Updated: 17 April 2013

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CEE 577: Surface Water Quality Modeling

Lecture #33

Toxics: Photolysis

(Chapra, L42)

Overall decay rate

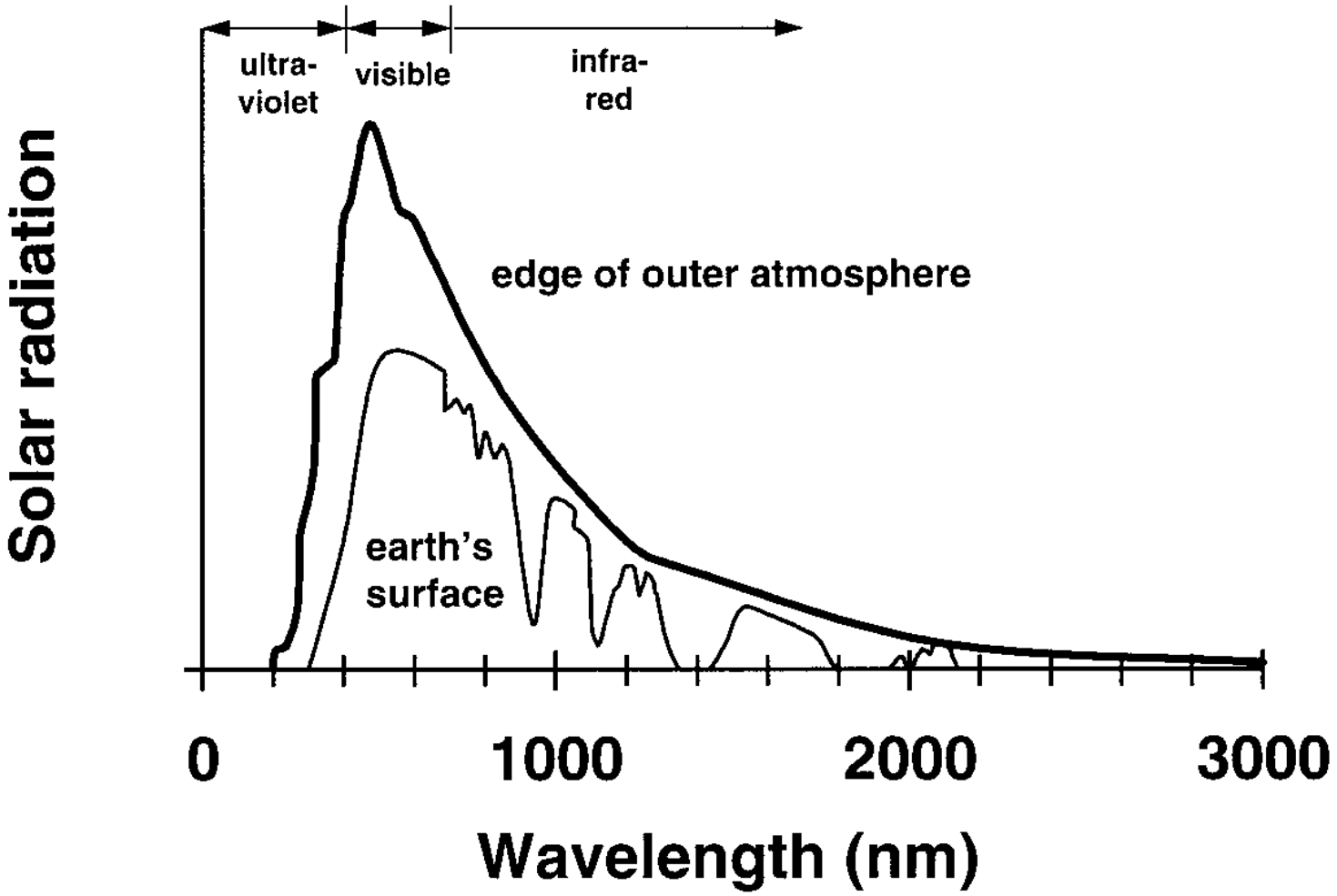
- k_1 is a combination of
  - Hydrolysis (k_h)
  - Photolysis (k_p)
  - Biodegradation (k_b)
  - Any other loss process not otherwise included in the model
- Any of these processes may be affected by sorption
  - Photolysis is most commonly attributed to dissolve forms only

$$k_1 = k_h + f_{p1} k_p + k_b$$

Photolysis

- Chemical breakdown initiated by light energy
- two types
  - direct photolysis
  - sensitized (or indirect) photolysis
- Several steps
  - some solar light reaches water surface
  - some of this light penetrates to the solute
  - some of this is absorbed by the solute
  - some of absorbed light is capable of causing a reaction

