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 photons corresponding to the levels $i$ and $j$ is

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

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

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

$$\frac{N_a}{N_c} = \frac{(n_1 B_{12} u_{12}) (n_2 B_{23} u_{23}) n_3 (A_{31} + B_{31} u_{13})}{(n_1 B_{13} u_{13}) n_3 (A_{32} + B_{32} u_{23}) n_2 (A_{21} + B_{21} u_{12})}$$

$$= \frac{u_{12} u_{23} B_{12} B_{23} B_{13} (2 h v_{13}^3 / c^2 + u_{13})}{u_{13} B_{13} B_{23} B_{12} (2 h v_{32}^3 / c^2 + u_{23}) (2 h v_{12}^3 / c^2 + u_{12})}$$

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) $u_{12} = B_{\nu_{12}} (T_\star) W$ where the dilution factor $W < 1$. Then

$$u_{12} = \frac{2 h v_{12}^3}{c^2 (e^{h v_{12} / k T_\star} - 1)} = \frac{2 h v_{12}^3}{c^2} K_{12}$$
So

\[
\frac{N_a}{N_c} = \frac{v_1^3 K_{12} v_3^3 K_{23} W^2 \nu_3^3 (1 + W K_{13})}{v_3^3 W K_{13} \nu_3^3 v_1^3 (1 + W K_{23})(1 + W K_{12})} \\
= \frac{K_{12} K_{23} W (1 + W K_{13})}{K_{13} (1 + W K_{23})(1 + W K_{12})} \\
= \frac{K_{12} K_{23} K_{13} W \left( \frac{1}{K_{13}} + W \right)}{K_{13} K_{23} K_{12} \left( \frac{1}{K_{23}} + W \right) \left( \frac{1}{K_{12}} + W \right)} \\
= \frac{W \left( \frac{1}{K_{13}} + W \right)}{\left( \frac{1}{K_{23}} + W \right) \left( \frac{1}{K_{12}} + W \right)}
\]

Now

\[W + \frac{1}{K} = W + e^{\nu/kT} - 1 = e^{\nu/kT} \left[ 1 + e^{-\nu/kT} (W - 1) \right] \equiv e^{\nu/kT} F\]

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.