Photochemical reactions

Light (photon)/matter interactions

- **Photon/matter interactions play roles in**
  - Transformations in
    - the atmosphere
    - surface water
    - water & wastewater treatment (e.g., disinfection, engineered wetland)
  - Analysis
    - Light absorption $f(\lambda, C_{compound})$ – determine $C_{compound}$ by a spectrophotometer

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

Light (photon)/matter interactions

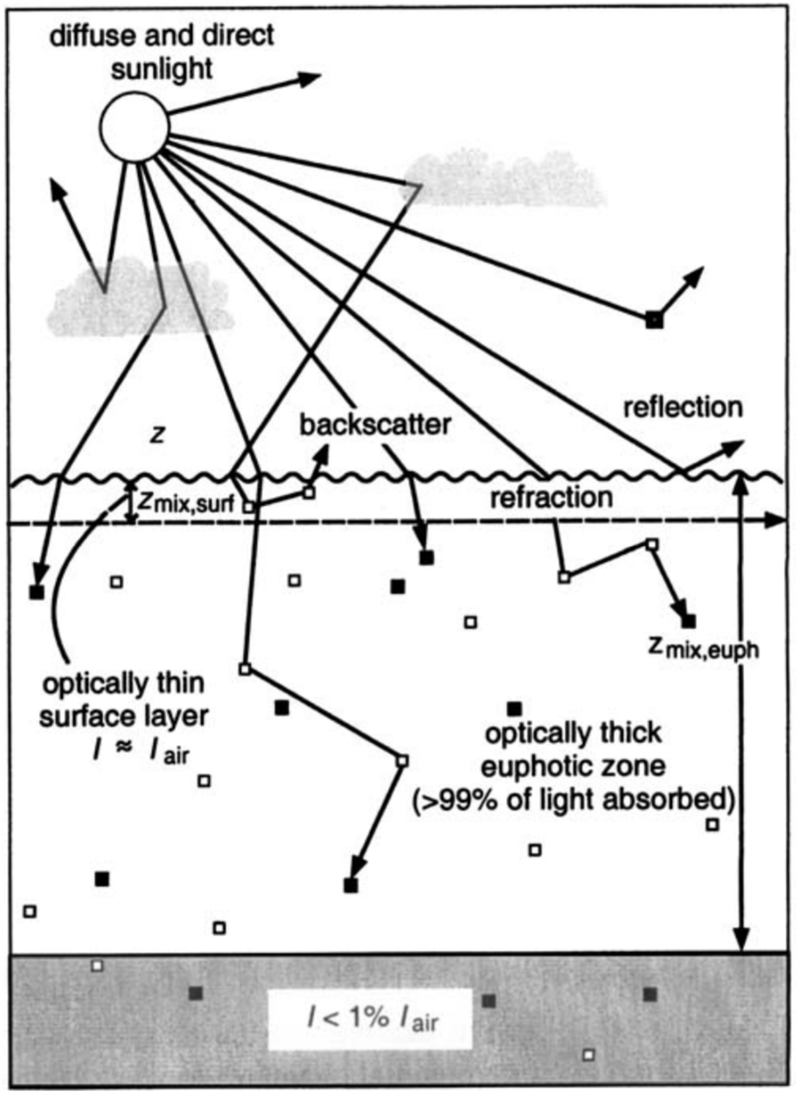
- **Light interact with matter in two ways**

  (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**

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

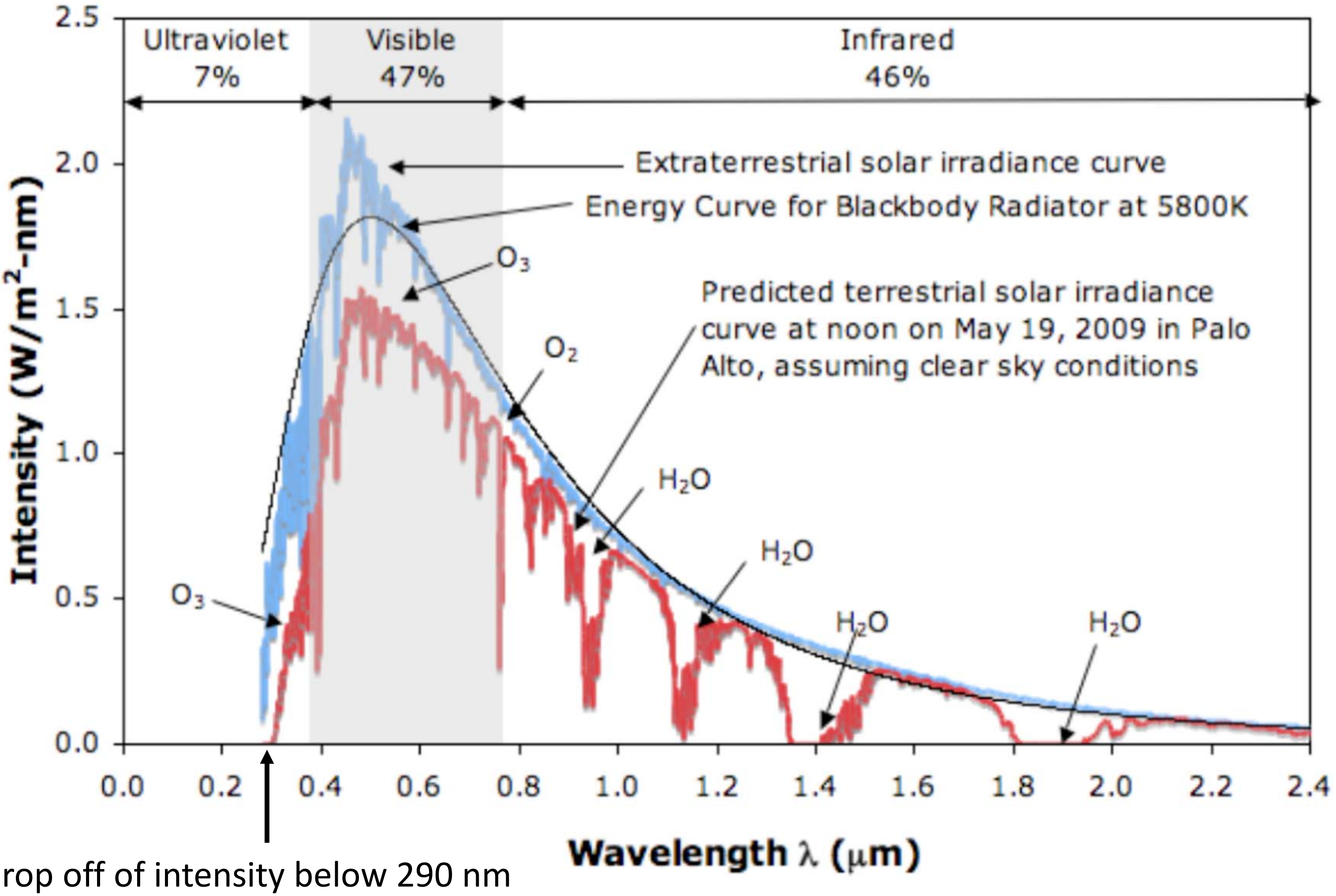
E = energy of a photon (J/photon)
h = 6.626 x 10^{-34} J·s, Planck constant
ν = frequency of light (s^{-1})
c = 3.0 x 10^{8} m/s, speed of light in a vacuum
λ = wavelength of light (m)

