Interaction Between Photon and Electron



Manifestations of Light-Matter Interactions

- Reflection
- Refraction
- Scatter
- Absorption process

Absorption



Photochemistry consists of two parts

- Photochemical
- Photophysical



The Basic Laws of Photochemistry

Grotthuss-Draper law

The First Law of Photochemistry: <u>light</u> <u>must be absorbed for photochemistry</u> <u>to occur</u>.



Theodor v. Grotthufs

Grotthus



John William Draper (1811-1882)

Stark-Einstein law

The Second Law of Photochemistry: for <u>each photon</u> of light absorbed by a chemical system, <u>only one molecule</u> is activated for a photochemical reaction.



Stark



Einstein

Third law of photochemistry

Probability of light absorption is related to the energy gap and wavelength of light

The energy conservation rule (Eq. 4.8): There must be an exact matching of the energy difference that corresponds to the energy required for the transition (ΔE) between orbitals and the energy of the photon $(h\nu)$; that is, ΔE must exactly equal $h\nu$ (Eq. 4.8).

$$\Delta E = E_1 - E_2 = hv$$
$$v = (E_1 - E_2)/h$$

$$R \longrightarrow \Psi_1$$

Same Rules Govern Excitation and De-excitation



Oscillator Strength-Absorption

Probability of light absorption is related to the oscillator strength 'f'

A perfectly allowed transition has f = 1



Absorption Spectra: Why the ε and f vary with the band?



	*R	*E		
	ε	k _e ⁰		
		$\Delta E = *E - E_0 =$	hv	
	R	E ₀		
		-NV	12.17 -3	
				201
$k_{\rm e}({\rm s}^{-1})$	Example	Transition type	$\varepsilon_{\rm max}$	f
10 ⁹	<i>p</i> -Terphenyl	$\mathrm{S}_1(\pi,\pi^*)\to\mathrm{S}_0$	3×10^4	1
10^{8}	Perylene	$S_1(\pi,\pi^*) \rightarrow S_0$	4×10^4	10^{-1}
10^{7}	1,4-Dimethyl-benzene	$S_1(\pi,\pi^*) \rightarrow S_0$	7×10^2	10^{-2}
10^{6}	Pyrene	$S_1(\pi,\pi^*) \rightarrow S_0$	5×10^2	10^{-3}
10^{5}	Acetone	$S_1(n,\pi^*) \rightarrow S_0$	10	10^{-4}

Jablonski Diagram





Alexander Jablonski (1898-1980)

Shapes of Absorption and Emission Spectra



Shapes of Absorption Spectra



Vibrational Part Limits the Electronic Transition Franck-Condon Principle



Electron jump between orbitals generally takes $\sim 10^{-15}$ to 10^{-16} s Nuclear vibrations take $\sim 10^{-13}$ to 10^{-14} s

Condon

Mirror Image Rule and Stoke's shift





G.G. Stokes (1819-1903)

Owing to a decrease in bonding of the molecule in its excited state compared to that of the ground state, the energy difference between S_0 and S_1 is lowered prior to fluorescence emission (in about 0.1 to 100 ps). This is called Stokes' shift. **Shapes of Absorption and Emission Spectra**

Mirror Image Rule and Stoke's shift



Mirror Image Rule and Stoke's shift



Importance of 0, 0 band

Triplet State and Phosphorescence



G. N. Lewis



Kasha



S. Vavilov



A. Terenin



Porter

Singlet-Triplet Crossing



El-Sayed's Rule

Intersystem crossing is likely to be very slow unless it involves a change of orbital configuration.





Spin-Orbit Coupling and Heavy Atom Effect

Field at a molecular level is generated from the *orbital motion* of the electron around the nucleus.

$$\hat{H}_{SO} = \zeta l \cdot s$$
$$\zeta_{n,l} \propto \frac{Z^4}{n^3 l(l+1/2)(l+1)}$$

The Spin-Orbit coupling constant depends on the fourth power of the atomic number and its effect is very large for heavy atoms.

Fluorescence and Phosphorescence



The heavy atom effect on spin transitions

The "heavy atom" effect is an "atomic number" effect that is related to the coupling of the electron spin and electron orbital motions (spin-orbit coupling, SOC).

Most commonly, the HAE refers to the rate enhancement of a spin forbidden photophysical radiative or radiationless transition that is due to the presence of an atom of high atomic number, Z.

