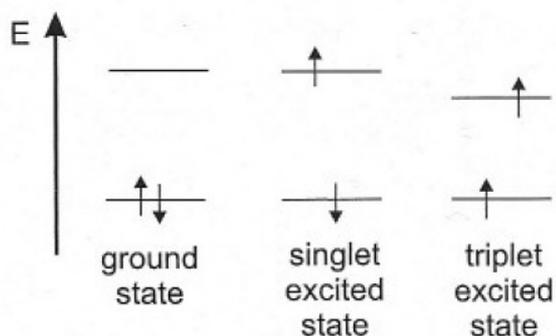


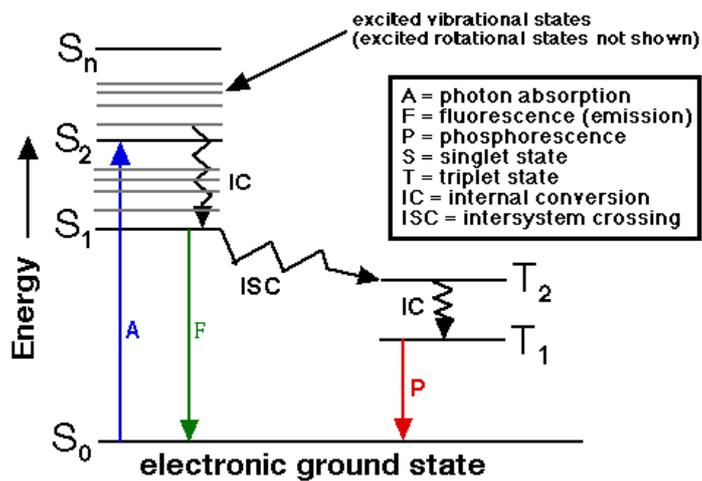
Kinetics of photochemical reactions

- **Primary photochemical process:**
products are formed directly from the excited state of a reactant.
- **Secondary photochemical process:**
intermediates are formed directly from the excited state of a reactant.
- Photophysical processes compete with the formation of photochemical products via deactivating the excited state

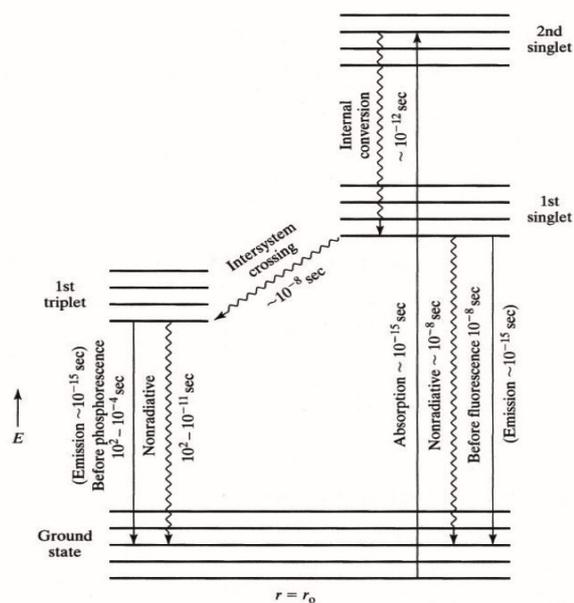
Distinction between singlet and triplet states



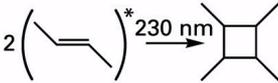
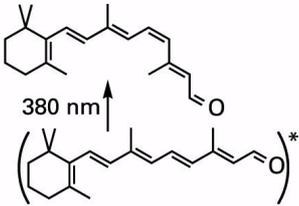
Jablonski's Diagram



