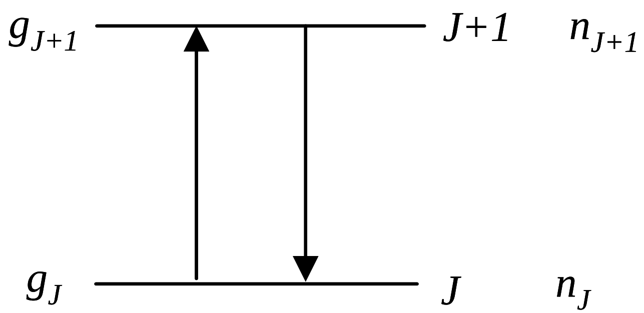
Appendix: Rotational linestrengths

Consider:



Spontaneous emission negligible, so :

$$\frac{dn_J}{dt} = -B_{J,J+1}\rho(\nu)n_J + B_{J+1,J}\rho(\nu)n_{J+1}$$

We know $\frac{B_{J,J+1}}{B_{J+1,J}} = \frac{g_{J+1}}{g_J} = \frac{2J+3}{2J+1}$ and $\frac{n_{J+1}}{n_J} = \frac{g_{J+1}}{g_J} exp\left(\frac{-\Delta E}{k_B T}\right) = \frac{2J+3}{2J+1} exp\left(\frac{-h\nu}{k_B T}\right)$

Boltzmann factor

Hence, $\frac{dn_J}{dt} = -B_{J,J+1}\rho(\nu)n_J\left[1 - exp\left(\frac{-h\nu}{k_B T}\right)\right]$ $h\nu << k_B T$

$\rightarrow$ expand as a power series:

$$\frac{dn_J}{dt} = -B_{J,J+1}\rho(\nu)n_J\left[1 - \left(1 - \frac{h\nu}{k_B T}\right) + \ldots\right] = -B_{J,J+1}\rho(\nu)n_J\frac{h\nu}{k_B T}$$

$$\boxed{\frac{dn_J}{dt} = -B_{J,J+1}\rho(\nu)(2J+1)\frac{N}{q} exp\left(\frac{-E_J}{k_B T}\right)\frac{h\nu}{k_B T}}$$

n.b., rate is –ve (absorption dominates emission)

Appendix: Rotational linestrengths

$$\frac{dn_J}{dt} = -B_{J,J+1}\rho(\nu)(2J+1)\frac{N}{q}exp\left(\frac{-E_J}{k_BT}\right)\frac{h\nu}{k_BT}.$$

A typical experiments measures the rate of absorption of energy (the power):

$$I = \frac{dn_J}{dt}h\nu \propto (J+1)\nu^2 exp\left(\frac{-E_J}{kT}\right)$$

This is subtly different from the expression obtained assuming the intensity distribution is due solely to population effects:

$$I \propto (2J+1)exp\left(\frac{-E_J}{kT}\right)$$

Calculated CO rotational spectrum for both expressions: