

# Chemical Dynamics Yr 2 T2

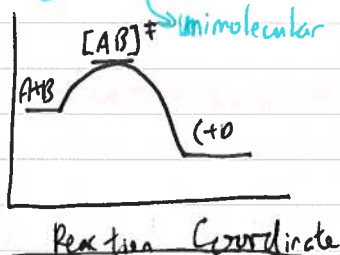
## Types of Reactions

Elementary: - take  $\text{Ⓐ}$

- a reaction for which no reaction intermediates have been detected or need to be postulated in order to describe the chemical Rx on a molecular scale

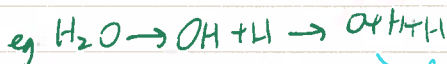
- assumed to occur in a single step & to pass thru a single transition state

eg. cis-trans isomerism

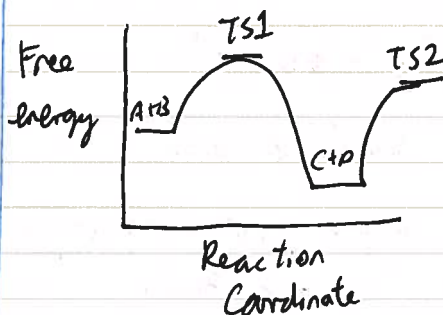


Complex - 需搭車

- a reaction sequence involving more than one elementary step



→ Bimolecular



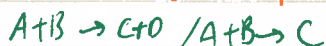
~~Uni / Bimolecular~~

→ tells you how many species involved

Unimolecular - rearrangement of a single molecule to produce one or more products



Bimolecular - reaction involving the collision of 2 reactants



Termolecular - same, but w/ 3

⚡ See the initial num of species being reacted.

Associative - bonds form during Rx

Dissociative - bonds broken during Rx

Photodissociative - light is used to energise the dissociation

Uni:  $k[\text{A}]$

Bi:  $k[\text{A}][\text{B}] / k[\text{A}]^2$

Tera:  $k[\text{A}][\text{B}][\text{C}] / k[\text{A}]^3 / k[\text{A}][\text{B}]^2$

## Types of collision

→ event in which 2 or more bodies exert forces on each other for a relatively short time

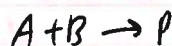
- Elastic  $KE_{tot}$  conserved  
[ 2 noble gas atoms ]  $\times$  transfer of  $KE$

- Inelastic  $KE_{tot}$   $\times$  conserved  
[ non-reactive collision between molecules ]  
→  $\therefore$  transfer of energy  
between translational & internal degrees of freedom  
ele, vib, rot

- Reactive collision - collisions that result in the making or breaking of bonds

## Collision Theory

rate of a bimolecular elementary reaction



$$v = - \frac{d[A]}{dt} = k_r [A][B]$$

$$k_r = A e^{-\frac{E_a}{RT}}$$

Simple Collision Theory [SCT]

[ assuming reaction between hard spheres ]

- Collide + have sufficient energy

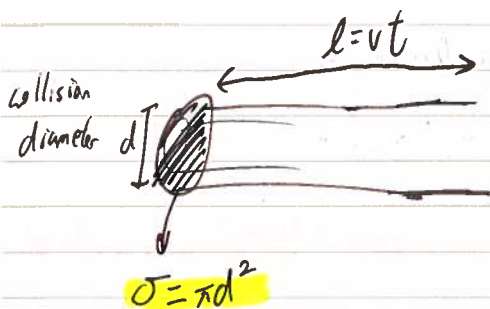
rate

$v \propto \text{Size} \times \text{velocity} \times \text{density of particles}$   
(rate)

\*  $KE$  must exceed a minimum value  $\Rightarrow E_a$

$\therefore v \propto (\text{collision frequency}) \times (\text{fraction w/ enough energy to react})$

## Collision Theory, the rate constant



\* the rate of change in the number density,  $n_A^*$ , of A molecules.

$$\frac{dn_A^*}{dt} = -Z_{AB} e^{-E_a/RT}$$

$n_A^* = \frac{N}{V} \Rightarrow$  number  $N$  of A molecules in a region of the sample per unit volume  $V$

$Z_{AB} \Rightarrow$  number of A-B collisions in the same region in an interval of time per  $V$  per  $t$  [duration of the interval]

determining  $Z$ :



volume of collision cylinder  $= \sigma v_{rel} \Delta t$

# of stationary molecules whose centres we expect to be contained in the cylinder

$$= n_A^* \times V = n_A^* \sigma v_{rel} \Delta t$$

collision frequency:

$$Z = \sigma v_{rel} n_A^*$$

[number of collisions divided by the time interval]

$\Rightarrow$  Total collision density:

collision of A w/ A:

$$Z_A = \frac{1}{2} Z n_A^* = \frac{1}{2} \sigma v_{rel} n_A^{*2}$$

↓  
avoid double counting

collisions of A w/ B:

$$Z_{AB} = \sigma v_{rel} n_A^* n_B^* \quad \left| \quad n_J^* = N_J [J] \right.$$

$$Z_{AB} = \sigma v_{rel} n_A^{*2} [A][B]$$

$$k_r = A e^{-E_a/RT} = \sigma v_{rel} n_A e^{-E_a/RT}$$

rewriting  $\frac{dn_A^*}{dt} = -Z_{AB} e^{-E_a/RT}$

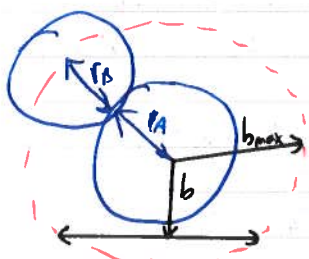
$$V = - \frac{d[A]}{dt} = \sigma v_{rel} n_A e^{-E_a/RT} [A][B]$$

$$v_{rel} = \sqrt{\frac{8k_B T}{\pi \mu}}$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

## Steric requirements for collision theory

↳ the relative orientations of the two reactive species



$$V(r) = \begin{cases} \infty & \text{for } b \leq r_A + r_B \\ 0 & \text{for } b > r_A + r_B \end{cases}$$

[interaction potential  $V(r)$ ]

Rates are very often overestimated

⇒ P-value for steric factor

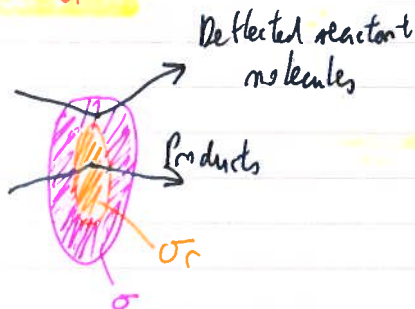
[steric factor]

$$\sigma_R = P\sigma$$

steric factor

correction for steric factors

$$\Rightarrow k_R = P\sigma v_{rel} N_A e^{-E_a/RT}$$



Some anomalies

## Harpoon Mechanism



Reaction sequence (thermal / photoinduced)

between neutral molecular / atomic entities

in which long-range e<sup>-</sup> transfer is

followed by a considerable reduction

of the distance between

donor & receptor sites, as a result

of the electrostatic attraction

in the ion pair created



- generally involve atoms / molecules w/

↳ low ionization energies  
[alkali metals]

↳ molecules w/ rather  
high e<sup>-</sup> affinity  
[halogens]





See curve in notes

Covalent: dominated by weak van der Waals attraction

$$\Rightarrow V(R) \sim -\frac{C_6}{R^6}$$

Ionic: dominated by electrostatic attraction

$$V(R) \sim -\frac{e^2}{4\pi\epsilon_0 R}$$

Crossing pt:

$$-\frac{e^2}{4\pi\epsilon_0 R_c} + \Delta E = -\frac{C_6}{R_c^6} \approx 0$$

$$R_c = \frac{e^2}{4\pi\epsilon_0 \Delta E}$$

Reaction cross section for a hapson  $R_c$ :

$$\sigma_R = \pi R_c^2$$

- large impact parameters +

large reaction cross-section [order of  $100 \text{ \AA}^2$ ]

$\therefore R_c \propto \frac{1}{\Delta E} \Rightarrow$  there are a # of periodic trends for hapson  $R_c$ s

Modelling  $R_c$ s requires:

- description of pair potentials

- assumption about value of  $\Delta E$

need require

$\rightarrow$  transition state theory for more complex  $R_c$ s.

## Dynamics of Collisions:

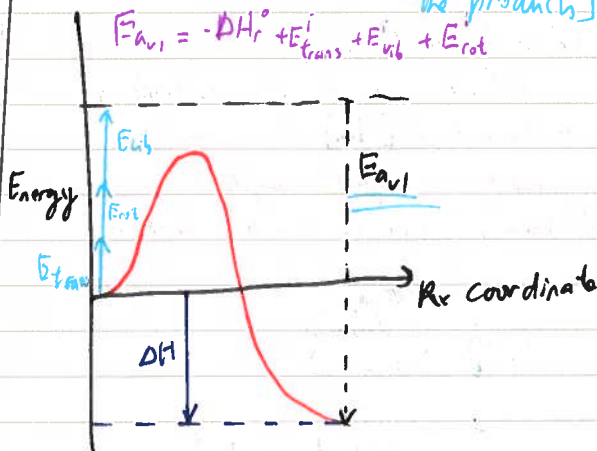
total energy & total momentum

must be conserved:

$$H^i + E_{\text{trans}}^i + E_{\text{vib}}^i + E_{\text{rot}}^i = H^f + E_{\text{trans}}^f + E_{\text{vib}}^f + E_{\text{rot}}^f$$

$$= E_{\text{av1}}$$

[energy available to the products]



$$\Delta H_r^0 = H^f - H^i \text{ enthalpy change of } R_c$$

fraction of energy in a particular degree of freedom

$$f_{\text{vib}} = E_{\text{vib}}^f / E_{\text{av1}}$$

\* internal energy of molecules can be

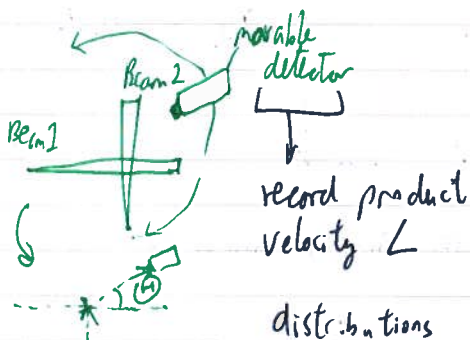
redistributed

## Molecular Beams

- collimated narrow beam of molecules  
[in terms of spatial distribution  
&  
internal dof]  
travelling through a vacuum vessel

### Crossed Molecular Beam expt

- 2 shooting 2 beams of atoms/molecules  
@ each other [beams]  
roughly w/ equal energies  
& quantum states in a vacuum chamber



## Scattering & impact parameter

[non-reactive] Scattering  $\angle_s$

Backward Scattering: scattering  $\angle > 90^\circ$



Forward Scattering: scattering  $\angle < 90^\circ$



Reflection  $\angle_s$

$$\theta = |\chi|$$

Scattering  $\angle$  often depends on  
impact parameter,  $b$

Small  $b$ : "head on" collisions

碰撞

- $\hookrightarrow$  velocity of particles reverses,  
 $\hookrightarrow$  backward scattering

Large  $b$ : "glancing blow"

- $\hookrightarrow$  little deviation in direction  
of particles  
 $\hookrightarrow$  forward scattering

Intermediate impact parameter

- $\hookrightarrow$  between small & large  $b$   
 $\hookrightarrow$  considering not necessarily  
hard sphere collisions

## See Elastic Scattering Between

Noble Gas Atoms in notes

\* Scattering is strongly peaked in the forward direction @  $\theta$

↳ zero degrees

\* P (high impact parameter collision) is greater

\* Broad Maxima at around

20-30 degrees [Or rainbow  $\angle$ ]

around which a range of impact parameters lead to scattering

\* Oscillations in intensity observed

quantum interference  $\Rightarrow$  different trajectories which led to same final state

\* Quick drop off in intensity

@ large  $\theta$

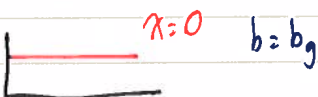
only the very smallest impact parameters lead to large deflections @  $180^\circ$  (very few of these)  
or - rainbow impact parameter: event,  $\frac{d\sigma}{db} \rightarrow 0$

$\rightarrow$  impact parameter @ which

the max -ve deflection  $\angle$  is obtained

$b_g$  - glory impact parameter:

$\rightarrow$  smallest impact parameter for which there is no net deflection



\* Observed deflection  $\angle$

is dependent on the impact parameter

$\Rightarrow$  @ large  $b$ : - attractive part of the potential is sampled

↳ slight attraction between the particles

↳ -ve deflection  $\angle \chi$

$\Rightarrow$  decreasing  $b$ : -ve deflection  $\uparrow\uparrow$  until reaching a maximum

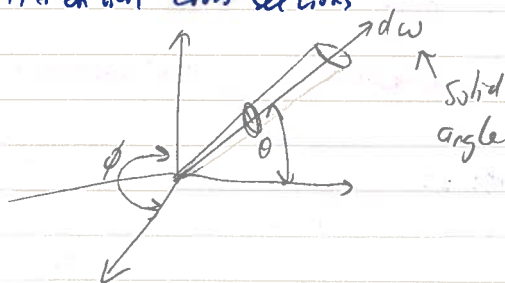
$\Rightarrow$  below  $b_g$ : (smaller impact parameters)

$\Rightarrow$  repulsion dominates & deflection  $\uparrow\uparrow$ s until @  $b=0$ ,  $\chi=180^\circ$

\* from scattering expts.

we can make inferences abt the shape of potential energy surface

## Differential cross sections



measurable rate

⇒ differential reaction cross-section

giving the angular dependence of reaction cross section

$$\sigma_r = \int_0^{2\pi} \int_0^{\pi} \frac{d\sigma_r}{d\Omega} \sin\theta d\theta d\phi$$

Reference frames relatively shift

- lab frame : real world frame of expt

- Centre of mass frame : independent of expt geometry

⇒ frame in which the origin is moving along w/ the velocity of the centre of mass of the system

Suppose  $A + B \rightarrow AB + C$

$$x_{cm} = \frac{m_A x_A + m_B x_B}{M} \quad \text{why?}$$

$$v_{cm} = \frac{m_A v_A + m_B v_B}{M} \quad [M = m_A + m_B]$$

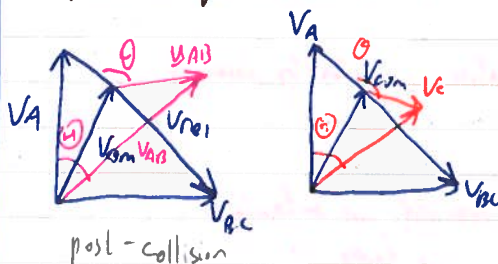
\* total momentum is zero

$$m_A u_A + m_B u_B = 0$$

$$u_A = v_A - v_{cm}$$

$$u_B = v_B - v_{cm}$$

Newton diagrams



\* products are likely to be

isotropically distributed

⇒ the distribution is the differential cross section in centre of mass coordinate

$$v_{cm} = v_A - u_A$$

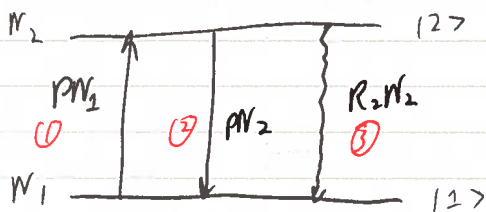
$$v_{cm} = v_A + \frac{m_B}{m_A + m_B} v_{rel}$$





