

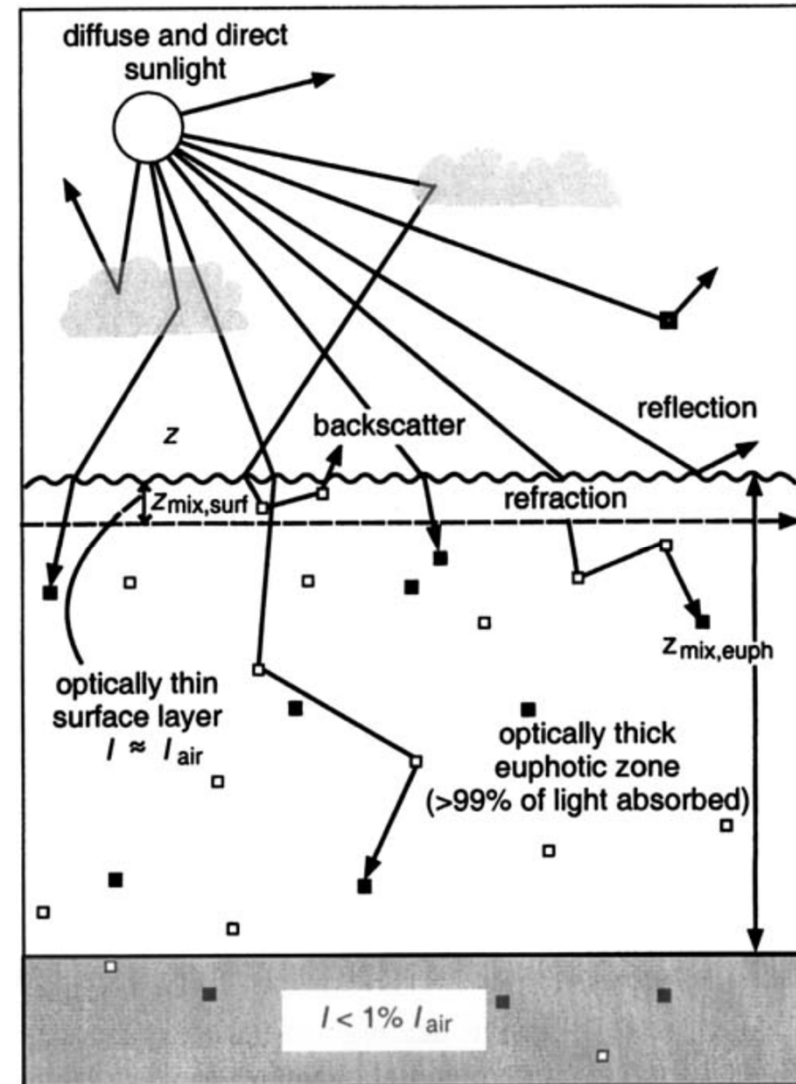
Photochemical reactions

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



(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 = 6.626×10^{-34} J·s, Planck constant

ν = frequency of light (s^{-1})

c = 3.0×10^8 m/s, speed of light in a vacuum

λ = wavelength of light (m)

On a molar basis,

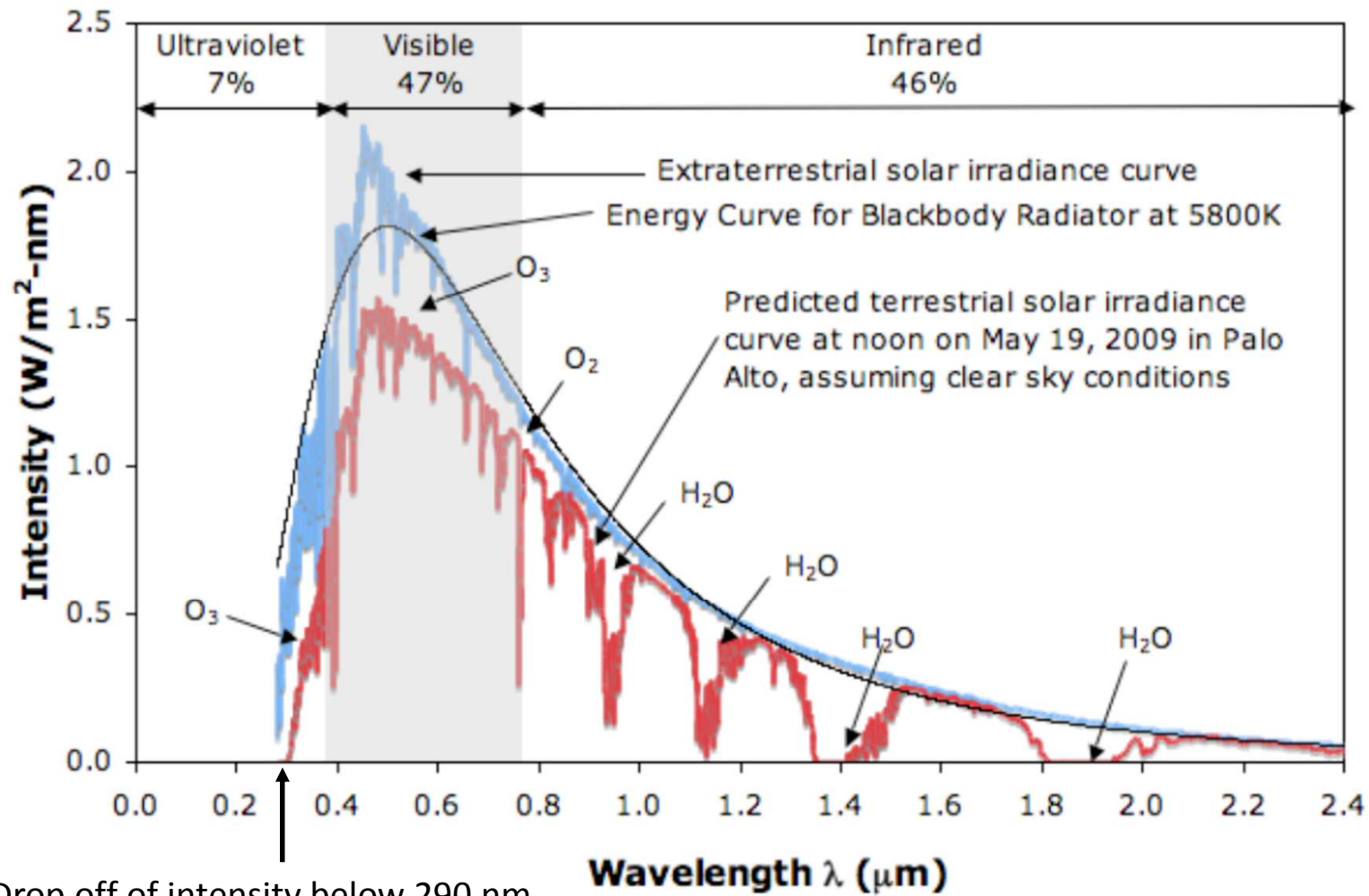
$$E = 6.02 \times 10^{23} \cdot h \frac{c}{\lambda} = \frac{1.196 \times 10^5}{\lambda} \text{ kJ/einstein}$$

