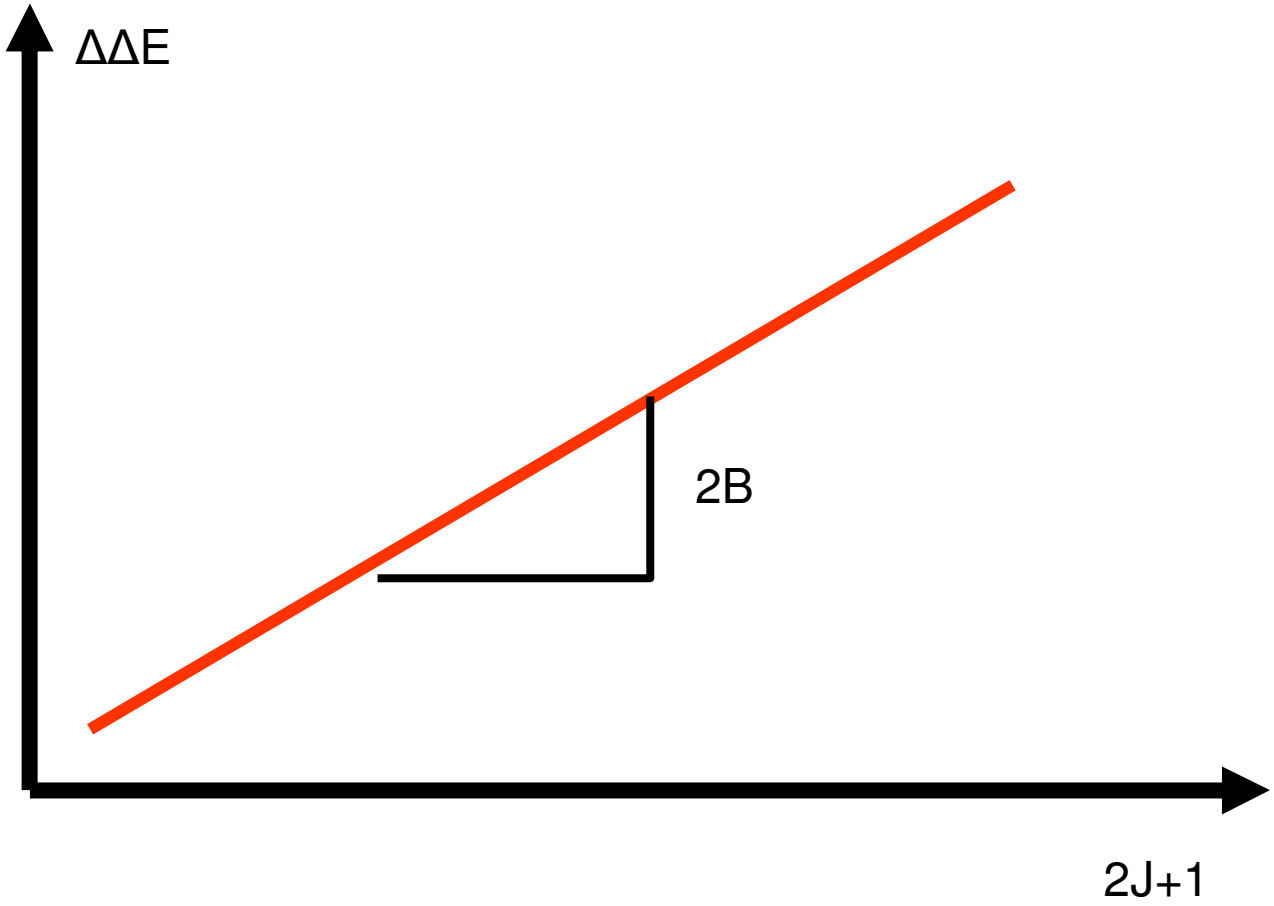
$$\Delta E(R) = \Delta E_{vib,1\leftarrow 0} + 2B(J+1)$$