## Power Broadening

Saturation: @ high laser intensities, excitation rate of an optical transition can become larger than the decay rate of the upper lvl  
 ↳ population of the lower level gets depleted



- Suppose  $g_1 = g_2 = 1 \Rightarrow B_{12} = B_{21}$
- optical pump rate:  $P = B_{12}P(\omega)$
- decay rate for upper state:  $R_2$

- ①  $PN_1 = B_{12}P(\omega)N_1$
- ②  $PN_2 = B_{12}P(\omega)N_2$
- ③  $R_2N_2 = A_{21}N_2$

rate of change of populations:

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} = -PN_1 + PN_2 + R_2N_2$$

→ under steady conditions:  $\frac{dN_1}{dt} = \frac{dN_2}{dt} = 0$

$$\Rightarrow PN_1 = (P + R_2)N_2$$

$$PN_1 = (P + R_2)(N - N_1)$$

$$N_1 = N \frac{P + R_2}{2P + R_2}$$

@ v. large pump rates  $P : P \gg R_2$

$N_1 = \frac{N}{2} \Rightarrow N_1 \approx N_2$  // Population inversion not possible

$$a(\omega) = \left[ N_1 - \frac{g_1}{g_2} N_2 \right] \sigma_{12}(\omega)$$

absorption coeff: vanishes i.e. transparent

## LASERS

active medium:

medium in which the EM wave is amplified by stimulated emission

Pumping: process of transferring energy into the active medium to create population inversion for amplification  
 ↳ more molecules in higher  $E$ -state than lower ones

2 methods of pumping

1. Optical pumping

exciting the active medium using a high-intensity light source (flash lamp / laser source)

2. Electrical pumping

creating population inversion using electrical discharge through the active medium

⇒ Stimulated emission is amplified in the optical resonator

⇒ require longitudinal resonator modes (integer of half wavelengths to equal the cavity length  $L_c$ )

$$n \frac{\lambda}{2} = L_c$$

$$\nu = \frac{nc}{2L_c}$$

⇒ output coupled coupler extracts the EM radiation (has a lower reflectivity than other cavity mirrors)

# Pressure Broadening/Collisional Broadening or Impact pressure Broadening

=> lifetime of the excited state can be reduced by collision w/ other gas molecules [quenching]

$$\Gamma_c = \frac{8\pi h \nu^3}{15c^3} \sigma_{eff} C \quad (\text{cm}^{-1})$$

effective collision cross section  
concentration / number density ( $\text{m}^{-3}$ )

$$C = \frac{N_A P}{RT}$$

$$P = \frac{n k_B T}{M_A + M_C}$$

## Doppler Broadening

- inhomogeneous line broadening  
↳ when all molecules in the sample contribute to different degrees of broadening OR if

if their central absorption frequencies are different

in Doppler Broadening, central absorption frequencies are different due to motion them having different velocities

$$\omega_a = \omega (1 - v_z/c)$$

$$\omega' = \omega \frac{1 + v_z/c}{1 - v_z/c}$$

$$= \frac{\omega - v_z t}{1 - v_z/c}$$

$$\omega_a = (1 - v_z/c) \omega$$

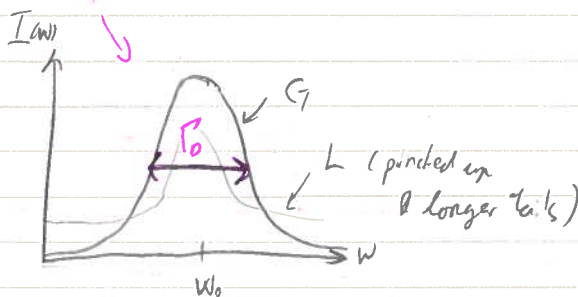


w/ Gaussian Profiles:

$$-\left(\frac{C(\omega - \omega_0)}{\omega_0 v_p}\right)^2$$

$$I(\omega) = I(\omega_0) e$$

$$v_p = \sqrt{\frac{2k_B T}{m}} \quad (\text{most probable velocity})$$



$\Gamma_0$  (FWHM):

$$\frac{\Gamma_0}{\omega_0} = \frac{1}{c} \sqrt{\frac{8k_B T \ln 2}{m}} \quad (\text{dimensionless})$$

$$= 7.16 \times 10^{-7} \sqrt{\frac{T}{M}} \quad \frac{M[\text{u}]}{M[\text{u}]} \quad M = \frac{M}{1000 N_A}$$

$$= \frac{\Gamma_0 [\text{cm}^{-1}]}{\omega_0 [\text{cm}^{-1}]}$$

## Natural line broadening

- excited states decay as a result of a dynamical process (eg. spontaneous emission)

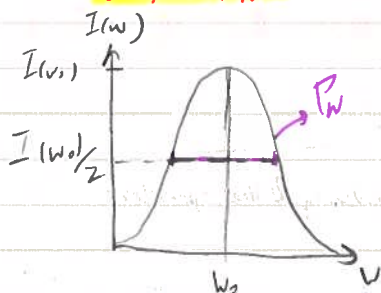
if excited state decays according to a first order law  $\Rightarrow$



shape of spectral line can be described by a Lorentz function

$$I(\omega) = \frac{I(\omega_0) \Gamma_N^2}{(\omega - \omega_0)^2 + \Gamma_N^2}$$

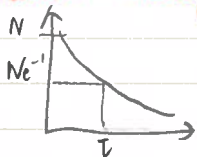
natural line broadening or lifetime broadening



$\Gamma_N$ : Full Width @ Half Maximum (FWHM)  
to characterize the linewidth

$\hookrightarrow$  arises from finite lifetime  $\tau$  of the excited state of the transition (natural linewidth)

$\tau$ : time it takes for the excited-state population to decay  $1/e$  of its initial value



$$\Gamma_N = \tau^{-1} \text{ (an angular frequency)}$$

$\Rightarrow$  tells us about decay processes

IF (excited state only decays)

by spontaneous emission

$$P_{N1} = A_{1k}$$

$$-\frac{dN_2}{dt} = A_{21} N_2$$

$$N_2 \in [N_2, N_2] \\ t \in [0, \infty)$$

$$-\int \frac{dN_2}{N_2} = \int A_{21} dt$$

$$-\ln N_2 \Big|_{N_2} = [A_{21} t]_0$$

$$\Rightarrow -\ln \frac{N_2}{N_2} = -\ln \frac{1}{e} = 1 = A_{21} \tau$$

$$A_{21} = \tau^{-1} = \Gamma_N$$

Homogeneous line broadening

$\Rightarrow$   $\therefore$  lifetime broadening is a consequence of the decay dynamics of the excited states of the molecule  
 $\therefore \hookrightarrow$  all molecules in the macroscopic sample contribute the same amount of broadening to the spectral lines

$$A_{1k} = \tau^{-1} = \Gamma_N$$

## Relationship between the Einstein coefficients

in thermal eq<sup>m</sup>:

$$N_i = N \frac{g_i}{Z} e^{-\frac{E_i}{k_B T}}$$

$i=1,2$  w/ the partition function:

$$Z = \sum_i g_i e^{-\frac{E_i}{k_B T}}$$

↳ degeneracy of levels  $|1\rangle$  &  $|2\rangle$

$$N = \sum_i N_i = N_1 + N_2$$

↳ total number of molecules per unit volume

or

Number density

for 2-level system:

Boltzmann distribution of populations is:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\frac{E_2 - E_1}{k_B T}}$$

⇒ @ eq<sup>m</sup> the total emission rate must be equal to the absorption rate

$$(B_{21} \rho(\nu) + A_{21}) N_2 = B_{12} \rho(\nu) N_1$$

emission

absorption

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\frac{(E_2 - E_1)}{k_B T}} = \frac{g_2}{g_1} e^{-\frac{h\nu}{k_B T}}$$

