(3) ΔJ Transition Probabilities and Einstein Coefficients

Above we discussed the transition probabilities for the Zeeman components of certain ΔJ transition. Now let us take a look at the total transition probability of the ΔJ transition and the spectral line intensity.

First, let us investigate the spontaneous emission problem. All three transitions of $\Delta M = 0, \pm 1$ are possible, and all directions of radiation are also possible. To obtain the total transition probability, let us integrate dW_{sp} over all possible directions:

$$\Delta M = 0, \quad W_{sp}(\alpha_a J_a M \rightarrow \alpha_b J_b M) = \int dW_{sp}(\alpha_a J_a M \rightarrow \alpha_b J_b M)$$

$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} \begin{pmatrix} J_b & 1 & J_a \\ -M & 0 & M \end{pmatrix}^2 |\langle \alpha_b J_b \| \vec{d} \| \alpha_a J_a \rangle|^2 \qquad (247)$$

$$\Delta M = \pm 1, \quad W_{sp}(\alpha_a J_a M \mp 1 \rightarrow \alpha_b J_b M) = \int dW_{sp}(\alpha_a J_a M \mp 1 \rightarrow \alpha_b J_b M)$$

$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} \begin{pmatrix} J_b & 1 & J_a \\ -M & \pm 1 & M \mp 1 \end{pmatrix}^2 |\langle \alpha_b J_b \| \vec{d} \| \alpha_a J_a \rangle|^2 \qquad (248)$$

These are the transition probability per unit time (in all solid angles) of each Zeeman component.

Second, let us derive the total transition probability of the ΔJ transition, i.e., including all Zeeman components. For the initial level J_a, it has many M_a sub-levels. For each M_a sub-level, it has maximum 3 transitions to the final state J_b ($\Delta M = 0, \pm 1$). Thus, the total transition probability from M_a to lower state J_b is given by

$$\sum_{M_b} W_{sp}(\alpha_a J_a M_a \rightarrow \alpha_b J_b M_b)$$

$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} |\langle \alpha_b J_b \| \vec{d} \| \alpha_a J_a \rangle|^2 \sum_{M_b} \begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a \end{pmatrix}^2 \qquad (249)$$

Using the following relationship of 3j-symbols,

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \frac{1}{2j_3+1} \delta(j_3, j_3') \delta(m_3, m_3') \quad (250)$$

We have

$$\sum_{M_b} \begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a \end{pmatrix}^2 = \frac{1}{2J_a+1} \quad (251)$$

Thus, Eq. (249) can be further derived as

$$\sum_{M_b} W_{sp}(\alpha_a J_a M_a \to \alpha_b J_b M_b)$$
$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} |\langle \alpha_b J_b \| \vec{d} \| \alpha_a J_a \rangle|^2 \frac{1}{2J_a+1} \quad (252)$$

Note: Eq. (252) is independent of M_a !!! This means that the transition probability from any one M_a of J_a to lower states is equal ! We also have another "surprising" conclusion: The Eq. (252) also gives the total transition probability from $\alpha_a J_a \to \alpha_b J_b$:

$$W_{sp}(\alpha_a J_a \to \alpha_b J_b) = \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} \cdot \frac{1}{2J_a+1} |\langle \alpha_b J_b \| \vec{d} \| \alpha_a J_a \rangle|^2 \quad (253)$$

Since for any single atom, it can only be in one M_a sub-level. So its total transition rate W_{sp} is given by Eq. (253). We should not multiply it by the degeneracy of J_a level ($2J_a+1$).