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

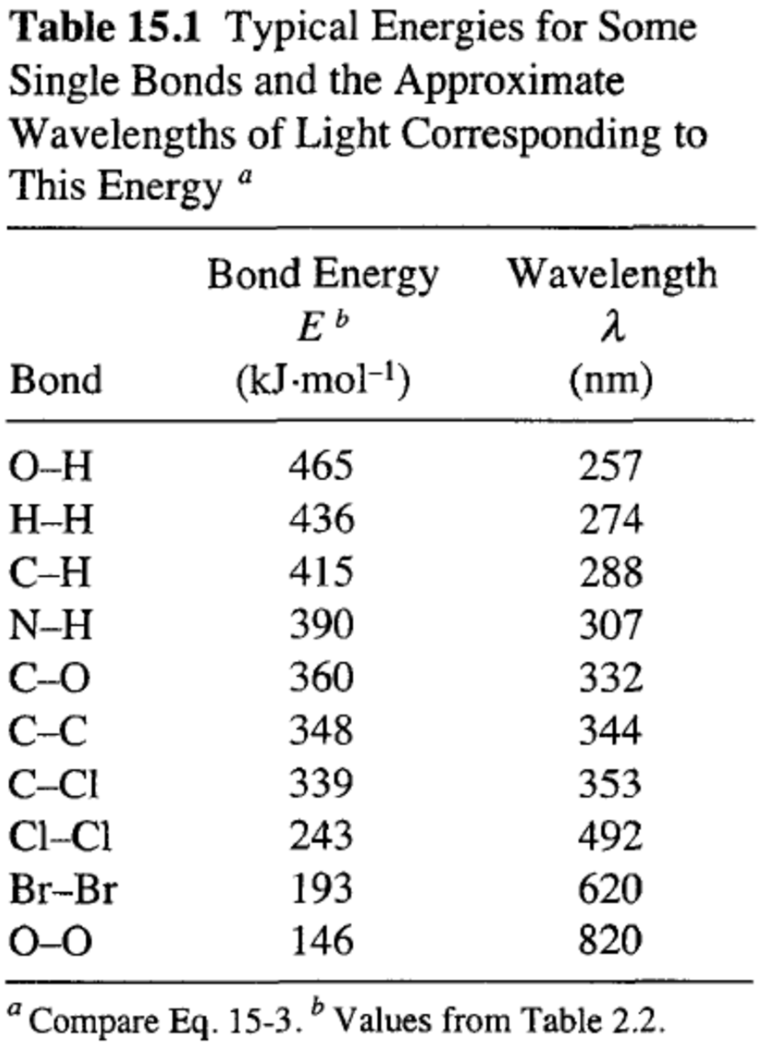


Table 15.1 Typical Energies for Some Single Bonds and the Approximate Wavelengths of Light Corresponding to This Energy [a]

Bond	Bond Energy E [b] (kJ·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})

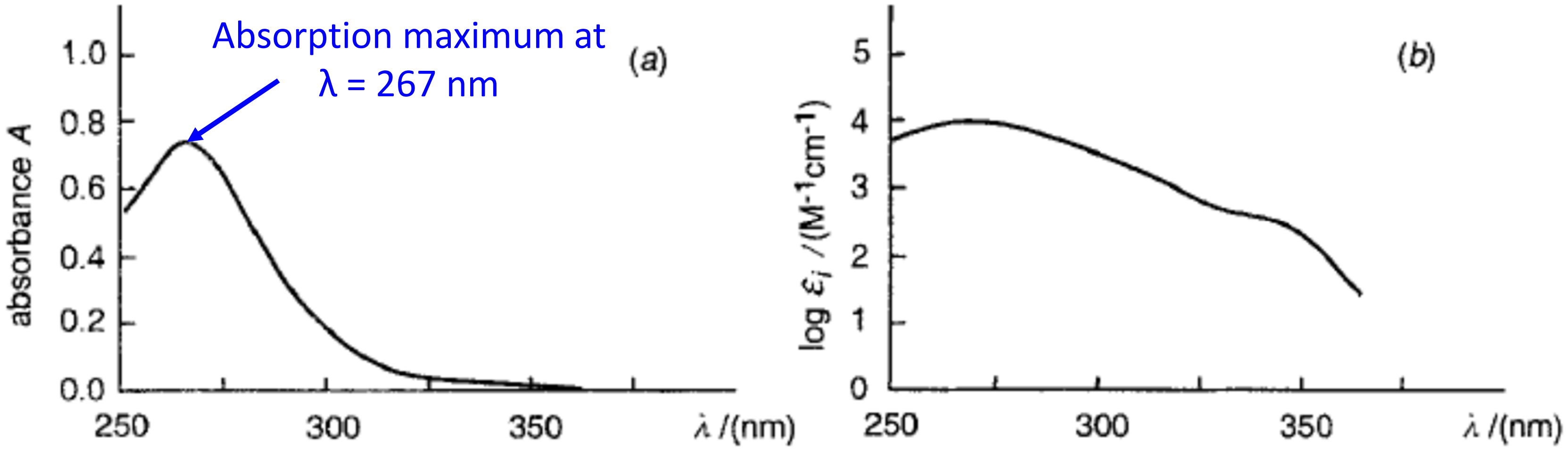
C_i = concentration of solute *i* (M)

l = path length of light (cm)