E = energy of light on a molar basis (kJ/einstein)

einstein: 1 mole of photons

λ = wavelength of light in nm

Solar flux & absorption



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:

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

- 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/cm²-s)

α = absorption coefficient of the solvent (cm⁻¹)

ε_i = molar absorption coefficient for solute i (M⁻¹·cm⁻¹)

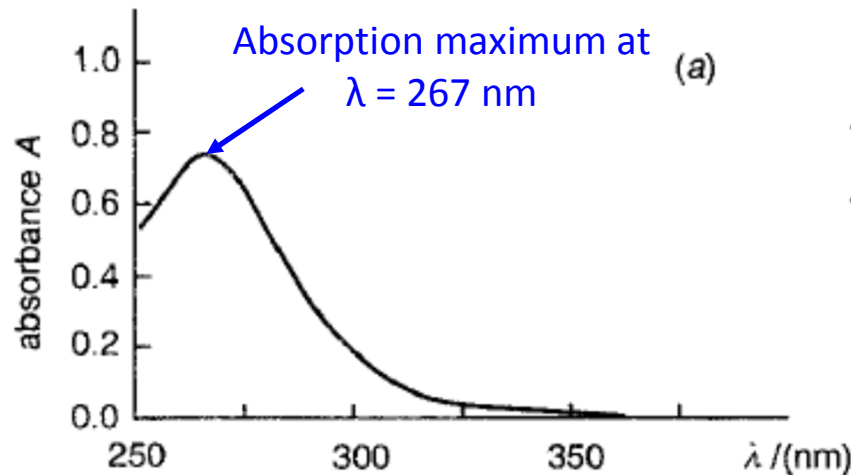
C_i = concentration of solute i (M)

l = path length of light (cm)

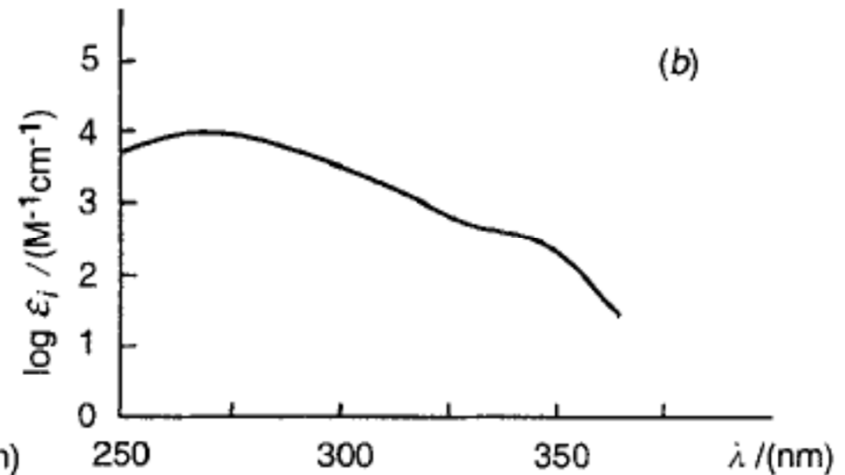
Absorption spectrum

- Absorption spectrum easily measurable by UV-Vis spectrophotometer

0.1 mM nitrobenzene in aqueous solution



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—NO ₂	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**