\* solving for  $\rho(\nu)$

$$N_2 B_{21} \rho(\nu) + A_{21} N_2 = B_{12} \rho(\nu) N_1$$

$$B_{12} \rho(\nu) N_1 - N_2 B_{21} \rho(\nu) = A_{21} N_2$$

$$\rho(\nu) = \frac{A_{21} N_2 / B_{21}}{(B_{12} N_1 - N_2 B_{21})}$$

$$\rho(\nu) = \frac{A_{21} / B_{21}}{\frac{B_{12} N_1}{B_{21} N_2} - 1}$$

$$\rho(\nu) = \frac{A_{21} / B_{21}}{\frac{B_{12} g_1}{B_{21} g_2} e^{\frac{h\nu}{k_B T}} - 1} = \frac{8\pi h \nu^3}{c^3 (e^{\frac{h\nu}{k_B T}} - 1)}$$

$$\Rightarrow \frac{A_{21} / B_{21}}{\frac{B_{12} g_2}{B_{21} g_1}} = \frac{8\pi h \nu^3}{c^3}$$

$$\Rightarrow \frac{A_{21} B_{12} g_2}{B_{21} B_{12} g_1} = \frac{8\pi h \nu^3}{c^3} \quad \frac{B_{21} g_2}{B_{12} g_1} = 1$$

$$A_{21} = \frac{8\pi h \nu^3}{c^3} B_{21}$$

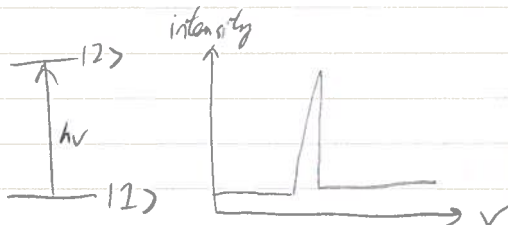
$$B_{12} = \frac{g_2}{g_1} B_{21}$$

Spectral line broadening & line profiles

spectrum: representation of  $\nu$  /  $\lambda$  /  $E$   
dependent absorption cross-section  
of a molecule / atom

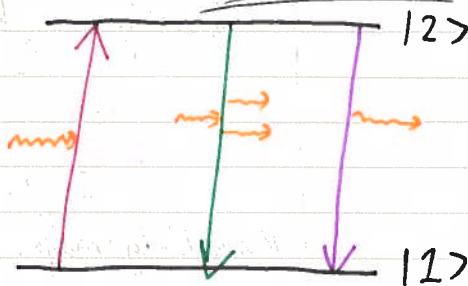
↳ tells us about the energy lvl structure  
& internal dynamics of a molecule

\* line of a spectrum has finite width  
↳ shape & width of spectral lines can be affected:





Level populations, absorption & emission  $\Rightarrow$  Einstein Model



What goes up must come down

## 1. Induced absorption

$\hookrightarrow$  absorption of a photon  
of energy  $\Rightarrow$  excitation from  $|1\rangle$  &  $|2\rangle$

$$-\frac{dN_1}{dt} = \frac{dN_2}{dt} = B_{12} \rho(\nu) N_1$$

"rate constant"

$B_{12}$  rate coefficient // Einstein coefficient  
for induced absorption ( $\text{m}^3 \text{J}^{-1} \text{s}^{-2}$ )

$\hookrightarrow$  (probability per second that  
a molecule will absorb a photon  
& be excited from  $|1\rangle$  &  $|2\rangle$ )

## 2. Stimulated emission: reverse of the upper case

$\Rightarrow$  radiation field induces a  
de-excitation of the upper level  
& generates a photon of frequency  $\nu$ :

$$-\frac{dN_2}{dt} = \frac{dN_1}{dt} = B_{21} \rho(\nu) N_2$$

$\star$  photon is emitted in the same mode  
as the radiation field that caused  
the emission

$\Rightarrow \nu$  &  $k$  are identical  
to those of the  
inducing radiation wave

$\star$  photon emitted in a particular direction

## 3. Spontaneous emission:

$\rightarrow$  statistical decay  
from higher to lower state  
to emit a photon:

$$-\frac{dN_2}{dt} = \frac{dN_1}{dt} = A_{21} N_2$$

$\star$  probability for spontaneous emission  
of a photon is independent of  
the external radiation field

$\rightarrow$  only depends on

$\rightarrow$  structure of molecule

$\rightarrow$  properties of transition  
from  $|1\rangle$  to  $|2\rangle$

$\Rightarrow$  usually isotropic, no particular  
direction is favoured

# LASERS:

EM Radiation:  $\underline{E} \perp \underline{B}$

for the electric field:

$$\underline{E} = A_0 e^{i(\omega t - \underline{k} \cdot \underline{r})}$$

$$|\underline{k}| = k \quad \underline{r} = \underline{r}(x, y, z)$$

$$k = \frac{2\pi}{\lambda} \text{ (angular wavenumber)}$$

$$\omega = 2\pi\nu$$

↳ choosing  $z$  as the axis of propagation

$$\underline{E} = A_0 e^{i(\omega t - k_z z)}$$

↳ for the real-valued superposition obtained from above & its complex conjugate

$$\begin{aligned} \underline{E} &= A_0 e^{i(\omega t - k_z z)} + A_0^* e^{-i(\omega t - k_z z)} \\ &= \underline{E} + \underline{E}^* \end{aligned}$$

$$= \underline{E}_0 \cos(\omega t - k_z z)$$

$A_0 = 2A_0$

↳ resolving  $A_0$  into 2 components

$$\underline{A}_0 = A_{0x} e^{i\phi_x} + A_{0y} e^{i\phi_y}$$

\* orientation of  $\underline{A}_0$  wrt direction of propagation  $\Rightarrow$  polarization

eg. Linearly polarized  $\Rightarrow \underline{E}$  oscillates in fixed plane

Circularly "  $\Rightarrow \underline{E}$  oscillates a plane rotating about a fixed axis

Unpolarised "  $\Rightarrow$  components of  $\underline{A}_0$  are uncorrelated & fluctuate randomly

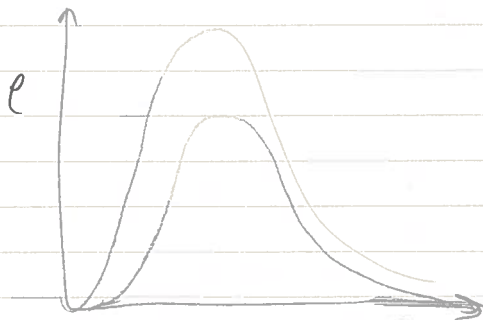
Intensity:  $(W m^{-2})$

$$I = c \epsilon_0 E_0^2$$

$I \propto E_0^2$

Black Body radiation & Planck's Law:

$$\rho(\nu, T) d\nu = \frac{8\pi h \nu^3}{c^3 (e^{\frac{h\nu}{k_B T}} - 1)} d\nu$$



$\rho(\nu) \Rightarrow$  spectral energy density

Diffusion w/ convection:

- transfer of molecules due to

a net motion of the

surrounding fluid solvent

$$J_{conv} = \frac{[B]v A \Delta t}{A \Delta t} = [B]v$$

$$\frac{\partial [B]}{\partial t} = \frac{J_{conv} - J_{conv}'}{\lambda}$$

$$= \frac{[B]v}{\lambda} - \left( [B] + \frac{\partial [B]}{\partial x} \lambda \right) \frac{v}{\lambda}$$

$$= -v \frac{\partial [B]}{\partial x} \quad \begin{array}{l} * \text{assuming} \\ \text{constant flow rate} \end{array}$$

generalized diffusion eq<sup>n</sup>

$$\frac{\partial [B]}{\partial t} = D_B \frac{\partial^2 [B]}{\partial x^2} - v \frac{\partial [B]}{\partial x}$$