$$\Delta\Delta E = \Delta E(R) - \Delta E(P)$$

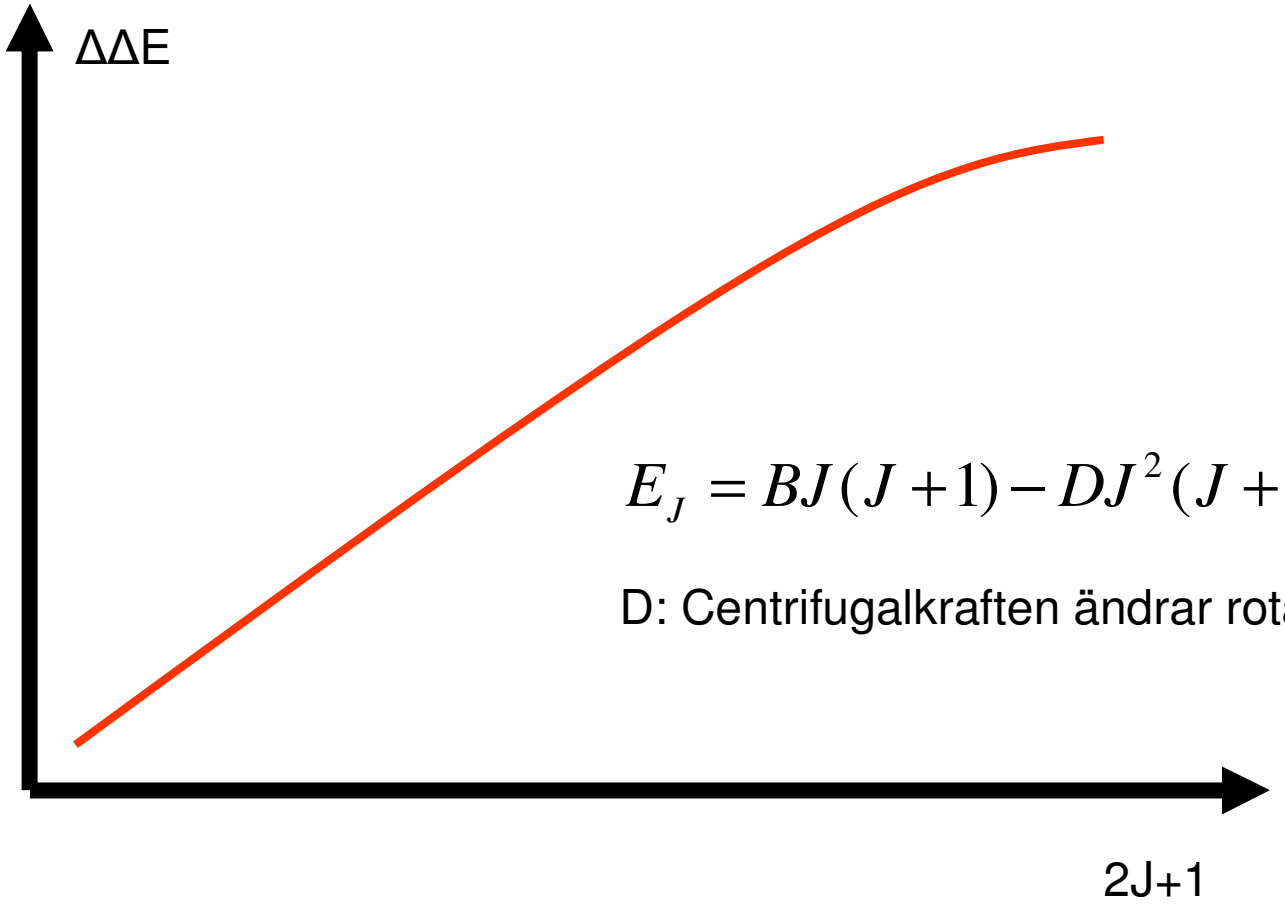
$$= 2B(2J+1)$$



Bättre metod



Varför bättre?