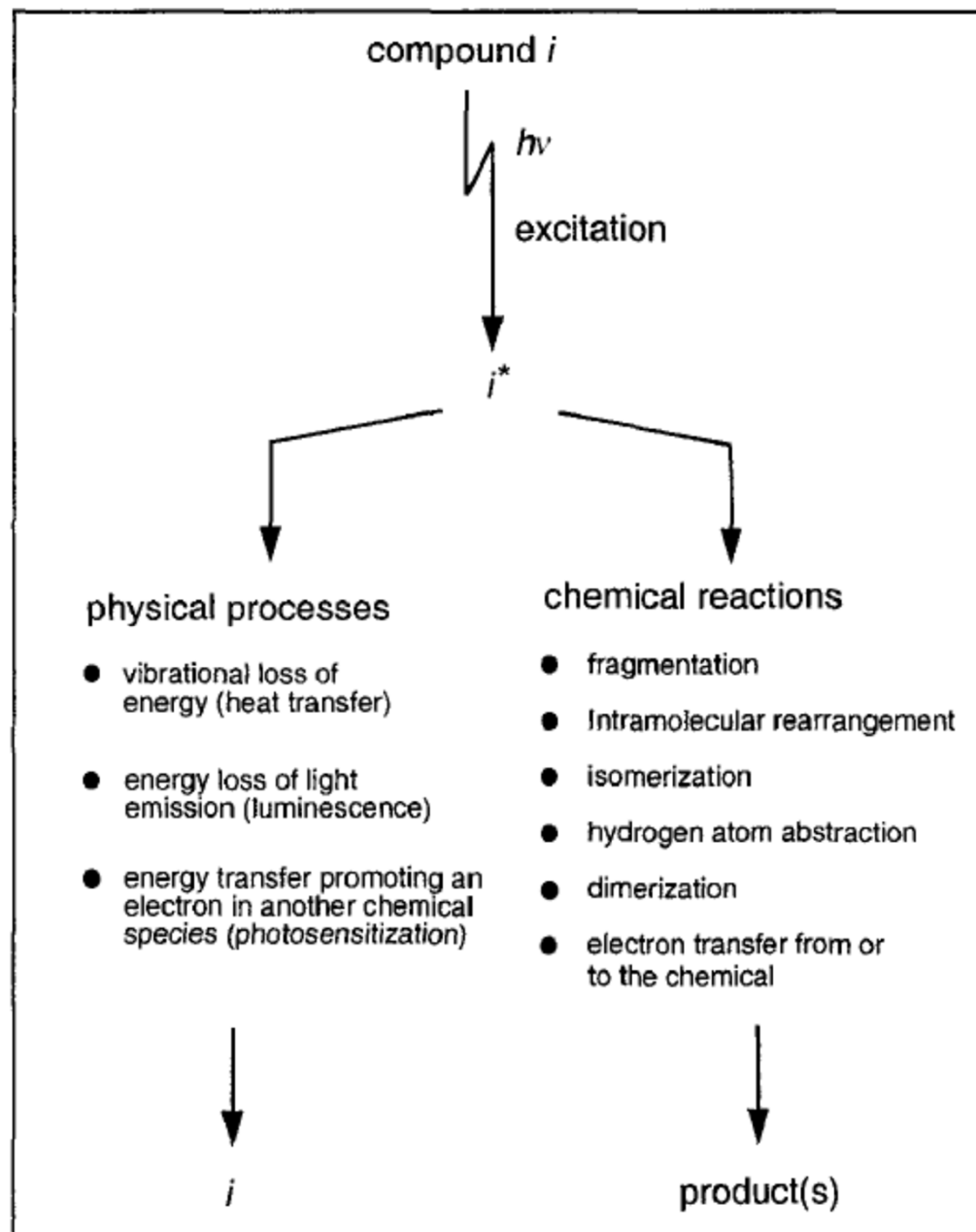
A structural moiety that exhibits a characteristic UV/Vis absorption spectrum

- Delocalized π electrons are often good chromophores
- $\lambda < 290$ nm strongly absorbed in the atmosphere \rightarrow not significant at natural conditions

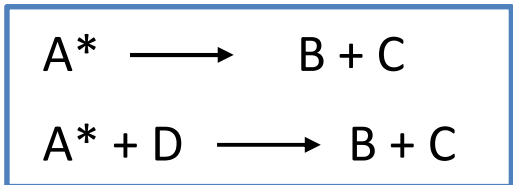
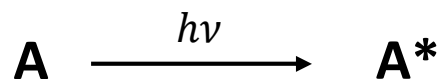
λ_{\max} : maximum absorption wavelength

ϵ : molar extinction coefficient

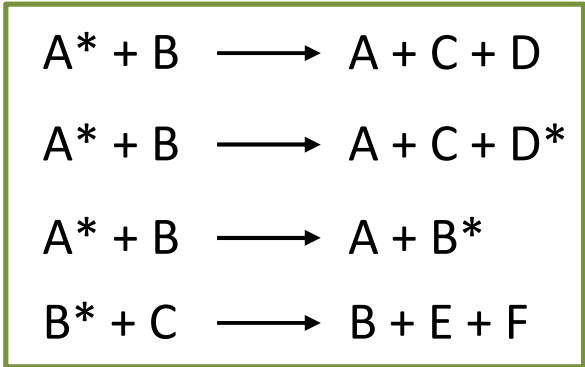
What happens after a molecule absorbs light?



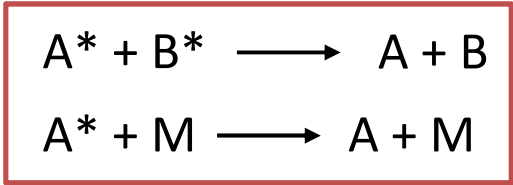
When molecule A absorbs a photon



- **Direct photolysis**
When the molecule being transformed is the same species that absorbed the photon