Material-Balance Eq<sup>n</sup>

description of reacting, diffusing  
& convecting systems

$$\frac{\partial [B]}{\partial t} = -k_r [B]$$

$$\frac{\partial [B]}{\partial t} = D_B \frac{\partial^2 [B]}{\partial x^2} - v \frac{\partial [B]}{\partial x} - k_r [B]$$

$$\partial_t [B] = D_B \nabla^2 [B] - v \nabla [B] - k_r [B]$$

Mass balance / diffusion eq<sup>n</sup>

$$\frac{\partial C_i}{\partial t} = \underbrace{D \nabla^2 C_i}_{\text{Diffusion}} - \underbrace{v C_i}_{\text{Convection}} + \underbrace{R_i}_{\text{Chemical rxns}}$$

Diffusion Control:

$$\frac{\partial C_i}{\partial t} \sim D \nabla^2 C_i$$

Degradation control / affinity control

$$\frac{\partial C_i}{\partial t} \sim R_i$$

Immobilized factors

$$\frac{\partial C_i}{\partial t} > 0$$

$C_i = \text{constant}$

# Diffusion

net motion of molecules from a region of high concentration [high chemical potential] to a region of low concentration [low chemical potential]

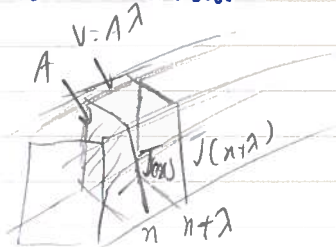
Fick's first law of diffusion:

$$J = -D_B \frac{\partial [B]}{\partial x}$$

↑ flux      ↑ diffusion coefficient      gradient of molar concentration

- only valid for when the concentration profile in space has reached a steady state [it does not change over time]  
[B] is not changing

Fick's 2nd Law:



$$\frac{\partial [B]}{\partial t} = \frac{JA}{A\lambda} = \frac{J}{\lambda}$$

$$\frac{\partial [B]}{\partial t} = -\frac{J'}{\lambda} \text{ leaving}$$

$$\frac{\partial [B]}{\partial t} = \frac{J - J'}{\lambda}$$

$$J - J' = -D_B \frac{\partial [B]}{\partial x} + D_B \frac{\partial [B]'}{\partial x}$$

using Fick's 1st Law

$$\frac{\partial [B]}{\partial t} = [B] + \frac{\partial [B]}{\partial x} \lambda$$

$$\begin{aligned} \hookrightarrow J - J' &= -D_B \frac{\partial [B]}{\partial x} + D_B \frac{\partial}{\partial x} \left( [B] \frac{\partial [B]}{\partial x} \lambda \right) \\ &= D_B \lambda \frac{\partial^2 [B]}{\partial x^2} \end{aligned}$$

$$\Rightarrow \frac{\partial [B]}{\partial t} = D_B \frac{\partial^2 [B]}{\partial x^2}$$

for a diffusion-controlled Rx

$$k_d = 4\pi R^* D_B N_A$$

$$D_A = \frac{kT}{6\pi\eta R_A}$$

$\eta$ : medium of viscosity

$$D_B = \frac{kT}{6\pi\eta R_B}$$

$R_i$ : hydrodynamic radius

assuming

$$\Rightarrow R_A = R_B = \frac{1}{2} R^*$$

$$k_d = \frac{8RT}{3\eta}$$

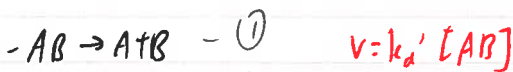
why???



Reactants in solutions  
from gas  $\rightarrow$  liquids / aqueous  
[larger number density]

Cage effect: where two molecules linger  
each other  $\therefore$  of the presence  
of solvent molecules

Setting up a simple kinetics scheme



$$\frac{d[AB]}{dt} = k_a [A][B] - k_a' [AB] - k_d [AB] = 0$$

$\star$  assuming steady state approximation

$\hookrightarrow$  concentration of intermediate  
molecules is small & constant  
during the course of the Rx

$$[AB] = \frac{k_a [A][B]}{k_a + k_a'} \quad \left| \quad k_r = \frac{k_a k_d}{k_a + k_d'} \right.$$

$$\frac{d[P]}{dt} = k_a [A][B] = k_r [A][B]$$

Limiting cases:

2. if the rate which reactants separate  
is slower than rate of when they react

$$\Rightarrow k_d' \ll k_a$$

$$\Rightarrow k_r \approx \frac{k_a k_d}{k_a} = k_d \quad [\text{quick Rx}]$$

orders of 100s of pico seconds  
or more

eg. Acid-Base Rx

2. Activation - controlled Rx

$\Rightarrow$  when a substantial activation  
energy is involved in  
the Rx  $AB \rightarrow P$

$$\Rightarrow k_a \ll k_d'$$

$$k_r \approx \frac{k_a k_d}{k_d} = k_a K \quad \uparrow$$

eq<sup>n</sup>/constant

## Early Barrier

transition state is closer to the reactant valley on the PES

- attractive PES / "entrance channel"

↳ exothermic  $\Delta H > 0$  available for products



Sometimes even when the system has enough energy to react, a reaction may not occur  
∴ available energy is not in the "correct" degree of freedom



- preferably translation energy [reactants]

- energy form of the products:

↳ highly vibrationally excited  
- relatively low translation energy

(why?)



⇒ produce vibrationally excited HF molecules

↳ in the  $v=2, 3, 4$  vib state

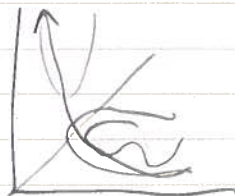
Population inversion ⇒ more molecules are in high vib states than in low vib states

## Late Barrier

transition state is closer to the product valley

- repulsive PES / "exit channel"

↳ endothermic



- preferably vibrational energy [reactants]

- energy form of the products:

↳ High translational energy  
- relatively low vib. excitation



## Case study III:

### Competing R mechanisms

- produces an almost forward-backwards symmetric distribution of products

[not completely symmetric]

- ↳ small preference for backwards scattering as the product molecules are also formed through a 2nd different R channel

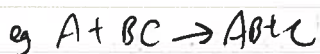
### Potential energy surfaces (PES)

for discussing results  
& calculating collision-cross-sections

[obtained from computer  
simulation methods]

$$F(r) = -\nabla V(r)$$

- Adiabatic separation of e<sup>-</sup> & nuclear motion  
↳ Born-Oppenheimer Approx



$$N=3 \Rightarrow \text{dof} = 3N - 6 = 3 \therefore 3 \text{ coordinates}$$

i) distance  $BC \Rightarrow$  length of bond which breaks in the  $BC$  molecule

ii) distance  $AB \Rightarrow$  length of new bond which is forming during the reaction

iii) Bond angle ( $\beta$ ) between  $BC$  &  $AB$  bonds

Minimum energy pathway:  
the route you follow

[most energetically favourable]

### MEP:

- ↳ steepest descent path  
connecting the transition w/  
the reactants & products  
or (ZVPA-C)

Path orthogonal to the eq. potential contours of a PES  
that connects the energy minima  
through a saddle point from  
which it slopes downwards along  
the steepest descending line  
in a  $3N-6$  configurational space  
↳ number of nuclei  
in the reacting system

### Transitional state (saddle point)

- ↳ highest energy point  
along the minimum energy pathway

### Polyanyi's Rules:

- symmetric
- early
- late

just a  
qualitative observation

Uniform distribution  $\leftrightarrow$  long-lived  
intermediate states

## Case 1: Harpoon Reactions:

- typically have large impact parameter & large  $R_x$  cross-section

$\Rightarrow$  lead to forward scattering

- a more general class of  $R_x$   
 $\hookrightarrow$  stripping  $R_x$ s

$\hookrightarrow$  the attacking atom/radical carries off part of the attached molecule in the forward direction



$\hookrightarrow$  rebound mechanism

- [backward scattering]  
 - had a smaller  $R_x$  cross section than  $K + I_2 \rightarrow KI + I$   $R_x$

$\hookrightarrow$   $\therefore CH_3I$  has a -ve e $\phi$  affinity  
 $\hookrightarrow$  K must go v. close to  $CH_3I$   
 $\hookrightarrow$  it can transfer its e $\phi$  to it

Case 2: Long-lived intermediates (indirect  $R_x$ )  
 Some  $R_x$ s involve transition complexes that survive for a relatively long time

- assuming reactive complex is incredibly short lived

\* long lived transition complex

$\hookrightarrow$  ~~some~~ one which survives for a few rotational periods [in picoseconds]

comparing to the mutual rotational periods of the reactants

eg.



indirect  $R_x$ s proceed via the formation of a long-lived  $R_x$  complex

$\Rightarrow$  collision partners lose part/all of the memory of their original orientation ???