Solar Radiation



Attenuation of light through water

- Beer-Lambert's Law

Attenuation coefficient (cm^{-1})

$$I(z,\lambda) = I(0,\lambda)e^{-\alpha_D(\lambda)z}$$

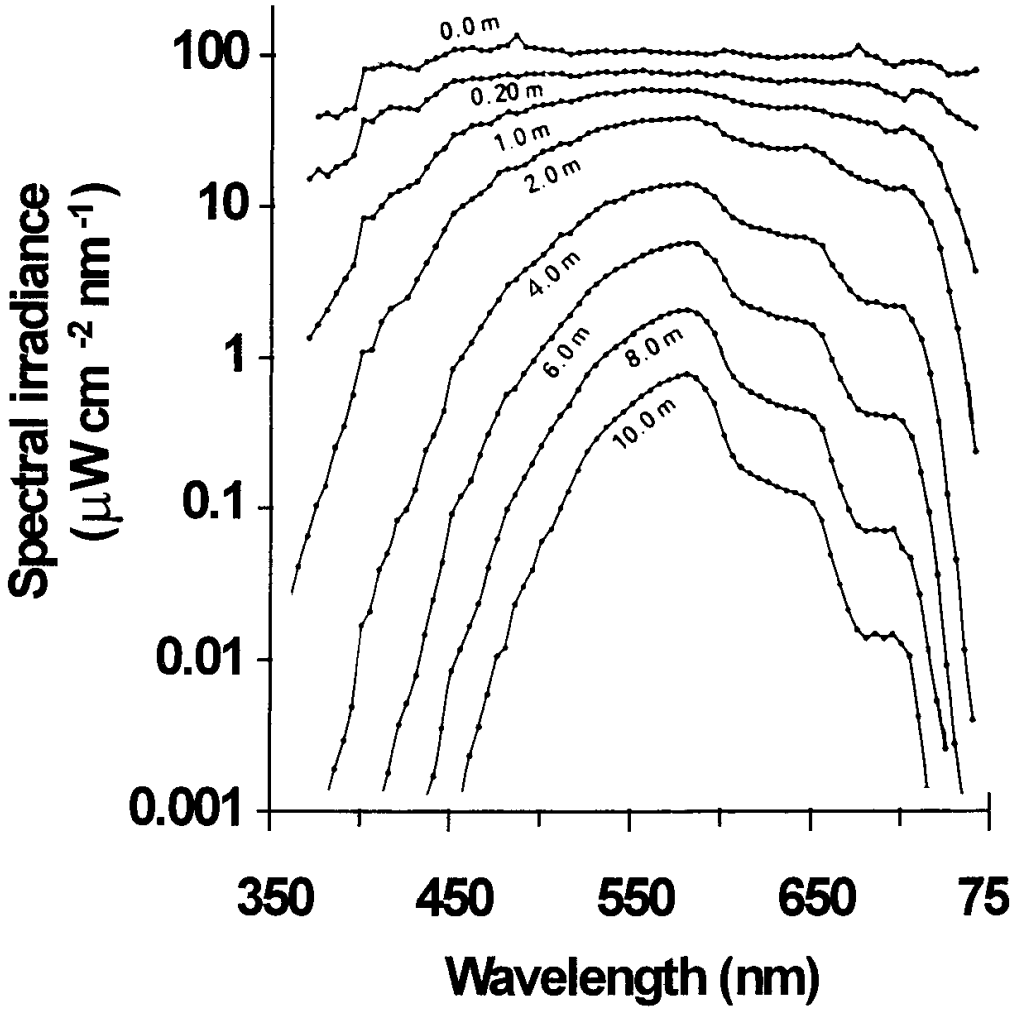
Light Intensity (einstein/cm^2/s) at depth z, and wavelength, λ

- and the attenuation coefficient is from:

$$\alpha_D(\lambda) = \frac{1}{H}\ln\left[\frac{I(0,\lambda)}{I(H,\lambda)}\right]$$

