

PHOTOCHEMISTRY NOTES

1st Law (Grotthus-Draper Law) – “Only absorbed radiation produces chemical change”.

Exception – inelastic scattering of X- or γ -rays (electronic Raman effect).

2nd Law (Stark-Einstein Law) – “The number of excited molecules produced is equal to the number of quanta absorbed”.

Exceptions – two-photon or multiphoton absorption (lasers).

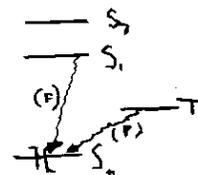
Luminescence

Fluorescence is fast (10^{-8} s). Transition between states of the same spin ($\Delta S=0$).

e.g. many aromatic hydrocarbons and dyes as vapours, in solution, or as solids, at room temperature. “Dayglo” paints. Highlighters.

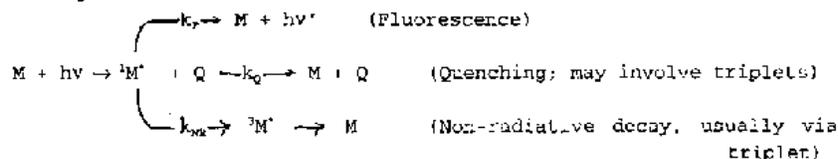
Phosphorescence is slow (10^{-3} -1s). The transitions are between states of different spin multiplicities, e.g. triplet to singlet ($\Delta S \neq 0$).

e.g. aromatic hydrocarbons, ketones, heterocyclic compounds in solid matrices at liquid nitrogen temperature. Glowstars.



Exceptions – in heavy atom compounds (e.g. I_2) the strong spin-orbit coupling makes the distinction between singlets and triplets invalid. In other words spin-orbit coupling makes spin-changing transitions relatively allowed.

Kinetics of Primary Photochemical Reactions



The steady state hypothesis is always valid for M^* :

$$\text{Rate of change of } [M^*] = I_{\text{abs}} - k_F[M^*] - k_{NR}[M^*] - k_Q[M^*][Q] = 0.$$

$$[M^*] = I_{\text{abs}} / \{ k_F + k_{NR} + k_Q[Q] \}$$

$$\text{Fluorescence intensity } F = k_F[M^*]$$

Quantum yield of fluorescence, Φ_F = photons emitted / photons absorbed:

$$\Phi_F = F/I_{\text{abs}} = k_F / \{ k_F + k_{NR} + k_Q[Q] \}$$

A similar expression is valid for any primary product.

First-order rate constant for decay of $[M^*]$, $k_{\text{eff}} = k_F + k_{NR} + k_Q[Q]$

The measured lifetime in all primary channels is the same, $\tau_{\text{obs}} = k_{\text{eff}}^{-1}$

{ τ is the mean lifetime, not half-life. $t_{1/2} = \tau \ln 2$ }

Hence, $\Phi_F = k_F \tau_{\text{obs}}$ and similarly for all primary products. k_F is obtained experimentally by measuring the quantum yield and lifetime.

Radiative Processes

Absorption Strength:

$$\text{Beer's Law: } I = I_0 e^{-\alpha[J]l} = I_0 10^{-\epsilon[J]l}$$

$\epsilon = \alpha / \ln 10$ = molar absorption coefficient, $[J]$ is concentration (mol dm^{-3}), l is length.

Typical values of ϵ_{max} ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) –

Allowed Transition	10^3 to 10^5	Ethene, double bond, $\pi \rightarrow \pi^*$
Symmetry forbidden	1 to 10^3	Ketones, aldehydes, $n \rightarrow \pi^*$
Spin forbidden (1 st row)	10^{-5} to 1	Singlet to triplet absorption in all molecules

Simple form of symmetry selection rule – initial and final state wavefunctions must differ by just one mode (parity change, $g \leftrightarrow u$).

Spin Selection Rule – initial and final state spin multiplicities must be the same ($\Delta S = 0$).

