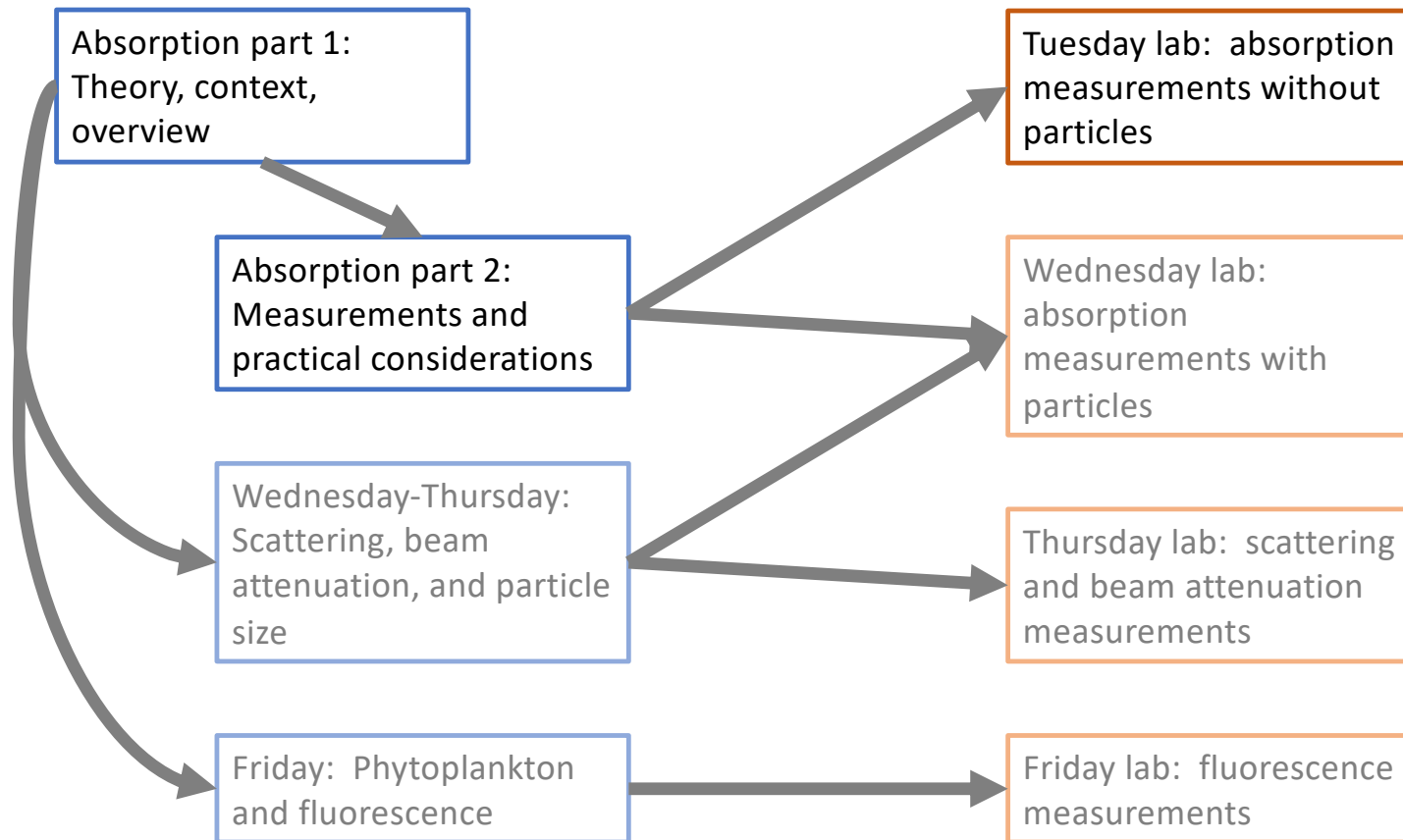


Absorption, Part 1

- Context (in this class, and broader disciplinary context)
- How does light energy interact with matter in the ocean?
- Overview of absorbing constituents in the ocean

Class context: Week 1 roadmap



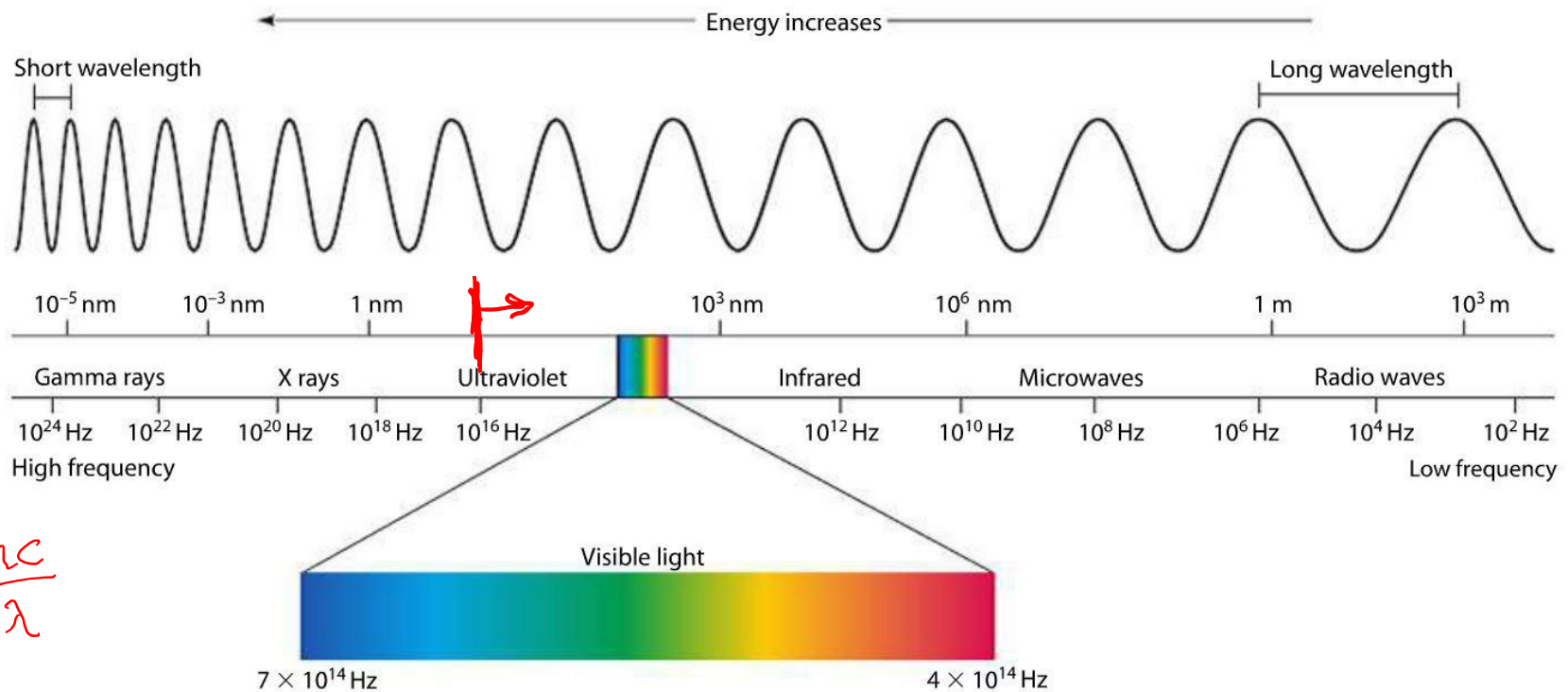
Disciplinary context

- Undergraduate physical chemistry connections (e.g., spectroscopy)
- Language to help you read about these concepts outside the field of oceanography and/or talk about them with non-oceanographers
- Foundation to support your future work in new directions that none of us have considered, yet!

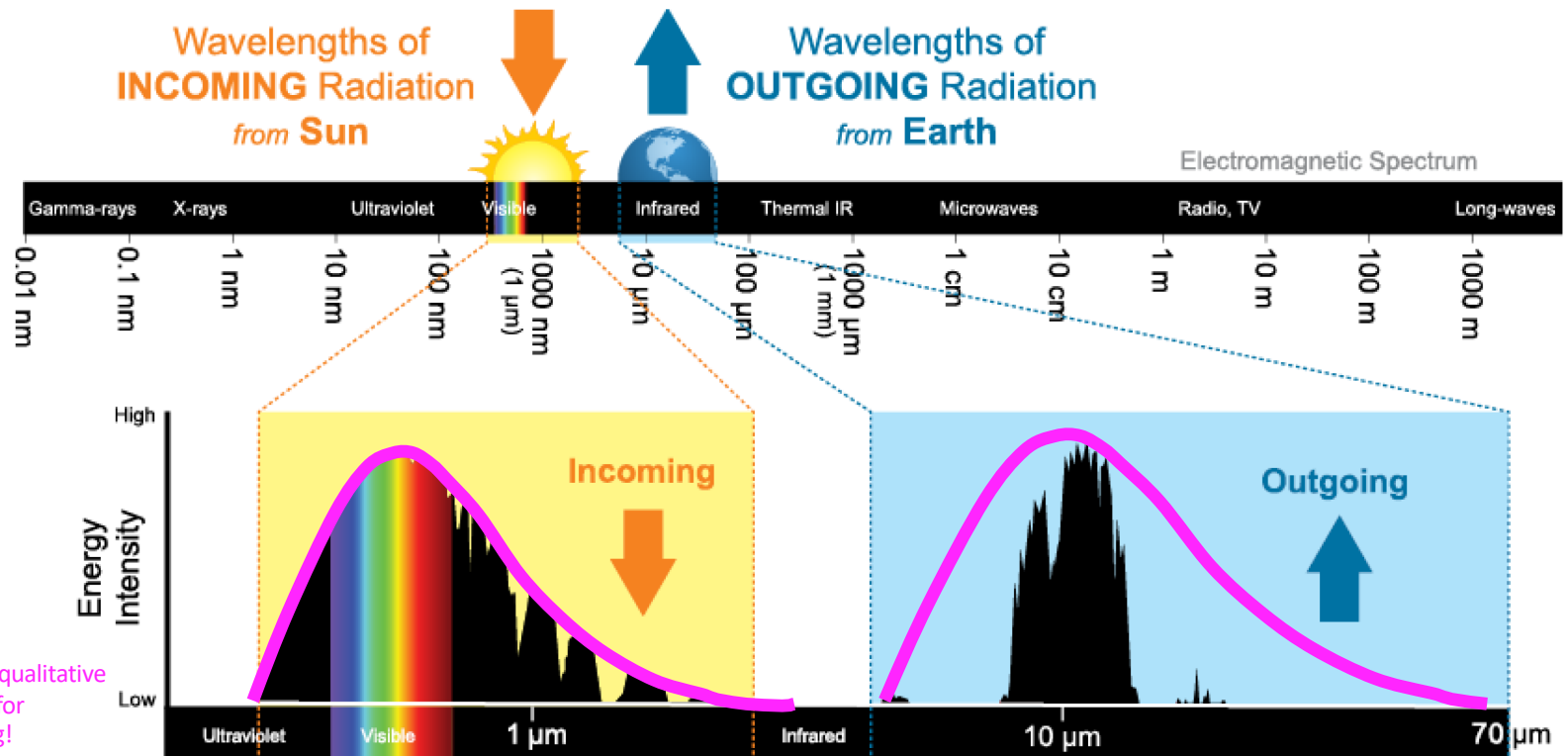
Absorption, Part 1

- Context (in this class, and broader disciplinary context)
- How does light energy interact with matter in the ocean?
 - Electromagnetic spectrum
 - Quantized absorption energies
 - Fate of energy after absorption
- Overview of absorbing constituents in the ocean

