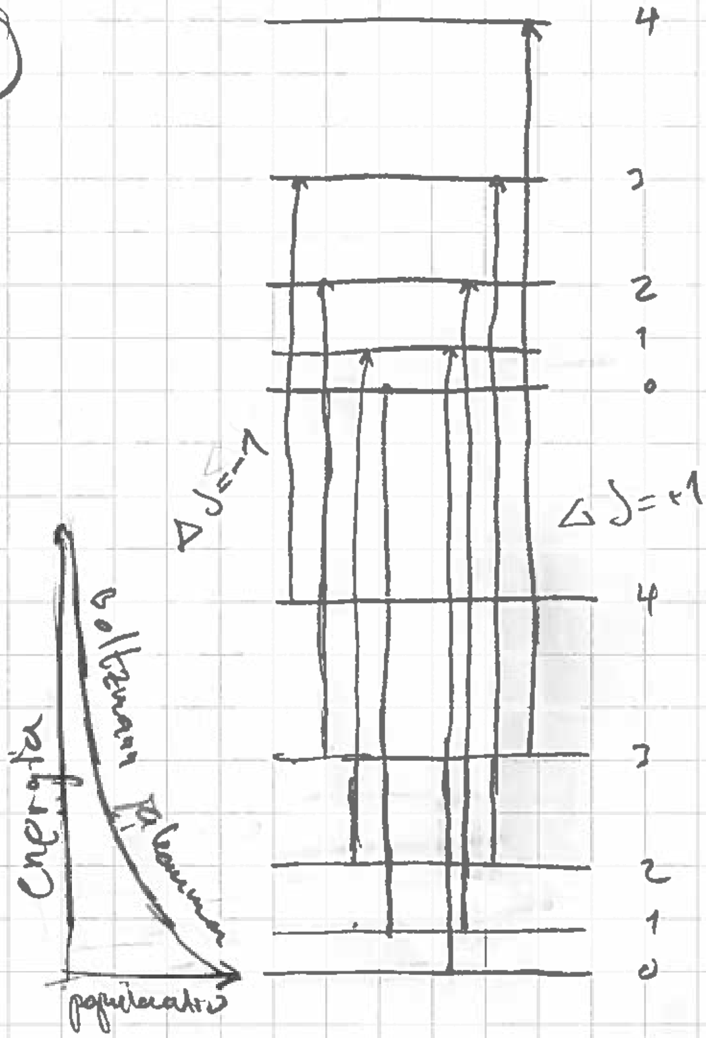
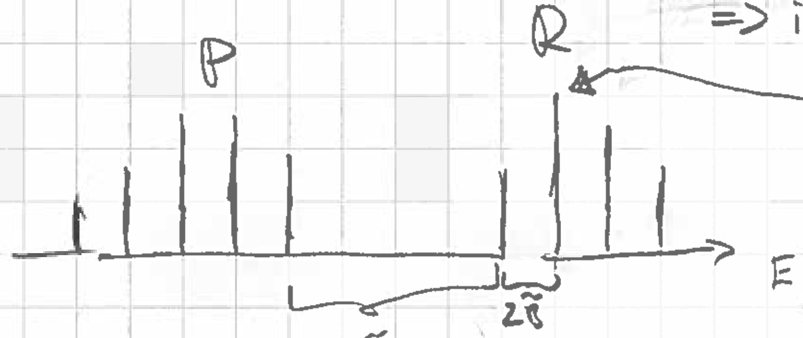
1



