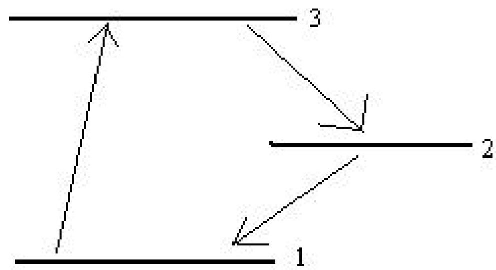
Fluorescence

Fluorescence occurs when an atom absorbs UV light and reradiates in the visible. The atomic levels look like this:



The number of absorptions from level i to level j is

$$n_i B_{ij} u_{ij}$$

where u_{ij} is the energy density of photons with frequency v_{ij}. The number of emissions of phtotons corresponing to the levels i and j is

$$n_j \left(A_{ji} + u_{ij} B_{ji} \right)$$

To simplify, we assume $g_i = g_j$ so that $B_{ij} = B_{ji}$. Also recall that$A_{ji} = B_{ji} \frac{2h\nu_{ij}^3}{c^2}$.

Now a cloclwise circuit of the diagram requires an absorption of a photon of frequency ν_{13} and emission of ν_{32} and $v_{21.}$ The number of anticloclwise circuits relative to the number of clockwise (fluorescent) circuits is

$$\begin{aligned} \frac{N_a}{N_c} &= \frac{(n_1 B_{12} u_{12}) (n_2 B_{23} u_{23}) n_3 (A_{31} + B_{31} u_{13})}{(n_1 B_{13} u_{13}) n_3 (A_{32} + B_{32} u_{23}) n_2 (A_{21} + B_{21} u_{12})} \\ &= \frac{u_{12} u_{23} B_{12} B_{23} B_{13} \left(2h\nu_{13}^3 / c^2 + u_{13} \right)}{u_{13} B_{13} B_{23} B_{12} (2h\nu_{32}^3/c^2 + u_{23}) (2h\nu_{12}^3/c^2 + u_{12})} \\ &= \frac{u_{12} u_{23} \left(2h\nu_{13}^3 / c^2 + u_{13} \right)}{u_{13} (2h\nu_{32}^3/c^2 + u_{23}) (2h\nu_{12}^3/c^2 + u_{12})} \end{aligned}$$

This result is independent of any atomic properties other than the frequencies.

Now if we are in the neighborhood of a black body (i.e. a star) $u_{12} = B_{\nu_{12}} (T_*) W$ where the dilution factor $W < 1$. Then

$$u_{12} = \frac{2hv_{12}^3}{c^2 \left(e^{h\nu_{12}/kT_*} - 1 \right)} = \frac{2hv_{12}^3}{c^2} K_{12}$$

So

$$\begin{aligned}
\frac{N_a}{N_c} &= \frac{v_{12}^3 K_{12} v_{23}^3 K_{23} W^2 \nu_{13}^3 (1 + W K_{13})}{v_{13}^3 W K_{13} \nu_{32}^3 \nu_{12}^3 (1 + W K_{23}) (1 + W K_{12})} \\
&= \frac{K_{12} K_{23} W (1 + W K_{13})}{K_{13} (1 + W K_{23}) (1 + W K_{12})} \\
&= \frac{K_{12} K_{23} K_{13} W \left(\frac{1}{K_{13}} + W\right)}{K_{13} K_{23} K_{12} \left(\frac{1}{K_{23}} + W\right) \left(\frac{1}{K_{12}} + W\right)} \\
&= \frac{W \left(\frac{1}{K_{13}} + W\right)}{\left(\frac{1}{K_{23}} + W\right) \left(\frac{1}{K_{12}} + W\right)}
\end{aligned}$$

Now

$$\begin{aligned}
W + \frac{1}{K} &= W + e^{h\nu/kT} - 1 \\
&= e^{h\nu/kT} \left[1 + e^{-h\nu/kT} (W - 1)\right] \equiv e^{h\nu/kT} F
\end{aligned}$$

where the factor F is of order 1. Thus

$$\frac{N_a}{N_c} = W \exp\left[(E_{13} - E_{12} - E_{23}) / kT\right] \frac{F_{13}}{F_{23} F_{12}}$$

But $E_{13} = E_{12} + E_{23}$, so

$$\frac{N_a}{N_c} = W \left(\frac{F_{13}}{F_{23} F_{12}}\right)$$

Since the factor in parentheses is of order 1, and $W < 1$, the preferred direction is *clockwise*, and the system fluoresces.