Electromagnetic (E-M) energy spectrum

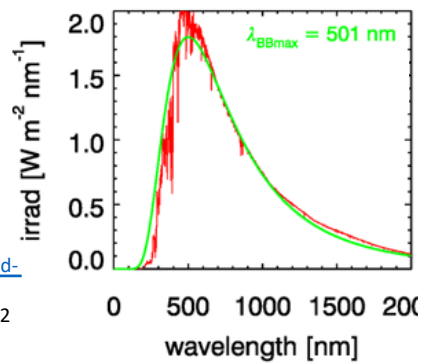


$$E = \frac{hc}{\lambda}$$

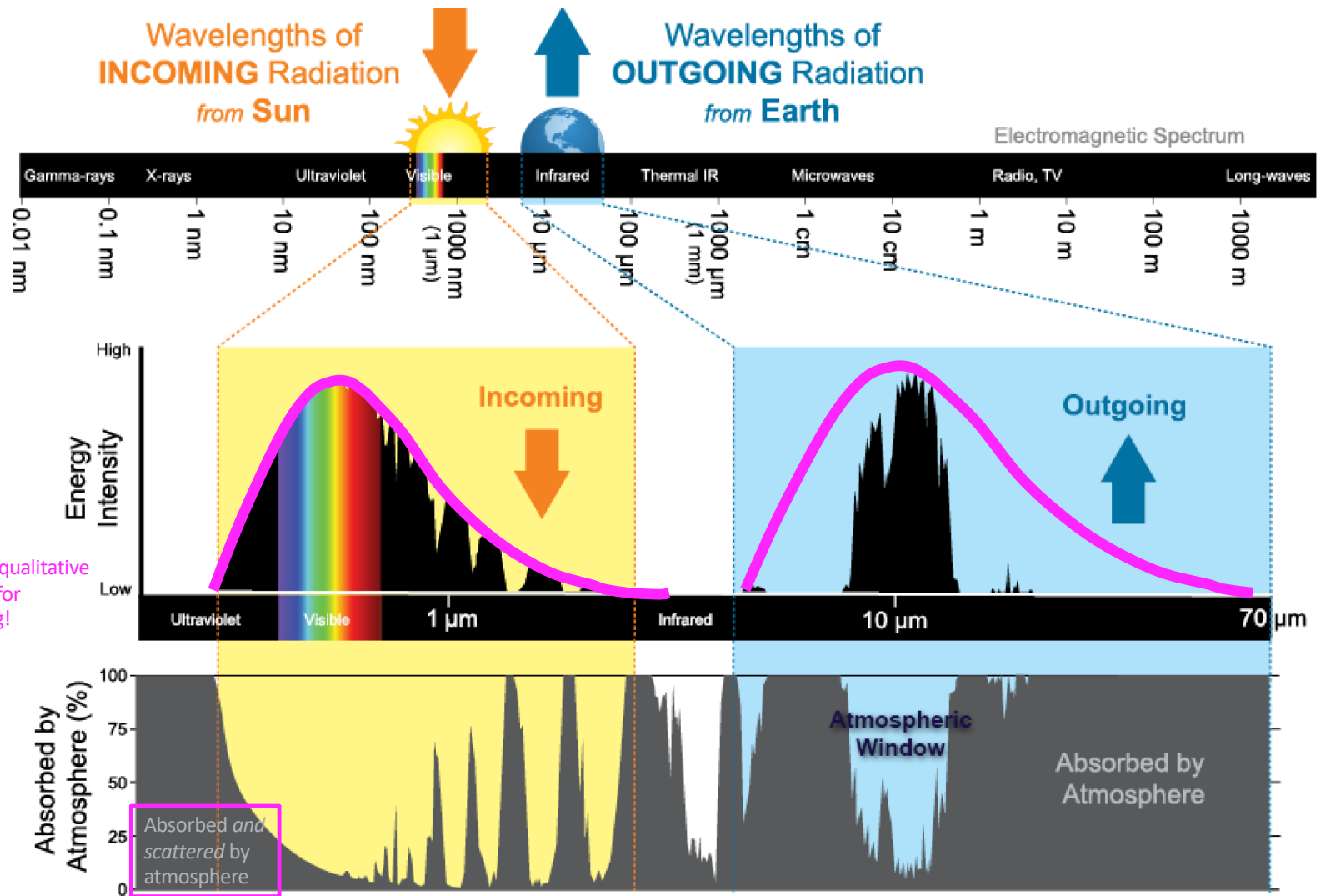


Vertical scales are qualitative and not the same for incoming/outgoing!

<https://www.noaa.gov/jetstream/satellites/absorb>



<https://www.oceanopticsbook.info/view/light-and-radiometry/level-2/common-misconception>
Figure 2.2, Mobley, *The Oceanic Optics Book*, 2022



Vertical scales are qualitative and not the same for incoming/outgoing!

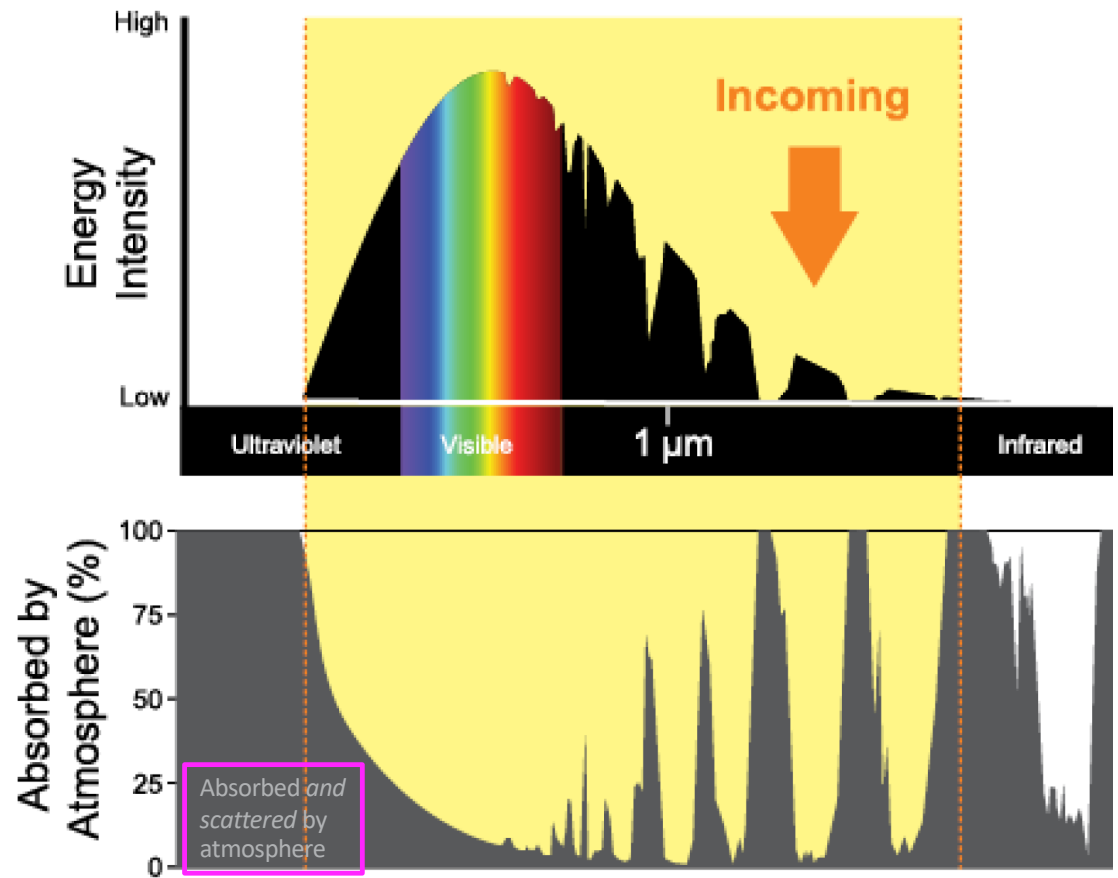
Examine the **spectral shape of the relative absorption** of incoming sunlight by Earth's atmosphere.

What notable features do you see?