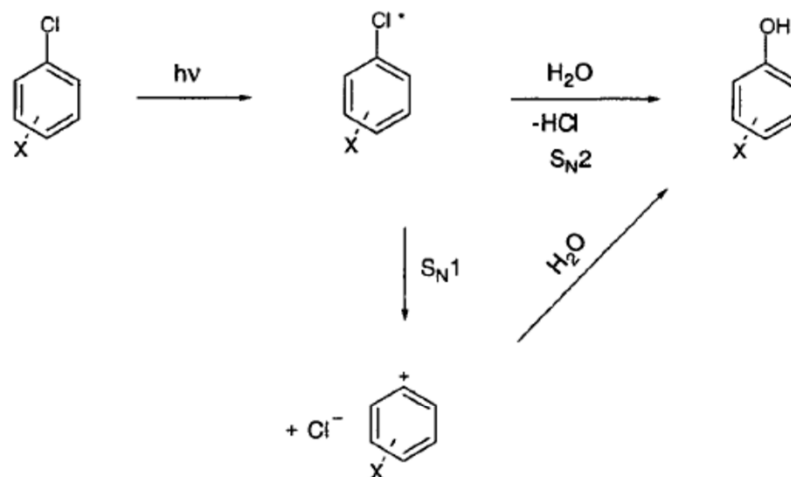
- **Indirect photolysis**
When the molecule being transformed is sensitized by other chemicals in the system excited by energy from light



- **Quenching**
A species accepts the electronic energy of the sensitized compound

Direct photolysis

(a)



(b)

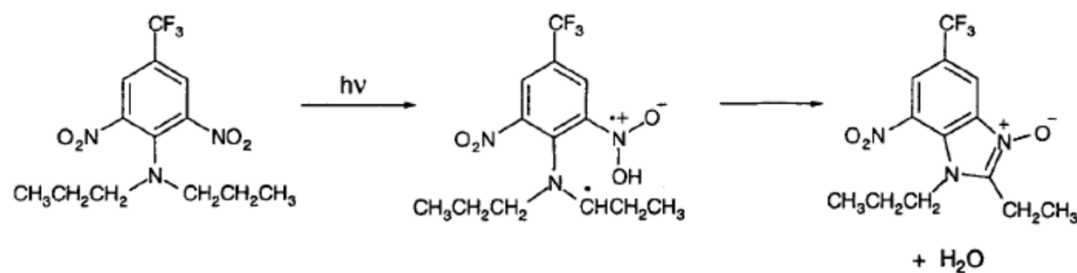


Figure 15.7 Examples of direct photochemical reaction pathways: (a) substituted chlorobenzenes, (b) trifluralin, and (c) a ketone (from Mill and Mabey, 1985).

Direct photolysis

(c)

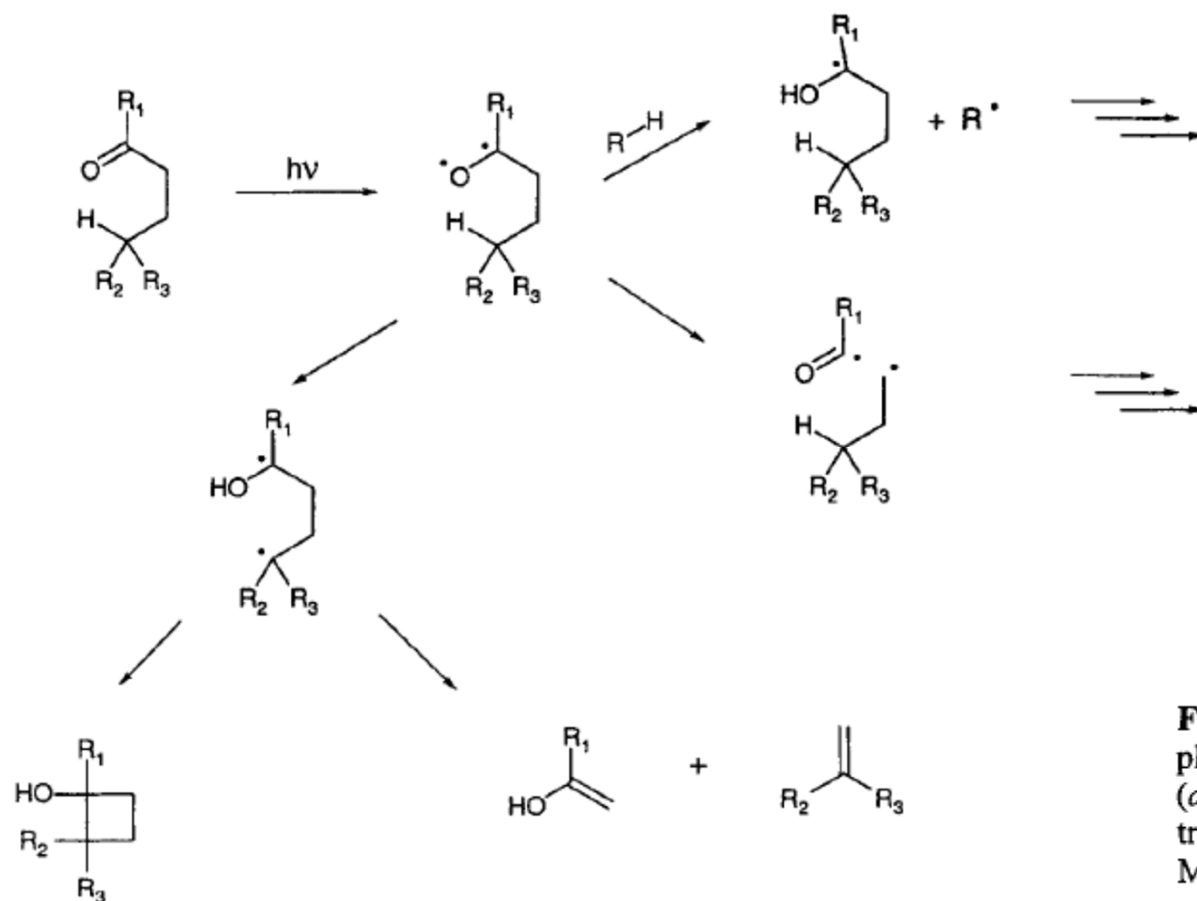


Figure 15.7 Examples of direct photochemical reaction pathways: (a) substituted chlorobenzenes, (b) trifluralin, and (c) a ketone (from Mill and Mabey, 1985).

