Physical Chemistry (Chem 132A)

Lecture 25
Wednesday, December 6

Homework 9 (last homework) Due on Saturday, December 9
Last homework of the quarter

Reminder: FINAL EXAM, DEC. 15,

8—10AM

Simple Collision Theory Picture

For a Bimolecular Reaction:

$$A + B \longrightarrow P$$

$$k \sim P\, \sigma\, (T/M)^{1/2}\, e^{-E'/RT}$$

Energy Dependence

$$k_r = \left\{ \int_0^\infty \sigma(E) \left(\frac{2E}{\mu} \right)^{1/2} 2\pi \left(\frac{\mu}{2\pi kT} \right)^{3/2} E^{1/2} e^{-E/kT} dE \right\} N_A$$

$$k_r = \left(\frac{8}{\pi\mu kT} \right)^{1/2} \left(\frac{1}{kT} \right) \int_0^\infty E\sigma(E) e^{-E/kT} \, dE$$

σ = 0 unless E > E_a

$$k_r = \left(\frac{8}{\pi\mu kT} \right)^{1/2} \left(\frac{1}{kT} \right) \int_{E_a}^\infty E\sigma(E) e^{-E/kT} \, dE$$

There are various approximations for the functional form of σ(E)

$$k_r = \sigma N_A \left(\frac{8kT}{\pi\mu} \right)^{1/2} e^{-E_a/kT}$$

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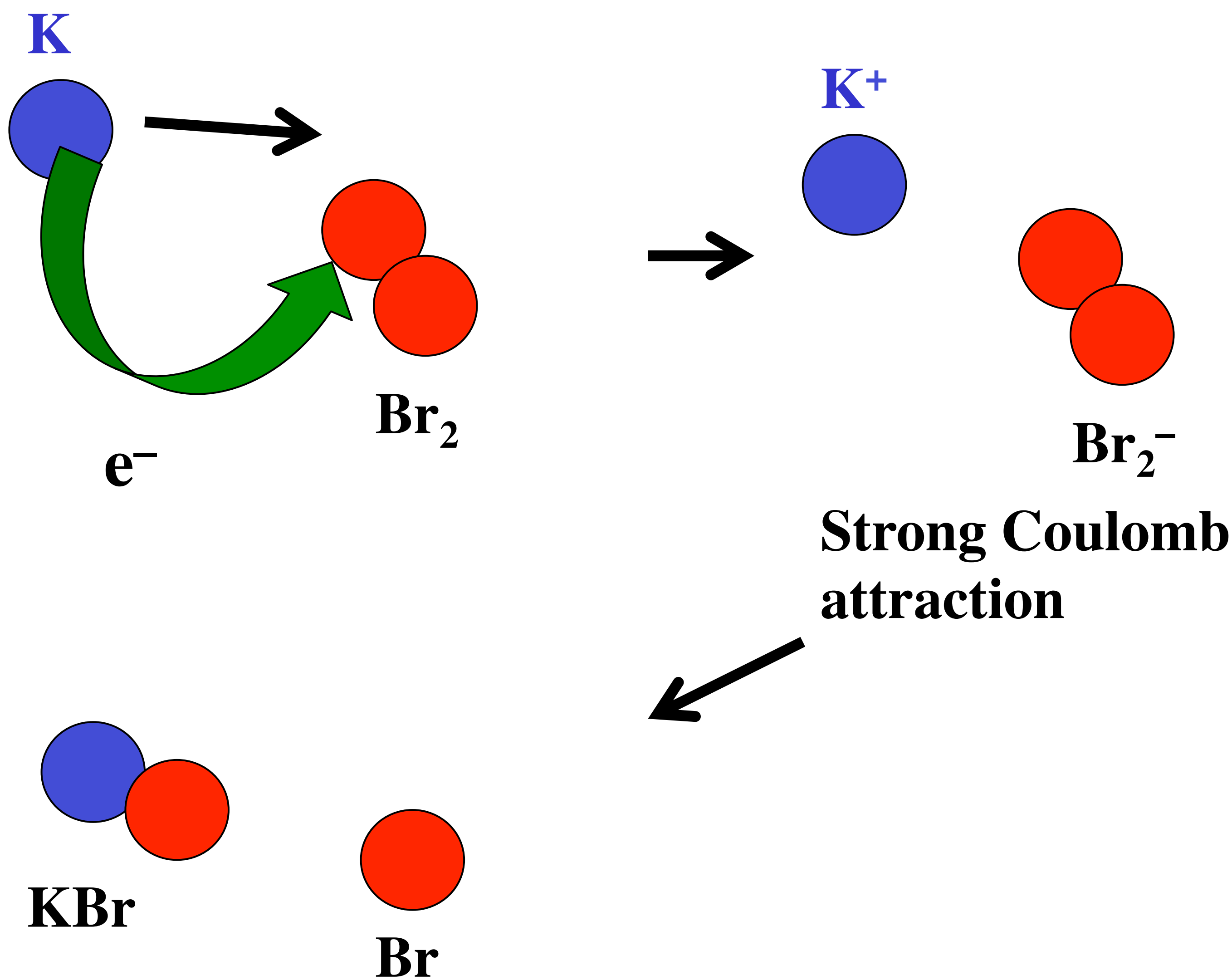
	$A/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$		$E_a/(\mathrm{kJ\,mol^{-1}})$
	Experiment	Theory	
$2\,NOCl \rightarrow 2\,NO + 2\,Cl$	9.4×10^{9}	5.9×10^{10}	102
$2\,ClO \rightarrow Cl_2 + O_2$	6.3×10^{7}	2.5×10^{10}	0
$H_2 + C_2H_4 \rightarrow C_2H_6$	1.24×10^{6}	7.4×10^{11}	180
$K + Br_2 \rightarrow KBr + Br$	1.0×10^{12}	2.1×10^{11}	0

