Photochemical reactions

Light (photon)/matter interactions

- **Photon/matter interactions play roles in**
  - Transformations
    - Atmospheric chemistry
    - Surface waters
    - Water & wastewater treatment (disinfection)
  - Analysis
    - Light absorption $f(\lambda, C_{compound})$

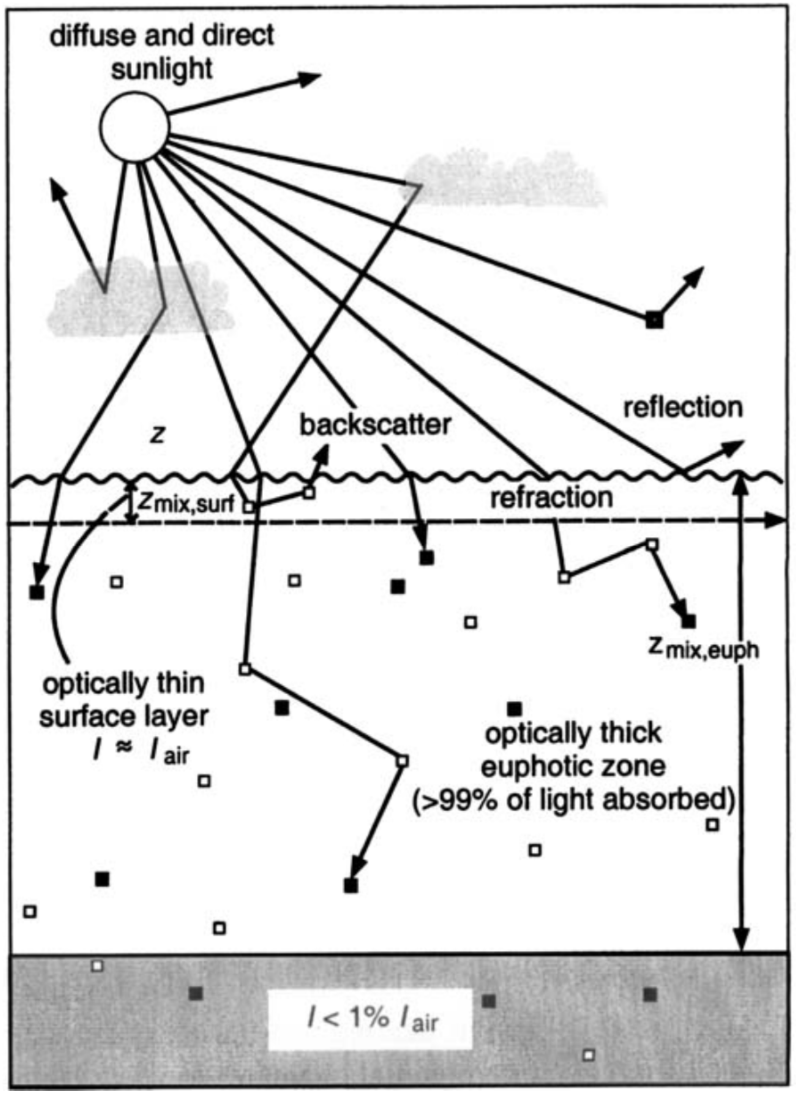
- **Photolytic transformations are often non-specific**
  - Attack bonds & structures resistant to biodegradation & other pathways
    - Growing concern about synthetic chemicals
  - Potential for complete mineralization – CO_2, H_2O, inorganic N & P
  - Combine with photocatalysts – visible light catalysis

Light (photon)/matter interactions

- **Light interact with matter in two ways**

  (1) Scattering
    - Elastic process (energy of light not substantially changed)

  (2) Absorption
    - Capture of the photon
    - Moves electron from low energy (ground) to high energy state



Basic laws of photochemistry

- **Grotthuss-Draper Law** (1st law of photochemistry):

  Light must be absorbed in order for a photochemical reaction to take place

- **Stark-Einstein Law** (2nd law of photochemistry):

  For each photon of light absorbed by a chemical system, only one molecule is activated

Photolysis – general

Molecule + photon $\longrightarrow$ Molecule* $\longrightarrow$ Products

(direct photolysis)

- **Photolysis**
  - Refers to light induced chemical transformations
  - Requires absorption of a photon by a molecule

- **Photon absorption**
  - As a consequence, electrons are excited: may break the covalent bond to produce a different compound
  - Absorptivity typically wavelength & solvent dependent

Photolysis – general

- **Light: source of energy**

$$E = h\nu = h\frac{c}{\lambda}$$

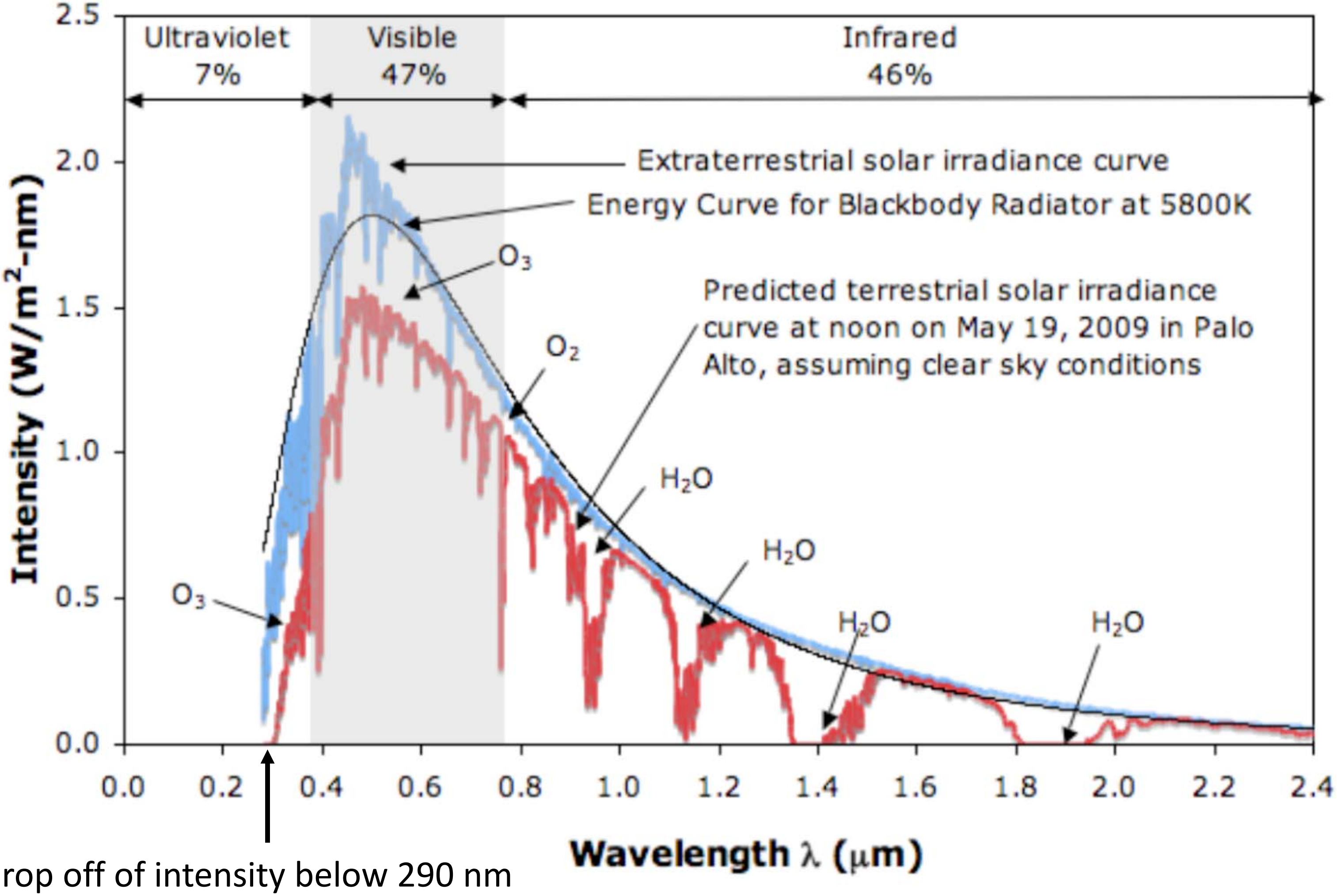
E = energy of a photon (J/photon)
h = 6.626 x 10^{-34} J·s, Planck constant
ν = frequency of light (s^{-1})
c = 3.0 x 10^{8} m/s, speed of light in a vacuum
λ = wavelength of light (m)

On a molar basis,

$$\boldsymbol{E} = 6.02 \times 10^{23} \cdot h\frac{c}{\lambda} = \frac{1.196 \times 10^{5}}{\lambda} kJ/einstein$$