Measured light intensity with depth

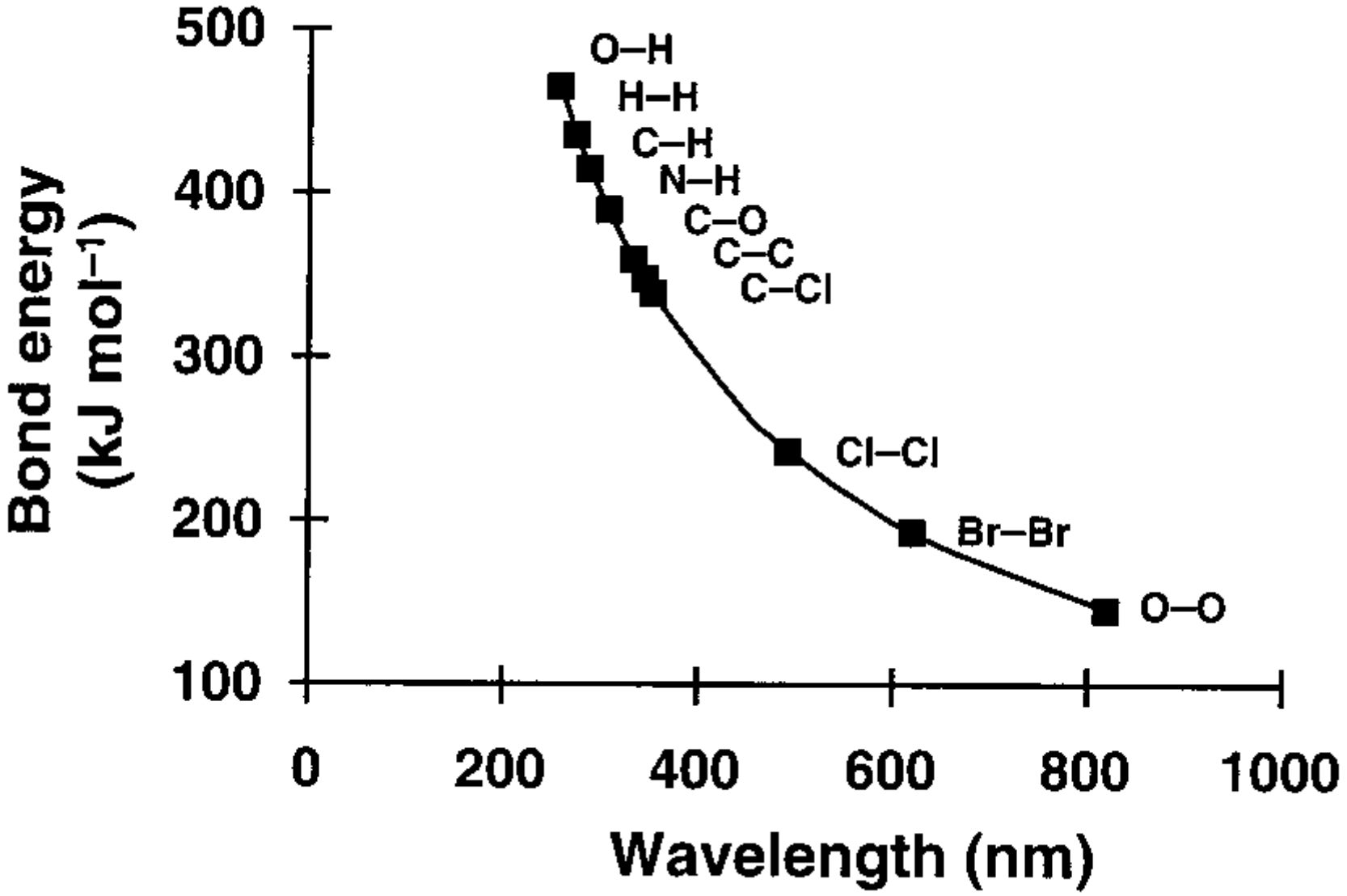
- Lake San Vincente
- Tyler & Smith, 1970