Introduce the Steric Factor

$$k_r = P\sigma N_A \left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-E_a/kT}$$

	$A/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$		$E_a/(\mathrm{kJ\,mol^{-1}})$	P
	Experiment	Theory		
$2\,NOCl \rightarrow 2\,NO + 2\,Cl$	9.4×10^{9}	5.9×10^{10}	102	0.16
$2\,ClO \rightarrow Cl_2 + O_2$	6.3×10^{7}	2.5×10^{10}	0	2.5×10^{-3}
$H_2 + C_2H_4 \rightarrow C_2H_6$	1.24×10^{6}	7.4×10^{11}	180	1.7×10^{-6}
$K + Br_2 \rightarrow KBr + Br$	1.0×10^{12}	2.1×10^{11}	0	4.8

What's Going on with $K + Br_2 = KBr + Br$



Diffusion Controlled Reactions In Solution

$A + B \longrightarrow AB$ rate = $k_d[A][B]$

$AB \longrightarrow A + B$ rate = $k'_d[AB]$

$AB \longrightarrow P$ rate = $k_a[AB]$

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

Steady State approximation

$$[AB]_{ss} = \frac{k_d[A][B]}{k_a + k_d^{'}}$$

$$\frac{dP}{dt} = k_a[AB] = \frac{k_a k_d}{k_a + k_d^{'}}[A][B]$$

Photochemistry

Light is another way to initiate a reaction

A + photon (hν) $\Longrightarrow$ A*

$\nu = c/\lambda$

Energy = hν

UV light ~ 3.5 eV = 337.7 kJ/mol

A few Bond enthalpies:

Br–CH_3 293

O_2N–NO_2 54

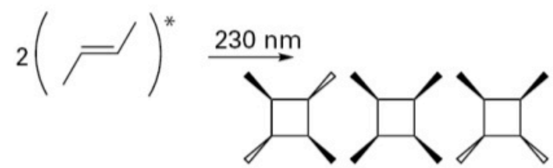
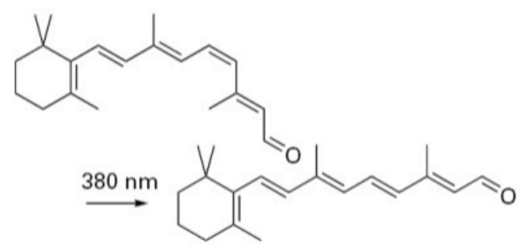
H–CH_3 435

