Advanced Organic Chemistry
Chm 512/412
Spring 2010

Handout I
“Photochemistry Part 1

Photophysical Processes
Quenching
Alkene cis-trans Isomerization
Importance of Photochemistry/Photophysics

**Organic Synthesis**
- strained multiple bonds
- cyclobutanes
- oxetanes
- 1,2 diols
- polycyclic compounds
- reactive intermediates: nitrenes; carbenes; radicals

**Analytical Chemistry**
Fluorescence Spectroscopy & Luminescence Imaging Techniques
Chemical sensors

**Material Sciences**
- Photopolymerization
- Photochromic Materials
- Photography
- Photolithography

**Photochromism**
Clean Energy through Photochemistry without CO$_2$ Emission

- Photovoltaic cells
- Photochemical splitting of water

$$\text{H}_2\text{O} \xrightarrow{\text{photocatalyst}} \text{H}_2 + \text{O}_2$$
**Photobiology**
Photochemistry of Biomolecules (Nucleic Acids, Amino acids, Proteins, Lipids)
Photosynthesis
Visual Transduction
Biological Effects of Solar Ultraviolet Radiation
Photocarcinogenesis

![Photobiology Diagram](image)

**Photomedicine**
Photochemotherapy
Photodynamic Phototherapy

![Photomedicine Diagram](image)
The Beginnings of Organic Photochemistry

1834: First photochemical transformation described by Trommsdorff: Exposed α-Santonin (1) crystals to sunlight and observed that they turned yellow and bursted. The mechanism was elucidated in 2007 by Arunkumar Natarajan et al.
Photochemistry

- Study of reactions that involve excited states of organic molecules

These reactions are initiated by the absorption of a photon by one reactant leading to its excited state \((\text{Excitation Process})\)
Grotthus-Draper Law
(First Law of Photochemistry)

“Only radiation absorbed in a system can produce a chemical change.”

\[ \text{hv} \quad \text{R} \rightarrow \text{R}^* \rightarrow \text{P} \]

ground state \quad \text{excited state}

Stark-Einstein Law of Photochemical Equivalence

“Number of activated molecules = number of quanta of radiation absorbed.”

\[ 1 \text{ hv} + 1 \text{ R}_0 \rightarrow 1 \text{ R}^* \]
Photochemistry

\[ \text{hv} \]

R \rightarrow R^* \rightarrow P
ground state \rightarrow \text{excited state}

Properties of Excited State: geometry; electronic configuration

Photophysical Processes

1) Relaxation Processes
- Dissipation of energy and change of electronic configuration after excitation
  - Vibrational Relaxation
  - Internal Conversion
  - Intersystem Crossing

2) Decay Processes
- Return to ground state with release of energy
  - Quenching – energy transfer
  - Fluorescence
  - Phosphorescence
  - Luminescence

Photochemical Processes

- Chemical reactions of the excited state
  - fragmentations
  - cis/trans isomerizations
  - rearrangements
  - addition/cyclization reactions
  - photo oxidations

Important Compound Classes

- alkenes, dienes & polyenes
- aromatic compounds
- carbonyl compounds
- nitrogen-containing compounds
  - (R-N_3, RR’C=N_2, R-NO_2, R-N=N-R, R-ONO)
- singlet oxygen
- halogen-containing compounds
Excited State of the Molecule

- Energy of the molecule has increased by the energy of the absorbed photon
- Photochemistry deals in part with properties of the excited state

\[
E_{\text{exc}} = E^* - E_0 = h\nu = hc/\lambda
\]

- Wavelength range of most photochemical reactions:
  UV/Vis region: \(200 \text{ nm} \leq \lambda \leq 700 \text{ nm}\); \(143 \text{ kcal/mol} \geq E \geq 40.8 \text{ kcal/mol}\)

With modern high intensity light sources (lasers) two photon excitation is possible (IR photolysis)
Photochemical Excitation

Adsorption of a photon is accompanied with an *electronic transition*

### Ground State vs. Excited States

- **Ground State**
  - $\pi_4$
  - $\pi_3$
  - $\pi_2$
  - $\pi_1$

- **Singlet Excited States**
  - $S_0$ (first excited state)
  - $S_1$
  - $S_2$
  - $S_3$

- **Triplet Excited States**
  - $T_1$ (first excited state)