Absorption spectrum

- Absorption spectrum easily measurable by UV-Vis spectrophotometer

0.1 mM nitrobenzene in aqueous solution

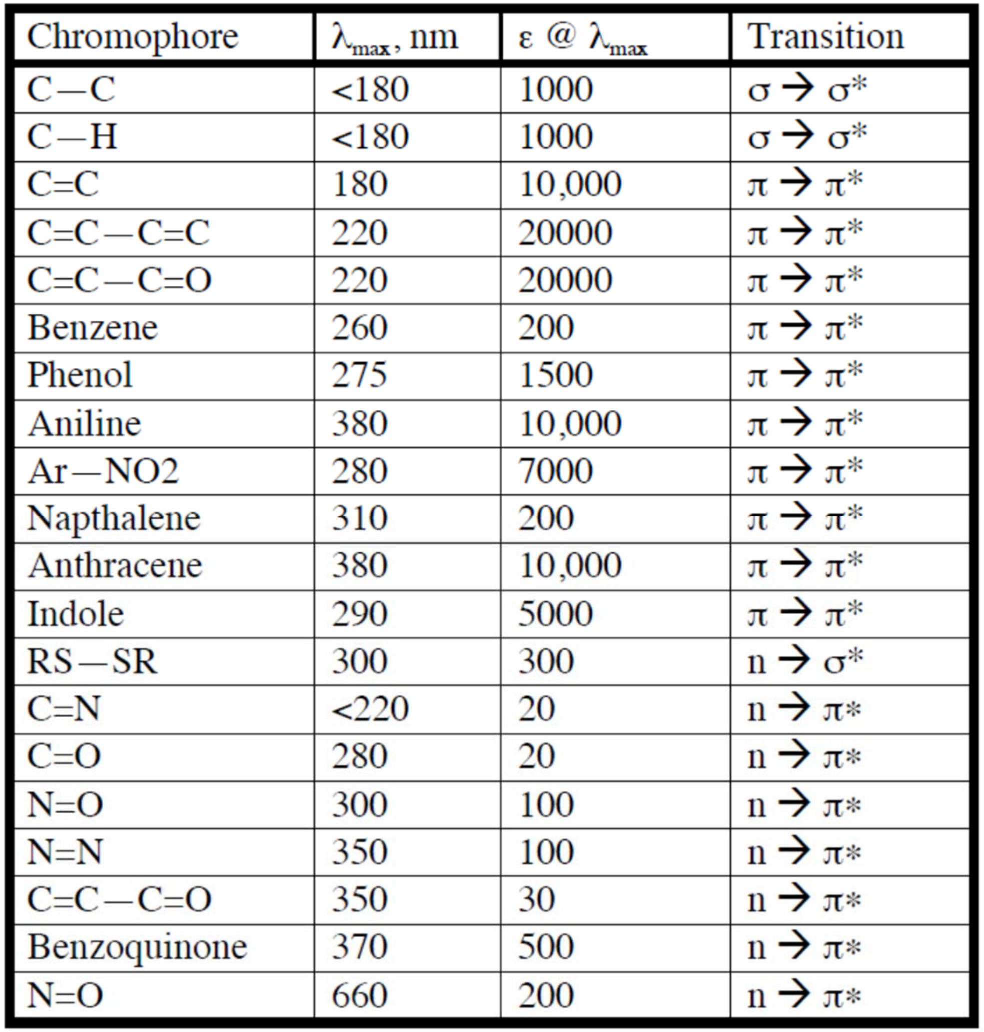


Absorption maximum at λ = 267 nm

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	$n \rightarrow \pi^*$

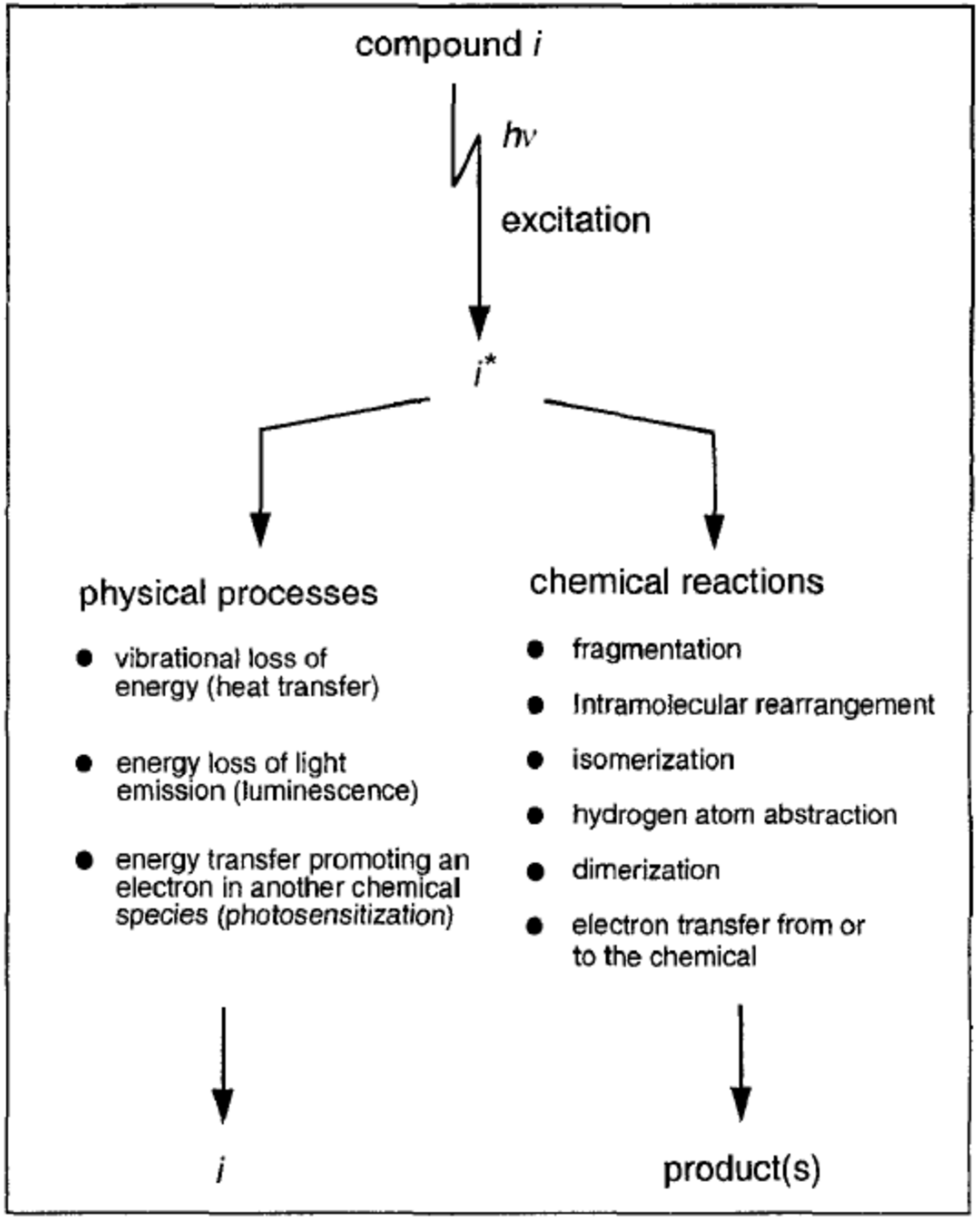
- **Chromophore**

  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*

$h\nu$

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

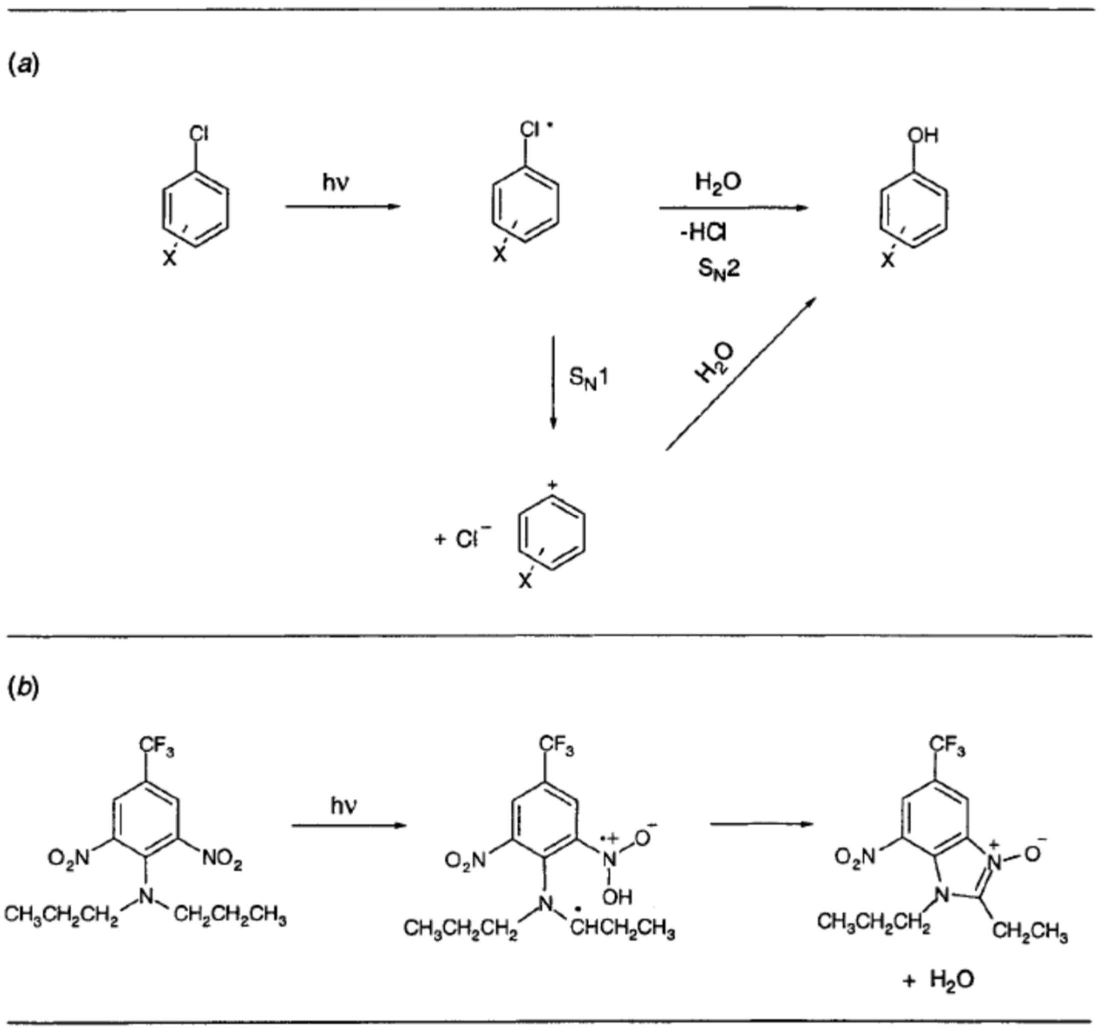


Figure 15.7 Examples of direct photochemical reaction pathways: (*a*) substituted chlorobenzenes, (*b*) trifluralin, and (*c*) a ketone (from Mill and Mabey, 1985).