When there is no external magnetic field, Zeeman components of the $\alpha_a J_a \to \alpha_b J_b$ transition own the same transition frequency. If we don't distinguish polarization, then only one spectral line is observed for $\alpha_a J_a \to \alpha_b J_b$ transition. If we assume each M_a sub-levels are homogeneously excited, and the population on each M_a is N_M, then the total population on J_a is

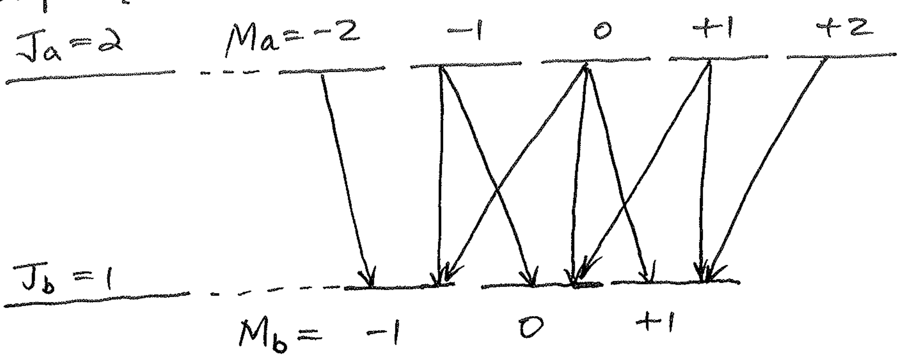
$$N_{J_a} = (2J_a+1) N_M = g_{J_a} N_M, \quad g_{J_a} = 2J_a+1 \quad (253)$$

Thus, the $\alpha_a J_a \to \alpha_b J_b$ spectral line intensity is

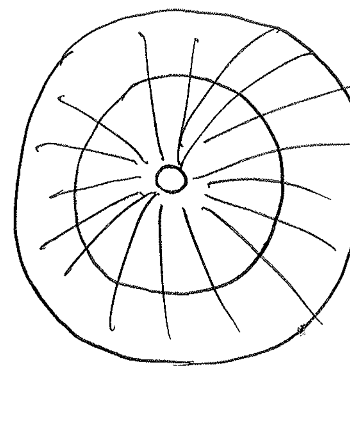
$$I \propto N_{J_a} W_{sp}(\alpha_a J_a \to \alpha_b J_b)\hbar\omega = g_{J_a} N_M W_{sp}(\alpha_a J_a \to \alpha_b J_b)\hbar\omega. \quad (254)$$

For angular distribution and polarization of $\alpha_a J_a \to \alpha_b J_b$ transition analysis, we need to start from Eqs. (242) and (244). For any arbitrary angle θ, add ~~the~~ the contributions from all Zeeman components together. We skip the procedure here. The results are that the radiation intensity is independent of θ angle, so the radiation is isotropic and non-polarized. This is required by the physics — a space without external magnetic / electric field should be isotropic. In such a space, a group of atoms that are excited homogeneously are also isotropic. The decay from each Ma sub-levels cannot have different speed — but the same spontaneous emission rate, i.e., no single orientation would show dominant feature. Thus, the radiation field from the group of atoms is also isotropic — the radiation is not dependent on angular direction. of course, if the group of atoms are not homogeneously excited, but Ma sublevels are selectively excited, then the isotropic properties are no longer valid.

Example :



Spontaneous emission is isotropic !



For stimulated transitions (emission and absorption), the situation is more complicated. Usually we shine a radiation field onto the atoms from one direction, and sometimes the radiation is polarized.

① If the incident light is polarized and can distinguish Zeeman components, also no optical pumping effect, then we should start from Eq. (225) $\left(dW_{st} = \frac{\pi e^2 I_{k\lambda}}{\mu^2 \varepsilon_0 \hbar^2 \omega^2 c} |\langle b| \hat{\vec{e}} \cdot \hat{\vec{P}} |a\rangle|^2 d\Omega \right)$, and derive equations similar to the spontaneous cases Eqs. (242) and (244)

$\Delta M = 0$, $dW_{st}(\alpha_a J_a M \to \alpha_b J_b M)$

$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\pi^2}{\hbar^2 c} I_{k\lambda} |\langle \alpha_b J_b M | d_z | \alpha_a J_a M \rangle|^2 \sin^2\theta \, d\Omega \quad (255)$$

$\Delta M = \pm 1$, $dW_{st}(\alpha_a J_a M \mp 1 \to \alpha_b J_b M)$

$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\pi^2}{\hbar^2 c} I_{k\lambda} \left| \langle \alpha_b J_b M | \frac{1}{\sqrt{2}} (d_x \pm i d_y) | \alpha_a J_a M \mp 1 \rangle \right|^2 \cdot \frac{1}{2} (1 + \cos^2\theta) \, d\Omega \quad (256)$$

