

Non-radiative energy transfer - overview

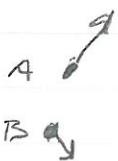
1) 2-body collisions

elastic - energy conserving

- can interrupt phase of excited state.

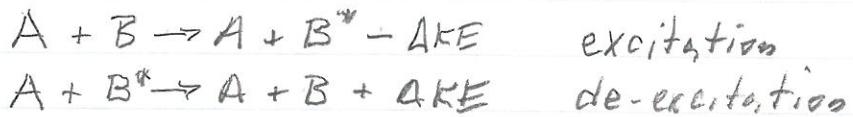
collision rate (microscopic)

$$\gamma_e = N_B \sigma_c V_A$$



thermal: average over all relative velocities
non-thermal: e.g. electron beam.

inelastic - internal energy changes



$$\frac{dN_{B^*}}{dt} = -k_{B^*A} N_A N_{B^*} + k_{BA} N_A N_B$$

rates w_{B^*A} w_{BA} $\propto N_A$

thermal eqn: $d/dt = 0$ "detailed balance"

"dynamic eqn"

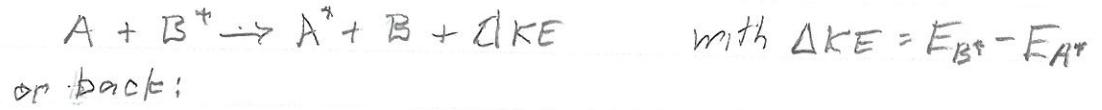
$$\rightarrow k_{B^*A} N_{B^*} = k_{BA} N_B$$

and $\frac{N_{B^*}}{N_B} = e^{-\Delta E/kT}$ Boltzmann

$$\therefore \frac{k_{B^*}}{k_B} = e^{+\Delta E/kT}$$

de-excitation rate is much higher for $\Delta E > kT$

Inelastic - excitation transfer



higher rate when ΔE is small, near-resonant.

- if all of species B, excitation hops, migrates
also cross-relaxation:



2) "non-collisional"

Forster transfer: dipole-dipole excitation transfer.

- through near-field interactions

$$W \propto 1/R^6 \quad \text{- exchange of virtual photons}$$

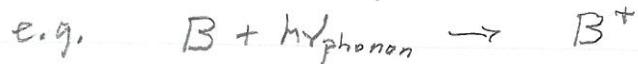
in gas: avg over all "collisions" \rightarrow avg rate

in solid (or liquid) \rightarrow non-exponential decay

since distribution is (nearly) fixed

phonon interactions in solid

can think of phonons like photons



there is a "blackbody" thermal distribution

- if $\Delta E \sim kT \rightarrow$ fast rate, up or down.

- if $\Delta E \gg kT \rightarrow$ slower, require multiphonon interactions

NR + R transitions:

$$\frac{dN_2}{dt} = -\frac{1}{\tau_r} N_2 - \frac{1}{\tau_{NR}} N_2 = -\frac{1}{\tau} N_2$$

- Quantum yield for fluorescence: τ / τ_R
- Rates add
- Lifetimes add like \parallel resistors.
- assumes rate is the same for all atoms (exponential decay)
- observed fluorescence: new τ , shorter

Degenerate states

N_1, N_2, etc = # density of an energy level,

If sublevels are degenerate = same energy,

$$\frac{N_2}{g_2} = \# \text{ density per state}$$

Boltzmann distribution applies for state populations

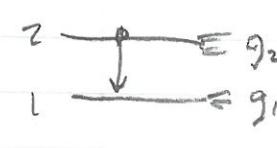
$$\frac{N_2^e}{N_1^e} = e^{-(E_2 - E_1)/kT}$$

$e = \text{exp}$

$$\rightarrow N_2^e = N_1^e \frac{g_2}{g_1} e^{-(E_2 - E_1)/kT}$$

If more states are available in upper level
 \rightarrow greater # at that energy level.