Time Scales



Examples of Photochemical Processes

Process	General form	Example
Ionization	$A^* \rightarrow A^+ + e^-$	$\text{NO}^* \xrightarrow{134 \text{ nm}} \text{NO}^+ + e^-$
Electron transfer	$A^* + B \rightarrow A^+ + B^-$ or $A^- + B^+$	$[\text{Ru}(\text{bpy})_3^{2+}]^* + \text{Fe}^{3+} \xrightarrow{452 \text{ nm}} \text{Ru}(\text{bpy})_3^{3+} + \text{Fe}^{2+}$
Dissociation	$A^* \rightarrow B + C$	$\text{O}_3^* \xrightarrow{1180 \text{ nm}} \text{O}_2 + \text{O}$
	$A^* + B-C \rightarrow A + B + C$	$\text{Hg}^* + \text{CH}_4 \xrightarrow{254 \text{ nm}} \text{Hg} + \text{CH}_3 + \text{H}$
Addition	$2 A^* \rightarrow B$	
	$A^* + B \rightarrow AB$	
Abstraction	$A^* + B-C \rightarrow A-B + C$	$\text{Hg}^* + \text{H}_2 \xrightarrow{254 \text{ nm}} \text{HgH} + \text{H}$
Isomerization or rearrangement	$A^* \rightarrow A'$	

* Excited state.

Common Photophysical Processes

Primary absorption	$S + h\nu \rightarrow S^*$
Excited-state absorption	$S^* + h\nu \rightarrow S^{**}$
	$T^* + h\nu \rightarrow T^{**}$
Fluorescence	$S^* \rightarrow S + h\nu$
Stimulated emission	$S^* + h\nu \rightarrow S + 2h\nu$
Intersystem crossing (ISC)	$S^* \rightarrow T^*$
Phosphorescence	$T^* \rightarrow S + h\nu$
Internal conversion (IC)	$S^* \rightarrow S$
Collision-induced emission	$S^* + M \rightarrow S + M + h\nu$
Collisional deactivation	$S^* + M \rightarrow S + M$
	$T^* + M \rightarrow S + M$
Electronic energy transfer:	
Singlet-singlet	$S^* + S \rightarrow S + S^*$
Triplet-triplet	$T^* + T \rightarrow T + T^*$
Excimer formation	$S^* + S \rightarrow (SS)^*$
Energy pooling	
Singlet-singlet	$S^* + S^* \rightarrow S^{**} + S$
Triplet-triplet	$T^* + T^* \rightarrow S^* + S$

† S denotes a singlet state, T a triplet state, and M is a third body.

Primary Quantum Yield

- The **primary quantum yield**, ϕ , the number of photophysical or photochemical events that lead to primary products divided by the number of photons absorbed by the molecules in the same interval, or the radiation-induced primary events divided by the rate of photo absorption:

$$\begin{aligned}\phi &= \frac{\text{number of events}}{\text{number of photons absorbed}} \\ &= \frac{\nu(\text{rate of the process})}{I_{abs} \text{ (intensity of light absorbed)}}\end{aligned}$$

Primary Quantum Yield

- The sum of primary quantum yields for all photophysical and photochemical events must be equal to 1:

$$\sum_i \phi_i = \sum_i \frac{\nu_i}{I_{abs}} = 1$$

- From the above relationship, the primary quantum yield may be determined directly from the experimental rates of **ALL photophysical** and **photochemical** processes that deactivate the excited state:

$$\phi_i = \frac{\nu_i}{\sum \nu_i}$$

Decay Mechanism of Excited Singlet State

- **Absorption:** $S + hv_i \rightarrow S^*$ $v_{\text{abs}} = I_{\text{abs}}$
- **Fluorescence:** $S^* \rightarrow S + hv_f$ $v_f = k_f[S^*]$
- **Internal conversion:** $S^* \rightarrow S$ $v_{\text{IC}} = k_{\text{IC}}[S^*]$
- **Intersystem crossing:** $S \rightarrow T^*$ $v_{\text{ISC}} = k_{\text{ISC}}[S^*]$

S^* is an excited singlet state, and T^* is an excited triplet state.