$\boldsymbol{E}$ = energy of light on a molar basis (kJ/einstein)
einstein: 1 mole of photons
λ = wavelength of light in nm

Solar flux & absorption



Drop off of intensity below 290 nm

Bond energies & light absorption

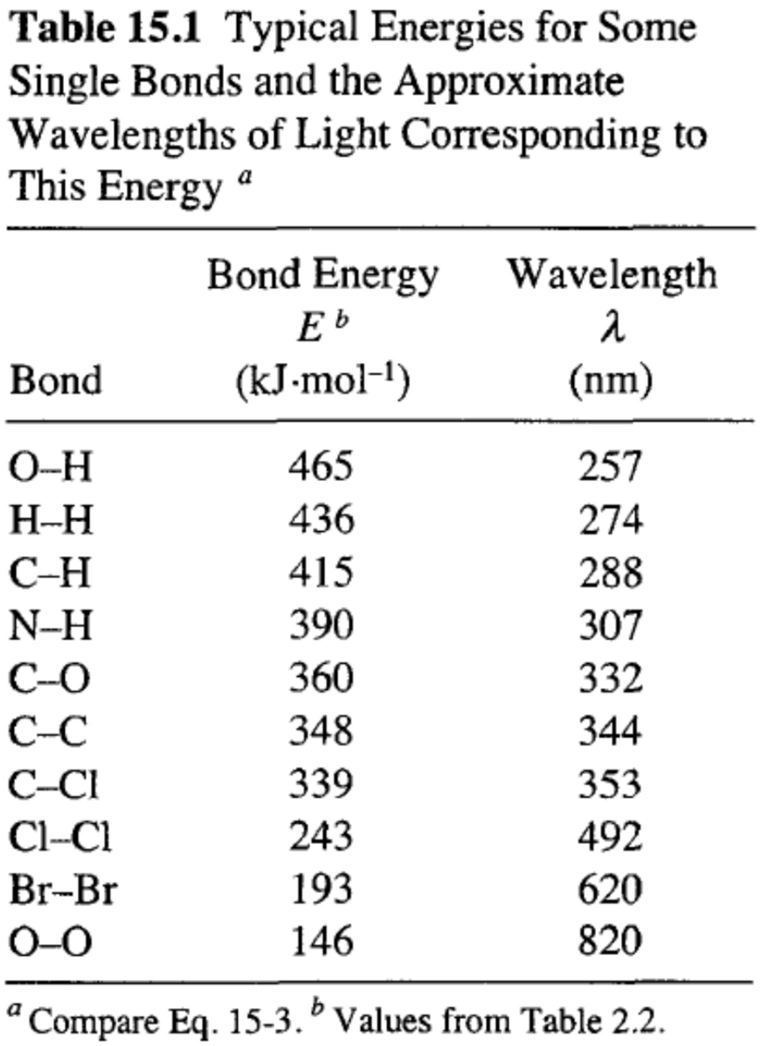


Table 15.1 Typical Energies for Some Single Bonds and the Approximate Wavelengths of Light Corresponding to This Energy [a]

Bond	Bond Energy E^b ($kJ \cdot mol^{-1}$)	Wavelength λ (nm)
O–H	465	257
H–H	436	274
C–H	415	288
N–H	390	307
C–O	360	332
C–C	348	344
C–Cl	339	353
Cl–Cl	243	492
Br–Br	193	620
O–O	146	820

[a] Compare Eq. 15-3. [b] Values from Table 2.2.

- Compare to:

$$\boldsymbol{E} = \frac{1.196 \times 10^5}{\lambda} kJ/einstein$$

- Energy of UV/visible light ~ covalent bonds

→ The covalent bonds may be cleaved as a consequence of UV/visible light absorption

Absorbance

- Whether the photochemical reactions will take place depends on
  i) The probability with which a given compound absorbs light of a given wavelength
  ii) The probability that the excited species undergoes a particular reaction

- **Absorbance: *Beer-Lambert law***

$$A(\lambda) = log_{10}\frac{I_0(\lambda)}{I(\lambda)} = [\alpha(\lambda) + \varepsilon_i(\lambda)C_i] \cdot l$$

A = absorbance

I_0 & I = light intensity at $x=0$ & l, respectively (e.g., in einstein/cm^2-s)

α = absorption coefficient of the solvent (cm^{-1})

ε_i = molar absorption coefficient for solute *i* (M^{-1}·cm^{-1})

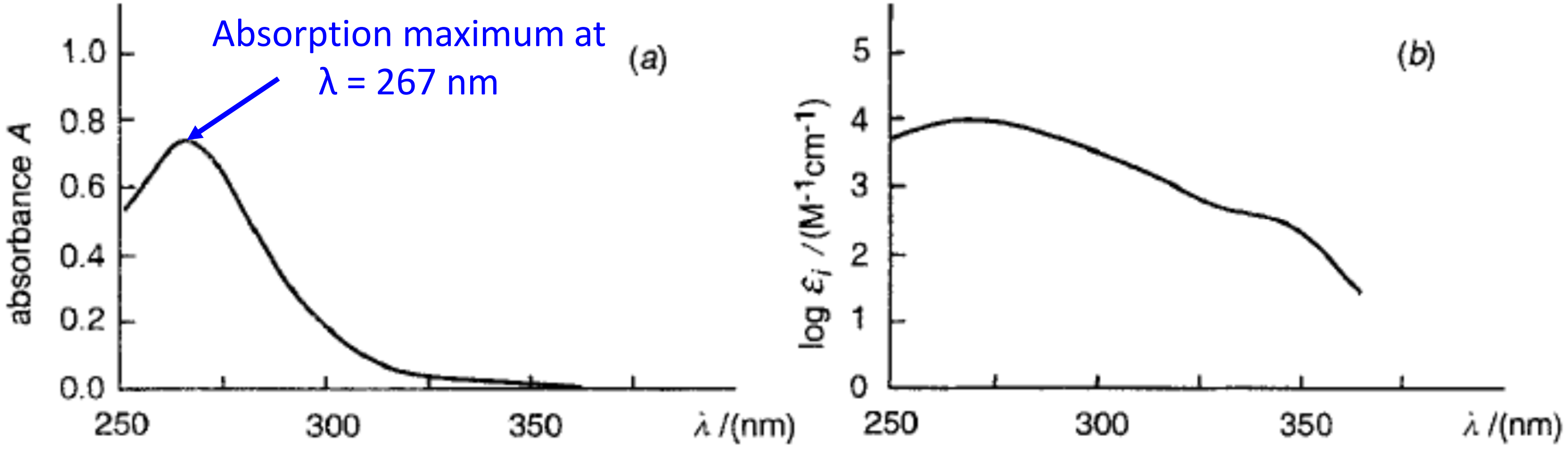
C_i = concentration of solute *i* (M)

l = path length of light (cm)