### Electronic Configurations

<table>
<thead>
<tr>
<th>Electronic State (enumerative)</th>
<th>Excited State (Kasha)</th>
<th>Electronic Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>-</td>
<td>$(\pi_1 \downarrow \uparrow)^2 (\pi_2 \downarrow \uparrow)^2 (\pi_3)^0 (\pi_4)^0$</td>
</tr>
<tr>
<td>$S_1$</td>
<td>$^1(\pi_2, \pi_3)$</td>
<td>$(\pi_1 \downarrow \uparrow)^2 (\pi_2 \downarrow)^1 (\pi_3 \uparrow)^1 (\pi_4)^0$</td>
</tr>
<tr>
<td>$S_2$</td>
<td>$^1(\pi_2, \pi_4)$</td>
<td>$(\pi_1 \downarrow)^1 (\pi_2 \uparrow \downarrow)^2 (\pi_3 \uparrow)^1 (\pi_4)^0$</td>
</tr>
<tr>
<td>$S_3$</td>
<td>$^1(\pi_1, \pi_3)$</td>
<td>$(\pi_1 \uparrow \downarrow)^2 (\pi_2 \downarrow)^2 (\pi_3)^0 (\pi_4 \uparrow)^0$</td>
</tr>
<tr>
<td>$T_1$</td>
<td>$^3(\pi_2, \pi_3)$</td>
<td>$(\pi_1 \uparrow \downarrow)^2 (\pi_2 \downarrow \uparrow)^1 (\pi_3 \downarrow)^1 (\pi_4)^0$</td>
</tr>
</tbody>
</table>
Symbolism to denote electronic states, excited states and electronic transitions

1. Electronic states and excited states
   (a) Enumerative system
   Used if the electronic configuration of the excited state is not known. States are labeled according to multiplicity and increasing energy.

   $S_0$ for ground state and $S_1$, $S_2$, … and $T_1$, $T_2$, … for first, second,… singlet and triplet states.

   (b) Kasha’s MO representation for excited states
   Used, if electronic configuration of excited states are known. Excited states are labeled by type of MOs involved and multiplicity.

   $1(\pi_2, \pi_3)$, $1(\pi_2, \pi_4)$, $3(\pi_2, \pi_3)$, $3(\pi_2, \pi_4)$ for $S_1$, $S_2$, $T_1$ and $T_2$

   Superscript 1 or 3 stands for multiplicity
   The two MOs are those involved in the transition.

2. Electronic Transitions
   (a) Enumerative system
   An arrow denotes the transition from the starting electronic state to the final electronic state.

   $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $T_1 \rightarrow S_1$

   (b) Kasha’s MO formalism
   Based on the type of ground state MO involved ($\sigma$, $\sigma^*$, $\pi$, $\pi^*$) in process. The transition is denoted by an arrow directed from the symbol of the initially occupied MO to the symbol of the initially unoccupied MO.

   $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$
Jablonski State Diagram

(1) Absorption
(2) Relaxation
(3) Fluorescence
(4) Internal Conversion
(5) Intersystem Crossing
(6) Phosphorescence
Example: Important electronic transitions of the carbonyl chromophore

<table>
<thead>
<tr>
<th>Transition</th>
<th>Excited State</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>n → π*</td>
<td>S_1</td>
<td>280-320 nm</td>
</tr>
<tr>
<td>n → σ*</td>
<td>S_2</td>
<td>~ 180 nm</td>
</tr>
<tr>
<td>π → π*</td>
<td>S_3</td>
<td>~ 160 nm</td>
</tr>
</tbody>
</table>

Dipole Moment

- S_0: 1.21 A
- S_1: 1.32 A

2.3 Debye

Electronic transitions involves a shift of one electrons from a lower to a higher energy molecular orbital. In most cases these molecular orbitals are associated with a specific part (e.g. functional group) of the molecule. *This part, that mainly absorbs the photon is termed the chromophore.*

Examples are aryl units, polyenes, and other pi-bonds, carbonyl, -NO$_2$, -N$_3$ and C-Hal groups.
Table 16.2
Typical Organic Chromophores

