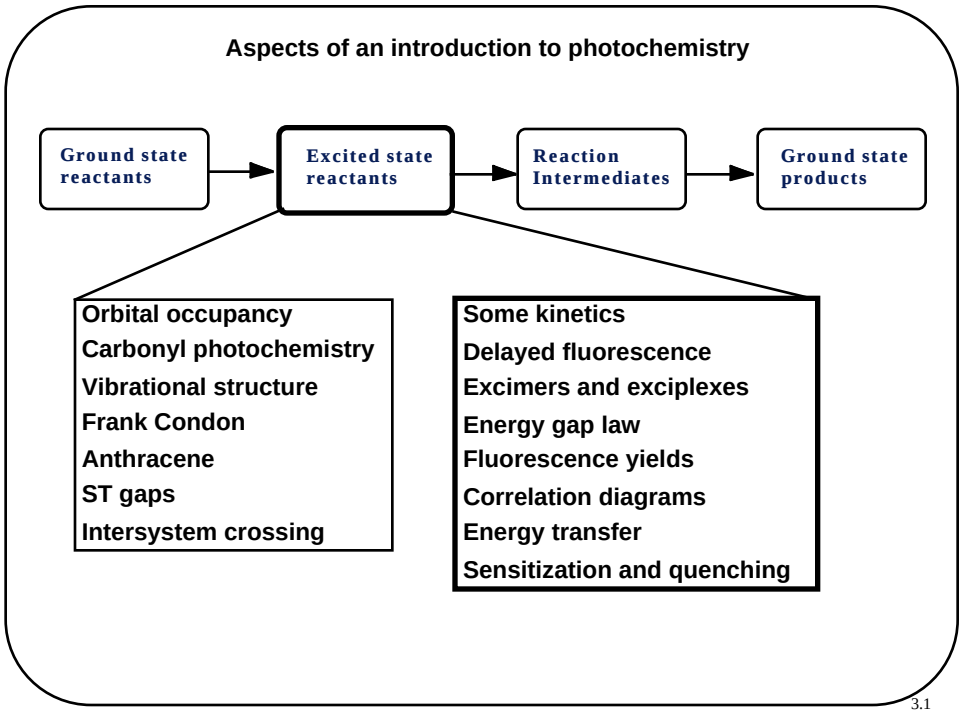
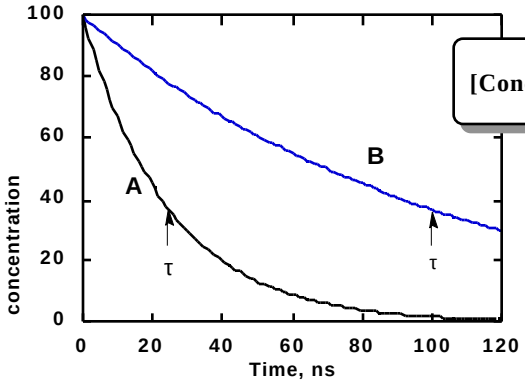

Aspects of an introduction to photochemistry
Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Orbital occupancy
Carbonyl photochemistry
Vibrational structure
Frank Condon
Anthracene
ST gaps
Intersystem crossing
Some kinetics
Delayed fluorescence
Excimers and exciplexes
Energy gap law
Fluorescence yields
Correlation diagrams
Energy transfer
Sensitization and quenching

Kinetic terms

Decay of reaction intermediates with lifetimes of 25 ns (A) and 100 ns (B).

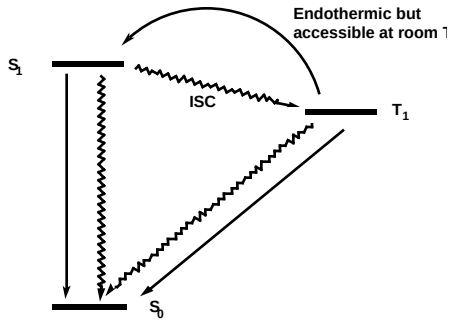


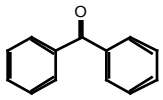
$$[Conc]_{\tau} = \frac{[Conc]_0}{2.718}$$