Absorption spectrum

- Absorption spectrum easily measurable by UV-Vis spectrophotometer

0.1 mM nitrobenzene in aqueous solution

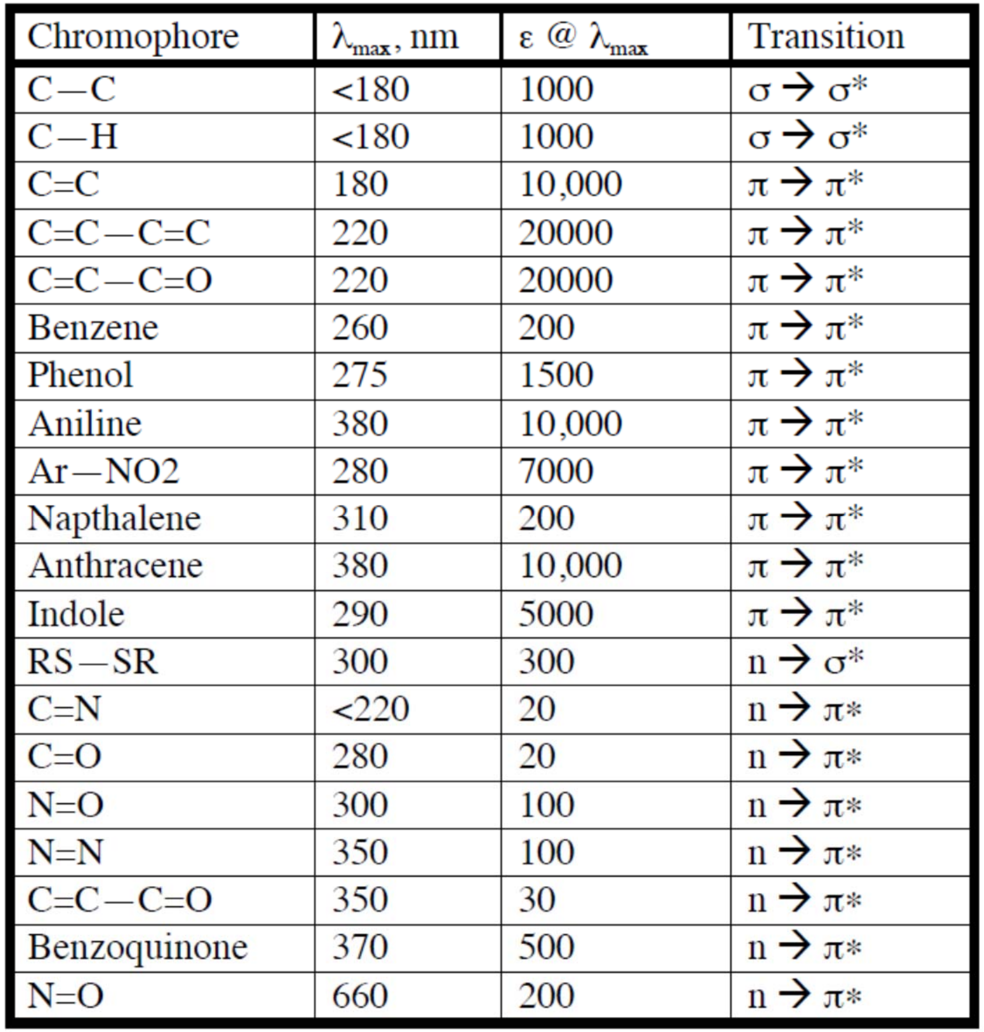


Absorption maximum at λ = 267 nm

Measure absorbance at each λ

Calculate molar extinction coefficient at each λ

Chromophores & light absorption



Chromophore	λ_{max}, nm	ε @ λ_{max}	Transition
C—C	<180	1000	$\sigma \rightarrow \sigma^*$
C—H	<180	1000	$\sigma \rightarrow \sigma^*$
C=C	180	10,000	$\pi \rightarrow \pi^*$
C=C—C=C	220	20000	$\pi \rightarrow \pi^*$
C=C—C=O	220	20000	$\pi \rightarrow \pi^*$
Benzene	260	200	$\pi \rightarrow \pi^*$
Phenol	275	1500	$\pi \rightarrow \pi^*$
Aniline	380	10,000	$\pi \rightarrow \pi^*$
Ar—NO2	280	7000	$\pi \rightarrow \pi^*$
Napthalene	310	200	$\pi \rightarrow \pi^*$
Anthracene	380	10,000	$\pi \rightarrow \pi^*$
Indole	290	5000	$\pi \rightarrow \pi^*$
RS—SR	300	300	$n \rightarrow \sigma^*$
C=N	<220	20	$n \rightarrow \pi^*$
C=O	280	20	$n \rightarrow \pi^*$
N=O	300	100	$n \rightarrow \pi^*$
N=N	350	100	$n \rightarrow \pi^*$
C=C—C=O	350	30	$n \rightarrow \pi^*$
Benzoquinone	370	500	$n \rightarrow \pi^*$
N=O	660	200	$n \rightarrow \pi^*$

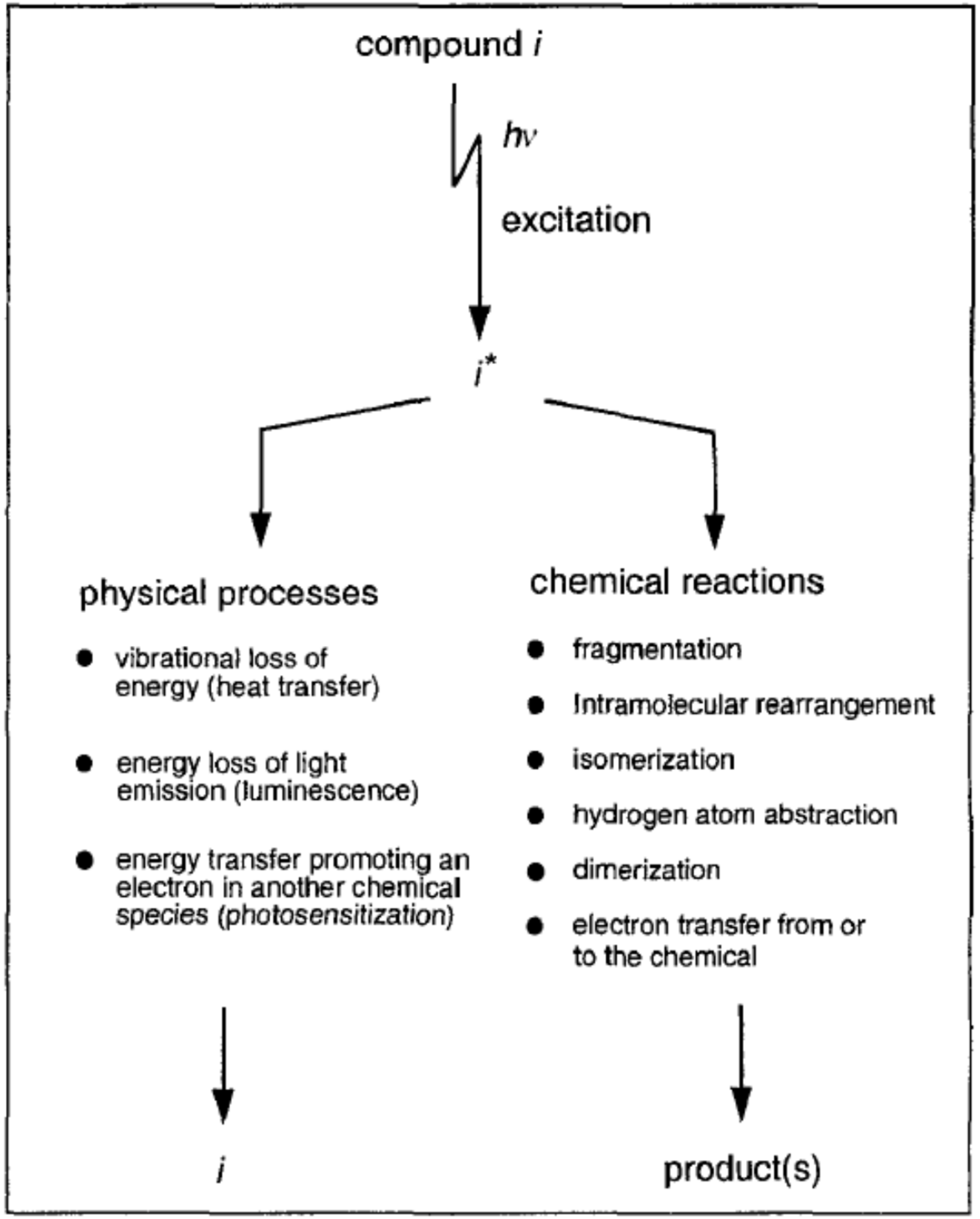
- **Chromophore**

  A structural moiety that exhibits a characteristic UV/Vis absorption spectrum
- Delocalized π electrons are often good chromophores
- λ<290 nm strongly absorbed in the atmosphere → not significant at natural conditions

λ_{max}: maximum absorption wavelength

ϵ: molar extinction coefficient

What happens after a molecule absorbs light?



compound *i*

hν

excitation

*i**

physical processes

- vibrational loss of energy (heat transfer)
- energy loss of light emission (luminescence)
- energy transfer promoting an electron in another chemical species (*photosensitization*)

i

chemical reactions

- fragmentation
- Intramolecular rearrangement
- isomerization
- hydrogen atom abstraction
- dimerization
- electron transfer from or to the chemical

product(s)

