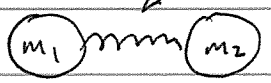


$$V = \frac{1}{2} k (r - r_e)^2$$

r_e = equilibrium bond length

$$\mathcal{E} = \mathcal{E}_{trans} + \mathcal{E}_{elect} + \mathcal{E}_{vib} + \mathcal{E}_{rot}$$

$$q(V,T) = q_{trans}(V,T)\, q_{elect}(T)\, q_{vib}(T)\, q_{rot}(T)$$

$$q_{trans} = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \qquad M = m_1 + m_2$$

$$q_{elect} = g_1 e^{\beta D_e} + g_2 e^{-\beta \varepsilon_2} + \dots$$

↑ zero of energy is above bound state!

$$q_{vib} = \frac{e^{-\theta_{vib}/2T}}{1 - e^{-\theta_{vib}/T}} \qquad \theta_{vib} = \frac{h\nu}{k_B} = \frac{h\omega}{k_B} = \frac{h\sqrt{\frac{k}{\mu}}}{k_B}$$

μ = reduced mass $= \frac{m_1 m_2}{m_1 + m_2}$

What about rotations?

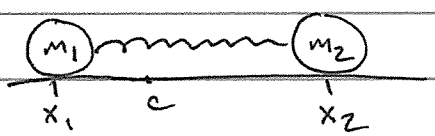
Quantum Mechanically $\quad \varepsilon_J = \frac{h^2}{2I} J(J+1) \qquad J = 0, 1, 2, \dots$

$g_J = 2J + 1$ ← degeneracy of rotational level J

I is the moment of inertia

For diatomics: $\quad I = m_1 d_1^2 + m_2 d_2^2$

↑ distance from center of mass



$$c = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

$$d_1 = x_1 - c \quad , \quad d_2 = x_2 - c$$

a bit of tedious algebra →

$$I = \mu r_e^2 \quad \text{(for a diatomic)}$$

Rotational Partition Function

$$q_{rot} = \sum_{states} e^{-\beta E_{state}} = \sum_{levels} g_{level}\, e^{-\beta E_{level}}$$

$$= \sum_{J=0}^{\infty} g_J\, e^{-\beta E_J} = \sum_{J=0}^{\infty} (2J+1)\, e^{-\beta \frac{\hbar^2}{2I} J(J+1)}$$

$\frac{\hbar^2}{2Ik_B}$ has units of temperature, so let's define

$$\boxed{\Theta_{rot} = \frac{\hbar^2}{2Ik_B}}$$

← contains only constants and fixed properties of the molecule

↓ rotational temperature

$$\therefore \quad q_{rot} = \sum_{J=0}^{\infty} (2J+1)\, e^{-J(J+1)\Theta_{rot}/T}$$

If $T \gg \Theta_{rot}$, the rotational levels are nearly continuous, so

$$q_{rot} \approx \int_0^{\infty} (2J+1)\, e^{-J(J+1)\Theta_{rot}/T}\, dJ$$

let $\quad X = J(J+1) = J^2 + J$

$$dX = (2J+1)\,dJ$$

$$\therefore \quad q_{rot} = \int_0^{\infty} e^{-\Theta_{rot} X/T}\, dX = \frac{-T}{\Theta_{rot}} \left[e^{-\Theta_{rot} X/T} \right]_0^{\infty}$$

$$\therefore \quad \boxed{q_{rot} = \frac{T}{\Theta_{rot}}}$$

$$\boxed{q_{rot}(T) = \frac{2Ik_BT}{\hbar^2} = \frac{8\pi^2 Ik_BT}{h^2} = \frac{T}{\Theta_{rot}}}$$

Level Populations

How likely are we to see vibrational level 2 at temperature T?

$$f_2^{vib}(T) = \frac{\text{Boltzman weight for level 2}}{\text{sum over all Boltzmann weights}} = \frac{e^{-\beta h\nu (5/2)}}{q_{vib}}$$

$$= \frac{e^{-5h\nu/2k_BT}}{q_{vib}} = \frac{e^{-5\theta_{vib}/2T}}{e^{-\theta_{vib}/2T}\left(1-e^{-\theta_{vib}/T}\right)}$$

$$f_2^{vib}(T) = \underbrace{e^{-2\theta_{vib}/T}}_{\text{makes } f_2 = 0 \text{ at } T=0}\ \underbrace{\left(1-e^{-\theta_{vib}/T}\right)}_{\text{makes } f_2 \to 0 \text{ as } T\to\infty}$$