Direct photolysis

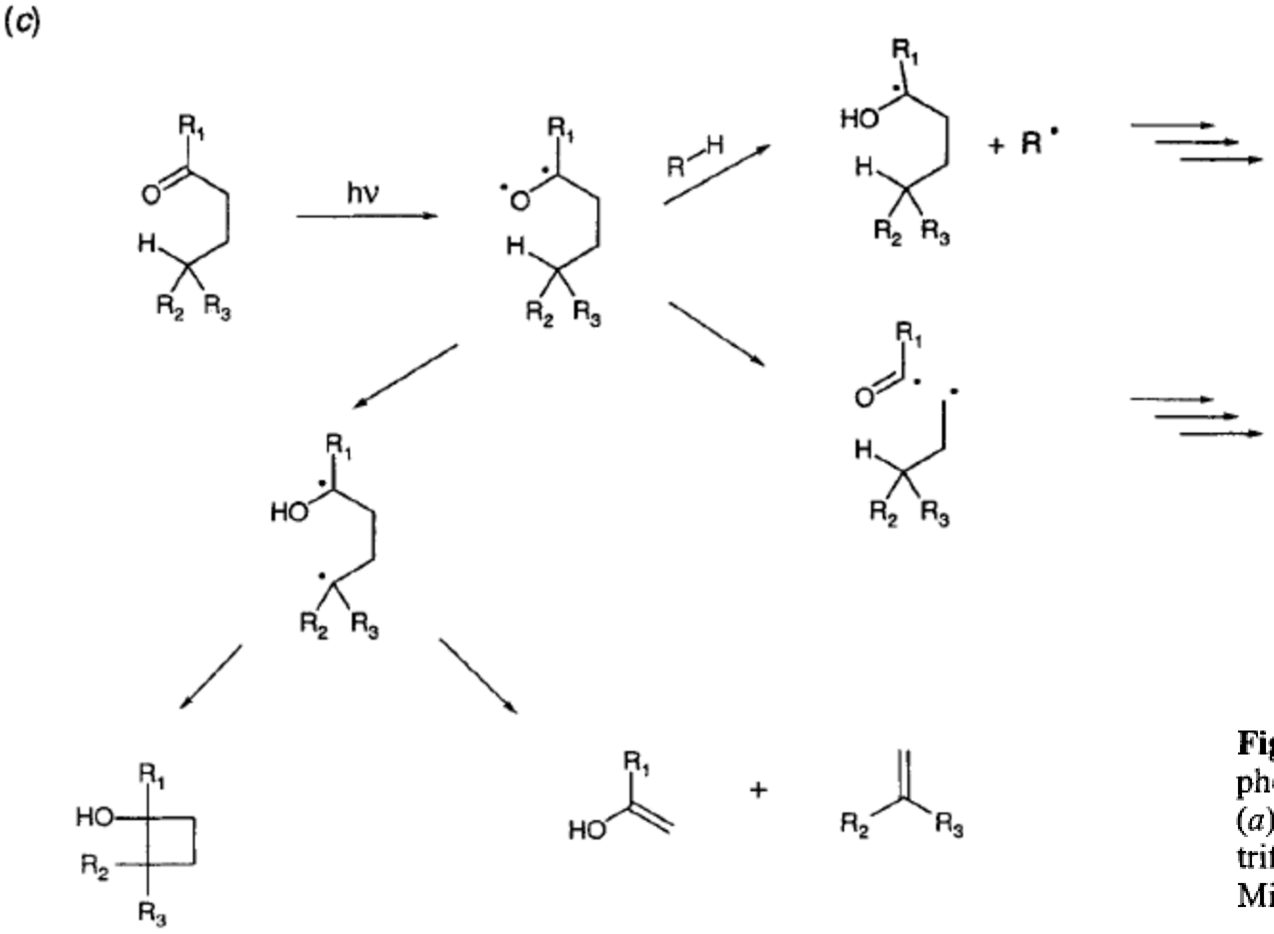


Figure 15.7 Examples of direct photochemical reaction pathways: (*a*) substituted chlorobenzenes, (*b*) trifluralin, and (*c*) a ketone (from Mill and Mabey, 1985).

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*

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

  - Reaction quantum yield (for all reaction pathways)

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

  - The reaction quantum yield has to determined by experiments

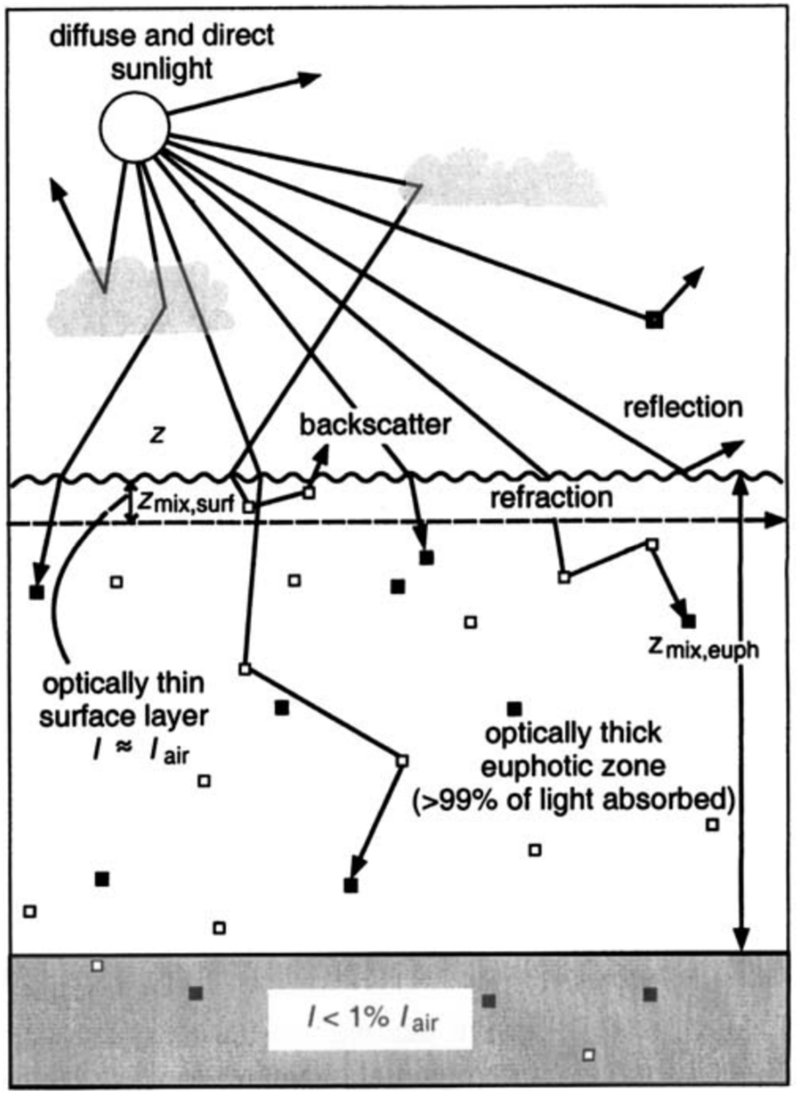
Direct photolysis – light absorption

$$A(\lambda) = log_{10}\frac{W_0(\lambda)}{W(\lambda)} = [\alpha(\lambda) + \varepsilon_i(\lambda)C_i] \cdot l$$

$W_0(\lambda)$ & $W(\lambda)$ = light intensity at the water surface & at the underwater position of interest, respectively (einstein/cm^2-s)

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

$$log_{10}\frac{W_0(\lambda)}{W(\lambda)} \approx \alpha(\lambda) \cdot l$$



Direct photolysis – light absorption

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

$\alpha_D(\lambda)$ = diffuse attenuation coefficient (cm^{-1})

$z_{mix} = V/A$ = depth of mixed water body (cm)

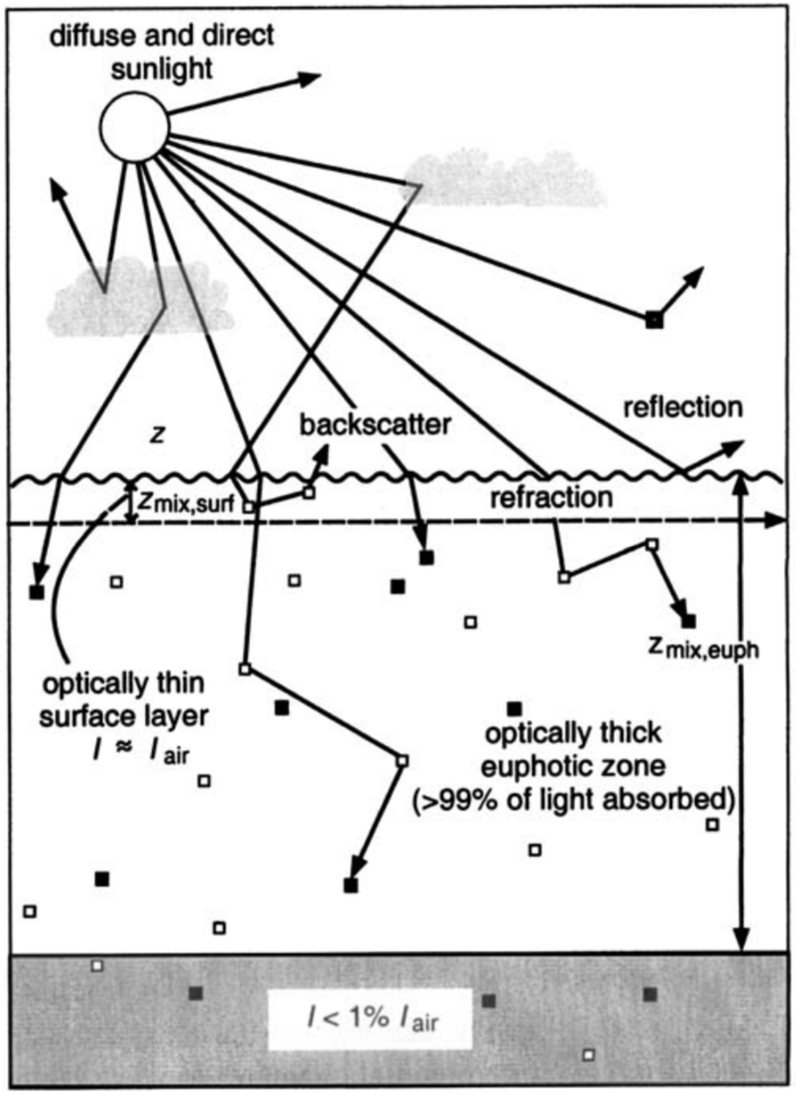
V = volume of the water body (cm^3)

A = surface area of the water body (cm^2)

$l \neq z_{mix}$ 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 – light absorption

so $W(z_{mix},\lambda) = W_0(\lambda)\cdot 10^{-\alpha_D(\lambda)\cdot z_{mix}}$

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

$D(\lambda)$ = distribution function

For non-turbid water, 1.05~1.3

For very turbid water, up to 2.0

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

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

Direct photolysis – light absorption

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)

$$= W_0(\lambda) - W(z_{mix}, \lambda) = W_0(\lambda)\left[1 - 10^{-\alpha_D(\lambda)\cdot z_{mix}}\right]$$