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$ (1/mol•cm)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C and C–H</td>
<td>&lt;180</td>
<td>1000</td>
<td>$\sigma \rightarrow \sigma^*$</td>
</tr>
<tr>
<td>C–O (alcohol)</td>
<td>≈180</td>
<td>200</td>
<td>$n \rightarrow \sigma^*$</td>
</tr>
<tr>
<td>C–S (alkyl sulfide)</td>
<td>210</td>
<td>1200</td>
<td>$n \rightarrow \sigma^*$</td>
</tr>
<tr>
<td>C–Br (alkyl bromide)</td>
<td>208</td>
<td>300</td>
<td>$n \rightarrow \sigma^*$</td>
</tr>
<tr>
<td>C–I (alkyl iodide)</td>
<td>260</td>
<td>400</td>
<td>$n \rightarrow \sigma^*$</td>
</tr>
<tr>
<td>C=C</td>
<td>180</td>
<td>10,000</td>
<td>$\pi,\pi^*$</td>
</tr>
<tr>
<td>C=C–C=C</td>
<td>220</td>
<td>20,000</td>
<td>$\pi,\pi^*$</td>
</tr>
<tr>
<td>C=C–C=C–C=C</td>
<td>260</td>
<td>50,000</td>
<td>$\pi,\pi^*$</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>260</td>
<td>200</td>
<td>$\pi,\pi^*$</td>
</tr>
<tr>
<td>Styrene</td>
<td>282</td>
<td>450</td>
<td>$\pi,\pi^*$</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>278</td>
<td>1100</td>
<td>$n,\pi^*$</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>310</td>
<td>200</td>
<td>$\pi,\pi^*$</td>
</tr>
<tr>
<td>Anthracene</td>
<td>380</td>
<td>10,000</td>
<td>$\pi,\pi^*$</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>330</td>
<td>125</td>
<td>$n,\pi^*$</td>
</tr>
<tr>
<td>C=O</td>
<td>280</td>
<td>20</td>
<td>$n,\pi^*$</td>
</tr>
<tr>
<td>N=N</td>
<td>350</td>
<td>100</td>
<td>$n,\pi^*$</td>
</tr>
<tr>
<td>−NO$_2$</td>
<td>270</td>
<td>20</td>
<td>$n,\pi^*$</td>
</tr>
<tr>
<td>N=O</td>
<td>660</td>
<td>200</td>
<td>$n,\pi^*$</td>
</tr>
<tr>
<td>C=C–C=O</td>
<td>350</td>
<td>30</td>
<td>$n,\pi^*$</td>
</tr>
<tr>
<td>C=C–C=O</td>
<td>220</td>
<td>20,000</td>
<td>$\pi,\pi^*$</td>
</tr>
</tbody>
</table>
Spin Selection Rule

An electronic transitions is allowed by the spin selection rule only if the multiplicity of the initial and final state are identical. E.g.

\[
\begin{align*}
S & \rightarrow S & T & \rightarrow T & \text{are allowed} \\
S & \rightarrow T & T & \rightarrow S & \text{are forbidden}
\end{align*}
\]

Symmetry Selection Rule

(restricted to most common electronic transitions)

\[
\begin{align*}
symmetry \text{ allowed are:} & \quad \pi & \rightarrow & \pi^*; & \quad \sigma & \rightarrow & \sigma^* \\
\text{symmetry forbidden are:} & \quad n & \rightarrow & \pi^*; & \quad n & \rightarrow & \sigma^*
\end{align*}
\]

Allowed transitions are strong (\(\epsilon \ 1000-10^5\))
Symmetry forbidden transitions are weak (\(\epsilon \ 1-1000\))
Symmetry and spin forbidden transitions are very weak (\(\epsilon \ 10^{-5} \ -1\))
Jablonski State Diagram

1. Absorption
2. Relaxation
3. Fluorescence
4. Internal Conversion
5. Intersystem Crossing
6. Phosphorescence
Internal Conversion: Transition between two surfaces having the same multiplicity

Rate $k_{IC}$ depends on energy difference between surfaces

Internal conversion is usually fast if vibrational level 0 of $S_{x+1}$ state overlaps with vibrational level of $S_x$ state. This is typically the case for $x > 1$ ($k'_{IC} > 10^9 \text{ s}^{-1}$). However, it is not the case for $S_1 \rightarrow S_0$ transitions, which is substantially slower ($k_{IC} < 10^6 \text{ s}^{-1}$).
Jablonski State Diagram

(1) Absorption
(2) Relaxation
(3) Fluorescence
(4) Internal Conversion
(5) Intersystem Crossing
(6) Phosphorescence
Excitation and Emission Spectrum of Fluorescein

\[ I_e = 2.3 I_0 \varepsilon \Phi_f b c \]

Figure 16.5
Overlay of the emission and excitation spectra of anthracene. Both are taken in toluene.