When molecule A absorbs a photon

$$\mathbf{A} \xrightarrow{h\nu} \mathbf{A^*}$$

$$A^* \longrightarrow B + C$$

$$A^* + D \longrightarrow B + C$$

- **Direct photolysis**

  When the molecule being transformed is the same species that absorbed the photon

$$A^* + B \longrightarrow A + C + D$$

$$A^* + B \longrightarrow A + C + D^*$$

$$A^* + B \longrightarrow A + B^*$$

$$B^* + C \longrightarrow B + E + F$$

- **Indirect photolysis**

  When the molecule being transformed is sensitized by other chemicals in the system excited by energy from light

$$A^* + B^* \longrightarrow A + B$$

$$A^* + M \longrightarrow A + M$$

- **Quenching**

  A species accepts the electronic energy of the sensitized compound

Direct photolysis

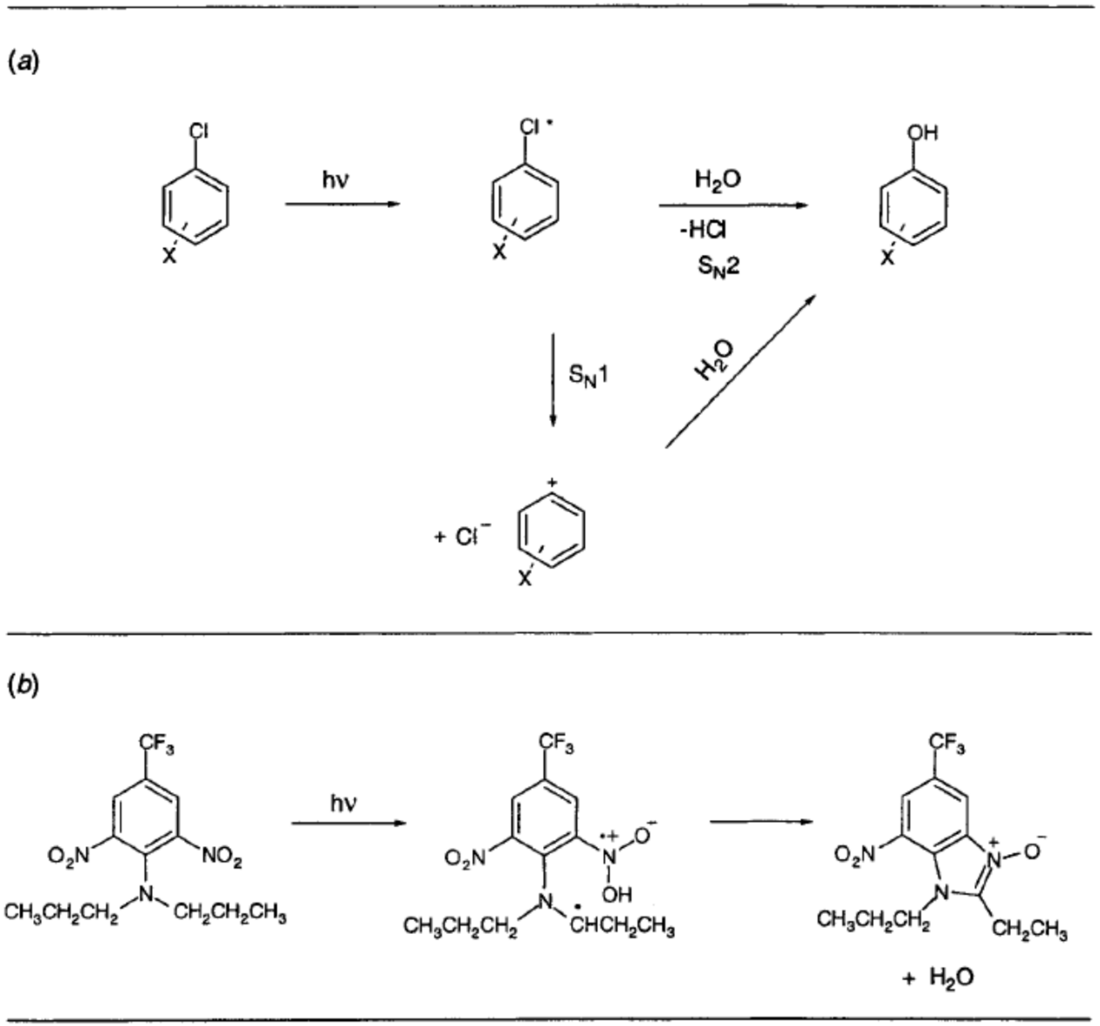


Figure 15.7 Examples of direct photochemical reaction pathways: (*a*) substituted chlorobenzenes, (*b*) trifluralin, and (*c*) a ketone (from Mill and Mabey, 1985).

Direct photolysis

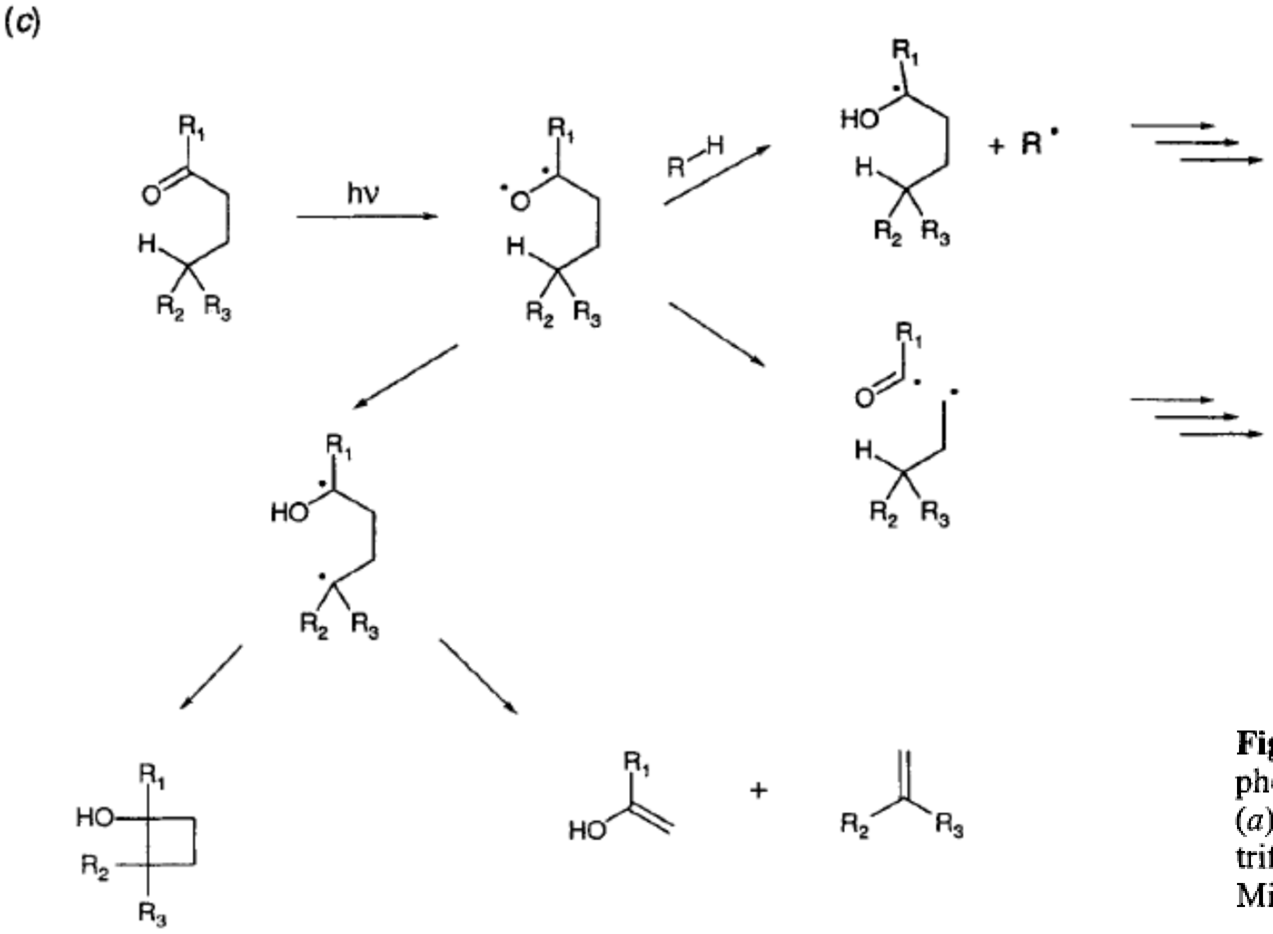


Figure 15.7 Examples of direct photochemical reaction pathways: (*a*) substituted chlorobenzenes, (*b*) trifluralin, and (*c*) a ketone (from Mill and Mabey, 1985).