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, $\Phi(\lambda)$**
 - Moles of compound transformed per moles of photons absorbed by the compound
 - Pathway specific or overall yields
 - Φ s are often $\ll 1$; $10^{-2} - 10^{-6}$

Direct photolysis – transformation issues

- **Quantum yield, $\Phi(\lambda)$**

- Quantum yield for reaction pathway j

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

- Reaction quantum yield (for all reaction pathways)

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

- The reaction quantum yield has to be determined by experiments

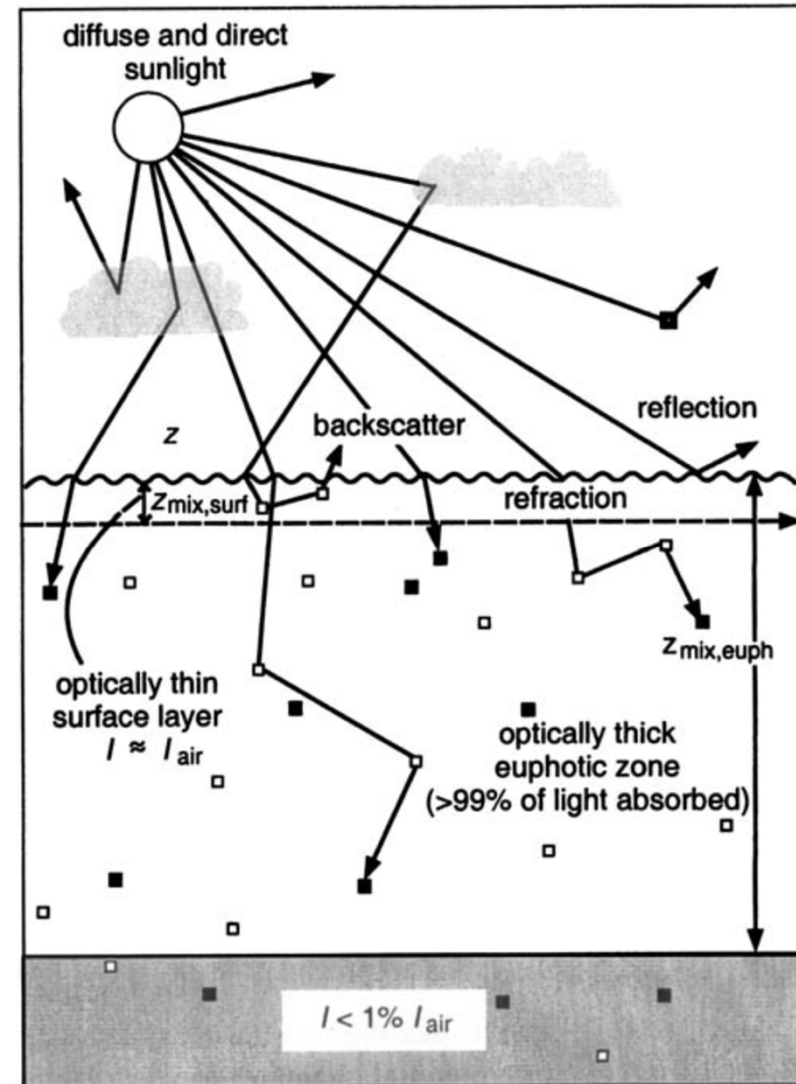
Direct photolysis – light absorption

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

$W_0(\lambda)$ & $W(\lambda)$ = light intensity at the water surface & at the underwater position of interest, respectively (einstein/cm²-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)

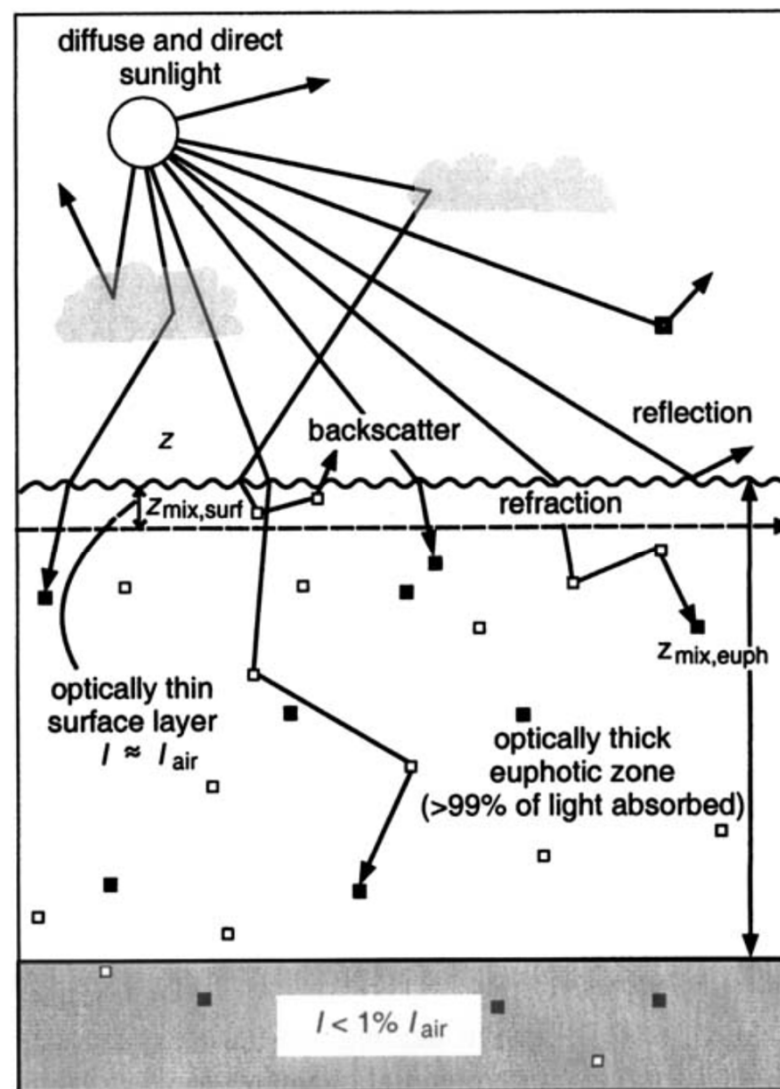
V = volume of the water body (cm^3)