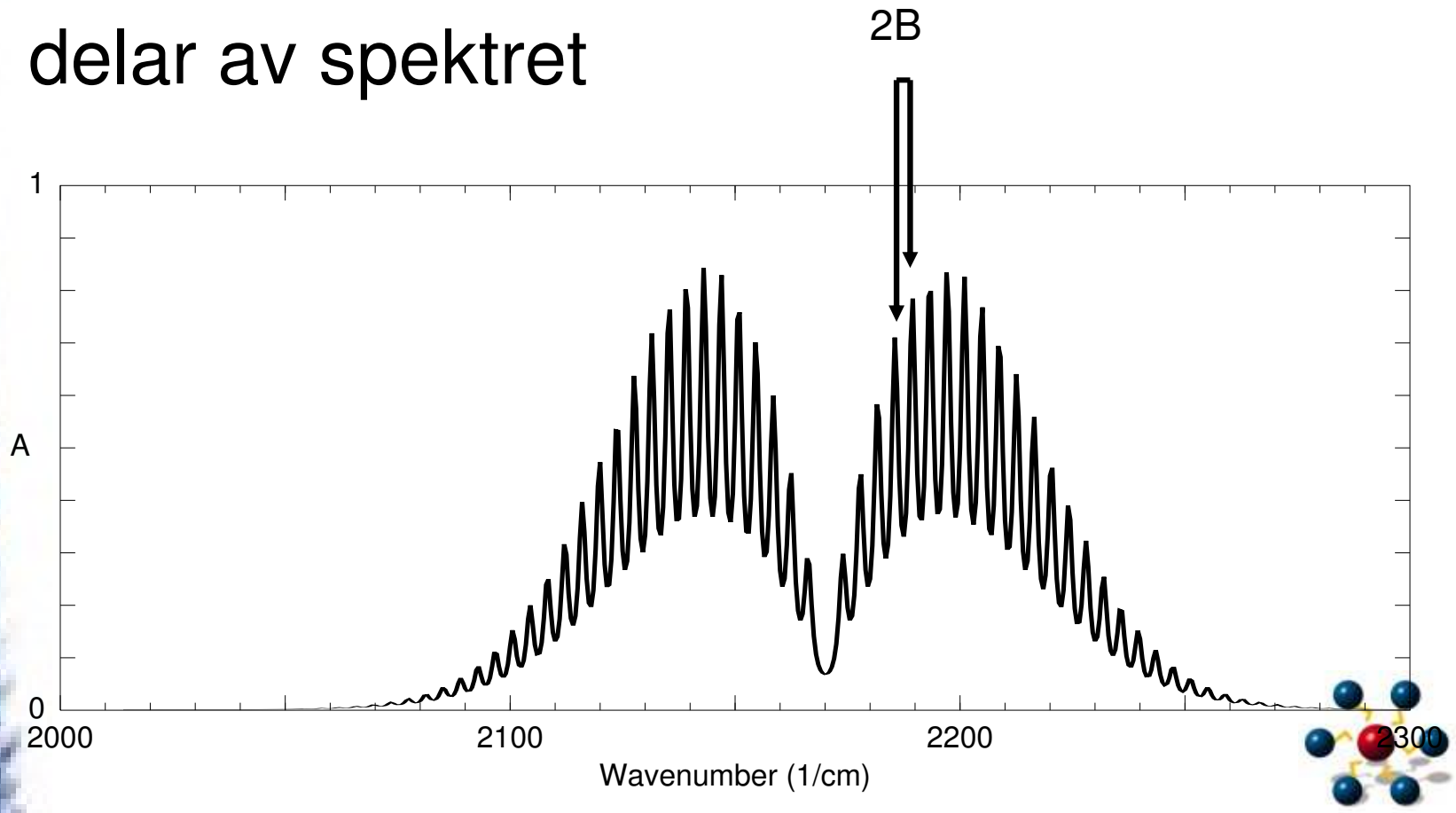


$$E_J = BJ(J+1) - DJ^2(J+1)^2$$

D: Centrifugalkraften ändrar rotationerna

Varför bättre?