Direct photolysis – transformation issues

- **Often have multiple pathways after photon absorption**
  - Multiple products
  - Multiple deactivation routes
    - Thermal
    - Phosphorescence/fluorescence
    - Interactions with solvent/solutes
- **Quantum yield, $\boldsymbol{\Phi(\lambda)}$**
  - Moles of compound transformed per moles of photons absorbed by the compound
    - Pathway specific or overall yields
      - Φs are often <<1; 10^{-2} – 10^{-6}

Direct photolysis – transformation issues

- **Quantum yield, $\boldsymbol{\Phi(\lambda)}$**
  - Quantum yield for reaction pathway *j*

$$\Phi_{ij}(\lambda) = \frac{(number\ of\ molecules\ i\ reacting\ by\ pathway\ j)}{\begin{matrix}(total\ number\ of\ photons\ of\ wavelength\ \lambda\ absorbed \\ by\ the\ system\ owing\ to\ the\ presence\ of\ the\ compound\ i)\end{matrix}}$$

  - Reaction quantum yield (for all reaction pathways)

$$\Phi_{ir}(\lambda) = \frac{(total\ number\ of\ molecules\ i\ transformed)}{\begin{matrix}(total\ number\ of\ photons\ of\ wavelength\ \lambda\ absorbed \\ by\ the\ system\ owing\ to\ the\ presence\ of\ the\ compound\ i)\end{matrix}}$$

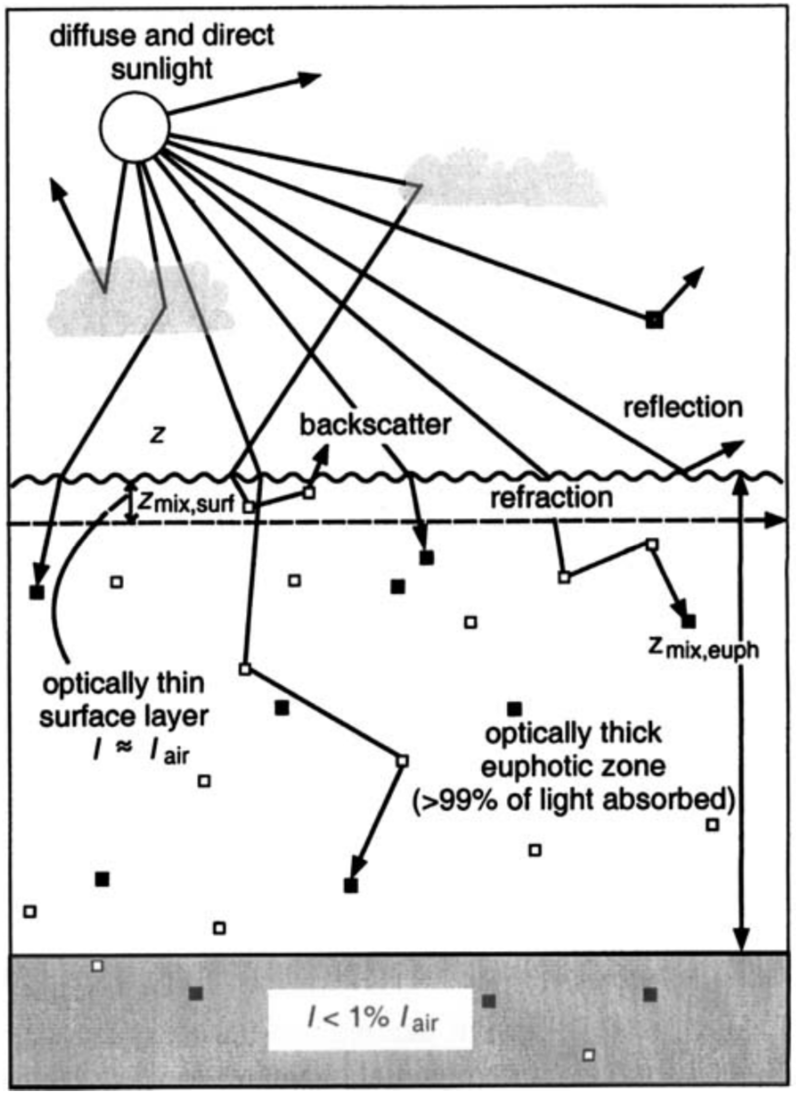
  - The reaction quantum yield has to determined by experiments

Direct photolysis – natural water

$$A(\lambda) = log_{10}\frac{I_0(\lambda)}{I(\lambda)} = [\alpha(\lambda) + \varepsilon_i(\lambda)C_i] \cdot l$$

Generally the light absorption by compound *i* is much smaller than other constituents in water

$$log_{10}\frac{I_0(\lambda)}{I(\lambda)} \approx \alpha(\lambda) \cdot l$$



Direct photolysis – natural water

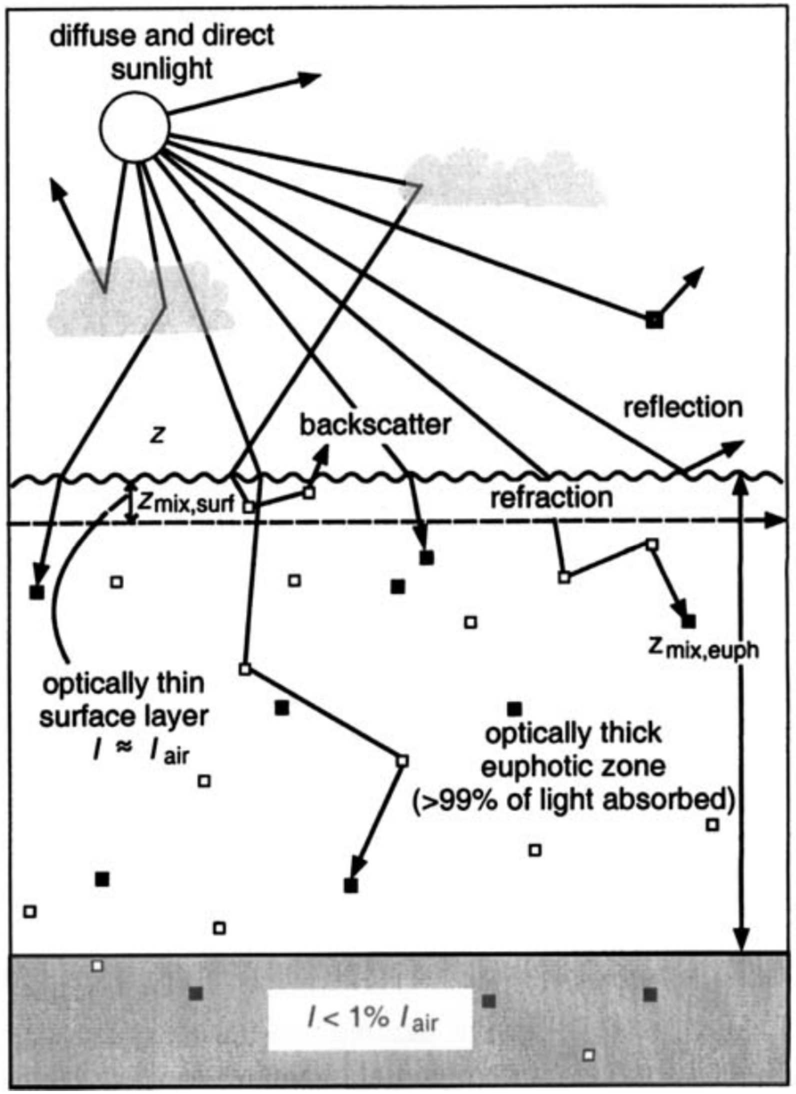
$$\alpha(\lambda) \cdot l = \alpha_D(\lambda) \cdot z_{mix}$$

$\alpha_D(\lambda)$ = diffuse attenuation coeff. (cm^{-1})
$z_{mix} = V/A$ = depth of mixed water body (cm)

$l \neq z_{mix}$ because:

i) The sunlight is not always perpendicular to water surface
ii) Light is scattered by suspended particles
iii) Light is absorbed and then reemitted by particles and dissolved matter

And l is a function of λ



Direct photolysis – natural water

so $I(z_{mix}, \lambda) = I_0(\lambda) \cdot 10^{-\alpha_D(\lambda) \cdot z_{mix}}$

Define $D(\lambda)$ as: $D(\lambda) = \dfrac{l(\lambda)}{z_{mix}}$

$$\alpha_D(\lambda) = D(\lambda)\alpha(\lambda)$$

$D(\lambda)$ = distribution function

For non-turbid water, 1.05~1.3

For very turbid water, up to 2.0

$\alpha(\lambda)$ -- can be determined by spectrophotometer;
$D(\lambda)$ -- can be determined by computer programs at the region of interest

Direct photolysis – natural water

Out interest: how much light will be absorbed between the depth of 0 to z_{mix} by a pollutant (per volume basis)

1) Rate of light absorption by all species in water (per surface area; in einstein/cm^2-s)

$$= I_0(\lambda) - I(z_{mix}, \lambda) = I_0(\lambda)\left[1 - 10^{-\alpha_D(\lambda)\cdot z_{mix}}\right]$$

2) Rate of light absorption by all species in water (per volume; in einstein/cm^3-s)

$$= \frac{I_0(\lambda)}{z_{mix}}\left[1 - 10^{-\alpha_D(\lambda)\cdot z_{mix}}\right]$$