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

$$= \frac{W_0(\lambda)}{z_{mix}}\left[1 - 10^{-\alpha_D(\lambda)\cdot z_{mix}}\right]$$

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

$$F_i =$$

Direct photolysis – light absorption

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

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

$$= \frac{W_0(\lambda)}{z_{mix}}\left[1 - 10^{-\alpha_D(\lambda)\cdot z_{mix}}\right]\frac{\epsilon_i(\lambda)}{\alpha(\lambda)}C_i$$

Rate of light absorption by compound *i*, $I_a(\lambda)$:

$$I_a(\lambda) = \frac{W_0(\lambda)\cdot\epsilon_i(\lambda)\cdot\left[1 - 10^{-\alpha_D(\lambda)\cdot z_{mix}}\right]}{z_{mix}\cdot\alpha(\lambda)}C_i$$

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

$I_a(\lambda)$ in einstein/L-s
$W_0(\lambda)$ in millieinstein/cm^2-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 light absorption rate*** (einsten/mole-s)

Direct photolysis rate at specific λ

(Photolysis rate) = (Light absorption rate) x (Transformation rate when light is absorbed)

$$-\left(\frac{dC_i}{dt}\right)_\lambda \qquad I_a(\lambda) \qquad \Phi_{ir}(\lambda)$$

$$-\left(\frac{dC_i}{dt}\right)_\lambda = \Phi_{ir}(\lambda) I_a(\lambda) = \Phi_{ir}(\lambda) k_a(\lambda) C_i$$

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

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

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

Direct photolysis – overall rate

- **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})

If Φ_{ir} is not a function of λ, then:

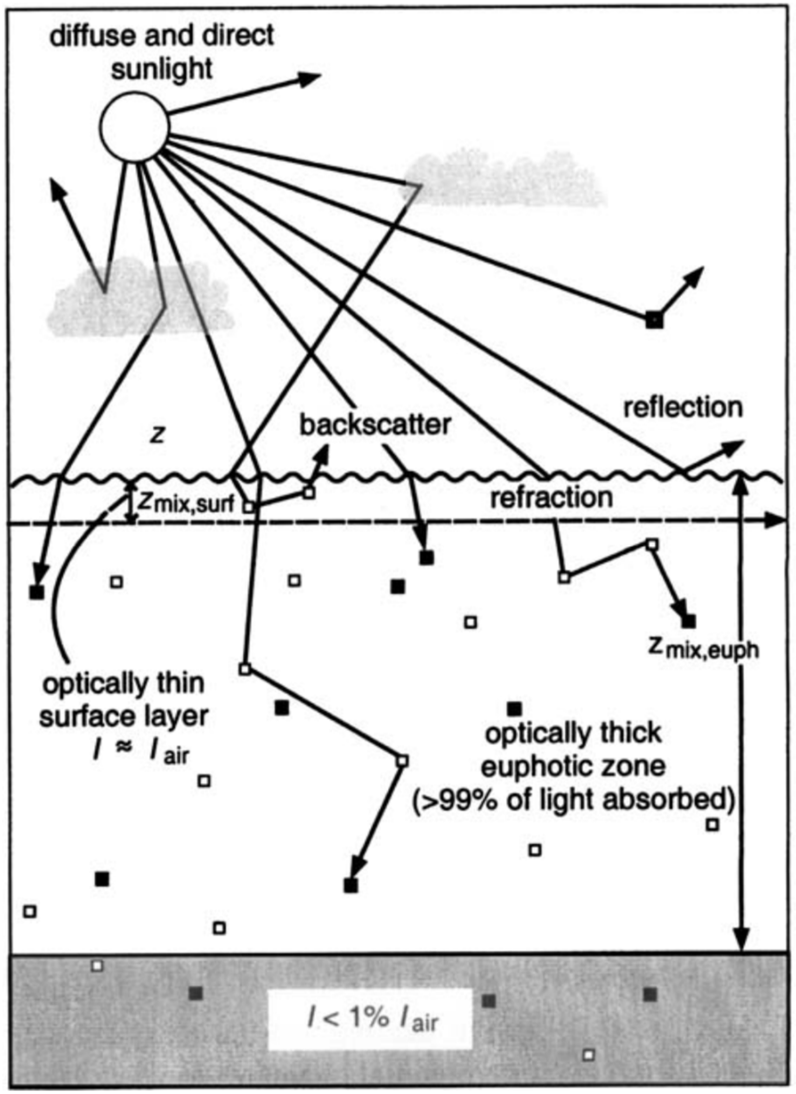
$$-\frac{dC_i}{dt} = \Phi_{ir}\left[\sum_{\lambda} k_a(\lambda)\right] C_i = \Phi_{ir} k_a C_i$$

k_a = ***the overall specific light absorption rate*** (einsten/mole-s)

Direct photolysis – natural water

- Two limiting cases:
  1) **Negligible light absorption**
     (clear lake surface, z_{mix} small)

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



1) Negligible light absorption (near surface)

We approximate our solution in the case of $\boldsymbol{\alpha_D(\lambda) z_{mix} \leq 0.02}$

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

$$= \left[\sum_{\lambda} \frac{\Phi_{ir}(\lambda) \cdot W_0(\lambda) \cdot \epsilon_i(\lambda) \cdot \left[1 - 10^{-\alpha_D(\lambda) \cdot z_{mix}}\right]}{z_{mix} \cdot \alpha(\lambda)}\right] C_i$$

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

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

$$= 2.303 \left[\sum_{\lambda} \frac{\Phi_{ir}(\lambda) \cdot W_0(\lambda) \cdot \epsilon_i(\lambda) \cdot {\alpha_D}^0(\lambda)}{\alpha(\lambda)}\right] C_i$$

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

Define

$$Z(\lambda) = \frac{W_0(\lambda) \cdot {\alpha_D}^0(\lambda)}{\alpha(\lambda)} = W_0(\lambda) \cdot D^0(\lambda)$$

($Z(\lambda)$ has a unit of millieinstein/cm^2/s)

1) Negligible light absorption (near surface)

So, in the case of $\alpha_D(\lambda) z_{mix} \leq 0.02$, the direct photolysis rate is given as:

$$-\frac{\boldsymbol{dC_i}}{\boldsymbol{dt}} = \mathbf{2.303}\left[\sum_{\boldsymbol{\lambda}} \boldsymbol{Z(\lambda) \cdot \epsilon_i(\lambda) \cdot \Phi_{ir}(\lambda)}\right]\boldsymbol{C_i} = \boldsymbol{k_p{}^0 C_i}$$

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

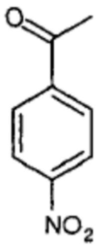
If Φ_{ir} is not a function of λ, then:

$$-\frac{dC_i}{dt} = 2.303\left[\sum_{\lambda} Z(\lambda) \cdot \epsilon_i(\lambda)\right]\Phi_{ir} C_i = k_a{}^0 \Phi_{ir} C_i$$

$k_a{}^0$= near surface specific light absorption rate (einsten/mole-s)

Realistic example – $k_a{}^0$

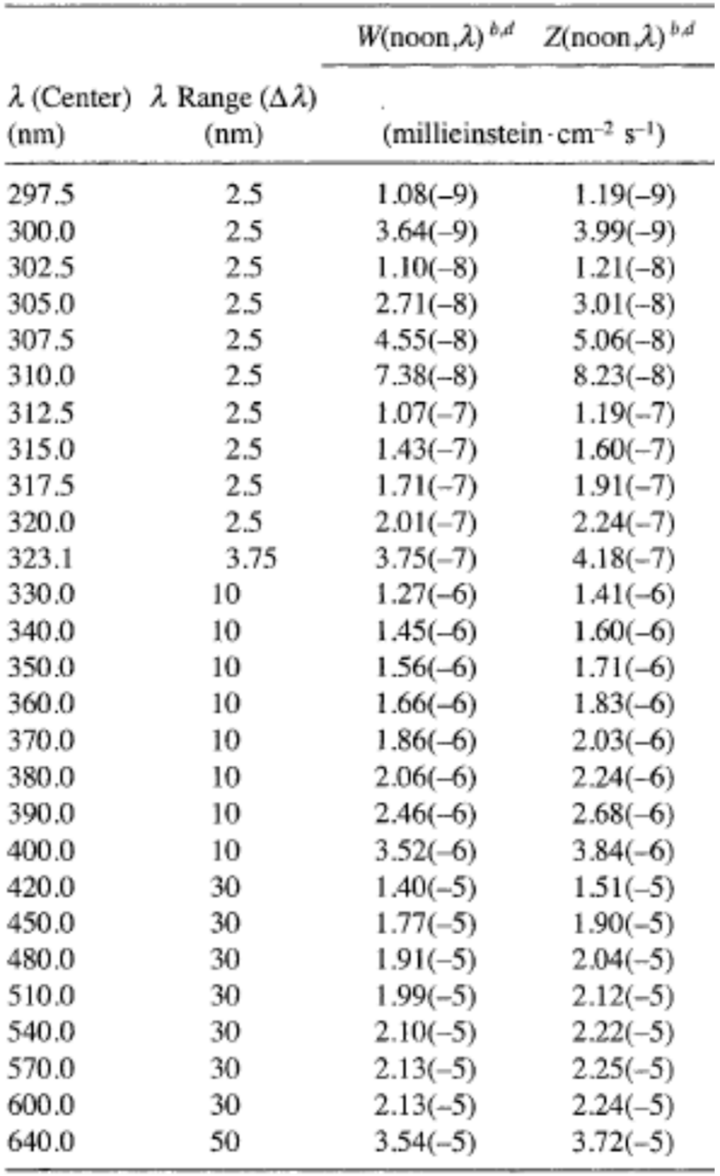
Q: Calculate $k_a{}^0$ of para-nitro-acetophenone (PNAP) at 40^{o}N altitude at noon on a clear midsummer day.