② If the incident light is non-polarized, then we will observe the total ΔJ transitions — ΔJ spectral line. Since the spontaneous emission from $\alpha_a J_a \to \alpha_b J_b$ is isotropic and non-polarized, the opposition process — absorption $\alpha_b J_b — \alpha_a J_a$ is isotropic, i.e., No matter which direction the radiation is incident, the stimulated transition probability should be the same. Therefore we can utilize the isotropic field results obtained above to derive the transition probability for non-polarized radiation interacting with atoms:

$$I_{k\lambda} = \frac{c}{2} \rho(\omega)$$

We define $E_a > E_b$, i.e., a level is higher than b level.

Thus, for stimulated absorption:

$$d W_{st} (\alpha_b J_b \to \alpha_a J_a) = \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\pi^2}{3\hbar^2} \rho(\omega) \frac{1}{2J_b+1} |\langle \alpha_a J_a \| \hat{\vec{d}} \| \alpha_b J_b \rangle|^2 d\Omega \tag{257}$$

for stimulated emission:

$$d W_{st} (\alpha_a J_a \to \alpha_b J_b) = \frac{1}{4\pi\varepsilon_0} \frac{4\pi^2}{3\hbar^2} \rho(\omega) \frac{1}{2J_a+1} |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 d\Omega \tag{258}$$

Einstein A and B coefficients are obtained in isotropic radiation field, which corresponds to the total ΔJ transition (includg all Zeeman components).

Thus, $$A_{a\to b} = W_{sp} (\alpha_a J_a \to \alpha_b J_b) = \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} \frac{1}{2J_a+1} |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \tag{259}$$

$$B_{a\to b} \rho(\omega) = W_{st} (\alpha_a J_a \to \alpha_b J_b)$$
$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\pi^2}{3\hbar^2} \rho(\omega) \frac{1}{2J_a+1} |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \tag{260}$$

$$B_{b\to a} \rho(\omega) = W_{st} (\alpha_b J_b \to \alpha_a J_a)$$
$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\pi^2}{3\hbar^2} \rho(\omega) \frac{1}{2J_b+1} |\langle \alpha_a J_a \| \hat{\vec{d}} \| \alpha_b J_b \rangle|^2 \tag{261}$$

From Eqs. (259–261), we obtain

$$A_{a\to b} = \frac{\hbar \omega^3}{\pi^2 c^3} B_{a\to b}, \qquad g_a B_{a\to b} = g_b B_{b\to a} \tag{262}$$

where $g_a = 2J_a + 1$, $\quad g_b = 2J_b + 1$.

(4) Oscillator strength, Line Strength, and A_{ki}

Equation (254) gives the spectral line intensity for spontaneous emission $\alpha_a J_a \to \alpha_b J_b$:

$$I(\alpha_a J_a \to \alpha_b J_b) \propto N(\alpha_a J_a)\, W_{sp}(\alpha_a J_a \to \alpha_b J_b)\, \hbar\omega$$

$$\propto N_M \frac{4\omega^3}{3\hbar c^3} \cdot \frac{1}{4\pi\varepsilon_0} \cdot \hbar\omega\, |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \qquad (263)$$

$$\boxed{\begin{array}{l} \text{Note: } N_{J_a} = N(\alpha_a J_a) = g_a N_M = (2J_a+1) N_M \\ W_{sp}(\alpha_a J_a \to \alpha_b J_b) \propto \dfrac{1}{2J_a+1} \end{array} \Bigg\} \Rightarrow \text{Thus, the } (2J_a+1) \text{ factor is cancelled out.}}$$

Thus, the line intensity I is independent of quantum number J_a, but proportional to the square of the matrix element.