H–OH 492

R = 8.314 $JK^{-1}mol^{-1}$

RT = 337 kJ/mol at T = 40,534 K

Example Photochemical Reactions

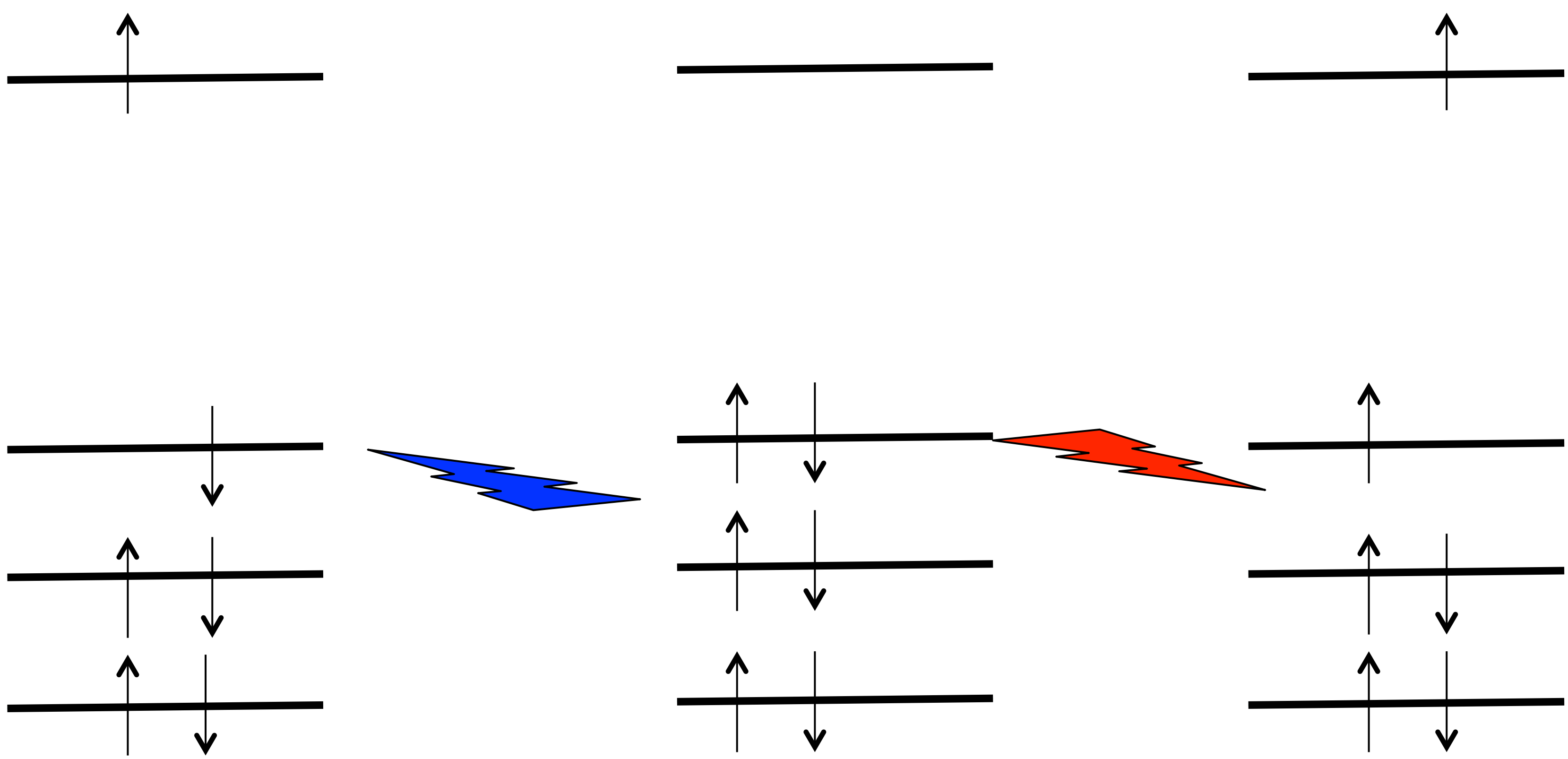
Process	General form	Example
Ionization	$A^* \rightarrow A^+ + e^-$	$NO^* \xrightarrow{134\,\text{nm}} NO^+ + e^-$
Electron transfer	$A^* + B \rightarrow A^+ + B^-$ or $A^- + B^+$	$\left[Ru(bpy)_3^{2+}\right]^* + Fe^{3+} \xrightarrow{452\,\text{nm}} Ru(bpy)_3^{3+} + Fe^{2+}$
Dissociation	$A^* \rightarrow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

Nature of Excited States

Singlet Excited State (S_1)