para-nitro-acetophenone
(PNAP)

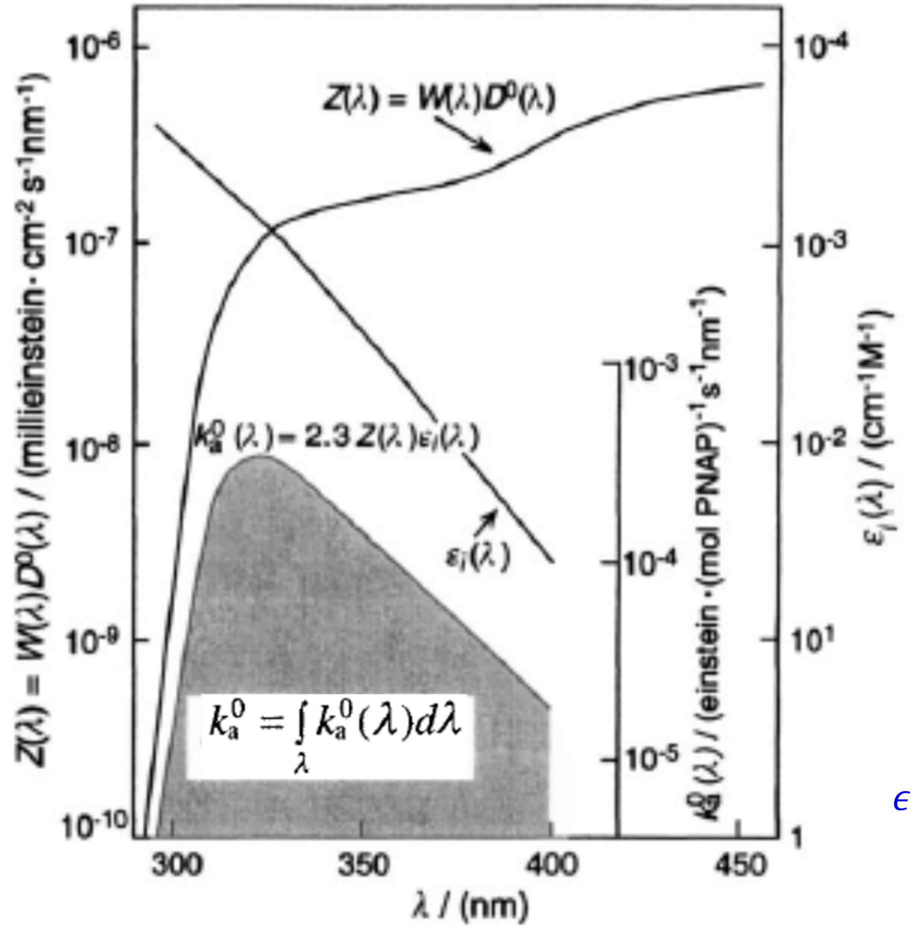
$W(noon,\lambda)$ is obtained from database or computer program

$Z(noon,\lambda) = W(noon,\lambda) \cdot D^0(\lambda)$, $D^0(\lambda)$ is obtained from database or computer program



λ (Center) (nm)	λ Range ($\Delta\lambda$) (nm)	$W(noon,\lambda)^{b,d}$ (millieinstein·cm^{-2} s^{-1})	$Z(noon,\lambda)^{b,d}$ (millieinstein·cm^{-2} s^{-1})
297.5	2.5	1.08(−9)	1.19(−9)
300.0	2.5	3.64(−9)	3.99(−9)
302.5	2.5	1.10(−8)	1.21(−8)
305.0	2.5	2.71(−8)	3.01(−8)
307.5	2.5	4.55(−8)	5.06(−8)
310.0	2.5	7.38(−8)	8.23(−8)
312.5	2.5	1.07(−7)	1.19(−7)
315.0	2.5	1.43(−7)	1.60(−7)
317.5	2.5	1.71(−7)	1.91(−7)
320.0	2.5	2.01(−7)	2.24(−7)
323.1	3.75	3.75(−7)	4.18(−7)
330.0	10	1.27(−6)	1.41(−6)
340.0	10	1.45(−6)	1.60(−6)
350.0	10	1.56(−6)	1.71(−6)
360.0	10	1.66(−6)	1.83(−6)
370.0	10	1.86(−6)	2.03(−6)
380.0	10	2.06(−6)	2.24(−6)
390.0	10	2.46(−6)	2.68(−6)
400.0	10	3.52(−6)	3.84(−6)
420.0	30	1.40(−5)	1.51(−5)
450.0	30	1.77(−5)	1.90(−5)
480.0	30	1.91(−5)	2.04(−5)
510.0	30	1.99(−5)	2.12(−5)
540.0	30	2.10(−5)	2.22(−5)
570.0	30	2.13(−5)	2.25(−5)
600.0	30	2.13(−5)	2.24(−5)
640.0	50	3.54(−5)	3.72(−5)

Realistic example – $k_a{}^0$



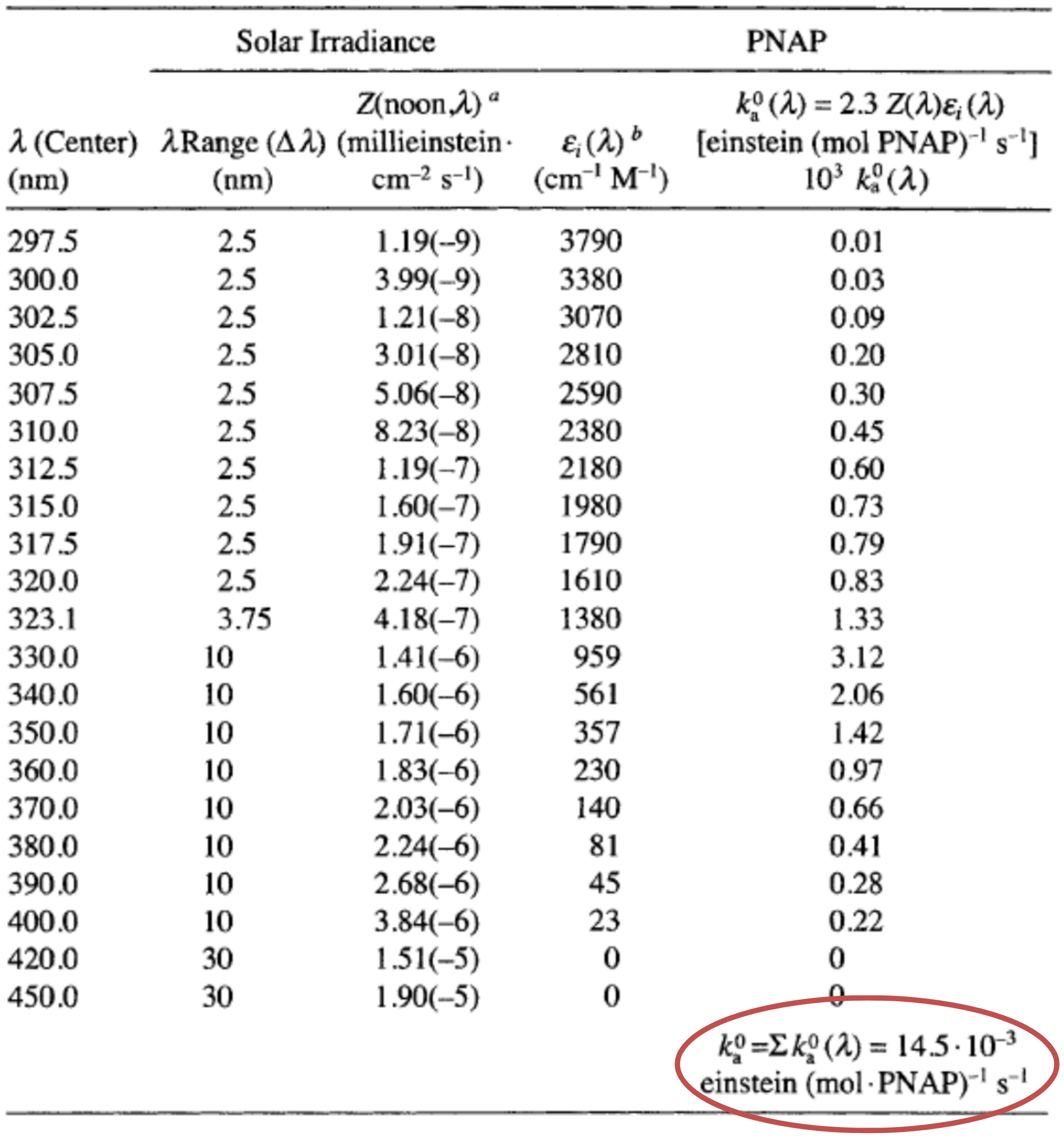
Obtain $k_a{}^0$ by

$$k_a{}^0 = \int k_a{}^0 d\lambda = 2.3 \int Z(\lambda)\epsilon_i(\lambda)\, d\lambda$$