Emission Strength and Lifetime –

Fluorescence intensity depends on competition:

$\Phi_F = k_F \tau_{obs}$

The radiative rate constant ($k_F = (\text{radiative lifetime})^{-1}$) is proportional to the integrated absorption coefficient for transition between the same states. k_F is exactly the same as the Einstein A coefficient for spontaneous emission. Einstein proved that there are three radiative processes:

Absorption	–	rate $\propto B [M] [h\nu]$
Spontaneous Emission	–	rate $\propto A [M^*]$
Stimulated Emission	–	rate $\propto B [M^*] [h\nu]$

Stimulated emission is the basis of laser operation. Fluorescence and phosphorescence are forms of spontaneous emission. A practical formula for k_F is:

$k_F \text{ (s}^{-1}\text{)} = 2.88 \times 10^{-9} n^2 (\bar{\nu} / \text{cm}^{-1})^2 \int \epsilon \text{ d}\nu$, where n is the refractive index of the solution, $\bar{\nu}$ is the average wavenumber, and the integral is taken over the absorption band.

Strong absorption \rightarrow large $k_F \rightarrow$ chance of strong emission

Weak absorption \rightarrow small $k_F \rightarrow$ long radiative lifetime \rightarrow more chance of quenching or internal non-radiative decay.

Examples:

Benzene at 260nm, $1/k_F = 414 \text{ ns}$ (symmetry forbidden)

Anthracene at 375nm, $1/k_F = 14 \text{ ns}$ (fully allowed)

Spectra

The shapes of electronic bands depend on vibrational Franck-Condon factors, which are absolute squares of vibrational overlap integrals between the initial and final vibrational levels.

Basic Theory:

Transition probability $\propto |\mu|^2$ where $\mu = \int \Psi_{final} \hat{\mu} \Psi_{initial} \text{ d}\tau$

By Born-Oppenheimer separation $\mu \approx \int \Psi_f \hat{\mu} \Psi_i \int \chi_f \chi_i$

Where μ is the electric dipole moment operator, ψ is the electronic wavefunction and χ is the vibrational wavefunction.

So transition probability $\propto \mu_{elec}^2 F$, where F is the Franck-Condon Factor $|\int \chi_f \chi_i|^2$

Semi-classical model

“Vertical” transitions are strongest, because nuclei cannot change their positions or momenta during an electron jump. If there is no change in equilibrium geometry on electronic excitation, $\Delta v = 0$ transitions are strongest. If there is a big change (e.g. bonding \rightarrow antibonding), many vibration levels may be reached giving a broad band.

Examples:

In $\pi \rightarrow \pi^*$ transitions such as the first singlet absorption in benzene, a strongly bonding electron goes into an antibonding orbital so there is a significant change in bond lengths and the band is broad with many vibration levels excited.

In $n \rightarrow \pi^*$ transitions a non-bonding electron goes into an antibonding orbital, but the change in bonding is less so the bands are narrower.

If a non-bonding electron is excited to a highly excited orbital (e.g. a Rydberg orbital) with no bonding properties, the band is essentially a single line showing no vibrational excitation at all.

The shapes of emission spectra (both fluor- and phosphorescence) in liquids are found to be independent of the exciting wavelength and are often mirror images of the corresponding absorption bands.

Exceptions: in molecules which change geometry on excitation (e.g. planar to non-planar), or which react rapidly in the excited state, there is no mirror image relationship.

Observations show:

1. Emission is always from the lowest state of each multiplicity (KASHA Rule)
2. Quantum yields are independent of absorbed wavelength (VAVILOV Rule)
Exceptions – Azulene, thiocarbonyls emit from S_2 .
3. Emission wavelengths change with changes of solvent.

Explanation – absorption goes from $v''=0$ to $v'=$ various. Vibrational relaxation brings all to $v'=0$ before emission. Franck-Condon factors are similar for $(n,0)$ and $(0,n)$ transitions. Solvation and solvent atmosphere relaxation cause levels to shift after each transition (absorption and emission), and these relaxation processes are much faster than emission.

Excited States

Energy – the energy left in $M^* = hv - \text{vib}$. Relaxation (in solution).