We define the line strength $S(J_a \to J_b)$ as

$$S(J_a \to J_b) \equiv |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \qquad (264)$$

$$\text{Symmetry} \Rightarrow S(J_a \to J_b) = S(J_b \to J_a) \qquad (265)$$

We define the oscillator strength (f value) as

$$f(J_a \to J_b) = \frac{2\mu}{3\hbar e^2} \cdot \frac{\omega_{ba}}{2J_a+1} |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2$$

$$= \frac{2\mu}{3\hbar e^2} \cdot \frac{\omega_{ba}}{2J_a+1} S(J_a \to J_b) \qquad (266)$$

where $\omega_{ba} = (E_b - E_a)/\hbar$, $\quad \mu = \dfrac{m_e M}{m_e + M}$. $\qquad (267)$

For emission, $\omega_{ba} < 0$, $\therefore f_{ki} < 0$ $\qquad$ k — upper, i — lower.

For absorption, $\omega_{ab} > 0$, $\therefore f_{ik} > 0$.

$$f(J_b \to J_a) = \frac{2\mu}{3\hbar e^2} \frac{\omega_{ab}}{2J_b+1} |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \qquad (268)$$

$$= \frac{2\mu}{3\hbar e^2} \cdot \frac{\omega_{ab}}{2J_b+1} S(J_b \to J_a)$$

$\because S(J_a \to J_b) = S(J_b \to J_a)$

$\therefore -(2J_a+1) f(J_a \to J_b) = (2J_b+1) f(J_b \to J_a)$

i.e., $\quad -g_K f_{Ki} = g_i f_{iK} \qquad (269)$

Compare Eq. (259) with Eqs. (266) and (268), we have

$$A_{Ki} = \frac{e^2 \omega_{Ki}^2}{2\pi \varepsilon_0 \mu c^3} (-f_{Ki})$$

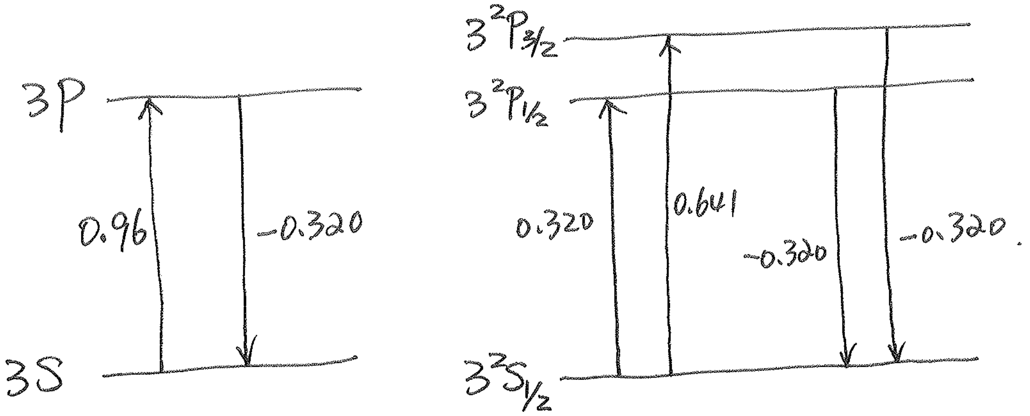
$$= \frac{e^2 \omega_{Ki}^2}{2\pi \varepsilon_0 \mu c^3} \frac{g_i}{g_K} f_{iK} \qquad (270)$$

$$\therefore f_{iK} = \frac{2\pi \varepsilon_0 \mu c^3}{e^2 \omega_{Ki}^2} \frac{g_K}{g_i} A_{Ki} \qquad (271)$$

Regard $\mu \approx m_e$, and $\omega_{Ki} = 2\pi \frac{c}{\lambda}$

$$\therefore f_{iK} = \frac{\varepsilon_0 m_e c \lambda^2}{2\pi e^2} \cdot \frac{g_K}{g_i} \cdot A_{Ki} \qquad (272)$$

Remember, absorption oscillator strength is positive, and the emission oscillator strength is negative.



Oscillator strength f for Na $3P \leftrightarrow 3S$ transitions

Note: $\sum_{J_b} f(J_a \to J_b) = 1 \qquad (273)$

$\begin{cases} 3S \to 3P & 0.96 \\ 3S \to 4P & 0.0153 \\ 3S \to 5P & 0.0025, \cdots \end{cases}$

i.e., all transitions from J_a (including absorption and emission) have the sum of oscillator strengths to be 1 for single electron transition.