- \( I_e \): Intensity of emitted light
- \( I_0 \): Irradiation intensity
- \( \varepsilon \): Extinction coefficient
- \( \Phi_f \): Fluorescence quantum yield
- \( b \): Path length of cell
- \( c \): Concentration

Excitation and Emission Spectrum of Fluorescein
Jablonski State Diagram

1. Absorption
2. Relaxation
3. Fluorescence
4. Internal Conversion
5. Intersystem Crossing
6. Phosphorescence

$S_0$ $S_1$ $S_2$ $T_1$

$E$

radiative

radiationless
**Intersystem Crossing**

Crossing of surfaces with different spin multiplicity

- singlet $\rightarrow$ triplet  \( S_1 \rightarrow T_1, T_2 \)  \( \text{non-radiative} \)
- triplet $\rightarrow$ singlet  \( T_1 \rightarrow S_0 \)  \( \text{non-radiative or radiative (phosphorescence)} \)

1) \( T_1 \) lower than \( S_1 \) (Hund’s Rule)

2) Intersystem crossing involves
   - **spin flip** ↔ change in spin angular momentum
   - quantum mechanically forbidden
   - $\Rightarrow$ slow

3) Intersystem crossing is fast (allowed)
   - if **change in spin angular momentum** is accompanied by
     - change in orbital angular momentum
   - $\Rightarrow$ total angular momentum conserved
**El Sayed’s Rules**

Predict, whether intersystem crossing in molecules without heavy atoms (molecules only containing 1\textsuperscript{st} and 2\textsuperscript{nd} row elements H, C, N, O) is allowed (favorable) or forbidden (unfavorable)

**Transition between excited states**

<table>
<thead>
<tr>
<th>Transition</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1(n, \pi^<em>) \leftrightarrow ^3(n, \pi^</em>)$</td>
<td>forbidden</td>
</tr>
<tr>
<td>$^1(\pi, \pi^<em>) \leftrightarrow ^3(\pi, \pi^</em>)$</td>
<td>forbidden</td>
</tr>
<tr>
<td>$^1(n, \pi^<em>) \leftrightarrow ^3(\pi, \pi^</em>)$</td>
<td>allowed</td>
</tr>
<tr>
<td>$^1(\pi, \pi^<em>) \leftrightarrow ^3(n, \pi^</em>)$</td>
<td>allowed</td>
</tr>
<tr>
<td>$^3(n, \pi^*) \leftrightarrow$ ground state</td>
<td>allowed</td>
</tr>
<tr>
<td>$^3(\pi, \pi^*) \leftrightarrow$ ground state</td>
<td>forbidden</td>
</tr>
</tbody>
</table>
Intersystem Crossing of Carbonyl Compounds
Spin-Orbit Coupling

\[ \text{S}_0 \rightarrow \text{S}_1 \]  

\[ \text{S}_1 \rightarrow \text{T}_1 \]  

\[ \text{ISC} \text{S}_1 \rightarrow \text{T}_2 \]
Rate constant of ISC depends on energy difference between S\textsubscript{1} and T\textsubscript{1}/T\textsubscript{2}

Strongly endotherm -> no intersystem crossing
Fastest if slightly exotherm or equal in energy

\[ k_{\text{ISC}} \sim 10^{11} \text{ s}^{-1} \]

\[ k_{\text{IC}} \sim 10^{9} \text{ s}^{-1} \]

\[ k_{\text{ISC}} \gg k_{\text{IC}} \text{ (S}_0 \rightarrow \text{S}_1) \]
Examples of Intersystem Crossing Rate Constants

$k_{ST}$ in $s^{-1}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>$5 \times 10^6$</td>
</tr>
<tr>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>$&lt;10^7$</td>
</tr>
<tr>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>$10^9$</td>
</tr>
<tr>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>$10^{10}$</td>
</tr>
<tr>
<td><img src="image5" alt="Chemical Structure" /></td>
<td>$10^{11}$</td>
</tr>
</tbody>
</table>

Heavy Atom Effect
Examples of Phosphorescence Lifetimes of Organic Compounds
In Ethanol at 77K

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau$ in s</th>
<th>$\lambda_{em}$ in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>0.007</td>
<td>415</td>
</tr>
<tr>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>0.007</td>
<td>445</td>
</tr>
<tr>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>0.002</td>
<td>507</td>
</tr>
<tr>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>2.3</td>
<td>515</td>
</tr>
<tr>
<td><img src="image5" alt="Chemical Structure" /></td>
<td>4.2</td>
<td>460</td>
</tr>
<tr>
<td><img src="image6" alt="Chemical Structure" /></td>
<td>6.6</td>
<td>440</td>
</tr>
</tbody>
</table>

Analytical Chemistry (1973) 45, 381.
Quenching

- Decay of excited state induced by a collision with another molecule (quencher). **Bimolecular process.**

\[
\begin{align*}
A^* & \xrightarrow{k_f} A \quad \text{lifetime of } A^* \text{ without } Q: \tau_f \sim 1/k_f \\
Q + A^* & \xrightarrow{k_q} A \quad \text{lifetime of } A^* \text{ with } Q = \tau_2
\end{align*}
\]

\[
1/\tau_2 = k_f + k_q [Q] = 1/\tau_f + k_q [Q] \quad \text{(Stern-Volmer Equation)}
\]