$\Rightarrow$  forward-backward symmetry

in the distribution of the scattered  $BrO$  product

Sprinkler model:

$\nearrow$  why  
 it is forget

model for a  $R_x$  in which the reactive complex sticks together for several rot periods  
 $\therefore$  making a uniform distribution in the plane of the collision of the scattered product

DCS in scattering & azimuthal  $\angle$ s:

$$\frac{d\sigma_r}{d\omega} = \frac{d\sigma_r}{\sin\theta d\theta d\phi}$$

avg all azimuthal orientations:

$$\frac{d\sigma_r}{d\omega} = \frac{d\sigma_r}{2\pi \sin\theta d\theta}$$

\* scattering & azimuthal  $\angle$ s are independent

$\nearrow$  how to derive

$\Rightarrow$  if no longer true [has]

$\Rightarrow$  give rise to forward backward symmetry



## Basic principles of lasing

absorption coeff:  $\alpha(\nu)$

$$\alpha(\nu) = \left[ N_1 - \left( \frac{g_1}{g_2} \right) N_2 \right] \sigma_{12}(\nu)$$

for population inversion:  $\frac{g_1}{g_2} N_2 > N_1$

$$\Rightarrow \alpha(\nu) < 0$$

[necessary for the rate of stimulated emission to exceed the rate of stimulated absorption]

$\Rightarrow$  using the Beer-Lambert law:

$$\ln\left(\frac{I_{\text{output}}}{I_{\text{input}}}\right) = \alpha(\nu) c L$$

$\downarrow$  output       $\uparrow$  input  $\alpha(\nu) c L$

$$I = I_0 e$$

when  $\alpha < 0$

$$e^{\alpha(\nu) c L} > 1$$

$\hookrightarrow$  increasing the output

$\rightarrow$  gain factor per round-trip ( $2L$ )

$$G(\nu) = \frac{I(\nu, 2L)}{I_0(\nu)} = e^{-2\alpha(\nu)L}$$

$\rightarrow$  loss coeff: parameterize general losses due to imperfect mirror reflectivity

$$I = I_0 e^{-\gamma}$$

$\Rightarrow$  Total intensity:

$$I(\nu, 2L) = I_0(\nu) e^{-2\alpha(\nu)L - \gamma}$$

\* For amplification

$$-2\alpha(\nu)L > \gamma$$

Obtaining a threshold condition for the population inversion

$\Rightarrow$  rewriting  $\alpha(\nu)$

$$\alpha(\nu) = - \frac{DN}{\sigma_{12}(\nu)} = - \left( \frac{g_1}{g_2} \right) N_2 - N_1$$

$$DN > DN_{\text{thresh}}$$

$$- \frac{\alpha(\nu)}{\sigma_{12}(\nu)} > \frac{\gamma}{2\sigma_{12}(\nu)L}$$

$DN_{\text{thresh}}$ : minimum population diff necessary to achieve amplification  $I > I_0$

## Properties of Laser radiation

coherence & directionality:

$\rightarrow$  photons created by stimulated emission have the same phase,  $\nu$ , propagation dir & polarization as those that stimulated them

$\rightarrow$  coherence enhanced by resonator which forces the photon to propagate along the resonator axis

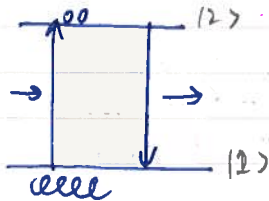
$\hookrightarrow$  amplifies radiation in a narrow frequency interval corresponding to one of the resonator modes

Brightness: from amplification, usually must more intense than light from thermal sources

Monochromaticity: from frequency selectivity of the resonator, laser is generated in very small frequency intervals  $\rightarrow$  finite width of the spectral emission determines the range of allowed frequencies

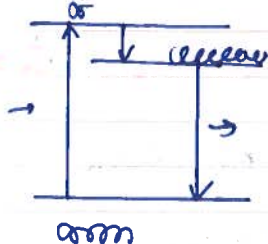
For population inversion for lasing:

a) 2 level system  $\rightarrow$  PI  
 $\times$  PI  $\Delta T$



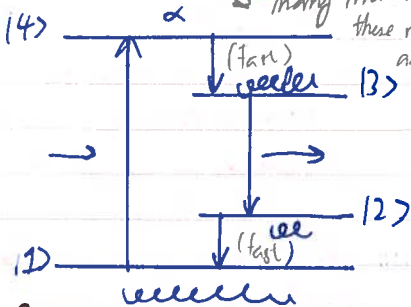
- $N_1 = N_2$  is possible
- population NOT possible in version

b. 3 Level system:  $\checkmark$  PI  
 Ruby



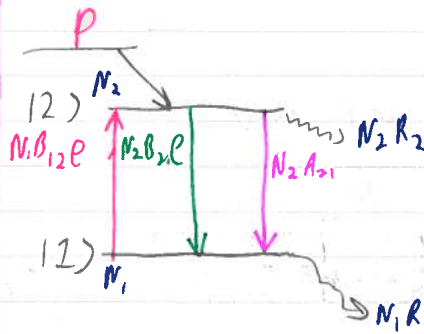
$\rightarrow$  PI requires more than half of the population to be transferred from the ground state into the upper lasing level

c. 4 level system:  $\checkmark$  PI  
 many materials fulfill these requirements and suitable for lasing medium



- lower lasing level |2> is not populated thermally
- efficient population transfer
- 1. from |4>  $\rightarrow$  |3> by a fast relaxation process
- 2. from |2>  $\rightarrow$  |1>

Rate eq<sup>s</sup> for 4-level system



$\Rightarrow$  consider equal statistical weights  
 $g_1 = g_2$

$\Rightarrow$  rate = P  $\because g_1 = g_2$   
 $B_{12} = B_{21}$

$\Rightarrow P = nh\nu$   
 $\swarrow \quad \searrow$   
 spectral energy density photon number density

$$(i) \frac{dN_1}{dt} = (N_2 - N_1)B_{21}P + N_2A_{21} - N_1R_1$$

$$(ii) \frac{dN_2}{dt} = P + N_1B_{12}P - N_2B_{12}P - N_2A_{21} - N_2R_2$$

$$= P - (N_2 - N_1)B_{21}P - N_2A_{21} - N_2R_2$$

$$\frac{dN_2}{dt} = P - (N_2 - N_1)B_{21}P - N_2A_{21} - N_2R_2$$

$$(iii) \frac{dN}{dt} = -\beta N + (N_2 - N_1)B_{21}P$$

$\beta = (s^{-1})$

rate constant for laser cavity losses

$$\delta = \frac{TP}{L} \quad (\delta: \text{loss per round trip})$$

$$T = \frac{2Lc}{c} \rightarrow \text{length of laser cavity}$$

Under steady-state / stationary condition

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = \frac{dN}{dt} = 0$$

(i) + (ii)

$$\Rightarrow N_2 B_{21} P - N_1 B_{21} P + N_2 A_{21} - N_1 P_1 + P - N_1 B_{21} P + N_1 B_{21} P - N_2 A_{21} - N_2 R_2 = 0$$

$$P = N_1 R_1 + N_2 R_2$$

(pump rate P compensates for loss rates)

ii + iii:

$$\Rightarrow P - (N_2 - N_1) B_{21} P - N_2 A_{21} - N_2 R_2 + \beta_1 + (N_2 - N_1) B_{21} P = 0$$

$$P = \beta_1 + N_2 (A_{21} + R_2)$$

$$N_1 R_1 + N_2 R_2 = \beta_1 + N_2 A_{21} + N_2 R_2$$

$$N_1 R_1 = \beta_1 + N_2 A_{21}$$

relaxation rate for lower level must be larger than its feeding rate due to spontaneous emission from upper level  $N_2 A_{21}$