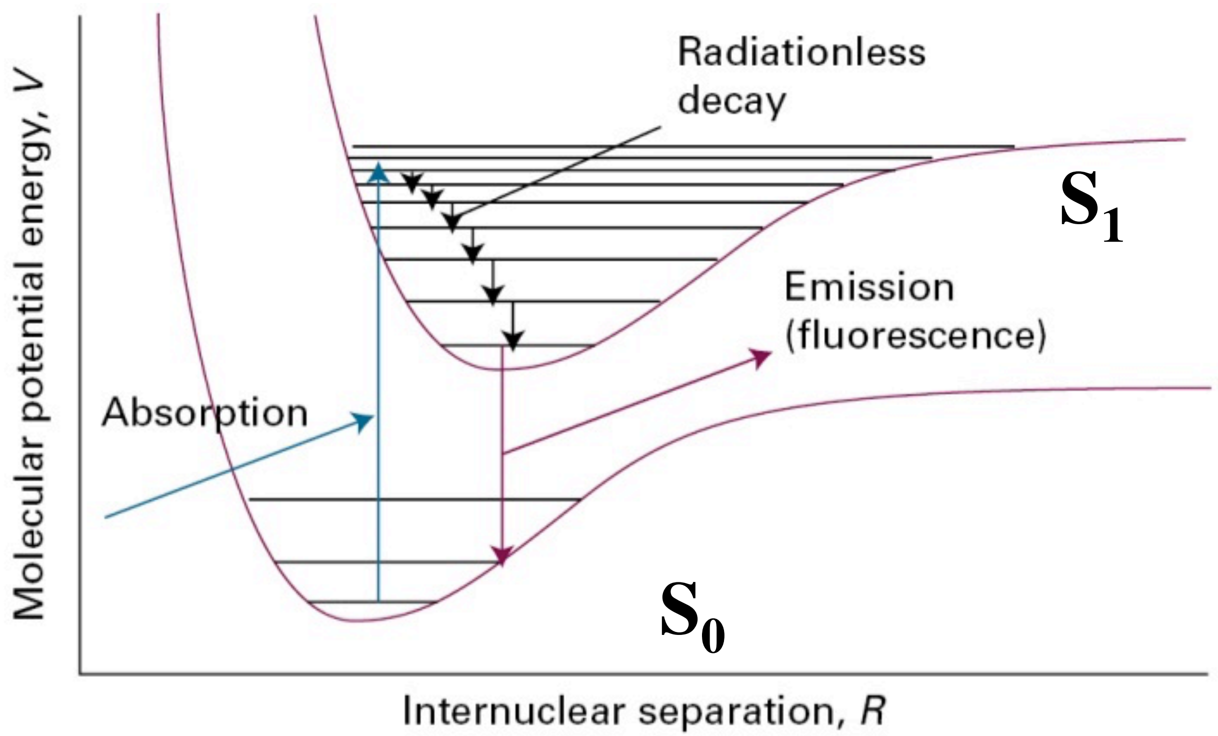
Ground state (S_0)

Excited Triplet State (T_1)