The heavy atom may be either <u>internal</u> to a molecule (molecular) or <u>external</u> (supramolecular).

Spin-orbit coupling energies for selected atoms

	Atomic			Atomic	
Atom	number	ζ (kcal mol ⁻¹)	Atom	number	ζ (kcal mol ⁻¹)
C ^c	6	0.1	Ι	53	14.0
N ^c	7	0.2	Kr	36	15
O ^c	8	0.4	Xe	54	28
F ^c	9	0.7	Pb	82	21
Si ^c	14	0.4	Hg	80	18
P ^c	15	0.7	Na	11	0.1
Sc	16	1.0	Κ	19	0.2
Cl ^c	17	1.7	Rb	37	1.0
Br	35	7.0	Cs	55	2.4

 Table 4.7
 Spin–Orbit Coupling in Atoms^{a,b}

Internal Heavy Atom Effect



External Heavy Atom Effect



External Heavy Atom Effect



Examples of internal heavy atom effect

Molecule	$k_{\rm F}^0$	$k_{\rm ST}$	$k_{ m P}^0$	$k_{\rm TS}$	$\Phi_{\rm F}$	$\Phi_{\rm P}$
Naphthalene	10 ⁶	10 ⁶	10^{-1}	10^{-1}	0.55	0.05
1-Fluoronaphthalene	10^{6}	10^{6}	10^{-1}	10^{-1}	0.84	0.06
1-Chloronaphthalene	10 ⁶	10^{8}	10	10	0.06	0.54
1-Bromonaphthalene	10 ⁶	10 ⁹	50	50	0.002	0.55
1-Iodonaphthalene	10 ⁶	10 ¹⁰	500	100	0.000	0.70





Fluorescence:

- High radiative rate constant, 10¹⁰ to 10⁸ s⁻¹
- Precursor state (S_1) has short lifetime
- · Generally not susceptible to quenching

Phosphorescence:

- \cdot Low radiative rate constant, 10° to 10 s^{-1}
- \cdot Precursor state (T₁) has long lifetime
- Very much susceptible to quenching
- \cdot Emission quantum yield depends on S1 to T1 crossing

FLUORESCENCE & PHOSPHORESCENCE

Luminescence is a property exhibited by minerals that emit visible light, usually as a result of irradiation by invisible light. Luminescence includes both FLUORESCENCE, the emission of light at the same time as the irradiation, and PHOSPHORESCENCE, the continued emission of light after irradiation has ceased. Luminescence is best shown in a darkened exhibit, using invisible ultraviolet radiation to demonstrate the property.

As ultraviolet radiation strikes the atoms of luminescent minerals, the energy causes electrons to move from their normal orbits to paths farther out. The return of the displaced electrons to their normal orbits is accompanied by a release of energy in the form of light. Thus, a fluorescent mineral will glow while being irradiated. In a phosphorescent mineral, return of the electrons is slower, so that a lingering emission of light occurs.

Luminescence is often related to a defect in the mineral's crystal lattice or to the presence of foreign ions. Thus, a typically fluorescent mineral may also occur in a nonfluorescent form.





Kasha's rule

Fluorescence occurs only from S_1 to S_0 phosphorescence occurs only from T_1 to S_0 S_n and T_n emissions are extremely rare.





Exceptions



Exceptions



Excimers ... 10 mM 1.5 --- 7.5 mM normalized fluorescence intensity Th. Förster 1.0 -5 mM in methylcyclohexane solution 2.5 mM 0.5 -1 mM 0.1 mM -- 0.01 mM 0.0 0 500 wavelength (nm) 350 400 450 550 600 650

Albert F. Weller

Pyrene as an exemplar of excimer formation

hν









Excimer







Bimolecular absorption and emission: Excited state complexes





Delayed Fluorescence



Fig. 1.11 Illustrating production of delayed thermal fluorescence (DTF).



Types of emissions

□ Fluorescence Phosphorescence Emission from upper excited states **D** Excimer emission Exciplex emission □ TICT emission Delayed fluorescence

Points to Remember

- Electronic Configuration of States, $n\pi^*$; $\pi\pi^*$
- Spin Configuration of States (S and T)
- Singlet-Triplet Gap, ΔE (S-T)
- Rules of Intersystem Crossing (El-Sayed's Rule)
- Heavy Atom Effect
- Absorption and Emission
- Fluorescence and Phosphorescence
- Radiative and Radiationless Transitions
- Kasha's Rule