Bands in NIR
- distinct

Large absorption/scattering
in UV

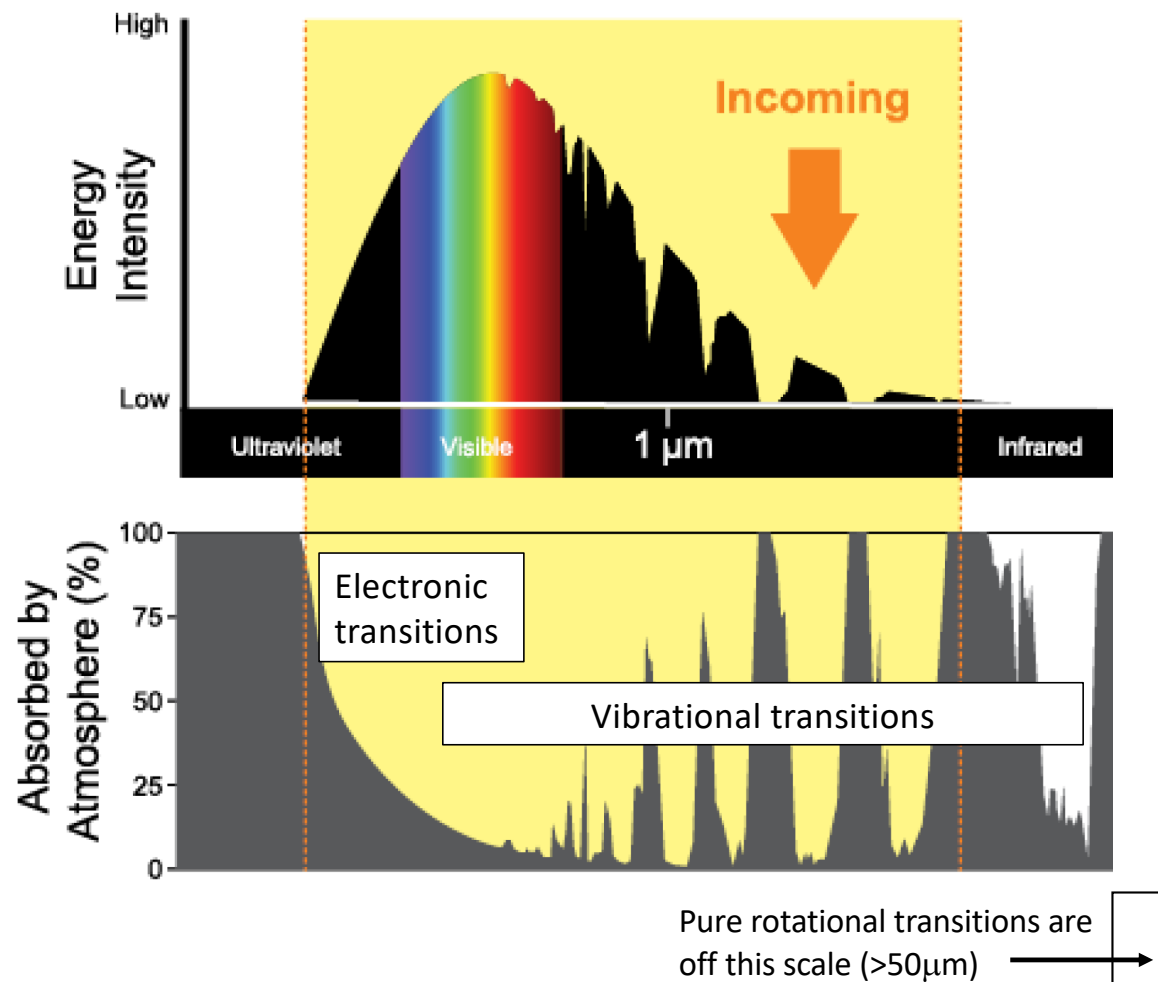
Decreasing intensity of
IR bands with
decreasing λ



Examine the **spectral shape of the relative absorption** of incoming sunlight by Earth's atmosphere.

What notable features do you see?

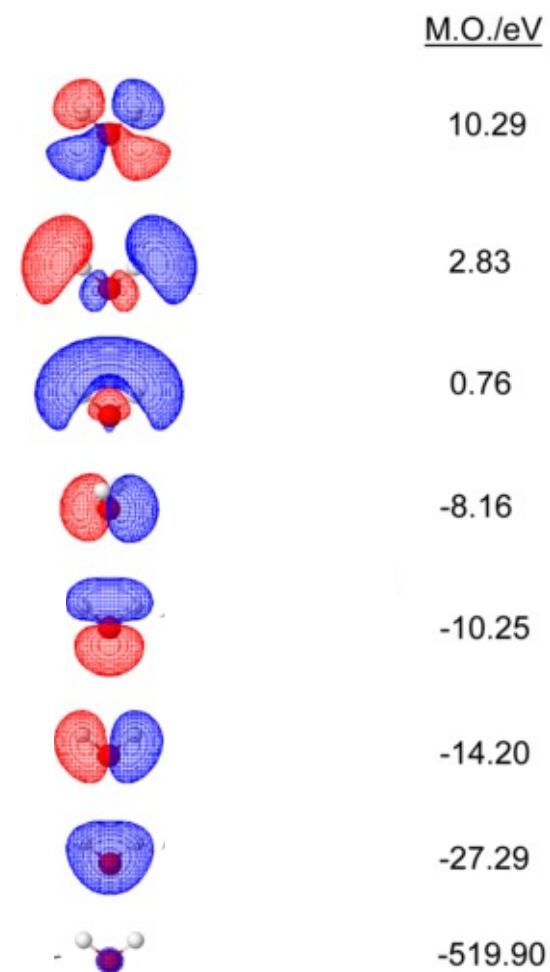
- Light is absorbed in discrete wavelength bands of varying width
 - **Absorption occurs only at specific, quantized energies**
- Light is strongly absorbed at ultraviolet wavelengths
 - UV light excites electrons (eg, O_3 bonds)
 - Shorter wavelengths undergo more Rayleigh scattering



Electronic transitions

- Red and blue blobs are molecular orbitals, the “probability regions” where the electrons are found around the molecule
- Electrons can *only* occupy these regions
- Going from bottom to top, the orbitals are arranged from lowest to highest energy (theoretical values on the right)
- For an electron to change shape between orbitals, it must absorb or release a photon with energy equal to the *difference* between those orbitals

Molecular Orbitals for Water Vapor

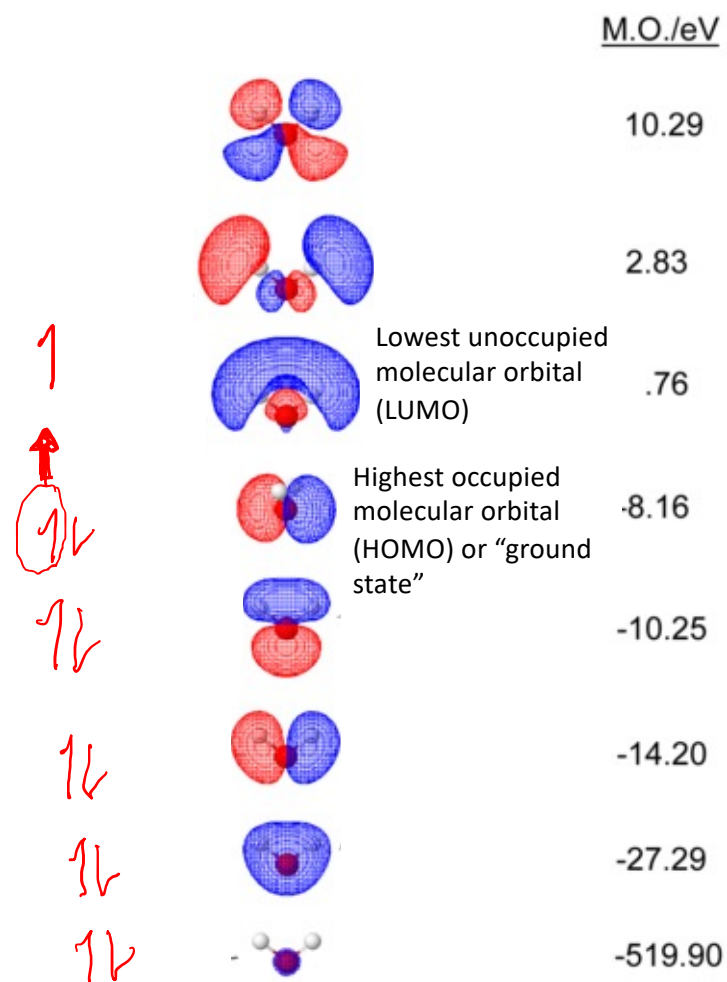


https://commons.wikimedia.org/wiki/File:Molecular_Orbitals_for_Water.png

Electronic transitions

- In its “ground” or lowest-energy state, water’s 10 electrons pair up in the bottom 5 orbitals
- If a water vapor molecule absorbs a photon with $\lambda = 166.5 \text{ nm}$ then an electron can be *excited* from the 5th to the 6th orbital in the diagram