- Average light absorption over depth H

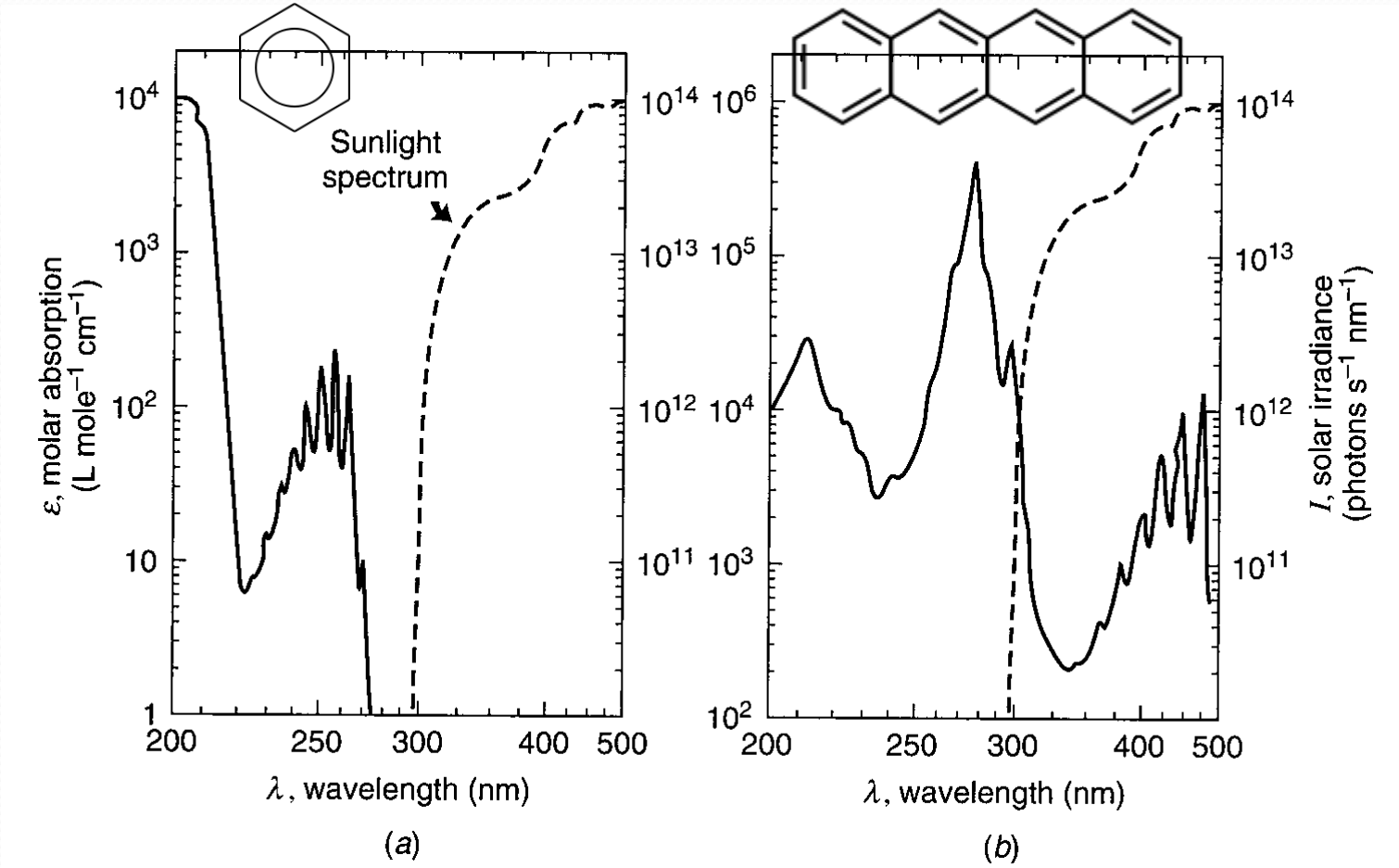
$$I = \frac{I(0,\lambda)}{H}\left(1 - e^{-\alpha_D(\lambda)H}\right)$$

einsteins/cm^3/s


Bond energy (kJ mol⁻¹)
500
400
300
200
100
0
200
400
600
800
1000
Wavelength (nm)
O–H
H–H
C–H
N–H
C–O
C–C
C–Cl
Cl–Cl
Br–Br
O–O

Spectral overlap

- (a) benzene; (b) naphthacene or tetracene



Absorption of Light

Molar extinction coefficient (L/mole/cm)