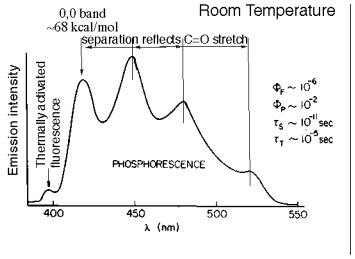
$$\tau = k^{-1} \quad ; \quad t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.69}{k}$$

Two mechanisms for delayed fluorescence

(A) Thermal population of the singlet state

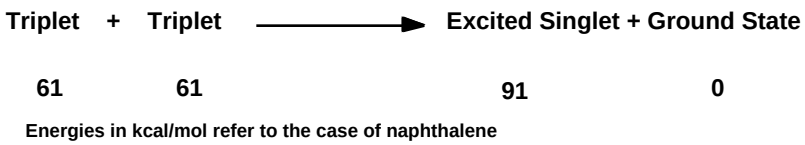






Two mechanisms for delayed fluorescence

Triplet-triplet annihilation in naphthalene



Energies in kcal/mol refer to the case of naphthalene

Spin considerations:

Triplet-triplet encounters

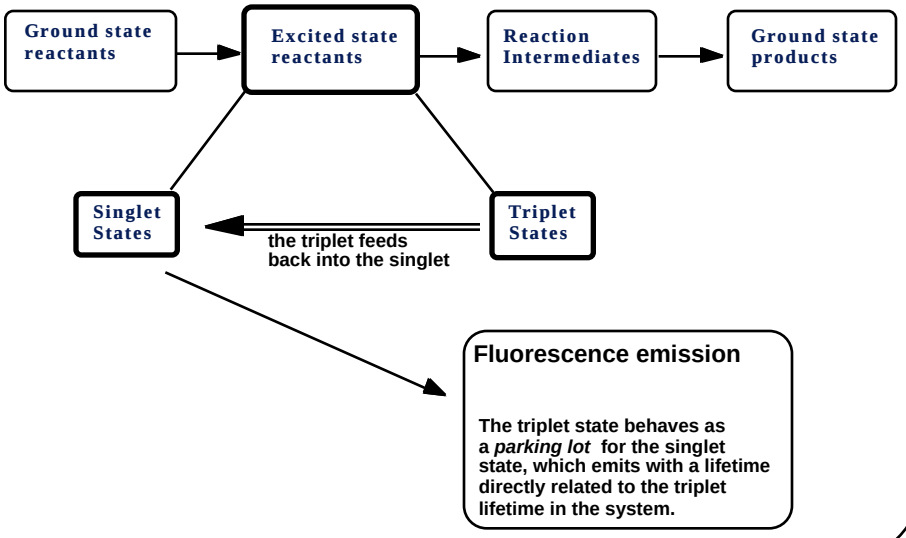
1/9 singlets

3/9 triplets

5/9 quintets

Two mechanisms for delayed fluorescence

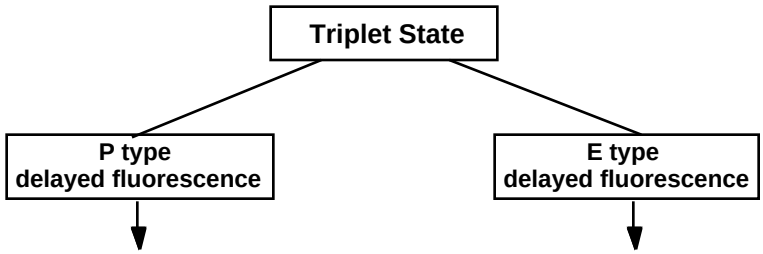
E and P mechanisms



Fluorescence emission

The triplet state behaves as a *parking lot* for the singlet state, which emits with a lifetime directly related to the triplet lifetime in the system.

E and P mechanisms



- **no thermal activation**
- **energy of TWO triplet exceeds requirements for one singlet**
- **spin allowed**
- **mobility required**
- ***usual observation in solution under laser excitation or very high sensitivity***

- **thermally activated**
- **requires only one triplet**
- **mobility not essential**
- ***usual observation in room temperature inert medium***

Stabilization by association

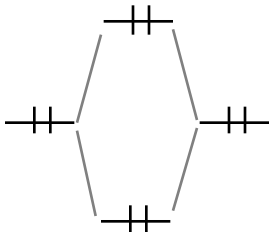
Excited stae molecules are stabilized by association in a manner that cannot be achieved by geornd state molecules.