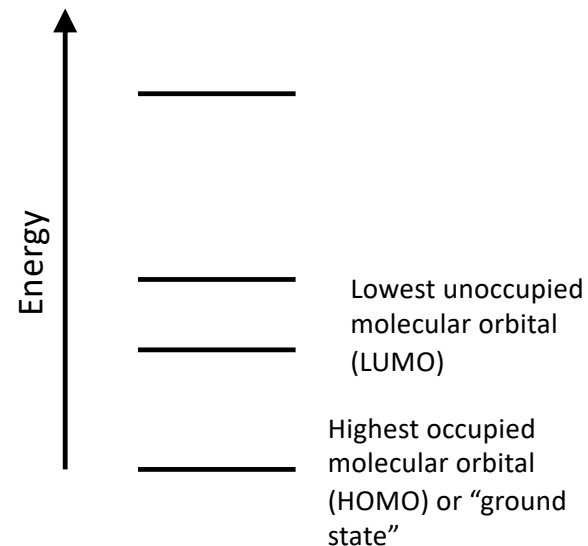
Molecular Orbitals for Water



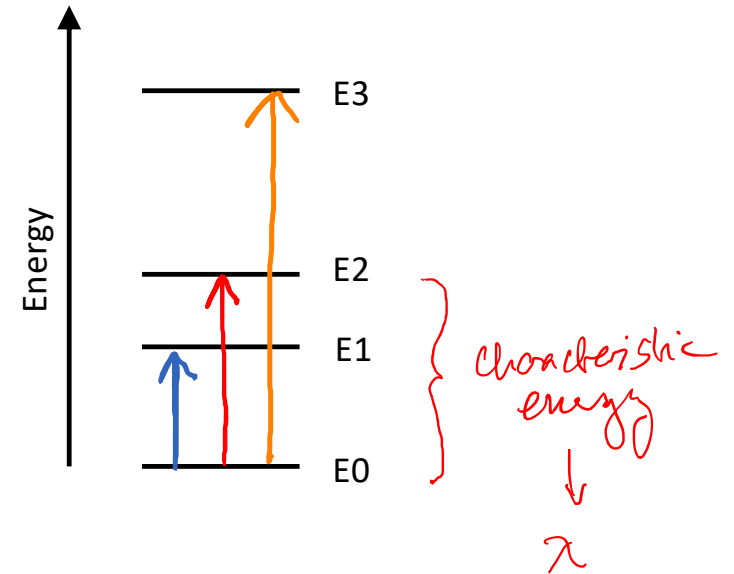
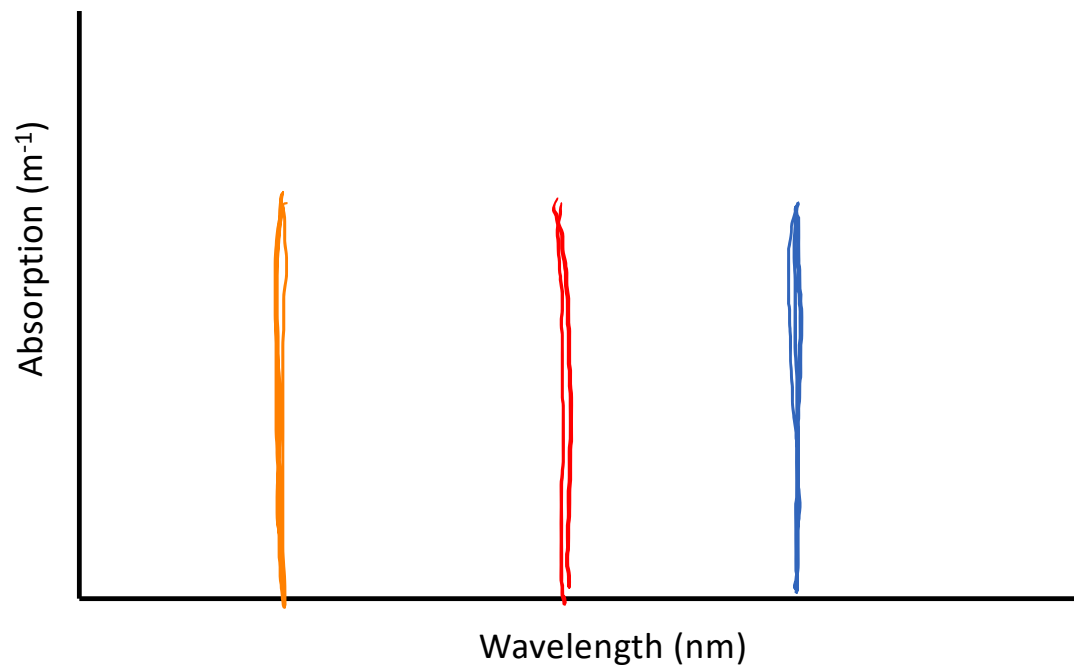
https://commons.wikimedia.org/wiki/File:Molecular_Orbitals_for_Water.png

Electronic transitions

- Most of the time we don't know the actual orbital shapes, instead we measure the energies that separate the states
- And often we don't bother showing states that don't interact with the part of the EM spectrum we're interested in

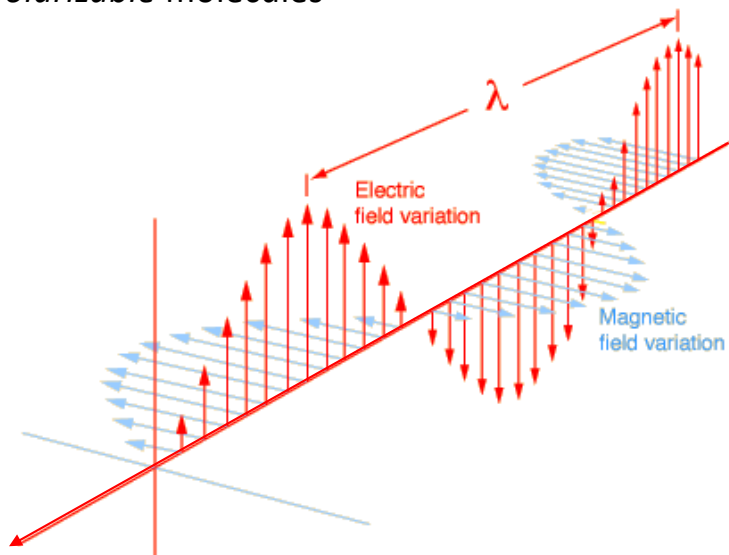


Electronic transitions



Vibrational states of a molecule

EM radiation interacts with vibrating, *polarizable* molecules



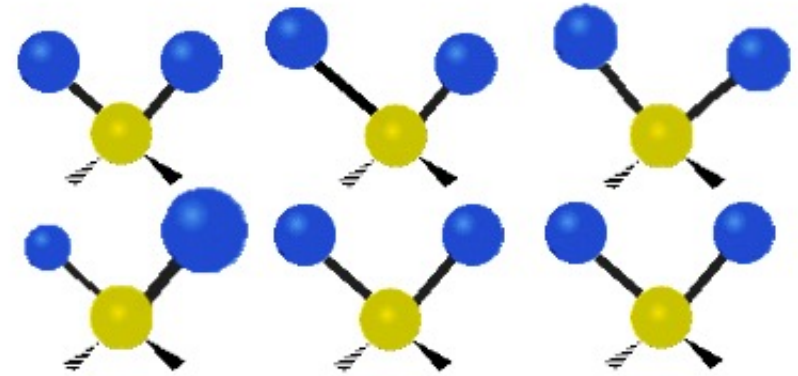
Simulation shows total vibrational *and* rotational states

A screenshot of a simulation interface showing several water molecules (represented by red and white spheres) in various vibrational and rotational states. The interface includes a "Thermometer" on the right side, a "Cool" button, a "Heat" button, and checkboxes for "Show hydrogen bonds", "Show partial charges", and "Slow motion". The logo for "The Concord Consortium" is visible in the bottom left corner.

<http://mw.concord.org/nextgen/#interactives/chemistry/intermolecular-attractions/hydrogen-bonds>

Vibrational “modes” of a molecule

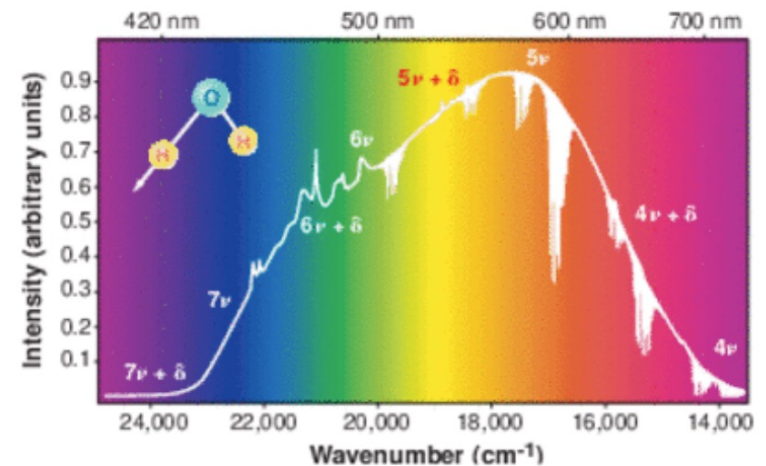
- Vibrational states include fundamental modes animated here, plus harmonics and higher order combinations
- The larger and more complex the molecule, the more possibilities there are...



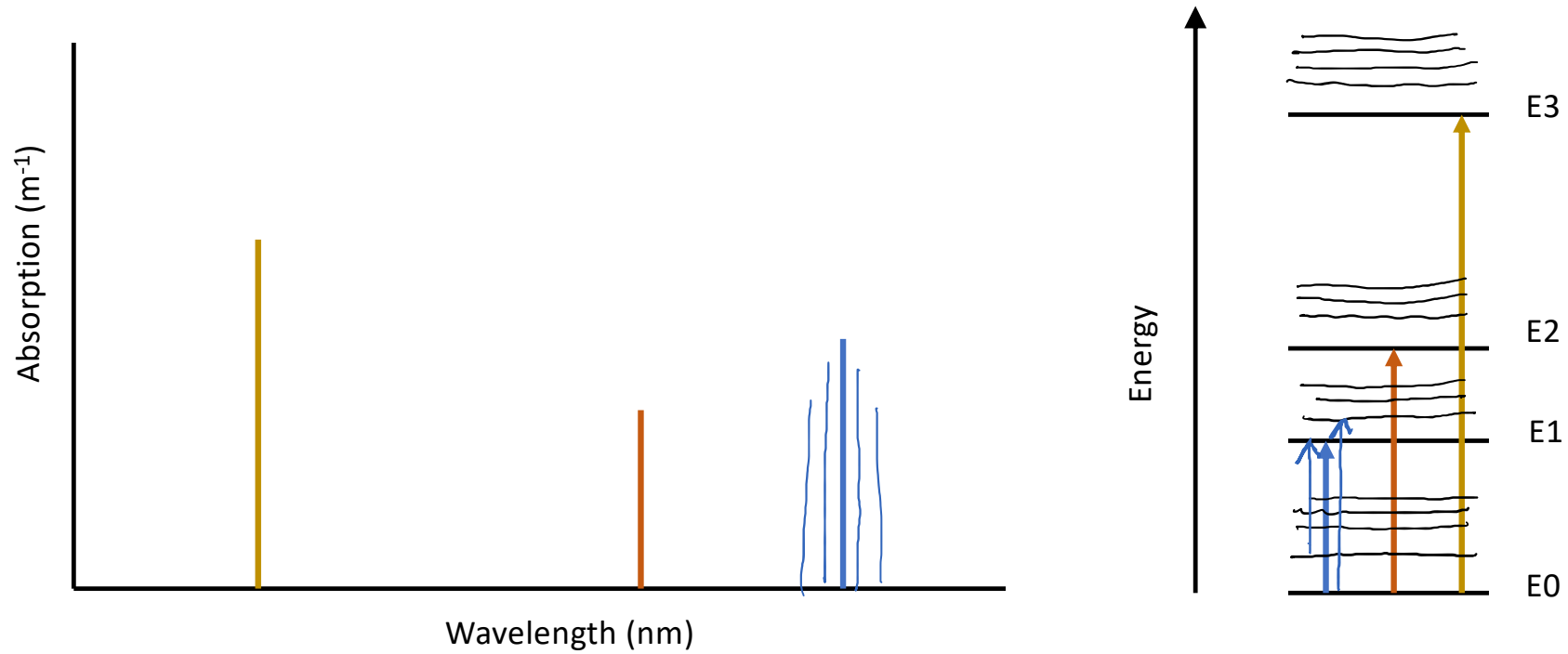
Animations:

<https://www.oceanopticsbook.info/view/absorption/physics-of-absorption>

FTIR spectrum of water vapor: Bernath, 2002.
<https://doi.org/10.1126/science.1075934>