Boltzmann jakauma
=> tilojen populaatio

← populaatio kertaa tilan degeneraatio $(2J+1)$
=> intensiteetti



$4\tilde{B}$ väli riippuu molekyylin rotaatiovakion arvosta

joka riippuu

hitausmomentista

2

$$G(v) = (v+\tfrac{1}{2})\tilde{\nu} - (v+\tfrac{1}{2})^2 x_e \tilde{\nu}$$

$$\Delta G(v+\tfrac{1}{2}) = G(v+1) - G(v)$$

$$= (v+\tfrac{3}{2})\tilde{\nu} - (v+\tfrac{1}{2})\tilde{\nu}$$

$$- (v+\tfrac{3}{2})^2 x_e \tilde{\nu} + (v+\tfrac{1}{2})^2 x_e \tilde{\nu}$$

$$= \tilde{\nu} - [\underbrace{(v+\tfrac{3}{2})^2 - (v+\tfrac{1}{2})^2}_{v^2+3v+9/4-(v^2+v+\frac{1}{4}) = 2v+2}] x_e \tilde{\nu}$$

$$= \tilde{\nu} - 2(v+1) x_e \tilde{\nu}$$

$$= \tilde{\nu}(1-2(v+1)x_e)$$

etsitään dissosiaatioraja:

$$\Delta G(v_{max}+\tfrac{1}{2}) = 0 = \tilde{\nu}(1-2(v_{max}+1)x_e)$$

$$2(v_{max}+1)x_e = 1$$

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

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

$$= \frac{2649\,cm^{-1}}{2\cdot 45{,}2\,cm^{-1}} - 1 = 28{,}29$$

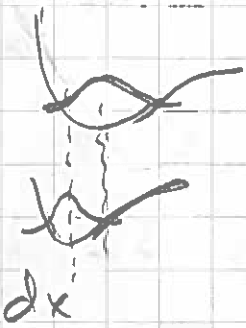
$$v_{max} = 28$$

$\Rightarrow 0 \ldots 28 \Rightarrow$ $\underline{\underline{29 \text{ tilaa}}}$

(3)

$$\psi_0 = N_0 e^{-ax^2}$$

$$\psi_0' = N_0' e^{-b(x-x_0)^2} \qquad b = \frac{a}{2}$$



Franck-Condon tekijä

$$S = \langle \psi_0 | \psi_0' \rangle$$

$$= \int_{-\infty}^{\infty} N_0 e^{-ax^2} N_0' e^{-\frac{a}{2}(x-x_0)^2} dx$$

$$= N_0 N_0' \int_{-\infty}^{\infty} \exp\left[-ax^2 - \frac{a}{2}\left(x^2 - 2xx_0 + x_0^2\right)\right] dx$$

$$= N_0 N_0' \underbrace{\int_{-\infty}^{\infty} \exp\left[-\frac{3a}{2}x^2 + ax_0 x - \frac{a}{2}x_0^2\right] dx}$$

$$\int_{-\infty}^{\infty} e^{-fx^2+gx+h} dx = \sqrt{\frac{\pi}{f}} \exp\left(\frac{g^2}{4f} + h\right)$$

wikipedia gaussian integral

$$f = \frac{3a}{2} \qquad g = ax_0 \qquad h = -\frac{a}{2}x_0^2$$

$$= N_0 N_0' \sqrt{\frac{\pi}{3a/2}} \exp\left(\frac{a^2x_0^2}{4\frac{3a}{2}} - \frac{a}{2}x_0^2\right)$$

$$= N_0 N_0' \sqrt{\frac{2\pi}{3a}} \exp\left(\frac{ax_0^2}{6} - \frac{ax_0^2}{2}\right)$$

$$= N_0 N_0' \sqrt{\frac{2\pi}{3a}} \exp\left(-\frac{2ax_0^2}{6}\right)$$

$$= N_0 N_0' \sqrt{\frac{2\pi}{3a}} \exp\left(-\frac{1}{3}ax_0^2\right)$$

Normitus:

$$N_0^2 \int_{-\infty}^{\infty} \left[e^{-ax^2}\right]^2 dx = N_0^2 \sqrt{\frac{\pi}{2a}} = 1 \Rightarrow N_0 = \left(\frac{2a}{\pi}\right)^{1/4}$$

$$N_0'^2 \int_{-\infty}^{\infty} \left[e^{-\frac{1}{2}ax}\right]^2 dx = N_0'^2 \sqrt{\frac{\pi}{a}} = 1 \Rightarrow N_0' = \left(\frac{a}{\pi}\right)^{1/4}$$