The rate of decay:

$$\frac{d[S^*]}{dt} = -k_f[S^*] - k_{\text{IC}}[S^*] - k_{\text{ISC}}[S^*]$$

When the incident light is turned off, the excited state decays exponentially:

$$[S^*]_t = [S^*]_0 e^{-t/\tau_0} \quad \text{with} \quad \tau_0 = \frac{1}{k_f + k_{\text{IC}} + k_{\text{ISC}}}$$

Fluorescence Quantum Yield

- If the incident light intensity is high and the absorbance of the sample is low, we may invoke the steady-state approximation for $[S^*]$:

$$I_{\text{abs}} - k_f[S^*] - k_{\text{IC}}[S^*] - k_{\text{ISC}}[S^*] = 0$$

Consequently,

$$I_{\text{abs}} = k_f[S^*] + k_{\text{IC}}[S^*] + k_{\text{ISC}}[S^*]$$

The expression for the quantum yield of fluorescence becomes:

$$\phi_{f,0} = \frac{v_f}{I_{\text{abs}}} = \frac{k_f}{k_f + k_{\text{IC}} + k_{\text{ISC}}}$$

Quenching

- The presence of a quencher, Q, opens an additional channel for deactivation of S*:



Now the steady-state approximation for [S*] gives:

$$I_{abs} - k_f[S^*] - k_{IC}[S^*] - k_{ISC}[S^*] - k_Q[Q][S^*] = 0$$

The fluorescence quantum yield in the presence of quencher becomes:

$$\phi_f = \frac{k_f}{k_f + k_{IC} + k_{ISC} + k_Q[Q]}$$

Quenching & Stern-Volmer Plot

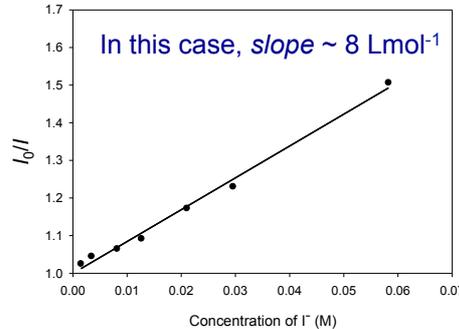
- The ratio of $\Phi_{f,0}/\Phi_f$ is then given by

$$\frac{\varphi_{f,0}}{\varphi_f} = 1 + \tau_o k_Q[Q]$$

- Therefore a plot of the left-hand side of the above equation against [Q] should produce a straight line with the slope $\tau_o k_Q$. Such a plot is called **Stern-Volmer** plot.

Quenching & Stern-Volmer Plot

Stern-Volmer plot, is shown below for the case of fluorescein quenched by iodide ion (I⁻).



Slope = $k_q \tau_0$ where k_q is the bimolecular quenching rate constant and τ_0 is the excited state lifetime in the absence of quencher.

In the case of purely collisional quenching, also known as **dynamic** quenching:

$$I_0/I = \tau_0/\tau$$

Hence in this case: $\tau_0/\tau = 1 + k_q \tau_0[Q]$

In the fluorescein/iodide system, $\tau = 4\text{ns}$ and $k_q \sim 2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$

- The fluorescence intensity and lifetime are both proportional to the fluorescence quantum yield, plot of $I_{f,0}/I_0$ and τ_0/τ against $[Q]$ should also be linear with the same slope and intercept as

$$\frac{\varphi_f}{\varphi} = 1 + \tau_0 k_Q [Q]$$

- The quenching of tryptophan fluorescence by dissolved O₂ gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the quenching rate constant for this process

[O ₂]/(10 ⁻² M)	0	2.3	5.5	8	10.8
Tau/(10 ⁻⁹ s)	2.6	1.5	0.92	0.71	0.57

3 Common Mechanisms for Bimolecular Quenching

1. Collisional deactivation:

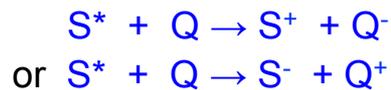


is particularly efficient when Q is a heavy species such as iodide ion.

2. Resonance energy transfer:



3. Electron transfer:



Energy Transfer Processes

- (Forster theory, 1952) Energy transfer is more efficient when:

1. The energy donor and acceptor are separated by a short distance, in the nanometer scale.
2. Photons emitted by the excited state of the donor can be absorbed directly by the acceptor.