This simple ideas mean that association will occur more readily in the excited than in the ground state.

Given the scheme that follows, why is it that not all excited molecules associate. Shouldn't they ALL associate?

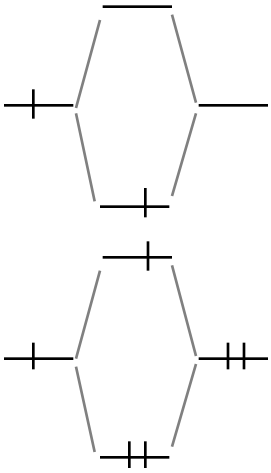
Stabilization by association

Ground state



no stabilization

Excited state



electron stabilization

The pyrene excimer

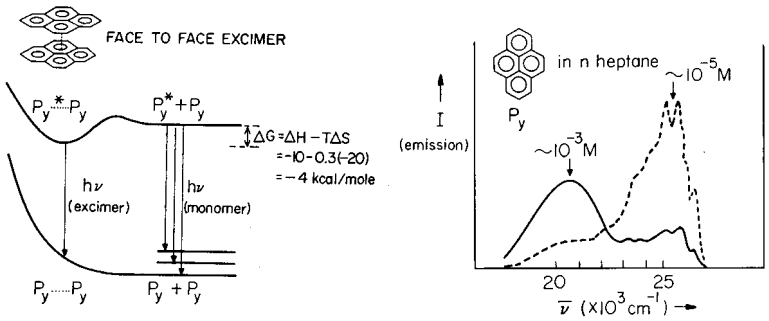
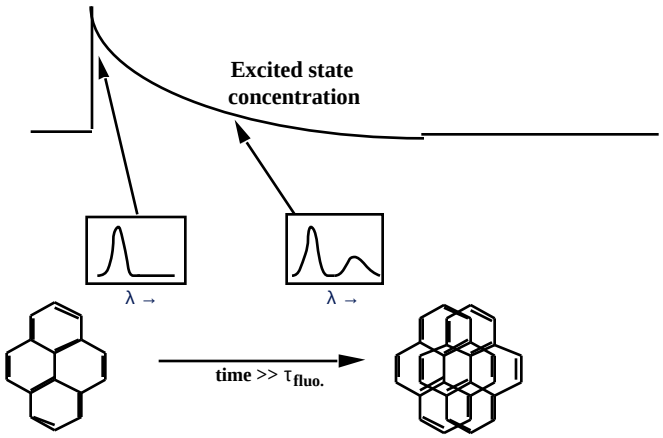


Fig. 5.31: Experimental example of the emission from pyrene and surface interpretation

from N.J. Turro, "Modern Molecular Photochemistry", 1978

Time evolution of excimer emission



Excited state complexes

Two identical molecules:

EXCIted diMER ⟹ EXCIMER

Two different molecules:

EXCIted comPLEX ⟹ EXCIPLEX

Exciplexes and emission

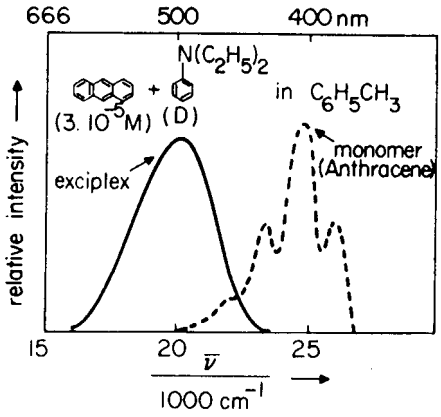
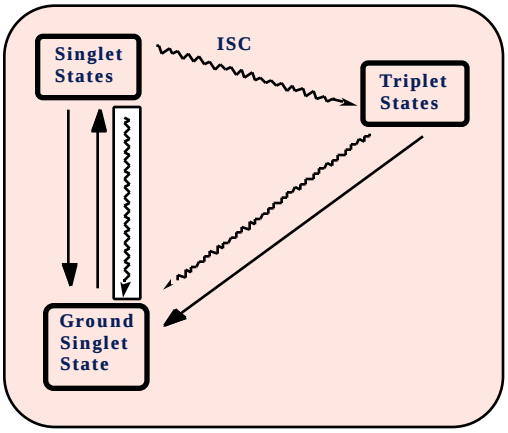


Figure 5.33
Exciplex and monomer emission of the anthracene-diethyl aniline system. The anthracene monomer is the light-absorbing species in this system.