3) Fraction of light absorbed by a pollutant *i*:

$$F_i =$$

Direct photolysis – natural water

4) Rate of light absorption by compound *i* per volume:

$$= (system\ light\ absorption, vol. basis) \times F_i$$

$$= \frac{I_0(\lambda)}{z_{mix}}\left[1 - 10^{-\alpha_D(\lambda)\cdot z_{mix}}\right]\frac{\epsilon_i(\lambda)}{\alpha(\lambda)}C_i$$

The specific rate of light absorption, $\boldsymbol{I_a(\lambda)}$

$$I_a(\lambda) = \frac{I_0(\lambda)\cdot\epsilon_i(\lambda)\cdot\left[1 - 10^{-\alpha_D(\lambda)\cdot z_{mix}}\right]}{z_{mix}\cdot\alpha(\lambda)}C_i$$

$$= k_a(\lambda)\cdot C_i$$

$I_a(\lambda)$ in einstein/L-s

$I(\lambda)$ in millieinstein/cm²-s

$\epsilon_i(\lambda)$ = molar absorption coeff. for compound *i* (L/mole-cm)

C_i = concentration of compound *i* (mole/L)

$k_a(\lambda)$ = ***specific rate of light absorption*** (einsten/mole-s)

Direct photolysis – natural water

- **The rate of direct photolysis at wavelength λ**

$$= -\left(\frac{dC_i}{dt}\right)_\lambda$$

$$= \Phi_{ir}(\lambda) I_a(\lambda)$$

$$= \Phi_{ir}(\lambda) k_a(\lambda) C_i$$

$$= k_p(\lambda) C_i$$

$k_p(\lambda)$ = ***the direct photolysis 1st-order rate constant at wavelength λ (s^{-1})***

The direct photolysis rate is in 1st order only if $\varepsilon_i(\lambda) C_i \ll \alpha(\lambda)$

- **The overall rate of direct photolysis**

$$= -\frac{dC_i}{dt} = \left[\sum_\lambda k_p(\lambda)\right] C_i = k_p C_i$$

k_p = ***the overall direct photolysis 1st-order rate constant (s^{-1})***

Direct photolysis – natural water

- Two limiting cases:

  1) **Negligible light absorption**
  (clear lake surface, z_{mix} small)

$$\alpha_D(\lambda) z_{mix} \leq 0.02$$

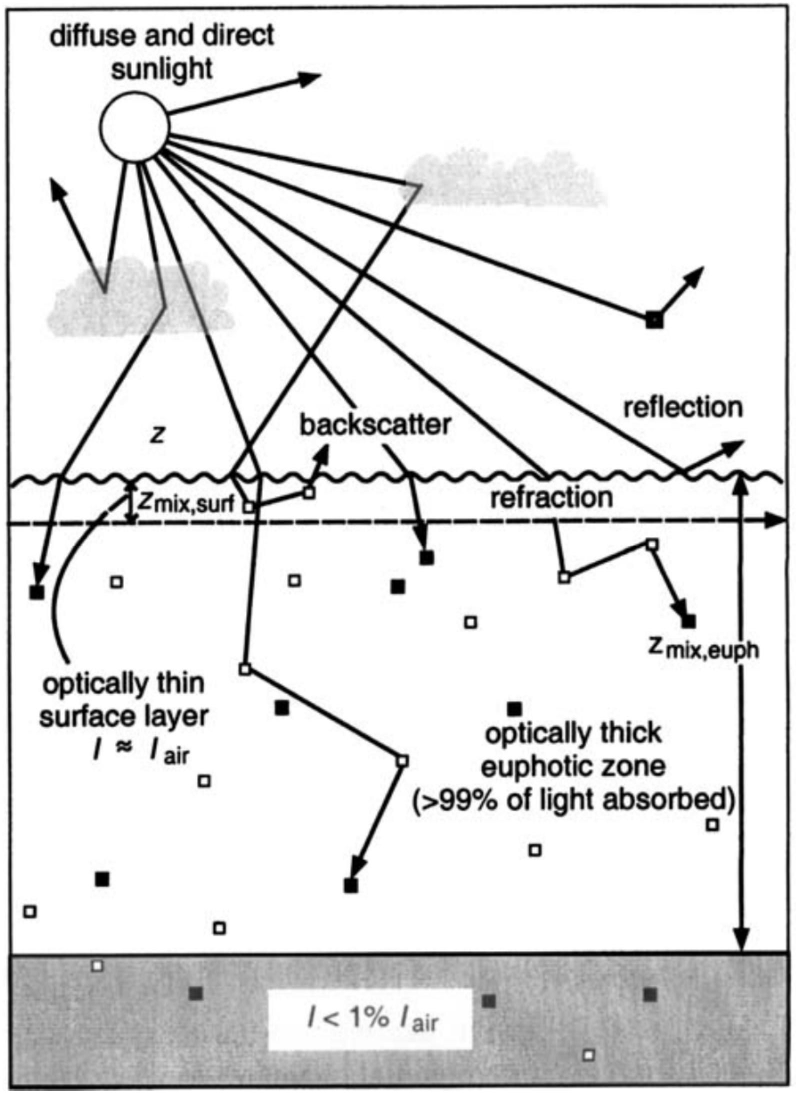
$$1 - 10^{-\alpha_D(\lambda)\cdot z_{mix}} \approx 2.303\alpha_D(\lambda) \cdot z_{mix}$$

$$-\frac{dC_i}{dt} = \left[\sum \frac{2.303 I_0(\lambda) \cdot \alpha_D(\lambda) \cdot \epsilon_i(\lambda) \cdot \Phi_{ir}(\lambda)}{\alpha(\lambda)}\right] C_i$$

$$= 2.303 \left[\sum Z(\lambda) \cdot \epsilon_i(\lambda) \cdot \Phi_{ir}(\lambda)\right] C_i$$

$$= {k_p}^0 C_i$$

${k_p}^0$ = near surface photolysis rate (s^{-1})



Direct photolysis – natural water

2) **Nearly all light absorbed**
(turbid water, z_{mix} large)

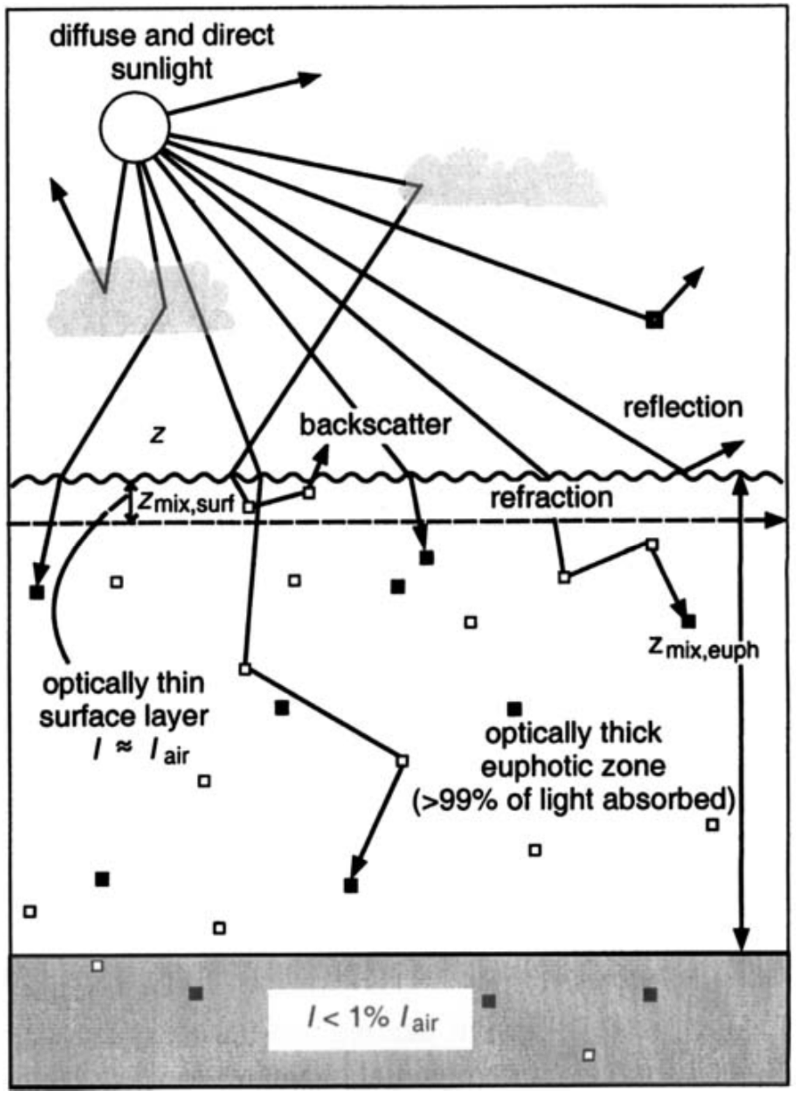
$$\alpha_D(\lambda) z_{mix} \geq 2$$

$$1 - 10^{-\alpha_D(\lambda) \cdot z_{mix}} \approx 1$$

$$-\frac{dC_i}{dt} = \left[\sum \frac{I_0(\lambda) \cdot \epsilon_i(\lambda) \cdot \Phi_{ir}(\lambda)}{\alpha(\lambda) z_{mix}}\right] C_i$$

$$= {k_p}^t C_i$$

${k_p}^t$ = photolysis rate of optically thick zone(s^{-1})