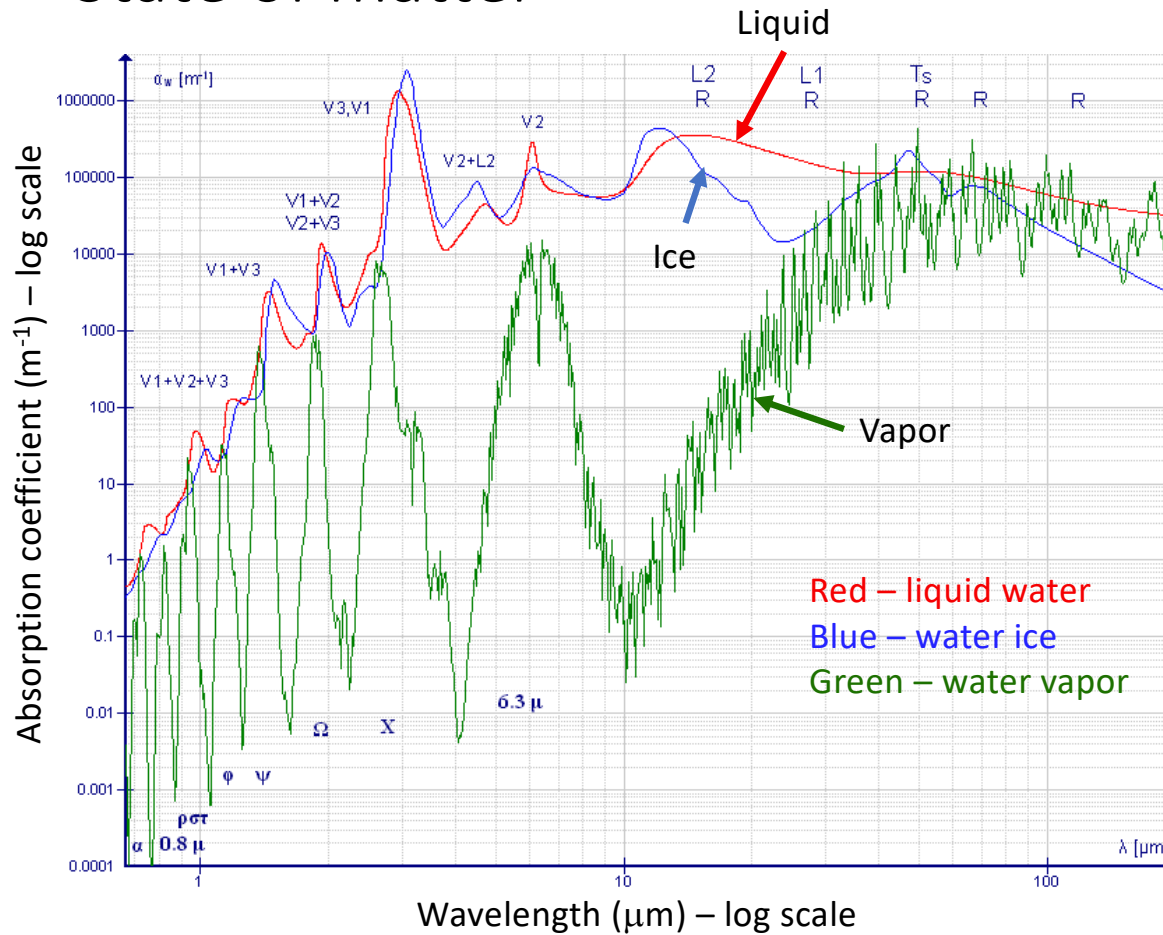
Electronic + vibrational + rotational? transitions



Factors that may modify absorbed energies

- State of matter (gas/liquid/solid)
- Internuclear distance
 - Temperature
 - Salinity
 - pH
 - Solvent effects

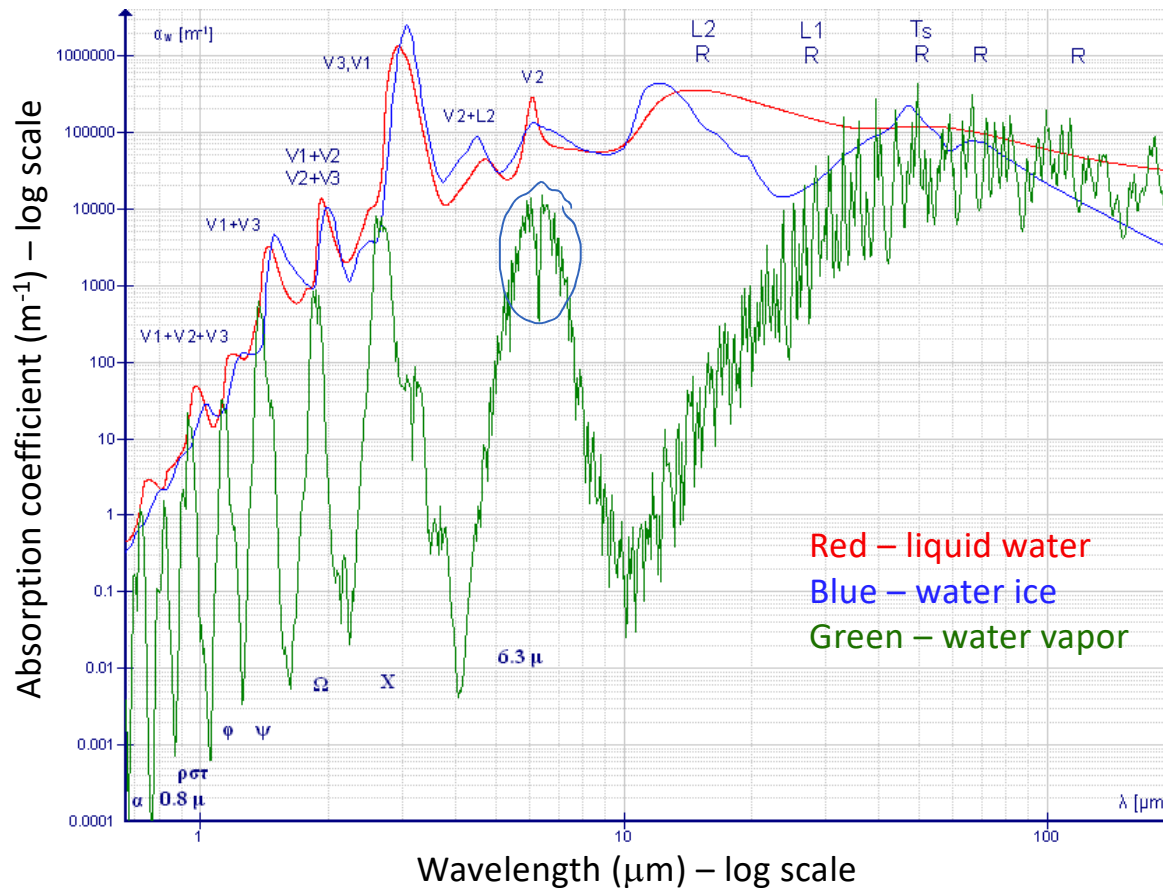
State of matter



What notable differences do you see?

*Vapor is different
 - More variable
 Vapor peaks are shifted*

State of matter (water)



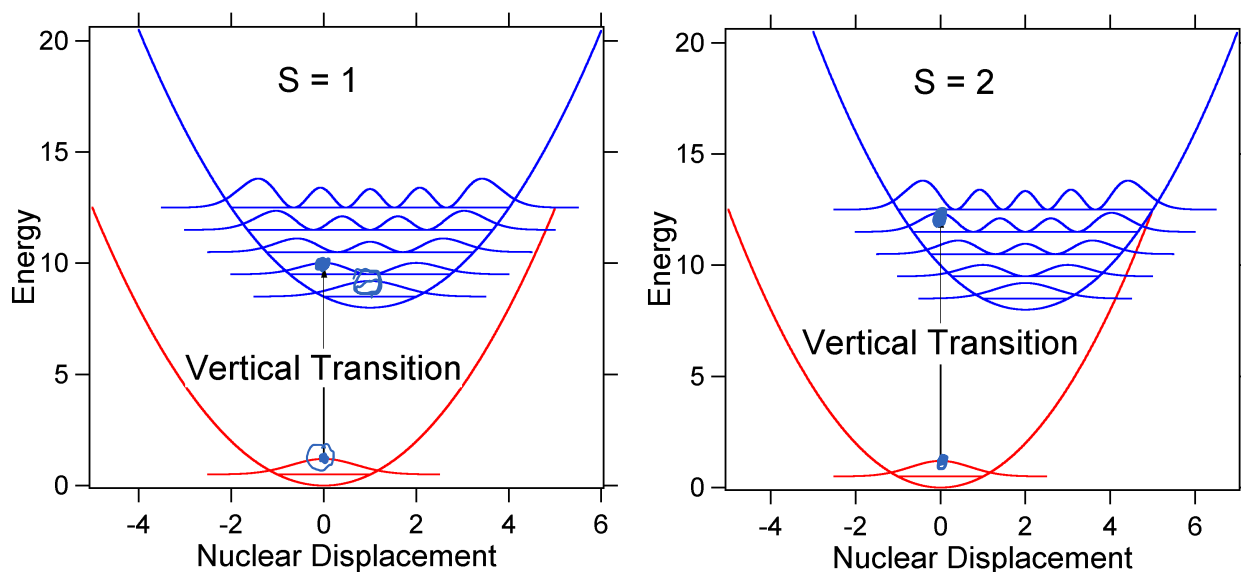
What notable differences do you see?

- **Liquid water and ice don't have the rotational structure.** Molecules in liquids and solids can't rotate as easily.
- **The wavelengths of the vibrational transitions are not the same.** Absorption energy depends on internuclear distance.

[Note: Narrow troughs in the middle of some vapor absorption bands shown here (e.g. 6.3 μm) probably arise because the absorption spectrum was derived from an atmospheric profile with a temperature inversion.]

Internuclear distance and transition probability

- Franck-Condon principle:
Nuclei are effectively motionless during the time it takes for an electron to change state
- The more two states are “in phase”, the higher the probability of an absorption (or fluorescence! more later) event
- It follows that anything affecting internuclear distance can alter the absorption energies.