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: $D(\lambda) = \frac{l(\lambda)}{z_{mix}}$

$D(\lambda)$ = 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/cm²-s)

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

2) Rate of light absorption by all species in water (per volume; in einstein/cm³-s)

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

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:

$$\begin{aligned} &= (\text{system light absorption, vol. basis}) \times F_i \\ &= \frac{W_0(\lambda)}{z_{mix}} \left[1 - 10^{-\alpha_D(\lambda) \cdot z_{mix}} \right] \frac{\epsilon_i(\lambda)}{\alpha(\lambda)} C_i \end{aligned}$$

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

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

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

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

$W_0(\lambda)$ in millieinstein/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 light absorption rate** (einsten/mole-s)

Direct photolysis rate at specific λ

$$\left(\text{Photolysis rate} \right) = \left(\text{Light absorption rate} \right) \times \left(\text{Transformation rate when light is absorbed} \right)$$

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

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

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

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

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

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)

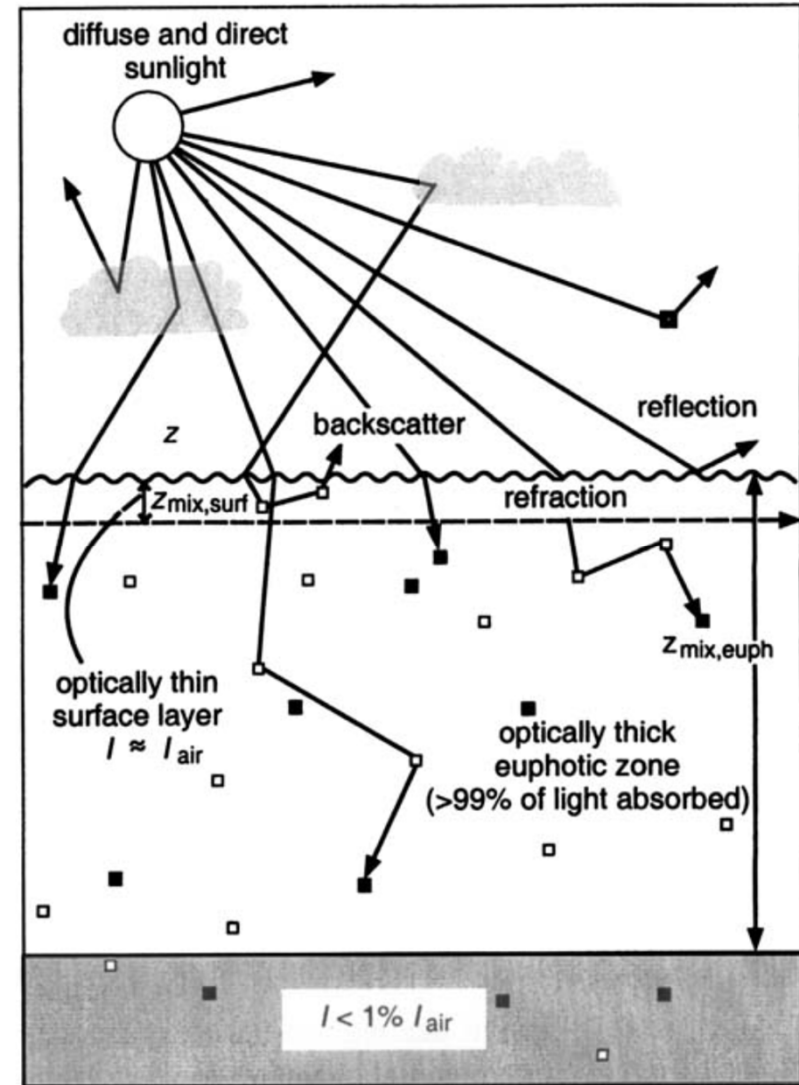
If Φ_{ir} is not a function of λ , then:

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

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

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

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

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

(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/cm²/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:

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

k_p^0 = near surface photolysis rate (s⁻¹)

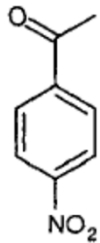
If Φ_{ir} is not a function of λ , then:

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

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°N altitude at noon on a clear midsummer day.