Exciplex formation normally involves charge-transfer interactions. Emission can be detected in non-polar media but usually not in polar solvents.

Energy gap law

$$k_{ic} = 10^{13} e^{-\alpha \Delta E} \ (sec^{-1})$$



Frank Condon factor:

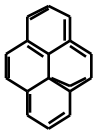
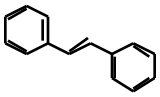
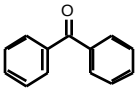
Proportional to the overlap of the wavefunctions for the initial and final states

$$f_v \qquad \exp(-\alpha \Delta E)$$

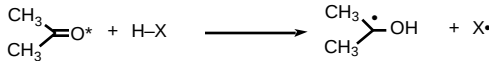
Quantum yields

$$\Phi = \frac{\text{Rate at which a process occurs of rate of formation of a product, or of disappearence of a reactant}}{\text{Intensity of light, i.e. rate of light absorption}}$$

Fluorescence quantum yields

	Φ_F	
	**0.2**	**π,π* , rigid**
	**0.7**	**π,π* , rigid**
	**0.05**	**π,π* , flexible**
	**0.001**	**n,π* , flexible, small ST gap**
	**< 0.0001**	**n,π* , flexible,very small ST gap**

Hydrogen abstraction by a carbonyl triplet



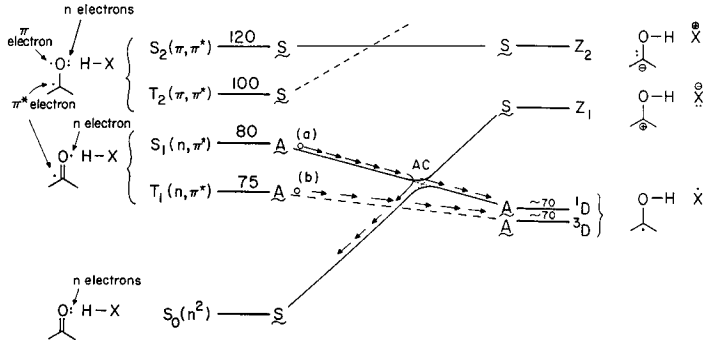
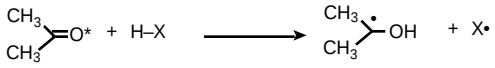


Figure 7.14
First Order correlation diagram for coplanar hydrogen abstraction. State energies in kcal/mole.

Some hydrogen abstraction rate constants

(in units of 10^6 $M^{-1}s^{-1}$)

	Benzophenone triplet	$(CH_3)_3CO\bullet$
Cyclohexane	**0.45**	**1.6**
Methanol	**0.21**	**0.29**
Benzhydrol	**7.5**	**7.2**
Triethylsilane	**9.6**	**5.7**



Energy transfer

$$M^* + Q \longrightarrow M + Q^*$$

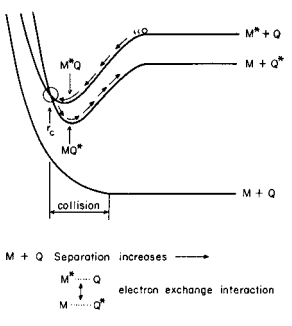


Figure 9.1
Schematic surface representation of collisional energy transfer.