[https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_\(LibreTexts\)/13%3AMolecular_Spectroscopy/13.07%3A_The_Franck-Condon_Principle](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_(LibreTexts)/13%3AMolecular_Spectroscopy/13.07%3A_The_Franck-Condon_Principle)

Temperature and salinity dependence of absorption by liquid water

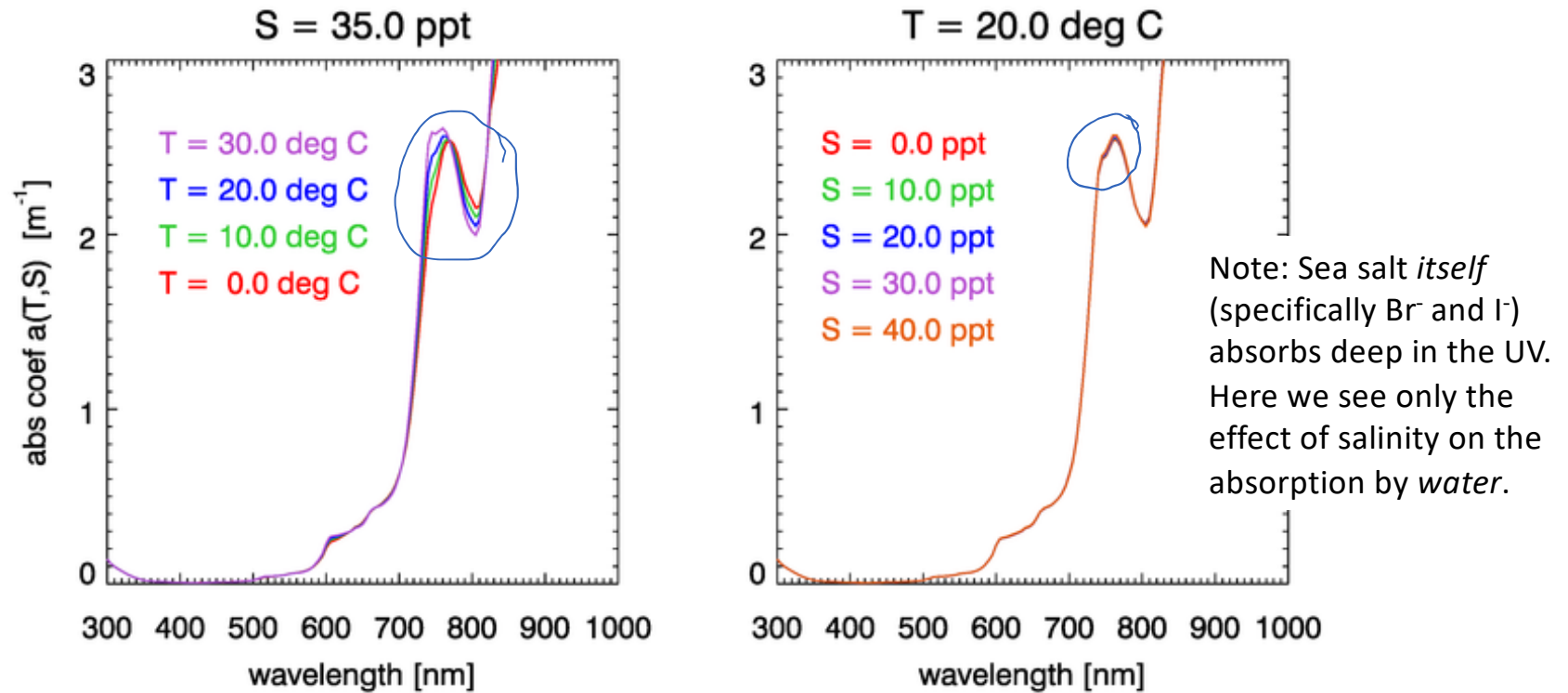


Figure 8.6: Dependence of the water absorption coefficient on temperature and salinity according to Roettgers et al. (2014).

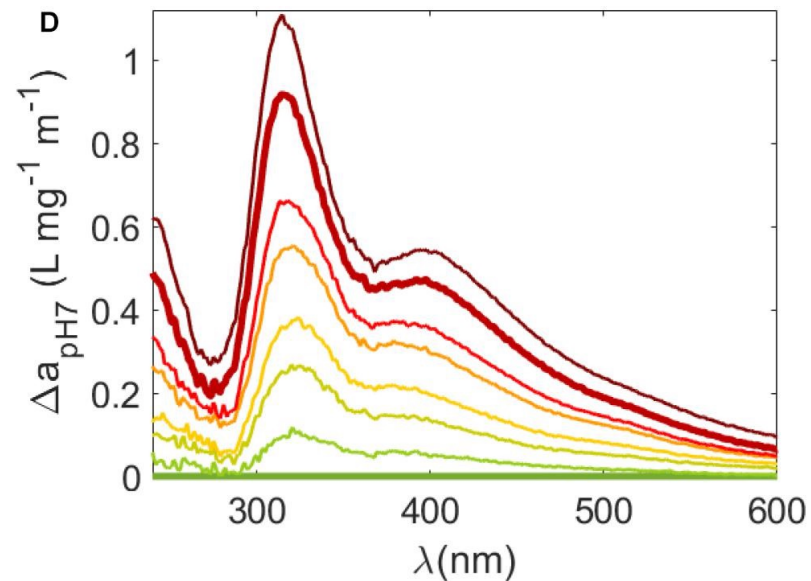
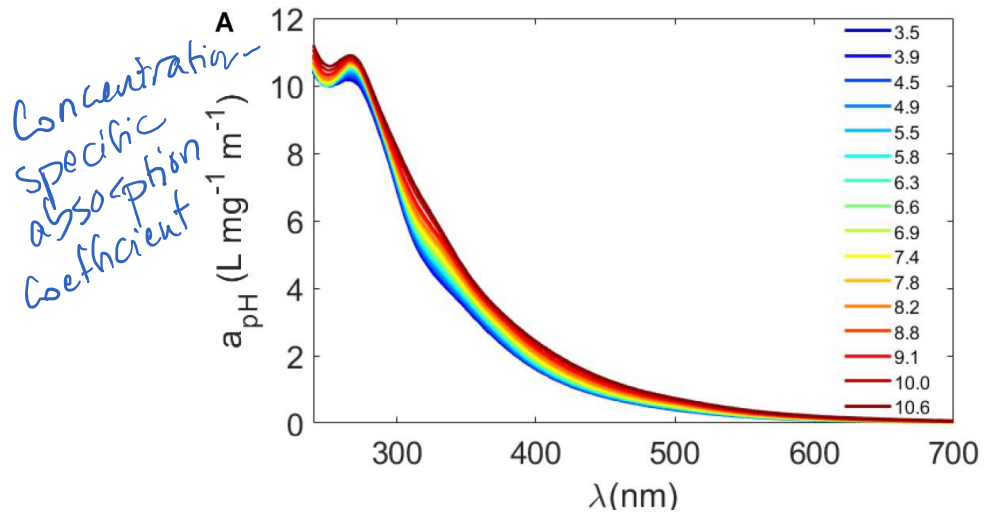
Figure 8.6, Mobley et al., *The Oceanic Optics Book*, 2022

pH dependence of absorption

- pH dependence of carbon-normalized absorption by colored dissolved organic matter (CDOM) isolated from the macroalgae *Sargassum*
- Changes broadly attributable to loss of protons from phenolic and carboxylic groups
- Δa_{pH} peak at 315 nm may be unique to brown algae?

Powers et al., 2020.

<https://www.frontiersin.org/articles/10.3389/fmars.2020.588287/full>



Solvent effects: Extracted vs. in vivo pigments

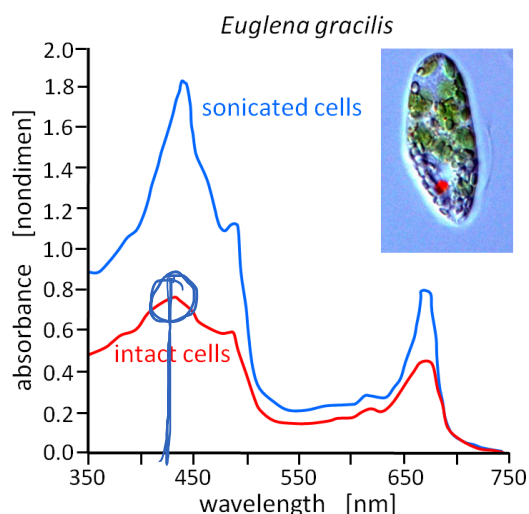


Figure 8.10, Mobley et al., *The Oceanic Optics Book*, 2022.

1. Pigment is “packaged” in the cell (more on this later)
2. Pigment absorption bands are shifted due to chemical environment in solvent, vs. in vivo.

Table 1. Absorption maxima, extinction coefficients (E) and wavelength shifts used for generating the “unpacked” in vivo specific absorption coefficients for the major algal pigment types (PE = phycoerythrin from specific clones of *Synechococcus* sp.). The absorption maxima reported for the chlorophylls and carotenoids were determined in this study.

Pigment	λ_{\max} (solvent)	E (L g ⁻¹ cm ⁻¹)	λ shift
Chlorophyll a	662 nm (acetone)	88.15 ¹²	>550 nm: +12 nm
	432 nm	-	<550 nm: +8 nm
Chlorophyll b	646 nm (90% acetone)	51.36 ¹²	>550 nm: +6 nm
	458 nm	-	<550 nm: +12 nm
Chlorophyll c ₁₊₂	630 nm (90% acetone)	42.6 ¹²	>550 nm: +6 nm
	444 nm	-	<550 nm: +16 nm
Fucoxanthin	450 nm (EtOH)	160.0 ¹³	>400 nm: +40 nm
β, β -carotene	452 nm (EtOH)	262.0 ¹⁴	>400 nm: +10 nm
WH7803 PE	547 nm (Pi buffer) ¹¹	25.5 ¹⁵	no shift
WH8103 PE	492 nm (Pi buffer) ¹⁶	11.6 ¹⁶	no shift

Table from Bidigare et al., 1990. doi:10.1117/12.21451

Fates of energy after it interacts with a molecule (and approximate timescales)

- Absorption: $\sim 10^{-15} - 10^{-13}$ s



Fig. 7.9, Mobley et al., *The Oceanic Optics Book*, 2022.

Fates of energy after it interacts with a molecule (and approximate timescales)

- Absorption: $\sim 10^{-15} - 10^{-13}$ s
- Rayleigh scattering: $\sim 10^{-13}$ s
 - Photon re-emission happens quickly, faster than vibration can occur
 - “Elastic scattering” = no change in wavelength (more tomorrow!)