$$S = \left(\frac{2a}{\pi}\right)^{1/4} \left(\frac{a}{\pi}\right)^{1/4} \sqrt{\frac{2\pi}{3a}}\, e^{-\frac{1}{3}ax_0^2}$$

$$= \left[\frac{2a \cdot a}{\pi \cdot \pi} \cdot \left(\frac{2\pi}{3a}\right)^2\right]^{1/4} e^{-\frac{1}{3}ax_0^2}$$

$$= \underline{\underline{\left(\frac{8}{9}\right)^{1/4} e^{-\frac{1}{3}ax_0^2}}}$$

tarkastus jos $x_0 = 0 \Rightarrow S = \left(\frac{8}{9}\right)^{1/4}$

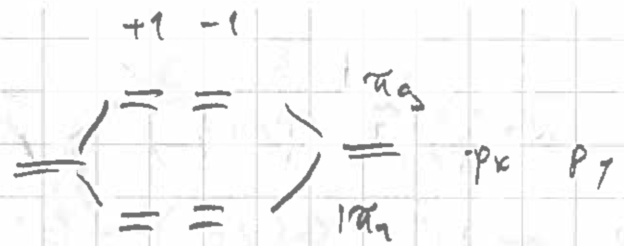
$$N_0 N_0' \int_{-\infty}^{\infty} e^{-ax^2} e^{-\frac{1}{2}ax^2} dx = N_0 N_0' \sqrt{\frac{\pi}{3a/2}}$$

$$= \left(\frac{8}{9}\right)^{\frac{1}{4}} \quad \underline{\underline{\text{ok}}}$$

Franck-Condon tekijä

$$\underline{\underline{|S|^2 = \sqrt{\frac{8}{9}}\, e^{-\frac{2}{3}ax_0^2}}}$$

4



	$\pi_u(+1)$	$\pi_u(-1)$	$\pi_g(+1)$	$\pi_g(-1)$	
$\pi_g^1 \pi_g^1$			↑	↑	$^3\Sigma_g$
$\pi_g^1 \pi_g^1$			↑	↓	$^1\Sigma_g$
$\pi_g^1 \pi_u^1$	↑		↑		$^3\Delta_u$
	↑		↓		$^1\Delta_u$
	↑			↑	$^3\Sigma_u$
	↑			↓	$^1\Sigma_u$
$\pi_g^2 \pi_g^0$			↑↓		$^1\Delta_g$

(5)

$$\mu_{fi,x} = N_{v_f} N_{v_i} \int_{-\infty}^{\infty} H_{v_f}\, x\, H_{v_i}\, e^{-y^2} dx$$

$$= \alpha^2 N_{v_f} N_{v_i} \int_{-\infty}^{\infty} H_{v_f}\, y\, H_{v_i}\, e^{-y^2} dy$$

$$x = \alpha y \qquad \alpha = \left(\frac{\hbar^2}{2 m_{eff} k}\right)^{1/4}$$

$$\left[\begin{array}{c} H_{v+1} - 2 y H_v + 2v H_{v-1} = 0 \\ y H_v = \frac{1}{2} H_{v+1} + v H_{v-1} \end{array}\right]$$

$$\mu_{fi,x} = \alpha^2 N_{v_f} N_{v_i} \int_{-\infty}^{\infty} H_{v_f} \left(\frac{1}{2} H_{v_i+1} + v H_{v_i-1}\right) e^{-y^2} dy$$

$$= \alpha^2 N_{v_f} N_{v_i}$$

$$\times \left[\frac{1}{2} \int_{-\infty}^{\infty} H_{v_f} H_{v_i+1} e^{-y^2} dy\right.$$

$$\left. + v \int_{-\infty}^{\infty} H_{v_f} H_{v_i-1} e^{-y^2} dy\right]$$

$$\left[\int_{-\infty}^{\infty} H_{v'} H_v e^{-y^2} dy = \begin{cases} 0 & v \neq v' \\ \sqrt{\pi}\, 2^v v! & v = v' \end{cases}\right]$$