- Attenuation due to background and contaminant

$$I(\ell,\lambda) = I(0,\lambda)e^{-[\alpha(\lambda)+\varepsilon(\lambda)c]\ell}$$

- Integrating over the depth and isolating on the contaminant we get:

$$I_a(\lambda) = \frac{\varepsilon(\lambda)I(0,\lambda)(1-e^{-\alpha_D(\lambda)H})}{H\alpha(\lambda)}c$$

Quantum Yield

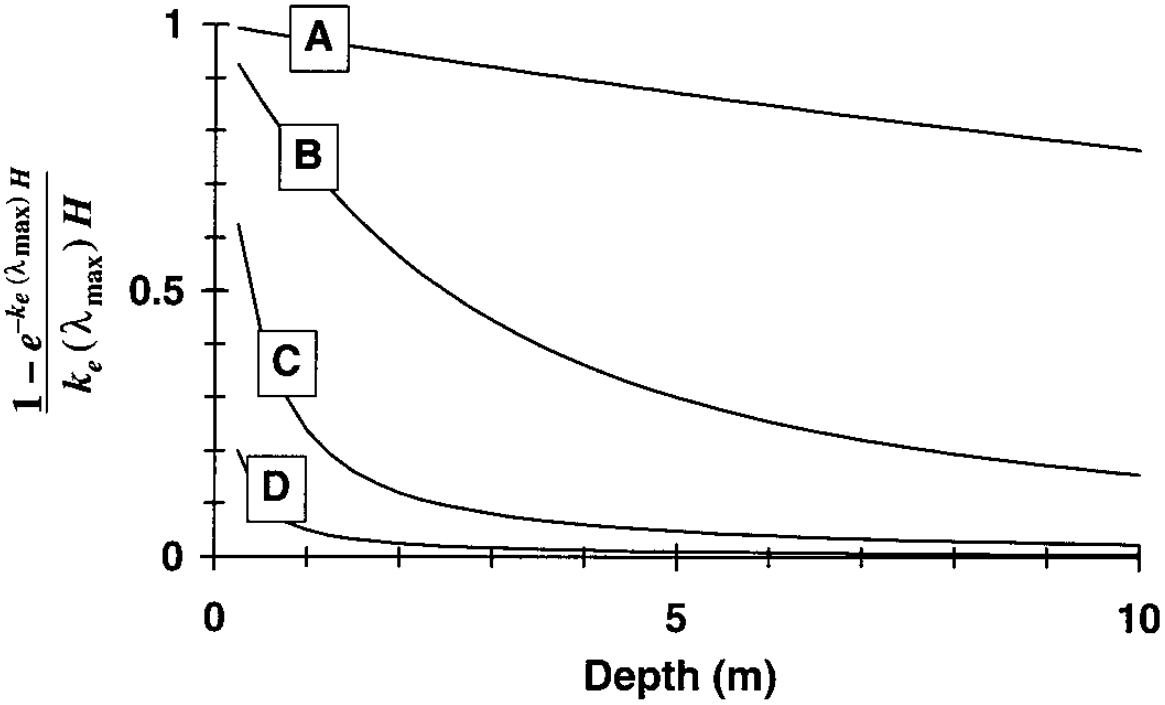
- Once absorption occurs, energy is dissipated by:
  - emission of heat
  - emission of light: luminescence
  - contact with another molecule: photosensitization
  - decomposition: direct photolysis
- Fraction following last pathway is quantum yield

$$\Phi_r(\lambda) = \frac{\text{number of moles transformed}}{\text{total moles of photons of wavelength } \lambda \text{ absorbed}}$$

- And combining with absorption equation:

$$k_p(\lambda) = \Phi(\lambda) k_a(\lambda) = \Phi(\lambda) \frac{\varepsilon(\lambda) I(0,\lambda)(1 - e^{-\alpha_D(\lambda) H})}{H\alpha(\lambda)}$$

	Water type	Chl*a* (mg L^{-1})	DOC (mg L^{-1})	ss (mg L^{-1})
A	Pure water	0	0	0
B	Lake Tahoe	0.001	0.1	0.5
C	Eutrophic	0.01	0.5	5
D	Hypereutrophic	0.1	2	20



- To next lecture