Direct photolysis – natural water

Q: Estimate the 24 h averaged direct photolysis half-life of 4-nitrophenol (4NP) near the surface of a lake (pH=7.5). Following 24-h averaged near-surface total specific light absorption rates have been determined for non-dissociated (HA) and dissociated (A^-) species (pK_a = 7.11):

$$k_a{}^0(HA) = 4.5 \times 10^3 \; einstein \cdot (mole\ HA)^{-1} \cdot d^{-1}$$

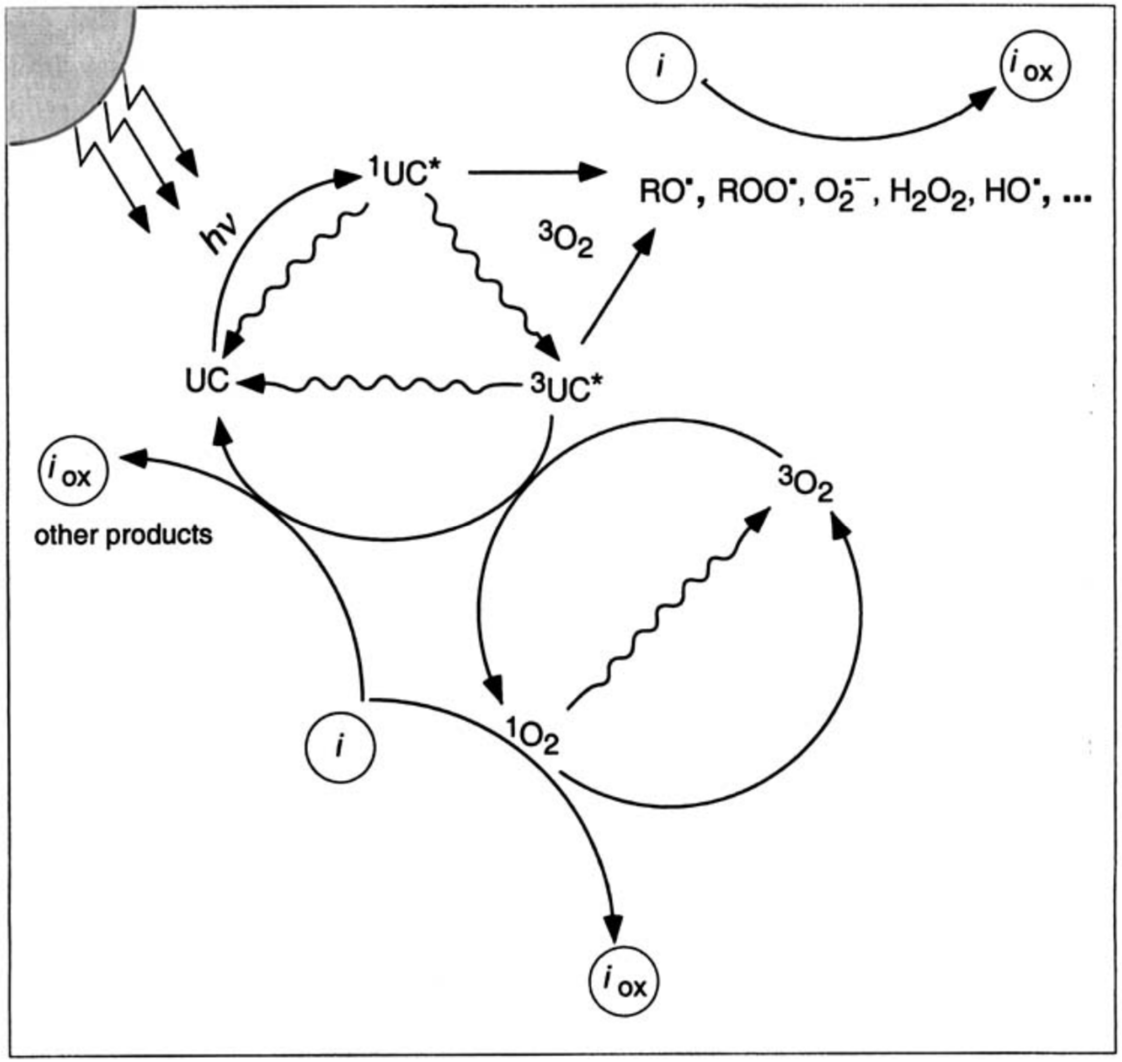
$$k_a{}^0(A^-) = 3.2 \times 10^4 \; einstein \cdot (mole\ A^-)^{-1} \cdot d^{-1}$$

The quantum yields for the two species are as follows (assume the quantum yields are identical for all wavelengths):

$$\Phi_{ir}(HA) = 1.1 \times 10^{-4} \; (mole\ HA) \cdot einstein^{-1}$$

$$\Phi_{ir}(A^-) = 8.1 \times 10^{-6} \; (mole\ A^-) \cdot einstein^{-1}$$

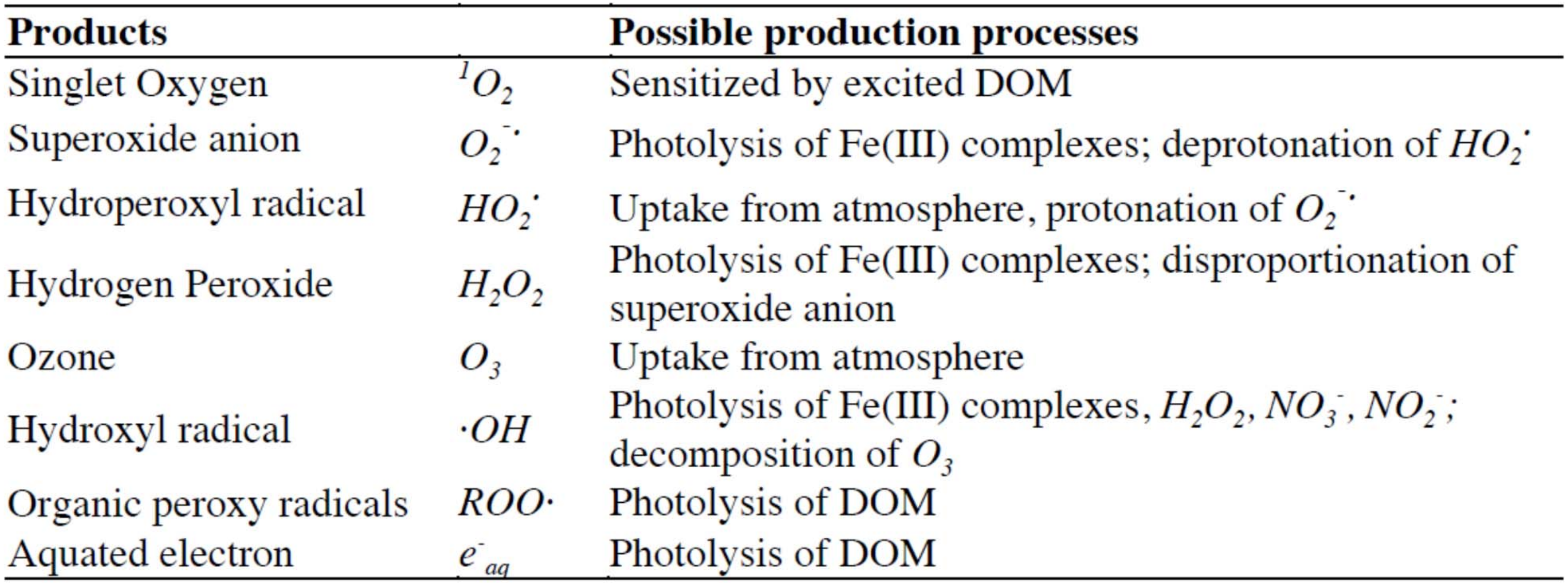
Indirect (sensitized) photolysis



- UC: Unknown chromophore
  ex) colored DOM (CDOM)
- Singlet oxygen ($^1O_2$): excited state
- Triplet oxygen ($^3O_2$): ground state
- Photochemically-produced reactive intermediates (PPRIs)

Figure 16.2 Pathways for indirect photolysis of an organic compound *i* involving excited natural organic matter constituents. UC refers to unknown chromophores. Wavy arrows symbolize radiationless transition (adapted from Zafiriou et al., 1984).