$$\boxed{\delta_{a,b} = \begin{cases} 1 & a = b \\ 0 & a \neq b \end{cases}}$$

$$\mu_{fi,x} = \alpha^2 N_{v_f} N_{v_i} \left[\frac{1}{2} \sqrt{\pi}\, 2^{v_f} v_f!\, \delta_{v_f, v_i+1}\right.$$

$$\left. + v \sqrt{\pi}\, 2^{v_f} v_f!\, \delta_{v_f, v_i-1}\right]$$

5

$$G(v) = \left(v+\tfrac{1}{2}\right)\tilde{\nu} - \left(v+\tfrac{1}{2}\right)^2 x_e \tilde{\nu}$$

$$\Delta G(v+1 \leftarrow v) = G(v+1) - G(v)$$

$$= \left(v+\tfrac{3}{2}\right)\tilde{\nu} - \left(v+\tfrac{3}{2}\right)^2 x_e \tilde{\nu}$$

$$- \left[(v+1)\,\tilde{\nu} - \left(v+\tfrac{1}{2}\right)^2 x_e \tilde{\nu} \right]$$

$$= \tilde{\nu} - \left[\left(v^2 + 2\tfrac{3}{2}v + \tfrac{9}{4}\right)x_e \tilde{\nu} - \left(v^2 + 2\tfrac{1}{2}v + \tfrac{1}{4}\right)x_e \tilde{\nu}\right]$$

$$= \tilde{\nu} - \left[(2v+2)\,x_e \tilde{\nu}\right]$$

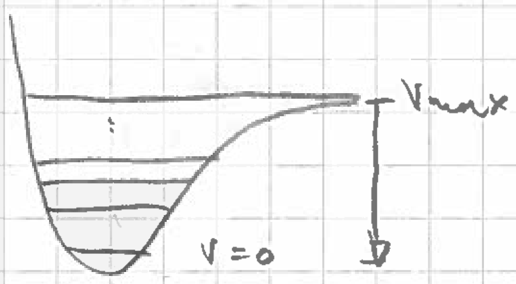
$$= \tilde{\nu}\left(1 - 2(v+1)x_e\right)$$

dissociation:

$$\Delta G(v+1 \leftarrow v) = 0$$
$$= \tilde{\nu}\left(1 - 2(v+1)x_e\right)$$

$$\Rightarrow \quad 1 - 2(v_{max}+1)x_e = 0$$

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



$$\tilde{D} = G(v_{max}) - G(0)$$

$$= \left(\frac{1}{2x_e} - 1 + \frac{1}{2}\right)\tilde{\nu} - \left(\frac{1}{2x_e} - 1 + \tfrac{1}{2}\right)^2 x_e \tilde{\nu}$$
$$- \left(\tfrac{1}{2}\tilde{\nu} - \tfrac{1}{4}x_e \tilde{\nu}\right)$$

$$= \frac{\tilde{\nu}}{x_e}\left[\tfrac{1}{2} - \tfrac{1}{2}x_e - \left(\tfrac{1}{2} - \tfrac{1}{2}x_e\right)^2\right] - \left[\tfrac{1}{2}\tilde{\nu} - \tfrac{1}{4}x_e\tilde{\nu}\right]$$

$$= \frac{\tilde{\nu}}{4x_e}\left[2 - 2x - 1 + 2x_e - e^2\right] - \left[\tfrac{1}{2}\tilde{\nu} - \tfrac{1}{4}x_e\tilde{\nu}\right]$$

$$\tilde{D} = \frac{\tilde{\nu}}{4x_e}\left[1 - x_e^2\right] - \frac{1}{2}\tilde{\nu} + \frac{1}{4}x_e\tilde{\nu}$$

$$= \frac{\tilde{\nu}}{4x_e}\left(1 - x_e^2\right) - \frac{1}{2}\tilde{\nu} + \frac{1}{4}x_e\tilde{\nu} \approx \frac{\tilde{\nu}}{4x_e}$$

$x_e \ll 1$