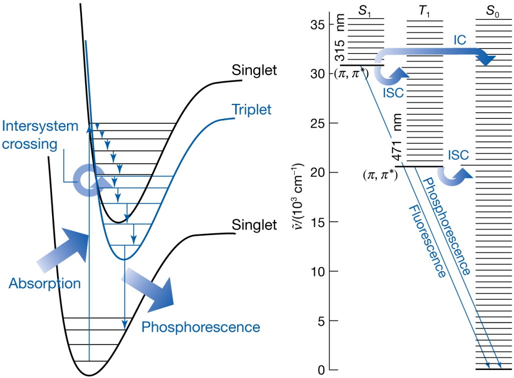
Photochemistry

- initiated by absorption of electromagnetic radiation
- most important : processes that capture solar energy
    - Some reactions lead to the heating of the atmosphere during the daytime by absorption of uv radiation.
    - Others include absorption of visible radiation during photosynthesis

Jablonski diagram

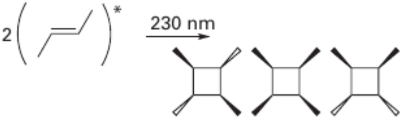
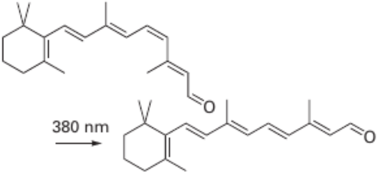


ground vibrational states correctly located vertically but other vibrational states are shown schematically
(IC: internal conversion; ISC: intersystem crossing)

primary process : products formed directly from excited state of reactant
Ex. : fluorescence and cis–trans photoisomerization of retinal

secondary process : products originate from intermediates formed directly from excited state of reactant,
Ex. : oxidative processes initiated by oxygen atom formed by ozone photodissociation

Competing with formation of photochemical products are numerous primary photophysical processes that can deactivate excited state
∴ it is important to consider timescales of formation and decay of excited states before describing mechanisms

Ionization	$A^* \rightarrow A^+ + e^-$	$NO^* \xrightarrow{134\,nm} NO^+ + e^-$
Electron transfer	$A^* + B \rightarrow A^+ + B^-$ or $A^- + B^+$	$\left[Ru(bpy)_3^{2+}\right]^* + Fe^{3+} \xrightarrow{452\,nm} Ru(bpy)_3^{3+} + Fe^{2+}$
Dissociation	$A^* \rightarrow B + C$	$O_3^* \xrightarrow{1180\,nm} O^2 + O$
	$A^* + B{-}C \rightarrow A + B + C$	$Hg^* + CH_4 \xrightarrow{254\,nm} Hg + CH_3 + H$
Addition	$2\,A^* \rightarrow B$	
	$A^* + B \rightarrow AB$	
Abstraction	$A^* + B{-}C \rightarrow A{-}B + C$	$Hg^* + H_2 \xrightarrow{254\,nm} HgH + H$
Isomerization or rearrangement	$A^* \rightarrow A'$	

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	$S^* + h\nu \rightarrow S + 2\,h\nu$
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	$T^* + T^* \rightarrow S^{**} + S$

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$\Longrightarrow$ excited triplet states are important photochemically; such species can undergo large number of collisions with other reactants before deactivation

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$$\Longrightarrow \phi_f + \phi_{IC} + \phi_{ISC} + \phi_p + \phi_R = 1; \qquad \phi_i = \frac{v_i}{\sum_i v_i}$$

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from a $P = 100$ W source

for 2700 s

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$$\phi = \frac{N_{decomposed}}{N_{absorbed}} = \frac{\left(0.344 \times 6.023 \times 10^{23}\right) \times 6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{0.6 \times 100 \times 2700 \times 490 \times 10^{-9}} = 0.52$$

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Assuming first order process:
$[\mathrm{S}^*]_t = [\mathrm{S}^*]_0 e^{-\frac{t}{\tau_0}}; \qquad \tau_0 = \frac{1}{k_f + k_{ISC} + k_{IC}}$

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tryptophan in water: $\phi_f = 0.20$; $\tau_0 = 2.6$ ns
$\therefore k_f = \frac{\phi_f}{\tau_0} = \frac{0.20}{2.6 \times 10^{-9} s} = 7.7 \times 10^7 s^{-1}$

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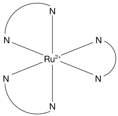
$= 1 + \tau_0 k_{\mathrm{Q}}[\mathrm{Q}]$: Stern-Volmer equation



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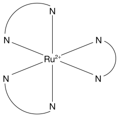

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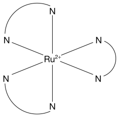

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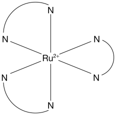
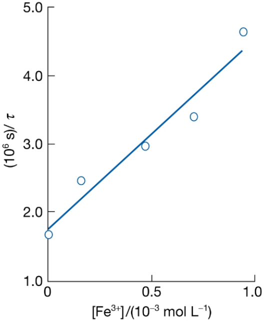


6

data:

$[Fe(H_2O)_6^{3+}]/(10^{-4}\ mol\ dm^{-3})$	0	1.6	4.7	7	9.4
$\tau/(10^{-7}\ s)$	6	4.05	3.37	2.96	2.17



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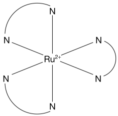

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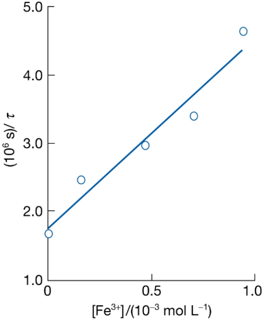

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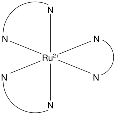

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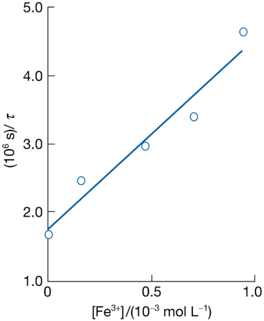

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Quenching of excited state of $Ru(bipy)_3^{2+}$ is a result of light-induced electron transfer to Fe^{3+}, but quenching data do not prove the mechanism

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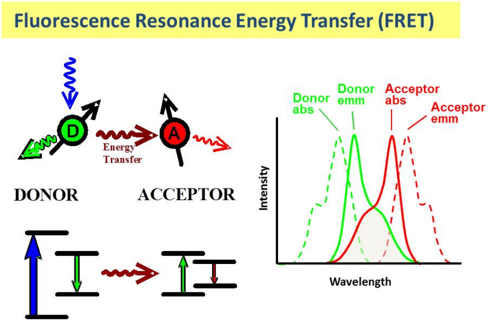
RET Efficiency : $E_T = 1 - \frac{\phi_f}{\phi_{f,0}}$



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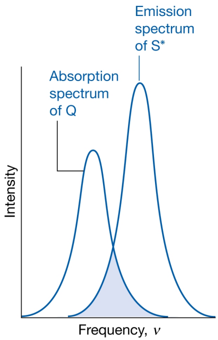
energy transfer is efficient when:

- Energy donor and acceptor are separated by short distance, $\mathcal{O}$ (1 nm)
- Photons emitted by excited state of donor can be absorbed directly by acceptor.
- $E_T = \frac{1}{1+\left(\frac{R}{R_0}\right)^6}$, R in nm and R_0 is a parameter

Donor[†]	Acceptor	R_0/nm
Naphthalene	Dansyl	2.2
Dansyl	ODR	4.3
Pyrene	Coumarin	3.9
IEDANS	FITC	4.9
Tryptophan	IEDANS	2.2
Tryptophan	Haem (heme)	2.9



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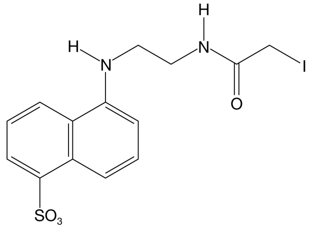

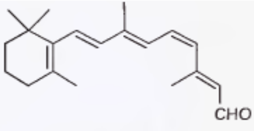

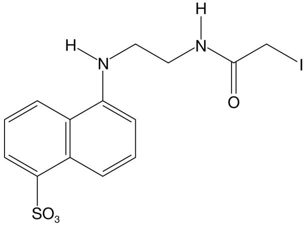

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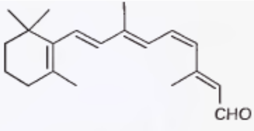

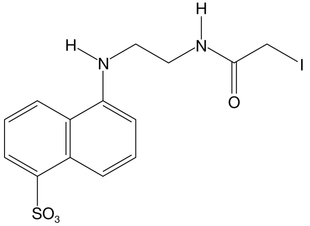

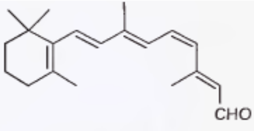

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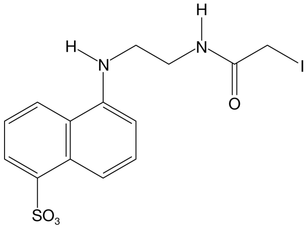

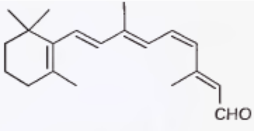

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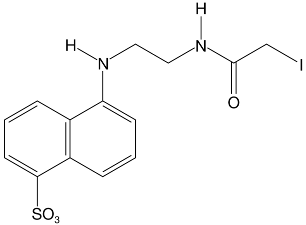

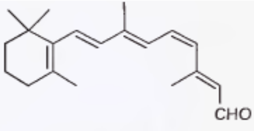

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using known value of $R_0 = 5.4$ nm for 1,5-I AEDANS/11-cis-retinal pair,
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Electron transfer can be studied by time-resolved spectroscopy.
Oxidized and reduced products often have electronic absorption spectra distinct from those of neutral parent compounds. Rapid appearance of such known features in absorption spectrum after excitation by laser pulse may be taken as indication of quenching by electron transfer

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example: $P \equiv$Haematoporphyrin; characteristics ?

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last step is termination by disproportionation rather than by combination