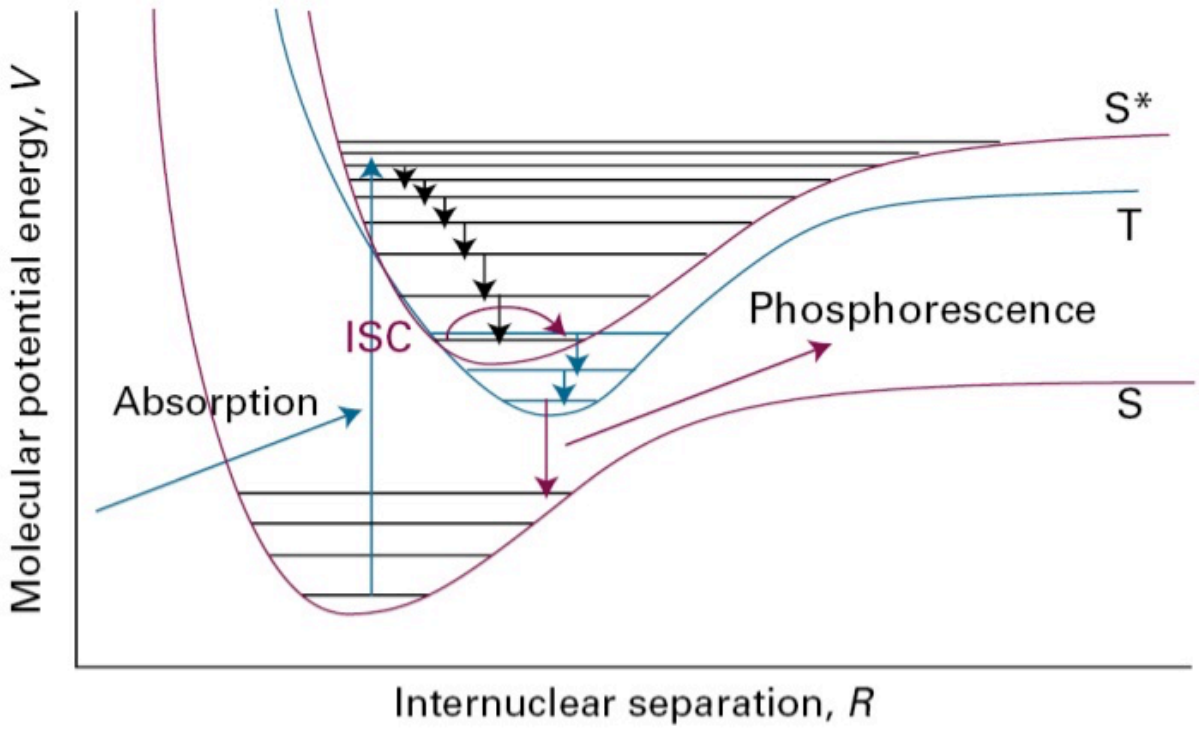


A More Detailed Picture

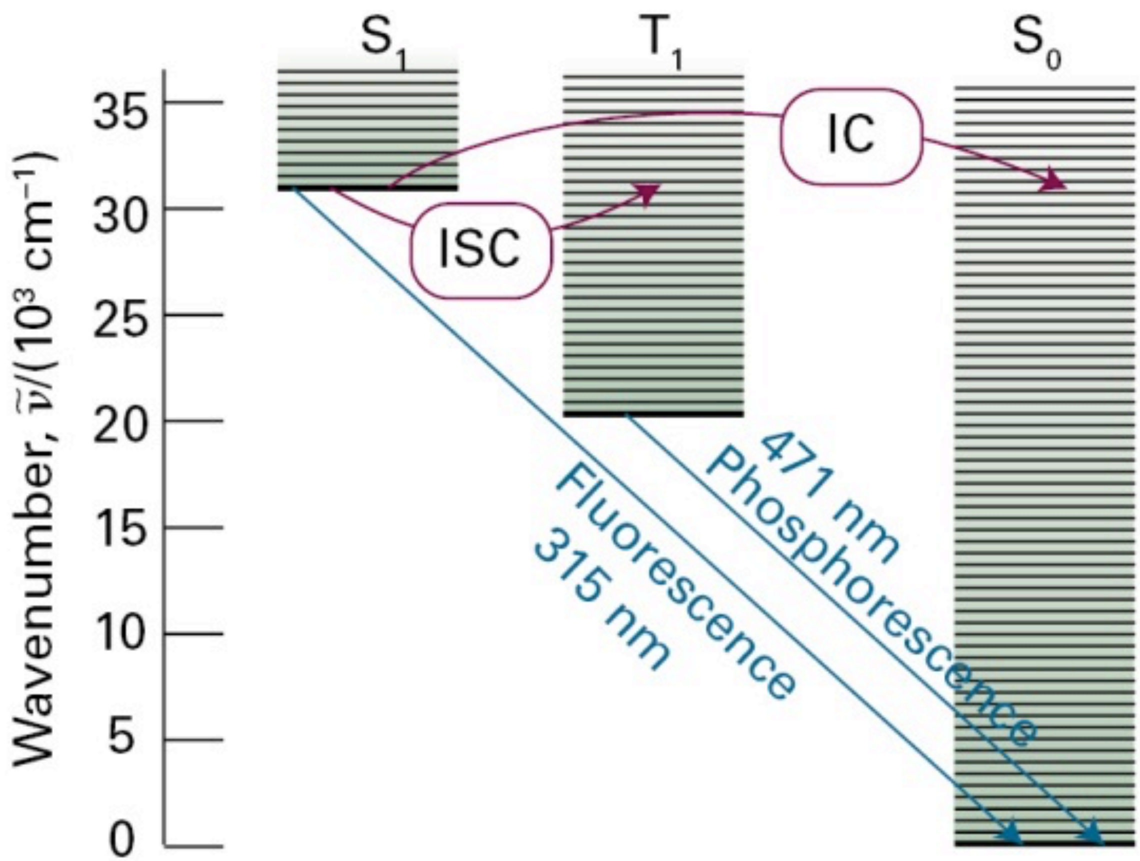
A Diatomic Molecule (A–B)

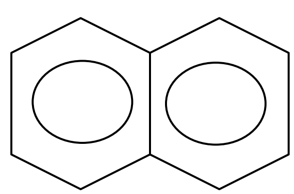


What Happens to S_1?