PPRIs



Products		Possible production processes
Singlet Oxygen	$^1O_2$	Sensitized by excited DOM
Superoxide anion	$O_2^{-\cdot}$	Photolysis of Fe(III) complexes; deprotonation of $HO_2^{\cdot}$
Hydroperoxyl radical	$HO_2^{\cdot}$	Uptake from atmosphere, protonation of $O_2^{-\cdot}$
Hydrogen Peroxide	H_2O_2	Photolysis of Fe(III) complexes; disproportionation of superoxide anion
Ozone	O_3	Uptake from atmosphere
Hydroxyl radical	$\cdot OH$	Photolysis of Fe(III) complexes, H_2O_2, NO_3^-, NO_2^-; decomposition of O_3
Organic peroxy radicals	$ROO\cdot$	Photolysis of DOM
Aquated electron	e^-_{aq}	Photolysis of DOM

Adapted from Stumm and Morgan (1996)

Steady-state concentrations of PPRIs

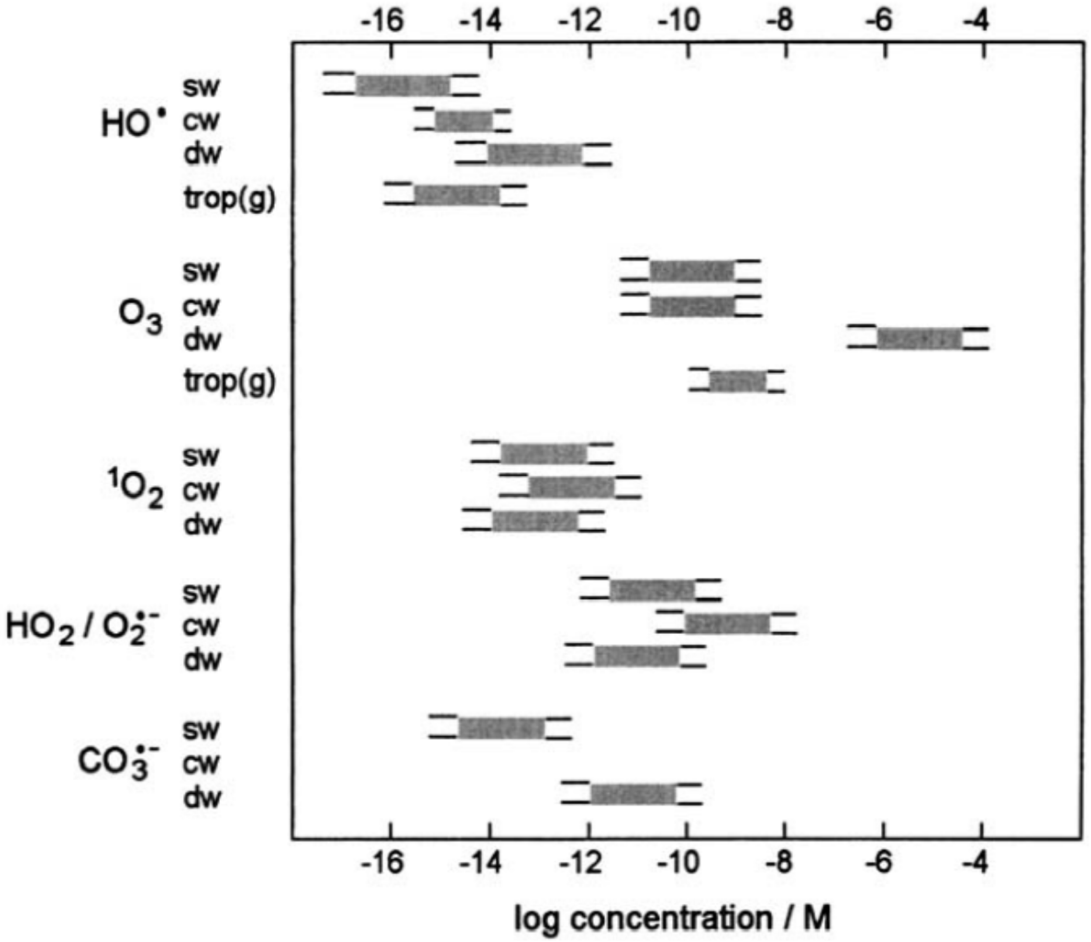


Figure 16.1 Ranges of steady-state concentrations of reactive oxygen species in sunlit surface waters (sw), sunlit cloud waters (cw), drinking-water treatment (dw), and the troposphere (trop(g)). Data from Sulzberger et al. (1997) and Atkinson et al. (1999).

ex)

$[^1O_2]_{ss} \sim 10^{-13}$ M

(summer, noon)

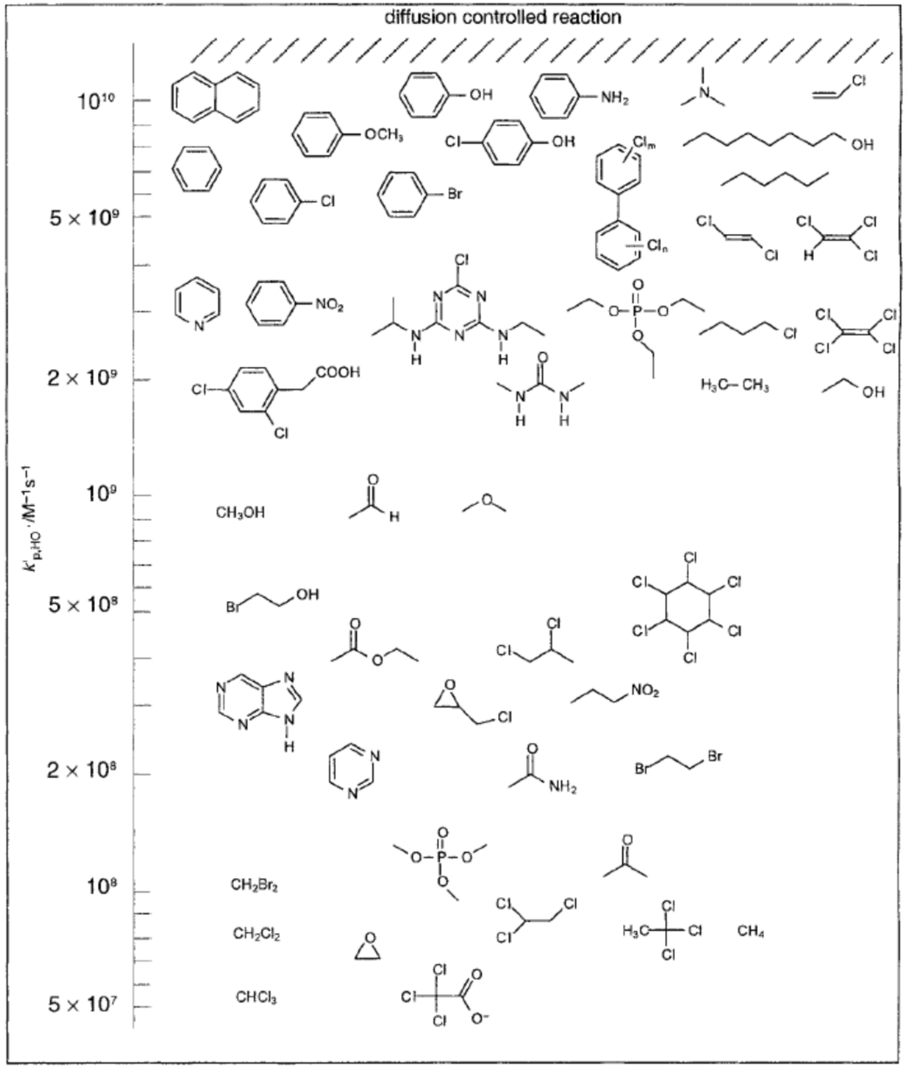
$k_{phenol} \sim 10^7\ M^{-1}s^{-1}$

$k_{phenolate} \sim 10^8\ M^{-1}s^{-1}$

$pK_a \sim 10$

$t_{1/2}$, phenol = ?

Reactions with hydroxyl radical



- **Especially important for advanced oxidation processes**
- **Major reaction pathways:**
  - Electrophilic addition to a double bond or aromatic ring
  - Abstraction of a hydrogen atom from a carbon atom

Figure 16.3 Second-order rate constants for reaction with $HO^\cdot$ in aqueous solution ($k'_{p,HO^\cdot}$; Eq. 16-7) for a series of organic compounds. Data from http://allen.rad.nd.edu, and Haag and Yao (1992).