Denna metod ger olika värden av 2B i olika delar av spektret



$CDBr_3$

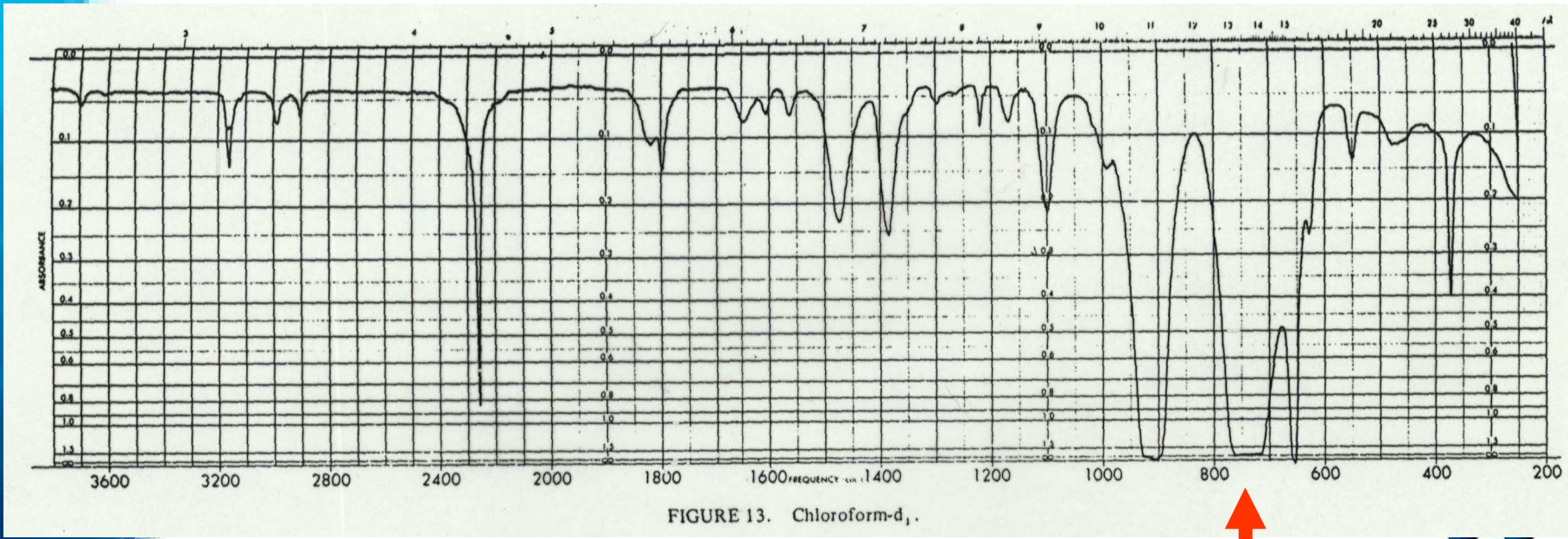
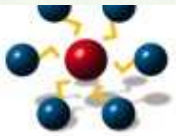
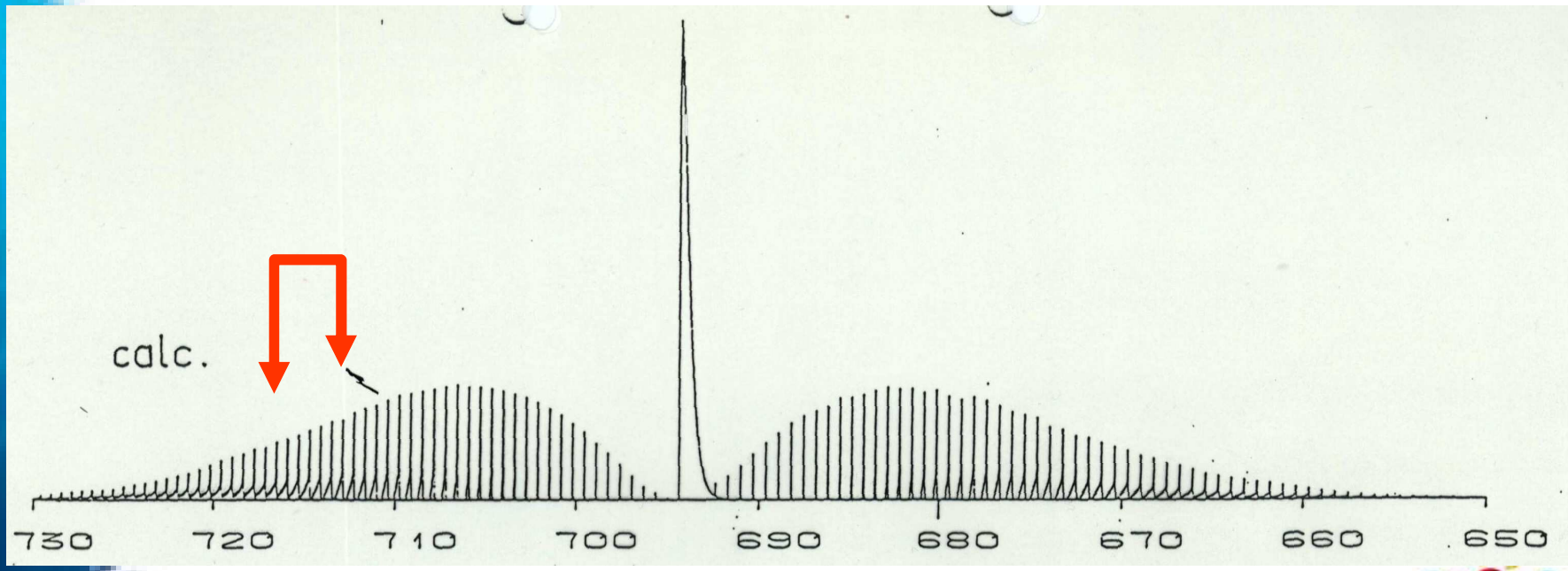


FIGURE 13. Chloroform-d_1.



$CDBr_3$



$CDBr_3$