$$\approx 2.3 \sum Z(\lambda)\epsilon_i(\lambda)$$

$\epsilon_i(\lambda)$ is obtained from experiments

Realistic example – $k_a{}^0$



	Solar Irradiance		PNAP	
λ (Center) (nm)	λRange ($\Delta\lambda$) (nm)	$Z(\text{noon},\lambda)$ [a] (millieinstein·$\text{cm}^{-2}\ \text{s}^{-1}$)	$\varepsilon_i(\lambda)$ [b] ($\text{cm}^{-1}\ \text{M}^{-1}$)	$k_a^0(\lambda) = 2.3\ Z(\lambda)\varepsilon_i(\lambda)$ [einstein (mol PNAP)$^{-1}$ s^{-1}] $10^3\ k_a^0(\lambda)$
297.5	2.5	1.19(–9)	3790	0.01
300.0	2.5	3.99(–9)	3380	0.03
302.5	2.5	1.21(–8)	3070	0.09
305.0	2.5	3.01(–8)	2810	0.20
307.5	2.5	5.06(–8)	2590	0.30
310.0	2.5	8.23(–8)	2380	0.45
312.5	2.5	1.19(–7)	2180	0.60
315.0	2.5	1.60(–7)	1980	0.73
317.5	2.5	1.91(–7)	1790	0.79
320.0	2.5	2.24(–7)	1610	0.83
323.1	3.75	4.18(–7)	1380	1.33
330.0	10	1.41(–6)	959	3.12
340.0	10	1.60(–6)	561	2.06
350.0	10	1.71(–6)	357	1.42
360.0	10	1.83(–6)	230	0.97
370.0	10	2.03(–6)	140	0.66
380.0	10	2.24(–6)	81	0.41
390.0	10	2.68(–6)	45	0.28
400.0	10	3.84(–6)	23	0.22
420.0	30	1.51(–5)	0	0
450.0	30	1.90(–5)	0	0
				$k_a^0 = \Sigma k_a^0(\lambda) = 14.5 \cdot 10^{-3}$ einstein (mol·PNAP)$^{-1}$ s^{-1}

2) Nearly all light absorbed

We approximate our solution in the case of $\boldsymbol{\alpha_D(\lambda) z_{mix} \geq 2}$

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

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

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

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

$k_p{}^t$ = 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):

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

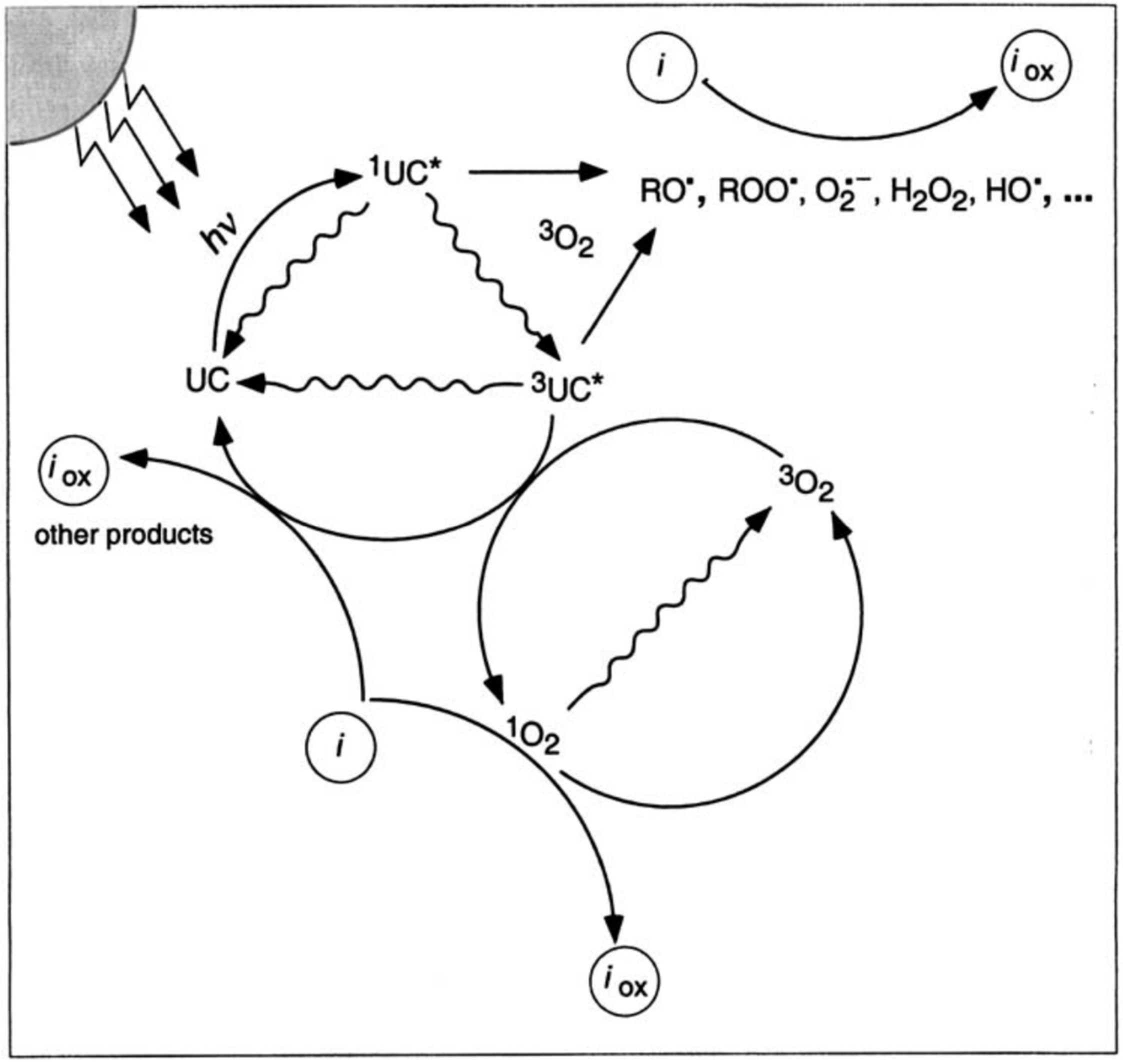
$$k_a{}^0(A^-) = 3.2 \times 10^4\ einstein \cdot (mole\ A^-)^{-1} \cdot d^{-1}$$