- **Chemical quenching:** Energy is transferred to quencher and converted into chemical energy. Quencher undergoes a chemical reaction.
- **Physical quenching:**
  - *self-quenching or impurity quenching:* energy transfer, electron transfer or heavy-atom quenching (accelerated decay of excited state upon collision with a molecule (e.g. solvent) containing a heavy atom (3rd row or higher)).
Eximer Spectrum of 9-Methylanthracene

Figure 2. Fluorescence spectra of 9-methylanthracene in benzene at R.T.; conc.
1: $10^{-4}$ M; 2: $10^{-2}$ M; 3: $2 \times 10^{-1}$ M.

(From: Brinks, J. B. & Aladekomo, J. B., Photochem. Photobiol., 1963, 2, 415-418)
**Exiplex**: Excited state complex or absorption complex. Complex between an excited state and a ground state molecule.

**Eximer**: Complex between two identical molecules of which one is in the excited state and the other in the ground state

Stabilized by *induced dipole-dipole interactions or dispersion interactions*, due to the high polarizability of the excited state, and by *donor-acceptor interactions*

Eximers are often observed for polyaromatic compounds such as anthracene and pyrene and can be identified in the fluorescence spectra of both compounds. The maximum of the emission spectrum of the eximer is shifted to higher wavelength (lower energy) relative to that of the monomeric excited state.

![Chemical structures](eximer Structures.png)
Common Organic and Inorganic Triplet Sensitizer and Triplet Energy $E_T$

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>$E_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mol</td>
</tr>
<tr>
<td>mercury</td>
<td>472</td>
</tr>
<tr>
<td>pyridine</td>
<td>355</td>
</tr>
<tr>
<td>benzene</td>
<td>351</td>
</tr>
<tr>
<td>anisole</td>
<td>339</td>
</tr>
<tr>
<td>acetone</td>
<td>326</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>322</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>301</td>
</tr>
<tr>
<td>benzophenone</td>
<td>288</td>
</tr>
<tr>
<td>biphenyl</td>
<td>276</td>
</tr>
<tr>
<td>trans-stilbene</td>
<td>209</td>
</tr>
<tr>
<td>anthracene</td>
<td>180</td>
</tr>
</tbody>
</table>

From Kavarnos & Turro, *Chem. Rev.* 1986, 86, 401
Diabatic photochemical process

\[ R \xrightarrow{h\nu} P \]

Adiabatic photochemical process

\[ R \xrightarrow{h\nu} P \]

Diabatic photochemical process:

- Reaction coordinate: R → TS → P
- Energy diagram: \( S_0 \) to \( S_1 \) to \( S_0 \)

Adiabatic photochemical process:

- Reaction coordinate: R → TS → P
- Energy diagram: \( S_0 \) to \( S_1 \) to \( S_0 \)
Quantum Yield

\[ \Phi_n = \frac{\text{number of molecules that undergo photochemical process } n}{\text{number of photons absorbed}} \]

Fluorescence quantum yield \( \Phi_f \)

\[ \Phi_f = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} < 1 \]

Quantum yield of a photochemical reaction \( \Phi_r \)

\[ \Phi_r = \frac{\text{number of product molecules formed}}{\text{number of photons absorbed}} \]

Typically \( \leq 1 \) but can be \( >> \) than 1, e.g. in photo polymerization or light initiated radical chain reactions.
Mechanism of the Photoinduced *cis-trans* Isomerization of Stilbene (PhCH=CHPh)
Triplet Sensitization or Organic Molecules

3.37 DIRECT IRRADIATION: EXCITATION $h\nu$

\[ S_0 \underset{h\nu}{\overset{S_1}{\longrightarrow}} T_2 \overset{T_1}{\underset{S'_1}{\longrightarrow}} \]

SENSITIZATION: EXCITATION $h\nu' < h\nu$

\[ S_0 \underset{h\nu}{\overset{S_1}{\longrightarrow}} T_2 \overset{T_1}{\underset{S'_1}{\longrightarrow}} \]

\[ S_0 \underset{h\nu'}{\overset{S_0}{\longrightarrow}} T_1 \overset{T_1}{\underset{S_0}{\longrightarrow}} \]

Compound A     Sensitizer

\[ E \]

planar ethylene  orthogonal ethylene  sensitizer
Dependence of the photostationary state of the triplet sensitized cis-trans stilbene isomerization on the triplet energy $E_T$ of the sensitizer.

![Diagram of stilbene isomerization](image)