We can do this for groundstate also

$$f_0^{vib}(T) = \frac{e^{-\beta h\nu/2}}{q_{vib}} = \frac{e^{-\theta_{vib}/2T}\left(1-e^{-\theta_{vib}/T}\right)}{e^{-\theta_{vib}/2T}}$$

$$f_0^{vib}(T) = \left(1-e^{-\theta_{vib}/T}\right)$$ ← exponentially dies off as $T\to\infty$

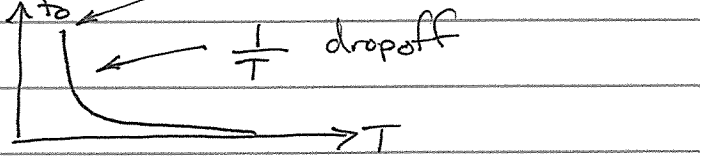
Rotational Populations (eg fraction of molecules with J=2)

$$f_J^{rot} = \frac{(2J+1)\, e^{-\theta_{rot} J(J+1)}}{q_{rot}}$$ ← $\frac{T}{\theta_{rot}}$ when $T >> \theta_{rot}$

$$f_J^{rot}(T) = (2J+1)\,\frac{\theta_{rot}}{T}\, e^{-\theta_{rot} J(J+1)/T}$$

doesn't work at very low T

$$f_0^{rot}(T) = \frac{\theta_{rot}}{T}$$



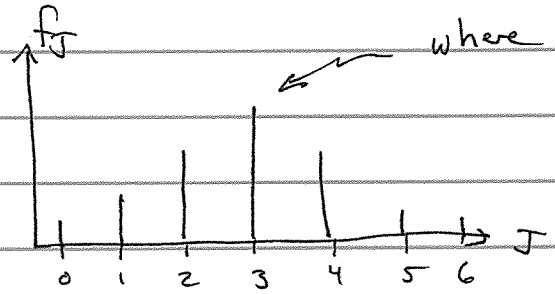
Let $J=2$:

$$f_2^{rot}(T) = 5\,\frac{\Theta_{rot}}{T}\,e^{-6\Theta_{rot}/T}$$

$e^{-6\Theta_{rot}/T} \approx 1$ at low T

So the $J=2$ level is more populated at the same temperature than the lower energy $J=0$ level. Why?

Degeneracy!



One good question: What is the most populated rotational level?

Set $\frac{df_J}{dJ} = 0$ to find J_{max}

$$f_J = (2J+1)\,\frac{\Theta_{rot}}{T}\,e^{-\Theta_{rot}\,J(J+1)/T}$$

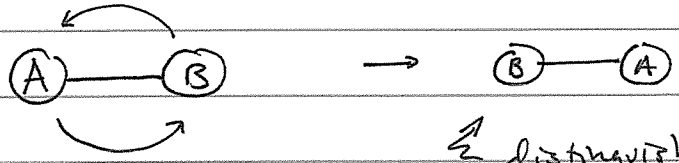
$$\frac{df_J}{dJ} = \frac{\Theta_{rot}}{T}\,e^{-\Theta_{rot}\,J(J+1)/T}\left(2 - (2J+1)^2\,\frac{\Theta_{rot}}{T}\right) = 0$$

$$\frac{2T}{\Theta_{rot}} = (2J+1)^2$$

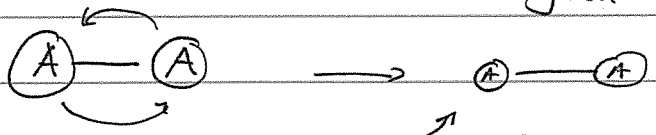
J_{max} increases with $\sqrt{T}$

$$J_{max} = \sqrt{\frac{T}{2\Theta_{rot}}} - \frac{1}{2}$$

Symmetry

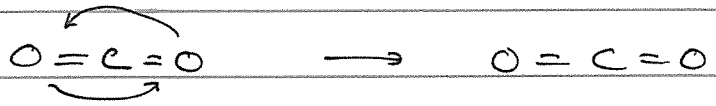
Heteronuclear: 

↳ distinguishable from original configuration

Homonuclear: 

↳ indistinguishable from original configuration

Likewise for CO_2:



For CO_2, twice per rotation we end up in the same configuration, so we need to adjust our rotational partition function to take this into account:

$$q_{rot}(T) = \frac{T}{\sigma\,\Theta_{rot}}$$

↳ symmetry # = number of indistinguishable rotations of the rotator

$N_2 \Rightarrow \sigma = 2$

$HCl \Rightarrow \sigma = 1$