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

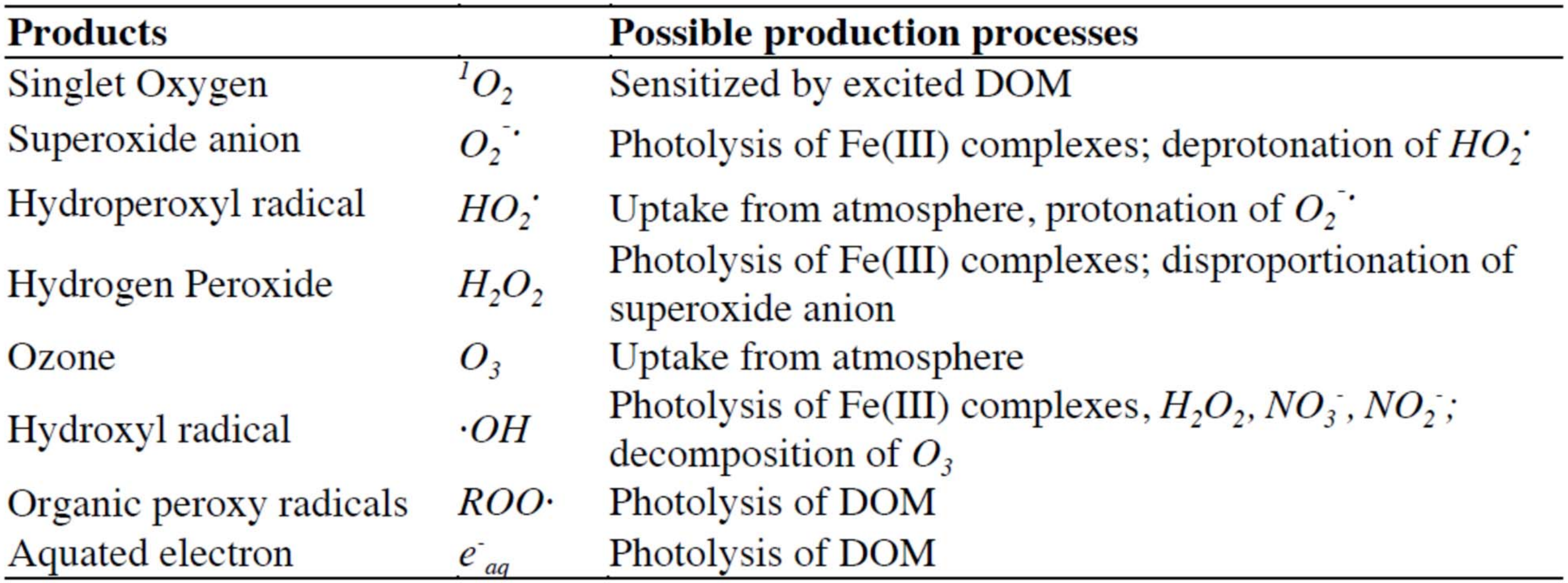


- UC: Unknown chromophore

  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

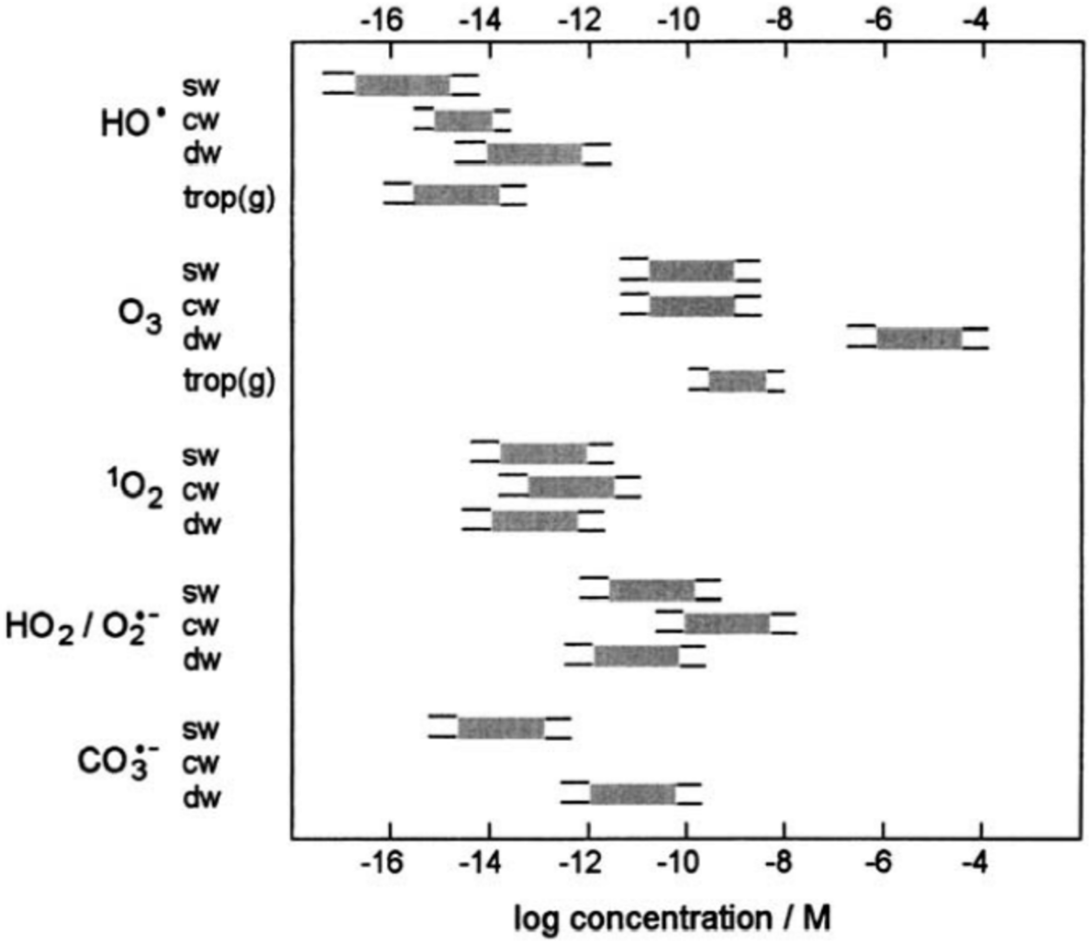


Figure 16.1 Ranges of steady-state concentrations of reactive oxygen species in sunlit surface waters (sw), sunlit cloud waters (cw), drinking-water treatment (dw), and the troposphere (trop(g)). Data from Sulzberger et al. (1997) and Atkinson et al. (1999).

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

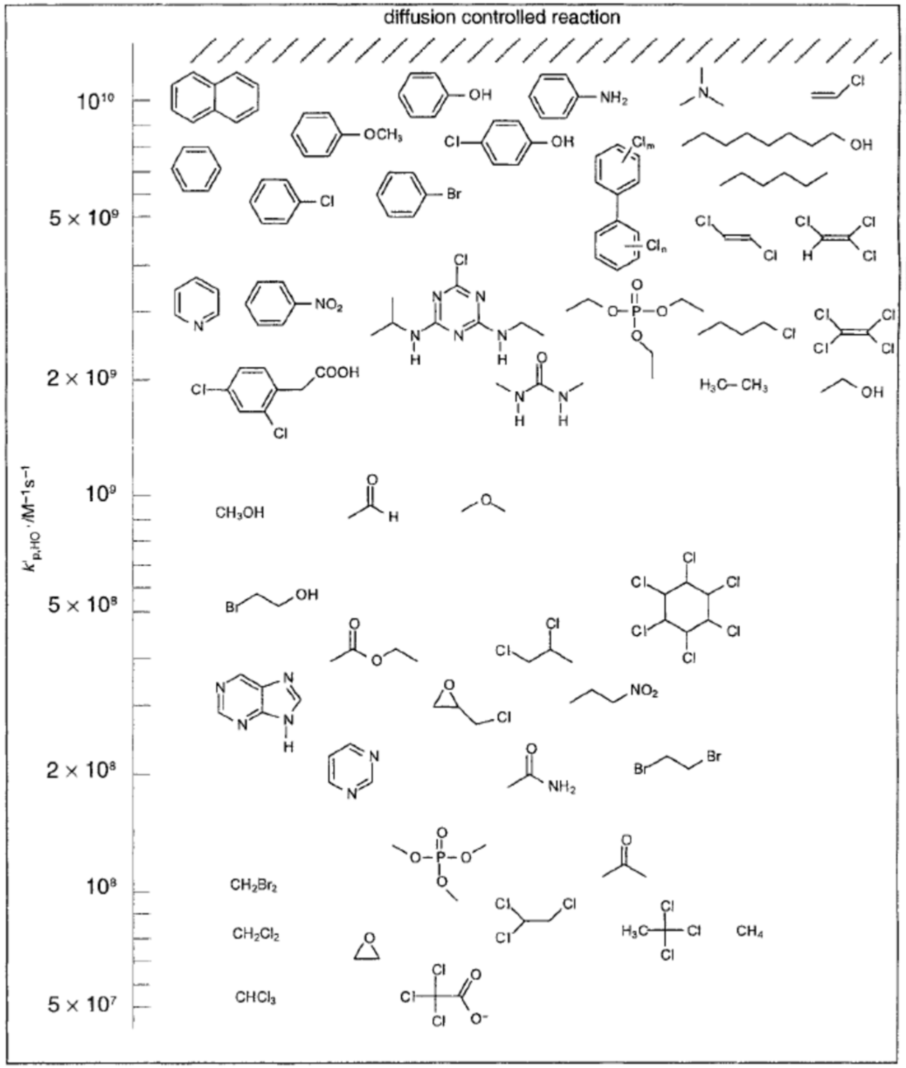


Figure 16.3 Second-order rate constants for reaction with HO• in aqueous solution ($k'_{p,HO^\bullet}$; Eq. 16-7) for a series of organic compounds. Data from http://allen.rad.nd.edu, and Haag and Yao (1992).

- **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