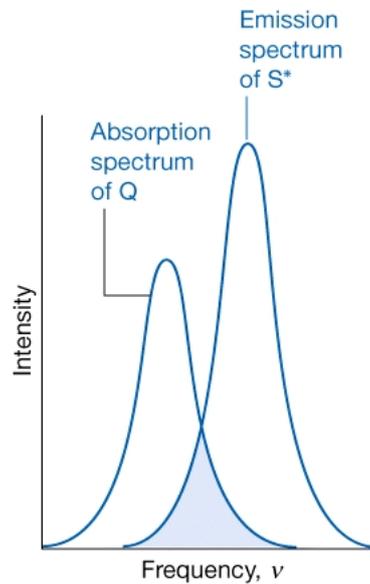
- The efficiency of energy transfer, E_T , equals

$$E_T = 1 - \frac{\phi_f}{\phi_{f,0}} \quad E_T = \frac{R_0^6}{R_0^6 + R^6}$$

Where R is the distance between the donor and the acceptor. R_0 is a parameter that is characteristic of each donor-acceptor pair.

- Fluorescence resonance energy transfer (FRET)

Quenching by Energy Transfer



Electron transfer reactions (Marcus theory)

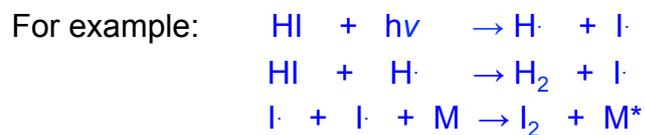
- The distance between the donor and acceptor, with electron transfer becoming more efficient as the distance between donor and acceptor decrease.
- The reaction Gibbs energy, $\Delta_r G$, with electron transfer becoming more efficient as the reaction becomes more exergonic.
- The reorganization energy, the energy cost incurred by molecular rearrangements of donor, acceptor, and medium during electron transfer. The electron transfer rate is predicted to increase as this reorganization energy is matched closely by the reaction Gibbs energy.

Complex photochemical processes

- The overall quantum yield of a photochemical reaction. (can be larger than 1)
- Rate laws of complex photochemical reactions.
- Photosensitization (no direct absorption).

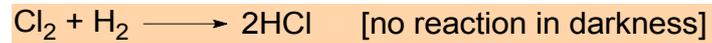
Quantum yield of a complex photochemical reaction

- **Overall quantum yield:** the number of reactant molecules consumed per photon absorbed:

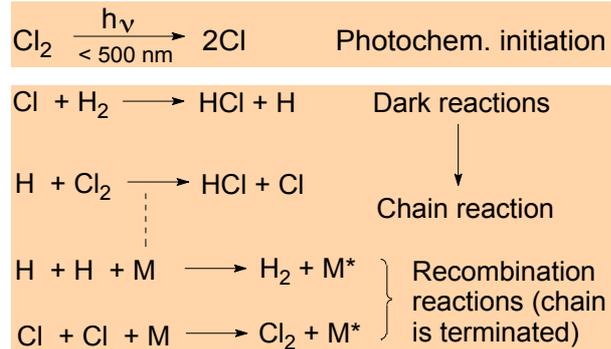


Here the overall quantum yield is **two**, because the absorption of one photon destroys two reactant molecules HI. Therefore, in a chain reaction the overall quantum yield can be very large.

The Photosynthesis of Hydrogen Chloride



Mechanism:



Quantum yield is about 10^6 (explosion)

Photosensitization

- Transfer of excitation energy from one molecule (the photosensitizer) to another nonabsorbing species during a collision.
- Example: hydrogen gas containing trace amount of mercury for the synthesis of formaldehyde:

$$\text{H}\cdot + \text{CO} \rightarrow \text{HCO}\cdot$$

$$\text{HCO}\cdot + \text{H}_2 \rightarrow \text{HCHO} + \text{H}\cdot$$

$$\text{HCO}\cdot + \text{HCO}\cdot \rightarrow \text{HCHO} + \text{CO}$$
- Basis for Photodynamic therapy.

Typical Example

When a sample of 4-heptane was irradiated for 100s with 313 nm radiation with a power output of 50W under conditions of total absorption, it was found that 2.8 mmol C_2H_4 was formed. What is the quantum yield for the formation of ethylene?

Solution: First calculate the number of photons generated in the interval 100s.

Then divide the amount of ethylene molecules formed by the amount of photons absorbed.

$$\begin{aligned}N_{(\text{photons})} &= P\Delta t/(hc/\lambda) \\ \Phi &= n(C_2H_4) \cdot N_A / N \\ &= 0.21\end{aligned}$$