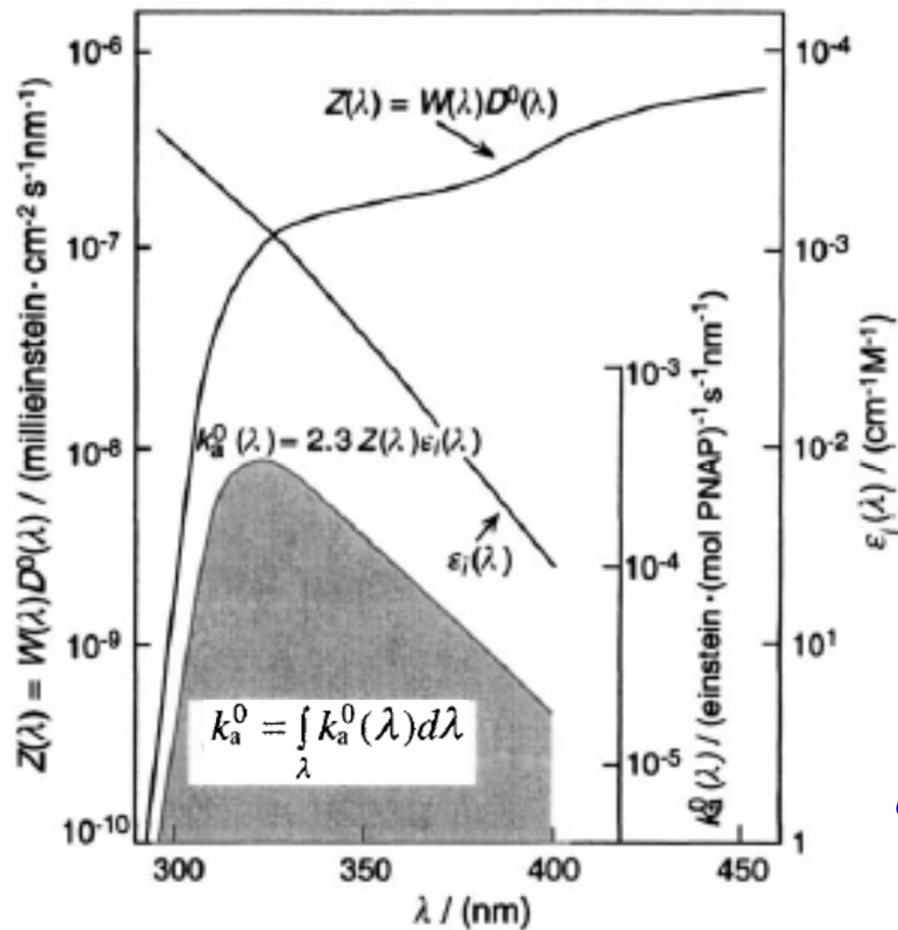
para-nitro-acetophenone
(PNAP)

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

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

λ (Center) (nm)	λ Range ($\Delta\lambda$) (nm)	$W(\text{noon}, \lambda)^{b,d}$ (millieinstein \cdot cm $^{-2}$ s $^{-1}$)	$Z(\text{noon}, \lambda)^{b,d}$
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)	λ Range ($\Delta\lambda$) (nm)	$Z(\text{noon}, \lambda)^a$ (millieinstein· $\text{cm}^{-2} \text{s}^{-1}$)	$\epsilon_i(\lambda)^b$ ($\text{cm}^{-1} \text{M}^{-1}$)	$k_a^0(\lambda) = 2.3 Z(\lambda)\epsilon_i(\lambda)$ [einstein (mol PNAP) $^{-1} \text{s}^{-1}$] $10^3 k_a^0(\lambda)$
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

$k_a^0 = \sum k_a^0(\lambda) = 14.5 \cdot 10^{-3}$
einstein (mol·PNAP) $^{-1} \text{s}^{-1}$

2) Nearly all light absorbed

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

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

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

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

$$-\frac{dC_i}{dt} = \left[\sum \frac{W_0(\lambda) \cdot \epsilon_i(\lambda) \cdot \Phi_{ir}(\lambda)}{\alpha(\lambda)z_{mix}} \right] C_i = k_p^t C_i$$

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 ($pK_a = 7.11$):

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

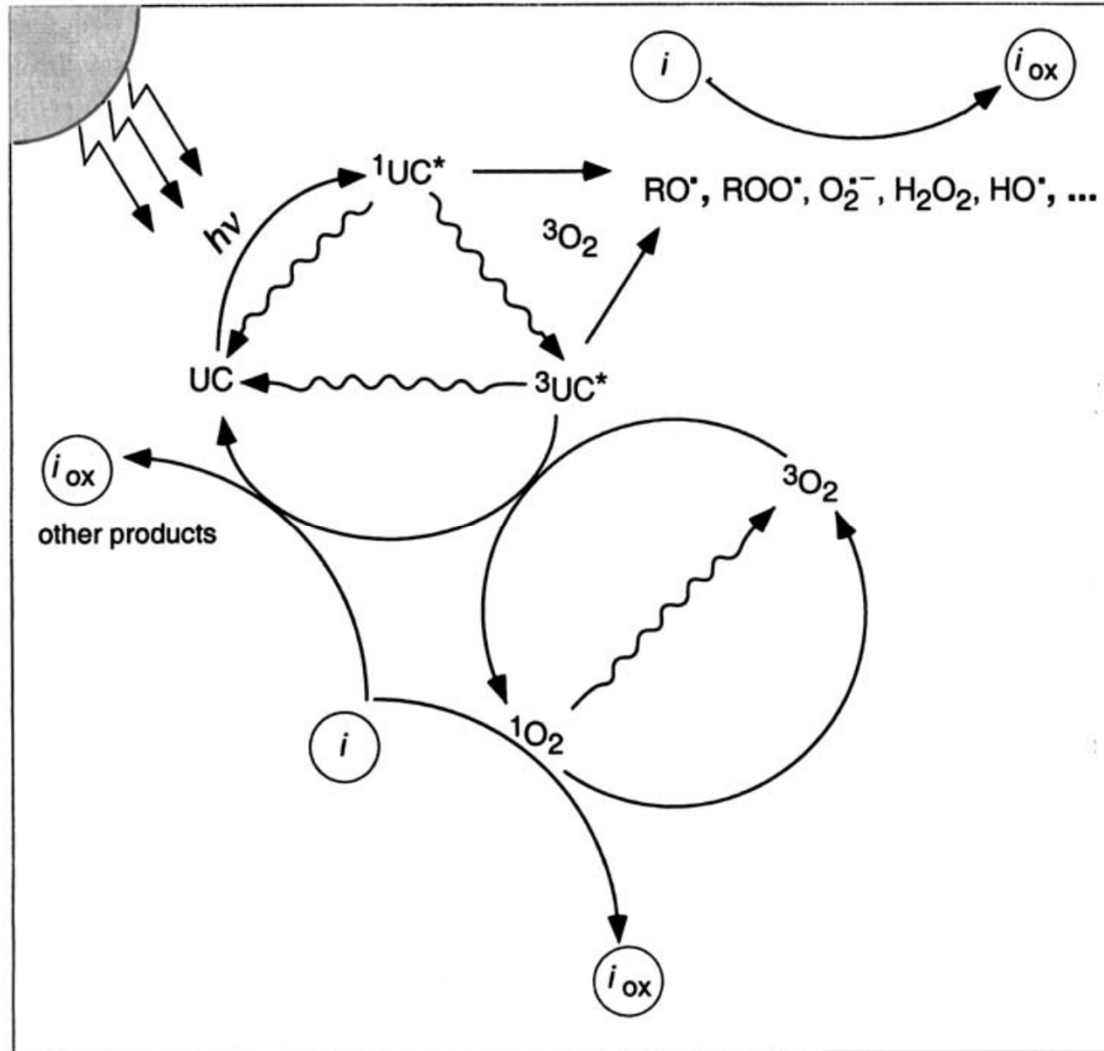
$$k_a^0(A^-) = 3.2 \times 10^4 \text{ einstein} \cdot (\text{mole } A^-)^{-1} \cdot d^{-1}$$