Typical bond energies are $350\text{--}450\text{kJ mol}^{-1}$, while one photon at 600nm (red) is equivalent to 200kJ mol^{-1} but 200nm (ultraviolet) is equivalent to 598kJ mol^{-1} .

Classification – orbital types, in typical E order $\sigma, \pi, n, \pi^*, \sigma^*$ give excitations $n \rightarrow \pi^*, \pi \rightarrow \pi^*$ etc.

Characteristics – the difference between excited states and ground states comes from their Energy, and also e.g. biradical properties (dimerisation), different polarity, acidity, redox properties, equilibrium geometry (C=C), orbital symmetry (pericyclics).

More About Photochemical Reactions

Spin Conservation –

A reaction $[AB] \rightarrow A + B$ is spin allowed if series $|S_A + S_B|, |S_A + S_B - 1| \dots |S_A - S_B|$ contains S_{AB} .

For example,

$^1AB \rightarrow ^1A + ^1B, ^2A + ^2B$, etc is allowed.

$^3AB \rightarrow ^1A + ^3B, ^3A + ^3B$, etc is allowed.

$^1AB \rightarrow ^1A + ^3B, ^2A + ^4B$, etc is forbidden.

Orbital symmetry has much less effect on a reaction rate than spin, but reactions which can happen on one single potential energy surface, without change of electronic state (“Adiabatic processes”, “homogeneous”) are the most favoured.

Any chemical change, whether light is involved or not, is said to be spin forbidden if $\Delta S \neq 0$. Because spin is flipped only by a magnetic field, but the fluctuating fields in normal matter are predominantly electric, such processes are generally slow.

Examples:

$N_2O \rightarrow N_2 (^1\Sigma) + O (^3P)$	Forbidden
$I_2 \rightarrow I(^2P) + I(^2P)$	Allowed
$O^+ (^4S) + H (^2S) \rightarrow H^+ (^1S) + O (^3P)$	Allowed
$O^+ (^4S) + CO_2 (^1\Sigma) \rightarrow O_2^+ (^2\Pi) + CO (^1\Sigma)$	Forbidden
$O^+ (^4S) + NO (^2\Pi) \rightarrow NO^+ (^1\Sigma) + O (^3P)$	Allowed
$N_2O^+ (^2\Pi) \rightarrow NO^+ (^1\Sigma) + N (^4S)$	Forbidden
$H_2S^+ (^2B_1) \rightarrow H_2 (^1\Sigma) + S^+ (^4S)$	Forbidden

Note: all the forbidden reactions do happen, but they are generally much slower than allowed ones.

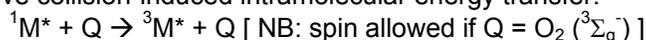
Quenching

Since $\Phi_F = \frac{k_F}{k_F + k_{NR} + k_Q[Q]}$ and $\Phi_0 = \frac{k_F}{k_F + k_{NR}}$ without quencher, and the observed lifetime without quencher $\tau_{obs} = 1/(k_F + k_{NR})$, it follows that:

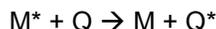
$$F^0/F = \Phi_0/\Phi_F = 1 = k_Q + k_Q\tau_{obs}[Q] \quad \text{[Stern-Volmer equation]}$$

Actual fluorescence yields are not needed. If the intensity of fluorescence without quencher divided by its intensity with quencher is plotted against [Q], the slope of the straight line is $k_Q\tau_{obs}$. If the lifetime is known, k_Q is determined, or vice versa. Often quenching in solution occurs on every encounter and so is *diffusion controlled*.

Quenching may involve collision-induced intramolecular energy transfer:

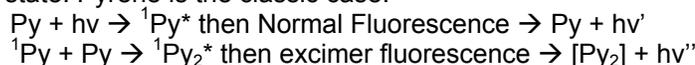


Or intermolecular energy transfer:

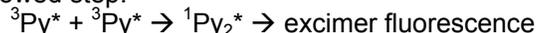


Excimers (Excited Dimers)

Two molecules may form a bound dimer in the excited state even though they do not bond in the ground state. Pyrene is the classic case.