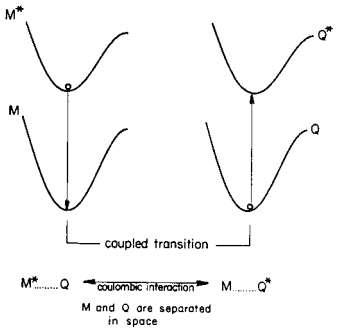
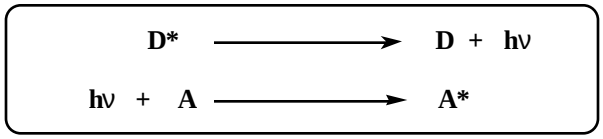


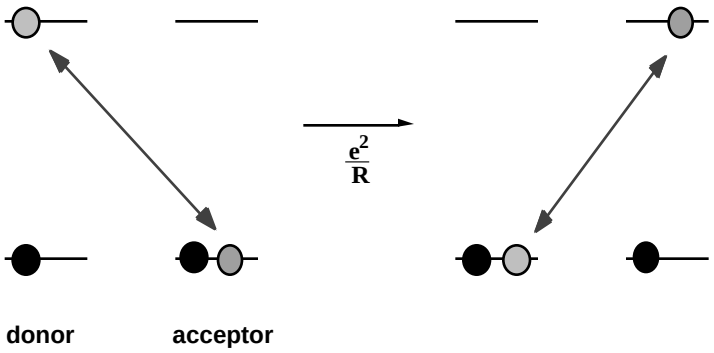
Figure 9.1
Schematic surface representation of collisional energy transfer.

Trivial mechanism for energy transfer

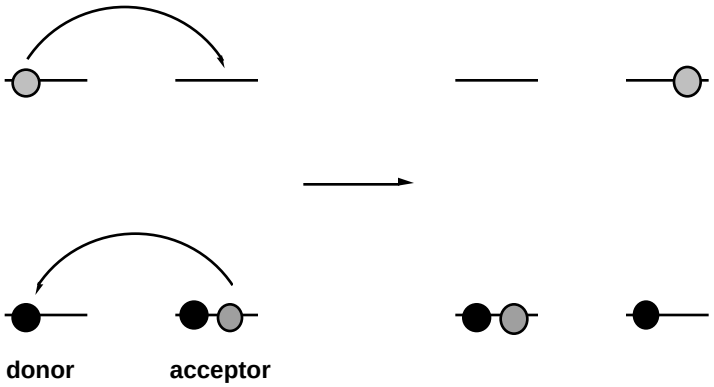


- High quantum yield for emission from D*
- High concentration of A
- High extinction coefficient for A
- Overlap of emission from D* and absorption from A

Coulombic energy transfer



Exchange energy transfer



Only mechanism of importance for triplet energy transfer

Exothermic energy transfer

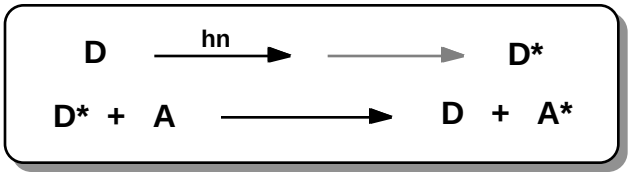
The rate constants for energy transfer processes which are exothermic by more than 3-4 kcal/mol and are spin allowed, frequently approach the diffusion controlled limit.

$$k_{diff} = \frac{8RT}{2000\eta} \qquad 2 \times 10^{5} \frac{T}{\eta}$$

Representative diffusion controlled rate constants in units of: 10^{10} M^{-1} s^{-1}

isopentane	4.6
benzene	1.6
water	1.1

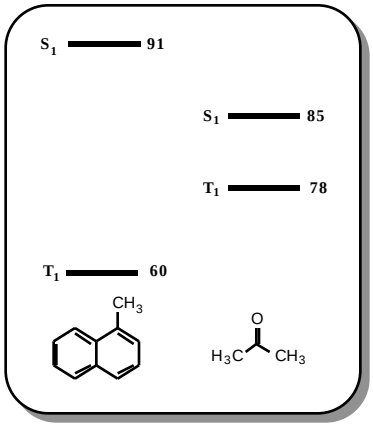
Sensitization and quenching
Two viewpoints for the same phenomena



D is a sensitizer for A

A is a quencher for D*

Energy transfer in the ketone naphthalene system



Approximate energies given in kcal/mol

$$N \xrightarrow{h\nu} {}^1N^*$$

$${}^1N^* + K \longrightarrow N + {}^1K^*$$

$${}^1K^* \longrightarrow {}^3K^*$$

$${}^3K^* + N \longrightarrow K + {}^3N^*$$

The consequence of this exchange is assisted intersystem crossing in naphthalene.

It also provides a way of 'isolating' the singlet chemistry of carbonyl compounds