Total transition rate: sum over all comb's

$$\frac{dN_2}{dt} = - \sum_{i=1}^{g_1} \sum_{j=1}^{g_2} \left(W_{ji} N_{2j} - W_{ij} N_{1i} - \frac{N_{2j}}{\tau_{ij}} \right)$$


$$\text{since } W_{ji} \propto |M_{ji}|^2 \quad W_{ij} = W_{ji}$$

$$\text{plus } N_{2j} = N_2/g_2 \quad N_{1i} = N_1/g_1$$

$$\text{and } \frac{1}{\tau} = \sum_{ij} \frac{1}{\tau_{ji}} \quad \text{total spontaneous rate}$$

$$\rightarrow \frac{dN_2}{dt} = -W \left(\frac{N_2}{g_2} - \frac{N_1}{g_1} \right) - \frac{1}{\tau} N_2$$

$$\downarrow \sum_{ij} W_{ij} \quad \text{sum over all combis}$$

cross-sections:

$$W = g_2 \sigma_{21} F \quad \text{more states, higher rate}$$

$$= g_1 \sigma_{12} F$$

$$\rightarrow \sigma_{21} = \frac{g_1 \sigma_{12}}{g_2} \quad \begin{matrix} \text{larger cross section with} \\ \text{more destination states} \end{matrix}$$

Einstein B's

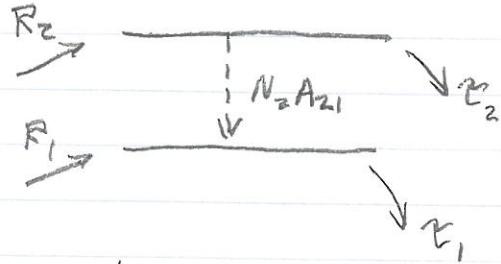
$$B_{21} \propto \sigma_{21} \quad \text{so} \quad B_{21} = \frac{g_1}{g_2} B_{12}$$

can also show in derivation of A, B coeff.

Condition for steady state inversion

$$\frac{dN_2}{dt} = R_2 - \frac{N_2}{\tau_2}$$

$$\frac{dN_1}{dt} = R_1 + N_2 A_{21} - \frac{N_1}{\tau_1}$$



τ_2 = fluorescence lifetime, includes $1/A_{21}$

$$\frac{d}{dt} \rightarrow 0 \text{ in steady state}$$

$$\rightarrow N_2 = \tau_2 R_2$$

$$N_1 = \underbrace{\tau_1 R_1 + \frac{R_2 \tau_2 A_{21}}{N_2} \tau_1}_{N_2} \tau_1$$

$$\text{For gain: } \frac{N_2}{g_2} > \frac{N_1}{g_1}$$

$$\frac{R_2 \tau_2}{g_2} - \frac{R_2 \tau_1 \tau_2 A_{21}}{g_1} > \frac{R_1 \tau_1}{g_1}$$

$$\rightarrow \frac{R_2 \tau_2}{g_2} > \frac{\tau_1}{g_1} (R_1 + R_2 \tau_2 A_{21})$$

$$\frac{R_2 \tau_2}{g_2} \left(\frac{1}{\tau_1} - \frac{\tau_1 A_{21}}{g_1} \right)$$

Steady-state inversion:

$$\frac{R_2}{R_1} \frac{\tau_2}{\tau_1} \frac{g_1}{g_2} \left(1 - \frac{g_1}{g_2} A_{21} \tau_1 \right) > 1$$

for gain:

$$\text{selective pump } R_2/R_1 > 1$$

favorable lifetime ratio $\tau_2 > \tau_1$

" degeneracy ratio $g_1 > g_2$

+ $A_{21} < \frac{g_1}{g_2} \frac{1}{\tau_1}$, necessary must empty out lower level faster.

Degenerate levels

So far, we have assumed that each level has only state at that energy.

In general, there are multiple states at the same energy level.

e.g. g_1, g_2

in thermal eqm. these degen. states have equal population.

Hence rate W is sum over all possible combinations, of levels

$N_1, N_2 = \# \text{ density for all degenerate states.}$

$$\frac{dN_2}{dt} = -W \left(\frac{N_2}{g_2} - \frac{N_1}{g_1} \right) - \frac{N_2}{\tau}$$

although the populations N_1, N_2 are reduced by g_1, g_2 , W 's are larger b/c of sum over all combinations.

In terms of cross sections:

$$g_2 \sigma_{21} = g_1 \sigma_{12}$$

typically $g_2 > g_1 \rightarrow \text{absorption has larger } \sigma_{12}$
b/c more upper states are available.

\rightarrow net gain coeff:

$$g = \sigma_{21} \left(N_2 - \frac{g_2}{g_1} N_1 \right)$$

Strongly-coupled levels: close enough ΔE to be thermally coupled.