There is some triplet formation by ISC in pyrene too, and two triplets can pool their energy in the spin-allowed step:



This produces "P-type delayed fluorescence" with a decay rate exactly twice that of the normal triplets.

$$\text{If } [T] = [T]_0 \exp \{ -k_T t \} \text{ then [excimer] (formed this way) } \propto [T]^2 = \exp \{ -2k_T t \}$$

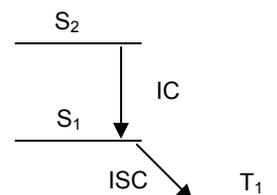
Thus the decay of the P-type delayed fluorescence has exactly half the lifetime of the triplet (i.e. the phosphorescence) under the same conditions.

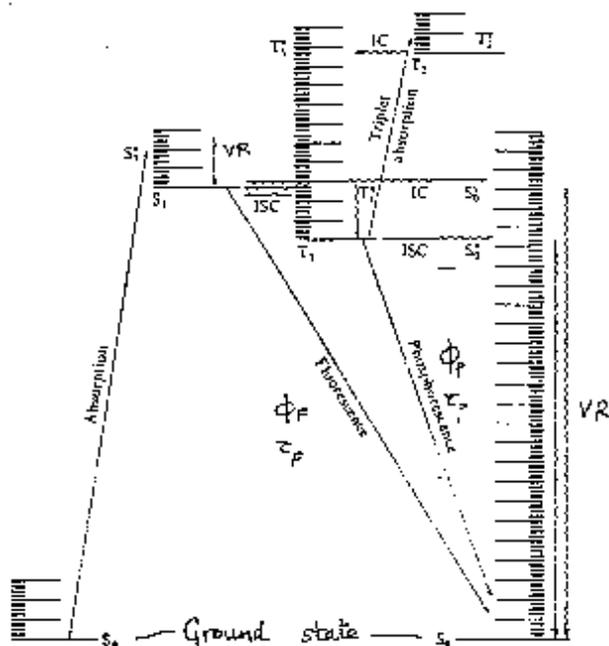
If different molecules are involved in a complex in the excited state, this is called EXCIPLEX.

Non-Radiative Transitions

The nature of any luminescence (F or P) and of photochemical reactions depend on the identity of the excited state populated, mainly S_1 , T_1 or S_2 .

Transitions between electronic states are summarised in the Jablonski diagram:





IC = Internal conversion

ISC = Intersystem crossing

NR = non-radiative

$$k_{NR} = k_{IC} + k_{ISC}$$

VR = vibrational relaxation

k_{ISC} is for $S_1 \xrightarrow{NR} T_1$

k'_{ISC} is for $T_1 \xrightarrow{NR} S_0$

Φ_T = quantum yield for formation of triplet T_1

The type of excited state active in different compounds depends on the rates of the non-radiative transitions, particularly $k_{ISC}(S_1 \rightarrow T_1)$. To determine them, first measure fluorescence quantum yield and lifetime (without quencher) as:

$$\Phi_F \frac{k_F}{(k_F + k_{NR})} = \tau_{obs} k_F$$

$$k_{NR} = k_{IC}(S_1 \rightarrow S_0) + k_{ISC}(S_1 \rightarrow T_1)$$

$$= \frac{\Phi_F}{\tau_{obs}} \left[\frac{1}{\Phi_F} - 1 \right] = \frac{1}{\tau_{obs}} [1 - \Phi_F]$$

If internal conversion from S_1 to S_0 is negligible, as is often the case, then $\Phi_F + \Phi_T = 1$ and the intersystem crossing rate $k_{ISC}(S_1 \rightarrow T_1)$ can be determined from the fluorescence lifetime and quantum yield.

If phosphorescence can be observed (usually at liquid nitrogen temperature), and its lifetime and quantum yield are measured, the radiative lifetime for phosphorescence and the intersystem crossing rate constant $k'_{ISC}(T_1 \rightarrow S_0)$ can be worked out in a similar way.

To determine triplet lifetimes we can also use flash photolysis to obtain relative values of triplet concentration immediately after a flash in solutions with different concentrations of quencher and extrapolate to zero concentration. This can be done at normal temperature.