1) finding the population difference:

$$\Delta N_{\text{stat}} = N_2 - N_1 = \Delta N$$

i)  $\times R_2$ :

$$\Delta N B_{21} R_2 + N_2 A_{21} R_2 - N_1 R_1 R_2 = \frac{dN_1}{dt} R_2$$

(ii)  $\times R_2$

$$\frac{dN_2}{dt} = P R_1 - \Delta N B_{21} P - N_2 A_{21} R_2 - N_2 R_2 R_1$$

$$P R_1 - \Delta N B_{21} P R_1 - N_2 A_{21} R_1 - N_2 R_2 R_1 - \Delta N B_{21} R_2 P - N_2 A_{21} R_2 + N_1 R_1 R_2 = 0$$

$$N_1 R_1 R_1 + N_2 R_2 R_1 - \Delta N B_{21} P (R_1 + R_2)$$

$$- N_2 A_{21} (R_1 + R_2) - R_1 R_2 (N_2 - N_1) = 0$$

$$N_1 R_1 R_1 + N_2 R_2 R_1 - N_2 R_1 A_{21} - R_2 N_2 A_{21} + \Delta N A_{21} R_1 = \Delta N (R_1 + R_2) B_{21} P + R_1 R_2$$

$$N_1 R_1 R_1 + N_2 R_2 R_2 - N_2 R_1 A_{21} - N_2 R_2 A_{21} + N_2 R_2 A_{21} - N_2 R_2 A_{21}$$

$$P R_1 - A_{21} (N_1 R_1 + N_2 R_2) = \Delta N (R_1 + R_2) B_{21} P + R_1 R_2$$

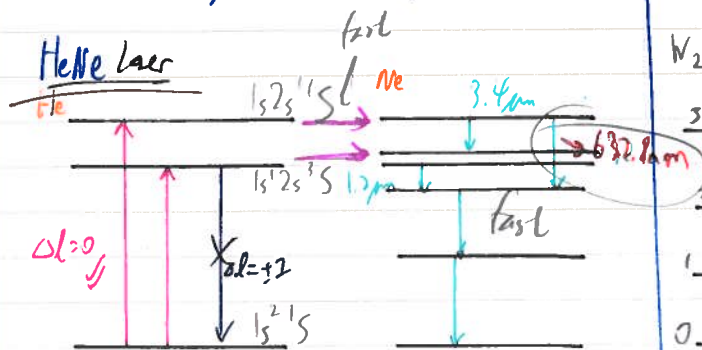
$$\Rightarrow \Delta N = \frac{P (R_1 - A_{21})}{B_{21} P (B_1 + B_2) + R_1 R_2 + A_{21} R_1}$$

for population inversion  $\Delta N_{\text{stat}} > 0$  can only be obtained if  $R_1 > A_{21}$

2) the decay rate from the lower level  $\checkmark$  repopulation rate from upper level



## Laser systems examples



why is it ok for  $\Delta l = 0$  when  $\uparrow$   
but not for  $\downarrow$ ?

- active medium: He:Ne  
= 10:1

Can use prism / diffraction grating to pick out the light we want

$\Rightarrow$  electronically excited states of He  
 $\hookrightarrow$  generated by collision w/ e<sup>-</sup>s  
in an electrical discharge  
a.k.a pump

(He<sup>\*</sup>): states decay rapidly until population  
is trapped in metastable  $1s^2 2s^1 S$  &  $1s^2 2s^1 S'$

\* optical selection rules forbid states  
radiative decay to the  $1s^2 1S$  ground state  
 $\hookrightarrow$  long-lived

(Ne<sup>\*</sup>) these metastable states l.u.s of He  
are in near-resonance  
with  $(1s^2 2s^1 2p^5 4s^1) \& (1s^2 2s^1 2p^5 5s^1)$  in Ne  
 $\Rightarrow$  energy is transferred efficiently  
from He to Ne by collisions

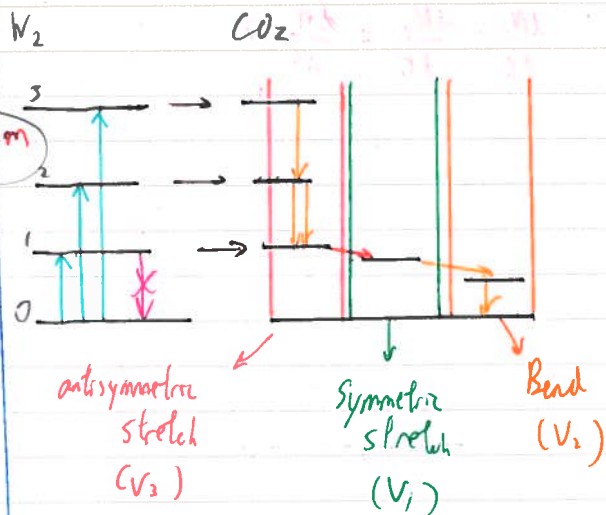
$\rightarrow$  several lasing transitions in Ne to  
lower-lying levels

\* \* 6p-3p @ 632.8nm (red) most  
important

$\rightarrow$  lifetimes of p-levels ( $\sim 10^{-8}$ s) are an order  
of magnitude less than those of s-levels ( $\sim 10^{-9}$ s)  
 $\hookrightarrow$  fulfills requirement for lasing

$$(R_1 > A_{21})$$

## CO<sub>2</sub> lasers



c) most important gas laser  
 $\hookrightarrow$  efficiency  $\approx 20\%$   
 $\rightarrow$  peak power up to 80kW  
in continuous wave (CW) operation  
 $\hookrightarrow$  used in welding & laser surgery

- active medium: mixture of  
CO<sub>2</sub>, N<sub>2</sub> & He

$\Rightarrow$  pump: electrical discharge which  
excites N<sub>2</sub> to  $v=1$  vib state

$\Rightarrow$  lack of a dipole moment forbids  
optical transitions back to ground state

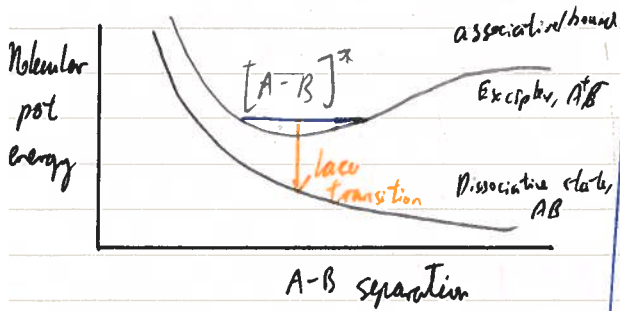
$\Rightarrow$  efficient collision quenching  
transfers energy from N<sub>2</sub> of the 6th l.u.s  
of the first asymmetric stretch of CO<sub>2</sub>,  $v_3$

$\rightarrow$  lower lasing are  $v_2$  &  $v_1$   
vib modes

$\Rightarrow$  lower lasing levels decay to  
ground state by  
collision w/ He



## Excimer Lasers (2-level laser system)



industrial excimer lasers employ  
halogen rare gas dimers



Most powerful UV-laser available  
(351-175 nm)