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

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

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

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

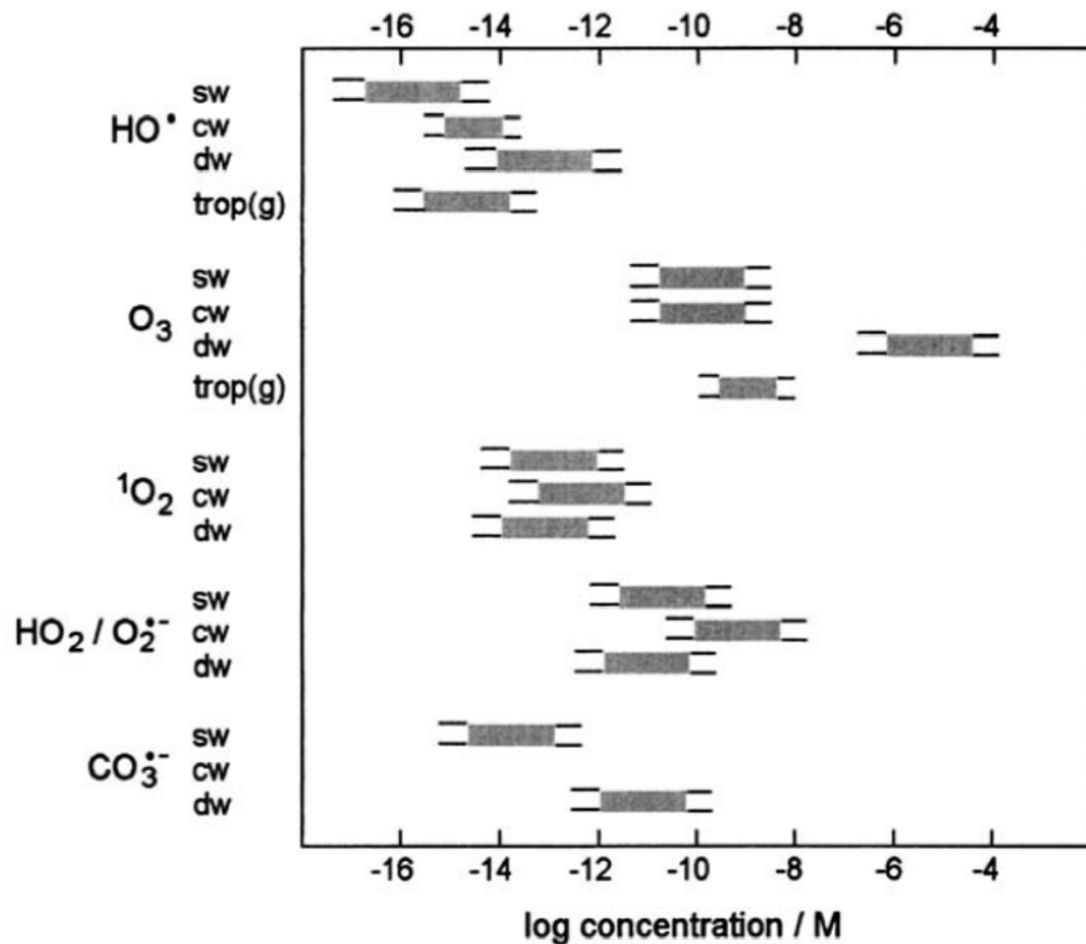


Figure 16.1 Ranges of steady-state concentrations of reactive oxygen species in sunlit surface waters (sw), sunlit cloud waters (cw), drinking-water treatment (dw), and the troposphere (trop(g)). Data from Sulzberger et al. (1997) and Atkinson et al. (1999).

ex)

$$[{}^1\text{O}_2]_{ss} \sim 10^{-13} \text{ M}$$

(summer, noon)

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

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

$$pK_a \sim 10$$

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