Summary of Theory:

When IC ($S_1 \rightarrow S_0$) can be neglected, all the rate constants can be found by measuring the quantum yields and lifetimes of fluorescence and phosphorescence.

Radiative lifetime,

$$k_F = \Phi_F / \tau_F$$

ISC ($S_1 \rightarrow T_1$),

$$k_{ISC} = (1 - \Phi_F) / \tau_F$$

Radiative lifetime,

$$k_P = \Phi_P / (1 - \Phi_F) \tau_P$$

ISC ($T_1 \rightarrow S_0$),

$$k'_{ISC} = (1 / \tau_P) - k_P$$

Important aspects of the measured rate constants are encapsulated in “El-Sayed’s rules”:

ISC: $^1n\pi^* \rightarrow ^3n\pi^*$ and $^1\pi\pi^* \rightarrow ^3\pi\pi^*$ are slow.

ISC: $^1n\pi^* \rightarrow ^3\pi\pi^*$ and $^1\pi\pi^* \rightarrow ^3n\pi^*$ are fast.

These determine how different classes of molecule behave photochemically, according to the form of their energy level patterns.

e.g. in aromatic ketones, the first medium strength (symmetry forbidden) absorption is to a singlet $^1n\pi^*$ state, but the lowest triplet state is usually a $^3\pi\pi^*$ state. So ISC is fast and the fluorescence yield is near zero, triplet yield is near one and phosphorescence or triplet reactions are observable.

Understanding Non-Radiative Transition Rates

Non-radiative transitions are internal energy transfers. In the large molecule limit their rates follow Fermi’s rule:

$$k_{NR} = (4\pi^2/h) H_{if}^2 \rho_f$$

ρ_f = density of final states (i.e. number of states per unit energy), and $H_{if} = \int \Psi_f H \Psi_i$.

where Ψ is the total wavefunction (electronic, nuclear, spin), and H is the operator which couples the initial and final states.

For ISC: H is the spin-orbit operator. For IC: H is the nuclear kinetic energy operator (B-O breakdown).

Approximately (mainly B-O) –

$$k_{NR} = (4\pi^2/h) H_{ei}^2 \rho_f F,$$

where F is a Franck-Condon factor.

H_{SO} has the symmetry of a rotation about one of the axes.

H_{KE} is totally symmetric.

Hence, H_{ei} (ISC) vanishes in this approximation for ISC between states with identical orbital symmetry.

H_{ei} (IC) vanishes except between states of the same symmetry.

The symmetry explains El-Sayed’s rules, but not the differences between $k_{IC}(S_2 \rightarrow S_1)$ and $k_{IC}(S_1 \rightarrow S_0)$ or $k_{ISC}(S_1 \rightarrow T_1)$ versus $k_{ISC}(T_1 \rightarrow S_0)$.

For a single, harmonic vibration the Franck-Condon factor can be calculated analytically. The largest arises for the smallest possible change in the number of vibrational quanta, and the rate can be written:

$$k_{NR} = A H_{ei}^2 \exp \{ -B\Delta E/h\nu_{max} \} \quad \text{The Energy Gap Law}$$

where A and B depend only weakly on ΔE or ν . The law predicts that in related compounds $\ln k_{NR}$ should be a linear function of the energy gaps, as observed, and non-radiative transitions should be slower in deuterated compounds than in hydrogenated ones, as also found. Applied to normal energy level schemes it explains the KASHA, VAVILOV and ERMOLAEV rules. It also explains the exceptional behaviour of azulene (large S_1 to S_2 gap, small S_0 to S_1 gap, so emission (fluorescence) $S_2 \rightarrow S_0$. Fast IC S_1 to S_0) and thiocarbonyls (large S_2 to S_1 gap. $S_2 = ^1\pi\pi^*$ so $S_2 \rightarrow T_2$ gap, slow ISC. $S_1 = n\pi^*$ so fast ISC $\rightarrow T_1$. Hence when absorption is to S_1 , reaction from T_1 . Absorption to S_2 , reaction/emission from S_2).