Jablonski Diagram





Nature of Excited States and 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	$S^* + h\nu \rightarrow S + 2\ h\nu$
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	$T^* + T^* \rightarrow S^{**} + S$

S = Singlet state

T = Triplet state

S → S can be fast

S → T slow

Photochemical Reaction Yields

Define what is called the "Quantum Yield" = Φ

$$\phi = \frac{number\_of\_events}{number\_of\_photons\_absorbed}$$

$$\phi = \frac{rate\_of\_process}{rate\_of\_photon\_absorption}$$

$$\phi = \frac{v}{I_{abs}}$$

Individual Quantum Yields

Fluorescence
Internal conversion
Intersystem crossing (S----T)
Phosphorescence
Reaction

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

$$\phi_F + \phi_{IC} + \phi_{ISC} + \phi_P + \phi_r = 1$$

Energy Transfer

Mechanisms:

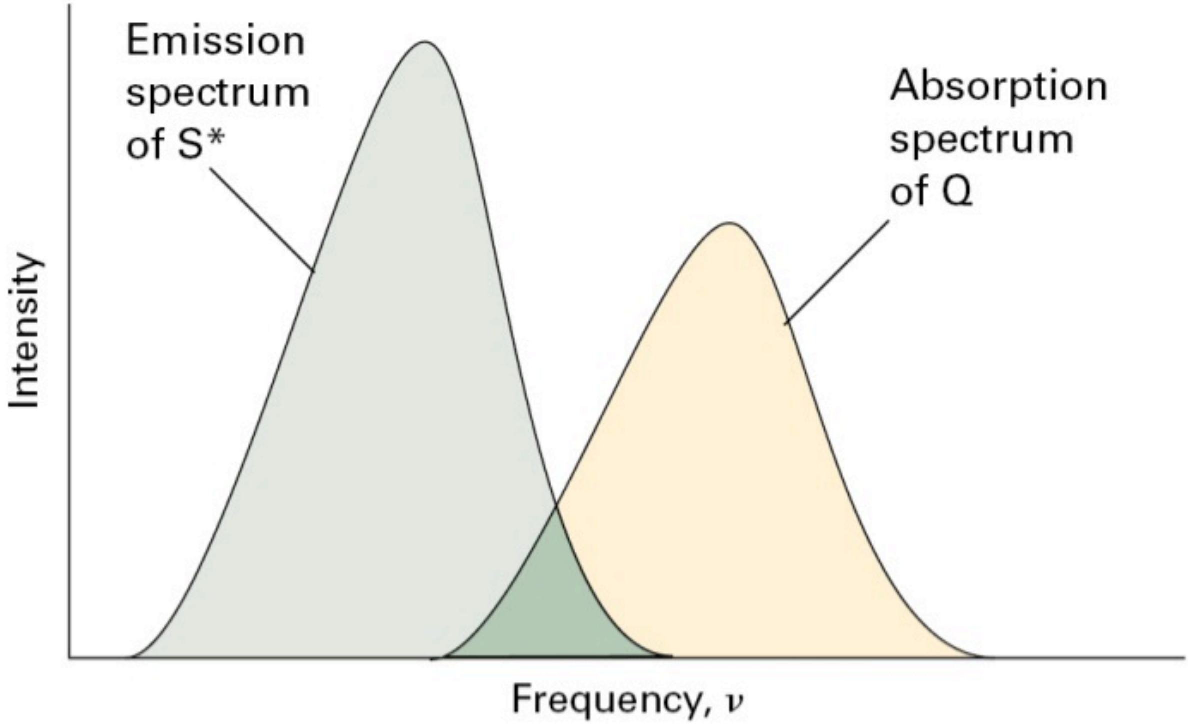
Collisional deactivation: $S^* + Q \longrightarrow S + Q$

Resonance Energy Transfer $S^* + Q \longrightarrow S + Q^*$

Electron Transfer $S^* + Q \longrightarrow S^{+/-} + Q^{-/+}$

Resonance Energy Transfer

$$S^* + Q \longrightarrow S + Q^*$$



Efficiency of Resonance Energy Transfer

Monitor Excited State S_1 by monitoring Fluorescence

$$\eta_T = 1 - \frac{\phi_f}{\phi_{F,0}}$$

Theory due to Forster:

$$\eta_T = \frac{R_0^6}{R_0^6 + R^6}$$

R_0 is a parameter dependent on the two chromophores

R is the distance between the two chromophores

A Molecular Ruler

THE END

SEE YOU ON FRIDAY