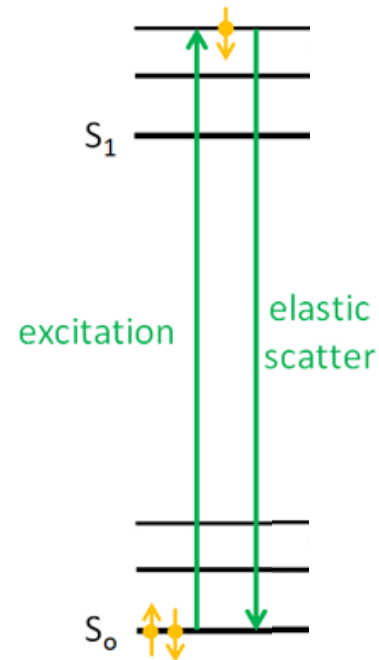


Fig. 7.9, Mobley et al., *The Oceanic Optics Book*, 2022.

Fates of energy after it interacts with a molecule (and approximate timescales)

- Absorption: $\sim 10^{-15} - 10^{-13}$ s
- Rayleigh scattering: $\sim 10^{-13}$ s
- Raman scattering: $\sim 10^{-13}$ s
 - Also very fast – before molecule can vibrate
 - “Inelastic” scattering
 - For water, characteristic shift in emitted photon of $\sim 3400 \text{ cm}^{-1}$ (tens to hundreds of nm)

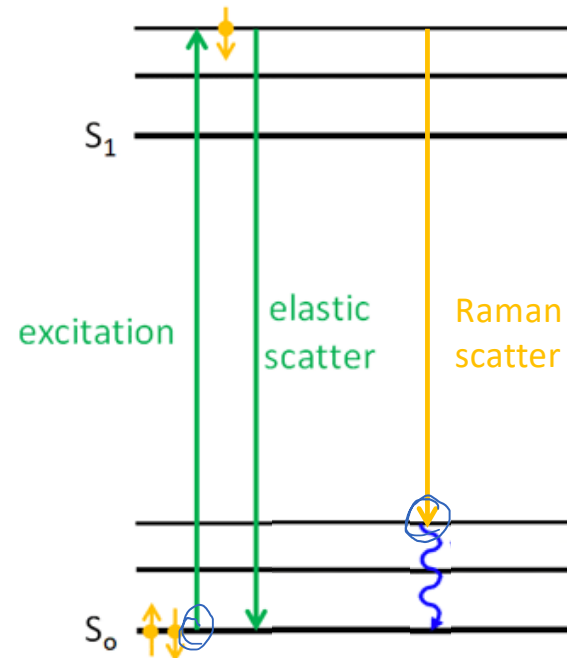


Fig. 7.9, Mobley et al., *The Oceanic Optics Book*, 2022.

(addition of Raman scatter is not in the Mobley figure – errors are mine!)

Fates of energy after it interacts with a molecule (and approximate timescales)

- Absorption: $\sim 10^{-15} - 10^{-13}$ s
- Rayleigh scattering: $\sim 10^{-13}$ s
- Raman scattering: $\sim 10^{-13}$ s
- Fluorescence: $\sim 10^{-9} - 10^{-7}$ s
 - Also “inelastic” scatter
 - Happens after vibrational relaxation – takes longer
 - Example: dissolved organic matter fluorescence. Also chlorophyll but biology complicates this example (more Friday)

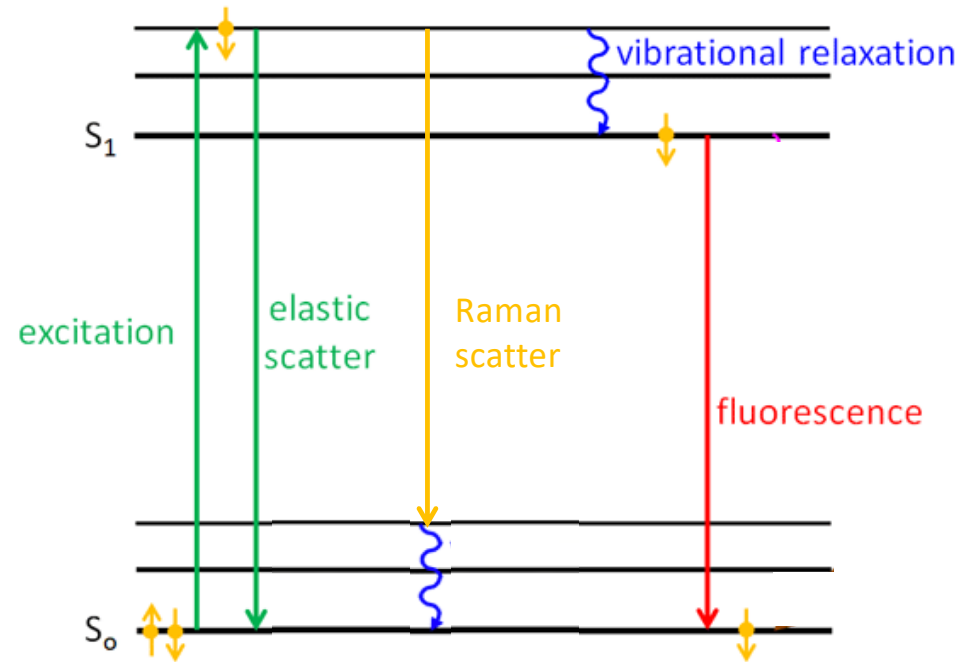


Fig. 7.9 et al., Mobley, *The Oceanic Optics Book*, 2022.

Fates of energy after it interacts with a molecule (and approximate timescales)

- Absorption: $\sim 10^{-15} - 10^{-13}$ s
- Rayleigh scattering: $\sim 10^{-13}$ s
- Raman scattering: $\sim 10^{-13}$ s
- Fluorescence: $\sim 10^{-9} - 10^{-7}$ s
- Phosphorescence: $\gg 10^{-9}$ s
 - Electron spin flip (intersystem crossing) leads to a “forbidden transition” and much slower re-emission of light
- Example = glow-in-the-dark T-shirts

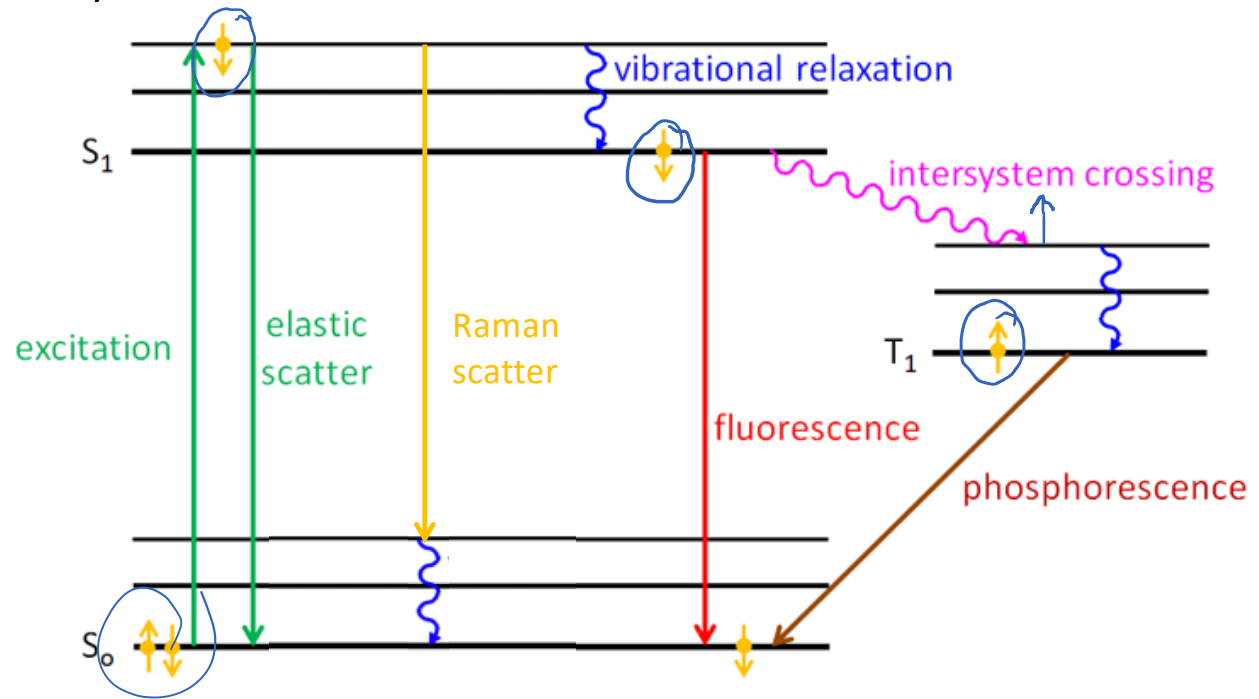


Fig. 7.9, Mobley et al., *The Oceanic Optics Book*, 2022.

Fates of energy after it interacts with a molecule (and approximate timescales)

- Absorption: $\sim 10^{-15} - 10^{-13}$ s
- Rayleigh scattering: $\sim 10^{-13}$ s
- Raman scattering: $\sim 10^{-13}$ s
- Fluorescence: $\sim 10^{-9} - 10^{-7}$ s
- Phosphorescence: $\gg 10^{-9}$ s
- Photochemical reaction
 - No re-emitted light – instead excited state molecule undergoes a chemical reaction
 - Examples: photosynthesis, photooxidation of CDOM