⇒ active medium: - halogen  
( $\text{X}_2 = \text{F}_2, \text{Cl}_2$ )  
- rare gas ( $\text{R} = \text{Ar}, \text{Kr}, \text{Xe}$ )  
- buffer gas ( $\text{Ne}$ )  
- inert gas ( $\text{He}$ )

⇒ pump: electrical discharge which  
excites the components of gas mixture  
to form the excimer / exciplex:



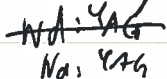
⇒ laser emission occurs from the  
strongly bound excited state



the dissociative ground state

in which the molecule cannot exist

See also tunable dye lasers,

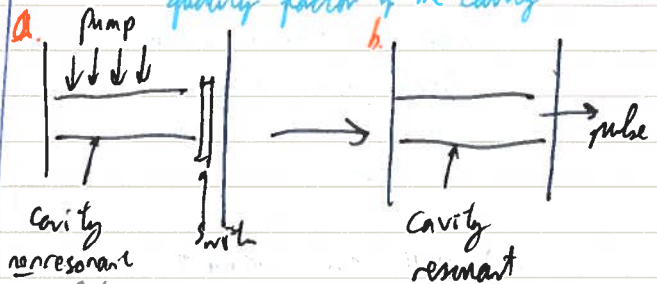


Ti: Sapphire

## Pulsed operation of lasers:

### 1. Q-switching

→ pulses of ~10 ns duration  
→ relies on a fast change of  
quality factor of the cavity



limited by switching speed of  
the high voltages required to  
cells sandwiched between  
a pair of crossed polarisers

### 1. Q is low

↳ substantial population inversion  
is allowed to build up

⇒ excited state is populated is populated  
while the cavity is non-resonant

2. A rapid switch to high Q then  
depletes the upper manifold.

↓  
resonance characteristic suddenly  
restored

↓  
stimulated emission releases energy  
as a giant pulse  
↳ short, intense pulse of laser  
radiation

## 2. Mode Locking

→ shorter pulses ( $\text{ps} \sim 10\text{fs}$ )

- multimode operation

↳ if freq-selective elements are not included in a laser resonator

↳ lasing will occur on several longitudinal modes within the spectral gain profile.

⇒ modes are incoherent

- if coherent (phase of resonator modes have a fixed relationship)

↳ coherent superposition can be made  
⇒ modes can interfere to generate very short laser pulses.

$$I(t) \propto E^*(t)E(t) = E_0^2 \frac{\sin^2(N\omega_c t/2L)}{\sin^2(\omega_c t/2L)}$$

min(pulse duration)

$$\hookrightarrow \tau = \frac{a}{\Delta\omega}$$

↑ gain bandwidth  
to.

a. depends on shape of laser pulse  
 $a \approx 0.441$  for Gaussian temporal profile.

## Non linear optics

→  $E$  interacts w/ charge distribution of atoms in the medium

↳ induces a dielectric polarisation

$$\underline{P} = \underline{P}^{(1)} + \underline{P}^{(2)} + \dots$$

$$= \sum_{n=1}^N \underline{P}^{(n)} = \epsilon_0 \sum_{n=1}^N \underline{\chi}^{(n)} E^n$$

$$\text{usually: } \underline{E} = \underline{E}_1 \cos(\omega_1 t - k_1 z) + \dots$$

## Laser Spectroscopy:

1. Laser Absorption spec
2. Cavity ring-down
3. Laser-induced fluorescence
4. Resonance-enhanced multiphoton-ionisation
5. Cooling in supersonic molecular expansions

Photofragment  $\text{KIE}$  release spectroscopy  
Suppose  $A \xrightarrow{h\nu} B + C$



#### 4. Intersystem crossing (ISC)

→ non-radiative change in electronic state

→ change in spin multiplicity  $\Delta S \neq 0$

→ Mononuclear:

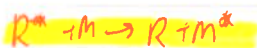
$$\Rightarrow \text{Rate} = k_{ISC} [R^*]$$

$$\Rightarrow k_{ISC} (T_1 \rightarrow S_0) \sim 10^5 - 10^8 \text{ s}^{-1}$$

$k$  depends exp (energy gap)

#### 5. Intramolecular energy transfer (IET)

→ electronic excitation transferred to another molecule



→ bimolecular

$$\text{Rate} = k_{IET} [R^*][M]$$

$$k_{IET} \sim 10^3 - 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

#### 6. Physical Quenching (Q)

→ loss of electronic excitation via collision w/ another molecule



→ bimolecular

$$\text{Rate} = k_q [R^*][Q]$$

See Jablonski diagram

&

energy state diagrams

#### Efficiencies



I Overall quantum yield:

$$\Phi = \frac{\# \text{ Reactants consumed}}{\# \text{ photons absorbed by R}}$$

II Overall product quantum yield:

$$\Phi = \frac{\# \text{ products produced}}{\# \text{ photon absorbed by R}}$$

\* assuming overall quantum yield refers to consumption of reactants

III Primary quantum yield for each specific process:

$$\phi_i = \frac{\# \text{ events of type } i}{\# \text{ photons absorbed by R}}$$

(for efficiencies of individual photochemical & photophysical process)

→ assuming  $R^*$  is formed only by absorption of photon & not by any secondary process

\*

$$\phi_f + \phi_{IC} + \phi_r + \phi_{ISC} = \frac{N_f + N_{IC} + N_r + N_{ISC}}{N_{abs}} = 1$$

$$\phi \rightarrow s = \sum_i \phi_i = 1$$

$$\phi_i = \frac{\text{rate of process } i}{\text{rate of photon absorption}} = \frac{\text{rate of } i}{I_{abs}}$$



Stern Volmer eq<sup>n</sup>:

$$\frac{I}{I_0} = \frac{1}{1 + k_f \tau_{s,0} [Q]}$$

Can use steady-state approx

$$\frac{d[S_1]}{dt} = 0$$

intensity of fluorescence decays  
~~exp<sup>ly</sup>~~ exponentially w/ time

$$I_f = I_0^{(0)} e^{-\frac{t}{\tau_{s,1}}}$$

$$\phi_f = \tau_{s,1} k_f$$

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Radiative transitions

$$Z_{AB} = \frac{\sigma v_{rel} N_A^2 [A][B]}{2}$$

$$\sigma = 0.43 \times 10^{-19} \text{ m}^2$$

$$v_{rel} = \sqrt{\frac{8k_B T}{\pi \mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m}{2}$$

$$= 671.191802 \text{ ms}^{-1} = \frac{28.02}{2}$$

$$\approx 474.492795 \text{ } 1401 \text{ u}$$

$$Z_{N_2} = 8.37 \times 10^7 \text{ m}^3 \text{ s}^{-1}$$



Exercise 2:

$$6.7 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$A = \pi r_{CH_3}^2$$

$$= 6.7 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$r_{CH_3} = \sqrt{\frac{4 \times 10^{-19}}{\pi}} = 3.5625 \times 10^{-10} \text{ m}$$

$$k_r = P \sigma v_{rel} N_A$$

$$r_{H_2} = \sqrt{\frac{2.7 \times 10^{-19}}{\pi}} = 2.971615 \times 10^{-10} \text{ m}$$

$$P = \frac{6.7 \times 10^6}{(1.3 \times 10^{-18})(1847)/(6.07 \times 10^{23})}$$

$$= 24.5 \times 10^3$$

$$A = (\pi r_{CH_3} + r_{H_2})^2 \pi = 1.3 \times 10^{-18} \text{ m}^2$$

$$v_{rel} = \sqrt{\frac{8k_B T}{\pi \mu}}$$

$$\mu = \frac{15 \times 2 \text{ u}^2}{(15+2) \text{ u}}$$

$$= \frac{30 \text{ u}}{17}$$

$$= \sqrt{\frac{8(1.38 \times 10^{-23})(300)}{\pi \mu}}$$

$$= 1847 \text{ ms}^{-1} = 1900 \text{ ms}^{-1}$$