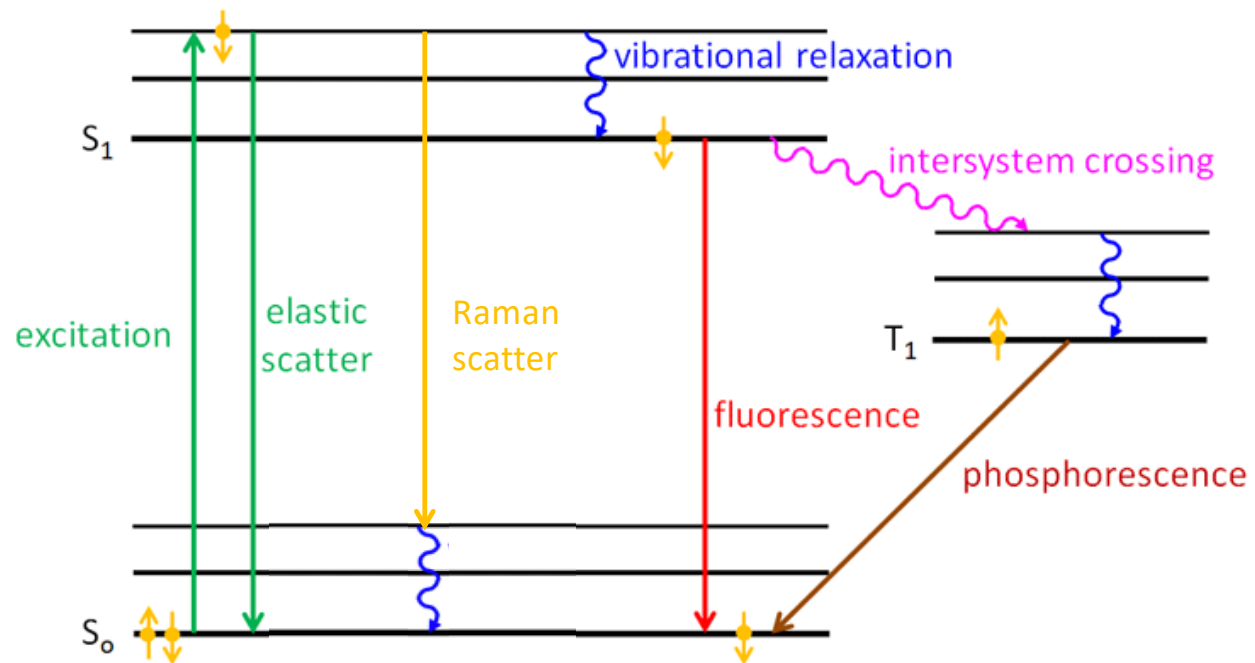


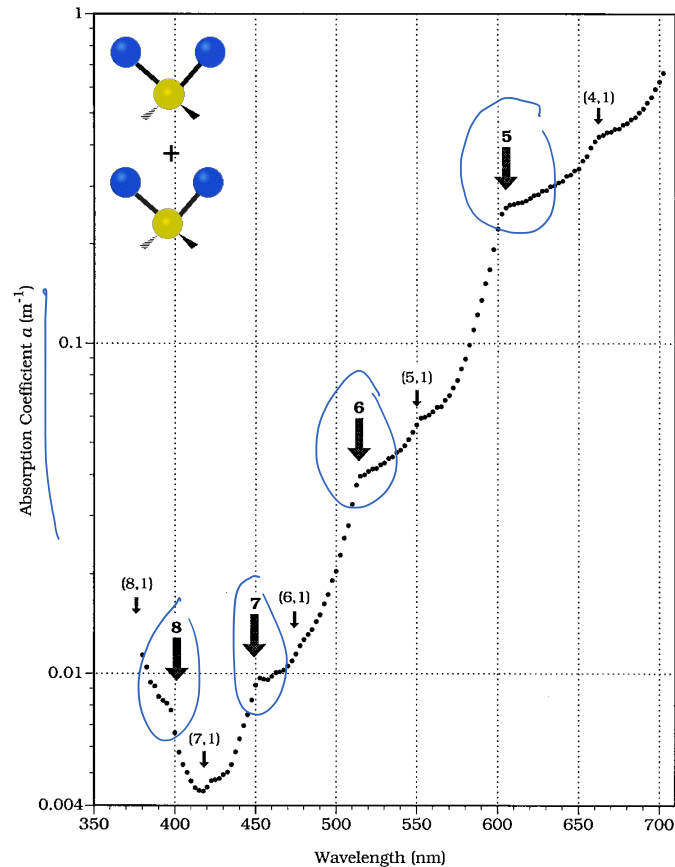
Fig. 7.9, Mobley et al., *The Oceanic Optics Book*, 2022.

Absorption, Part 1

- Context (in this class, and broader disciplinary context)
- How does light energy interact with matter in the ocean?
- Overview of absorbing constituents in the ocean
 - Water
 - Colored “dissolved” [[in?]organic?] matter (C“D”[O?]M)
 - Non-pigment particulate absorption (aka “non-algal particles”, NAP)
 - Phytoplankton pigments

Water

- Spectral absorption coefficient of water, $a_w(\lambda)$ [m^{-1}]
- Arises mainly from molecular vibrations (T, S dependence!) at visible-IR
- Difficult measurements to make...



Pope and Fry, 1997. *Appl. Opt.* 36(33): 8710-8723.

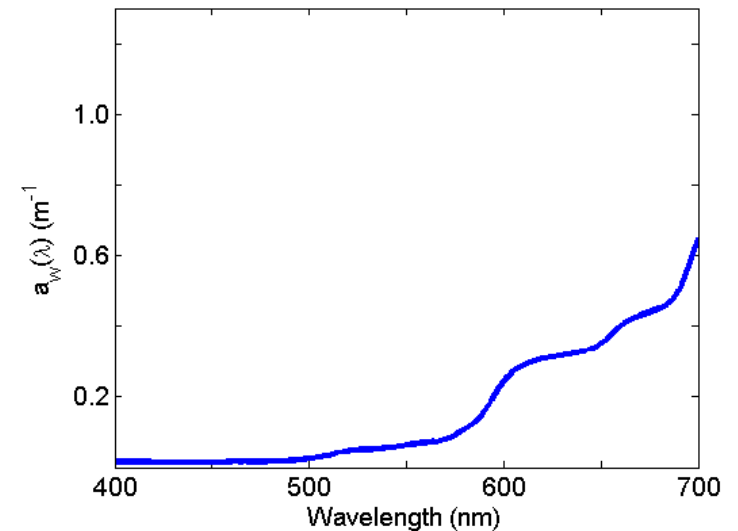


Figure 5.1 from Mobley et al., *The Oceanic Optics Book*, 2022. Data are from Pope and Fry, 1997.

Water

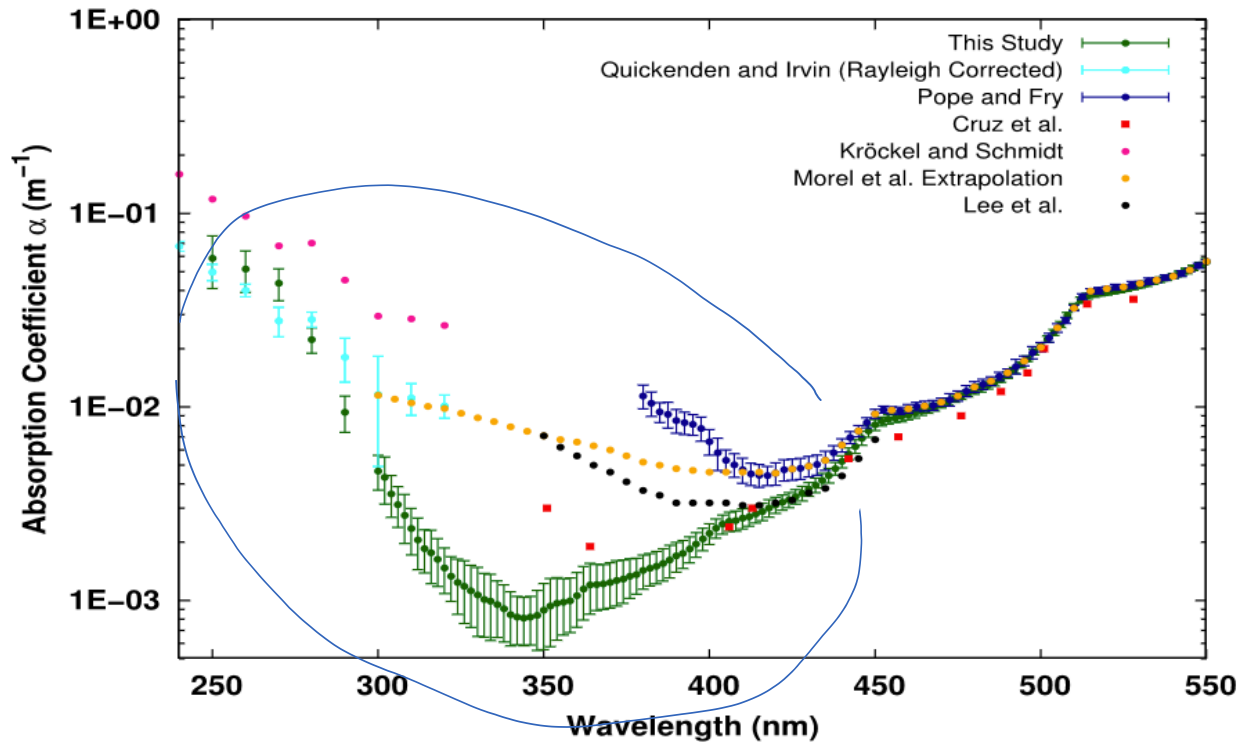


Fig. 11. Absorption coefficient, α , of pure water measured in this study along with the results from several other high-quality studies: Pope and Fry [8], the Rayleigh-scattering-corrected Quickenden and Irvin values [11], Cruz *et al.* [10], Lee *et al.* [30], and Morel *et al.* Extrapolation [17], and data at 10-nm intervals from Kröckel and Schmidt [14].

Issues arising in measurements of pure water absorption at UV-blue wavelengths:

- Organic contamination
- Scattering losses
- Absorption by dissolved oxygen
- Temperature and salinity??

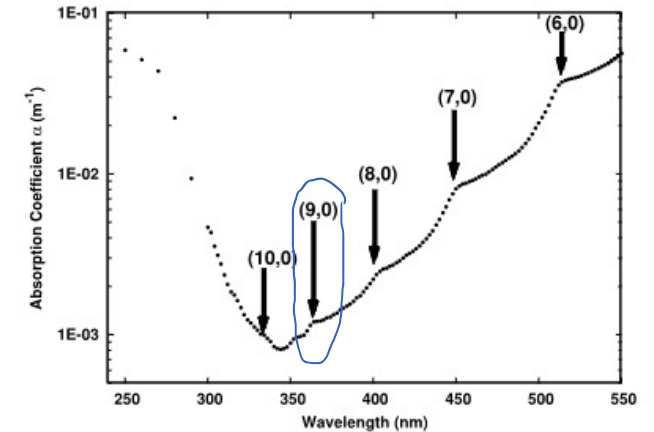


Fig. 12. Present results for pure water. $(n, 0)$ denotes the n th harmonic of the pure O-H stretch (no scissor mode combination). A large arrow is used to show the predicted locations of those harmonics.

Both figures are from Mason, Cone, and Fry, 2016. 10.1364/AO.55.007163

Correcting for temperature and salinity effects

- Temperature dependence Ψ_T [$\text{m}^{-1} \text{ } ^\circ\text{C}^{-1}$]
- Salinity dependence Ψ_S [$\text{m}^{-1} \text{ S}^{-1}$]
- Recall the salinity dependence arises from salt ions modifying the water absorption – not intrinsic absorption by the salt ions!
- Dependences in the UV...?

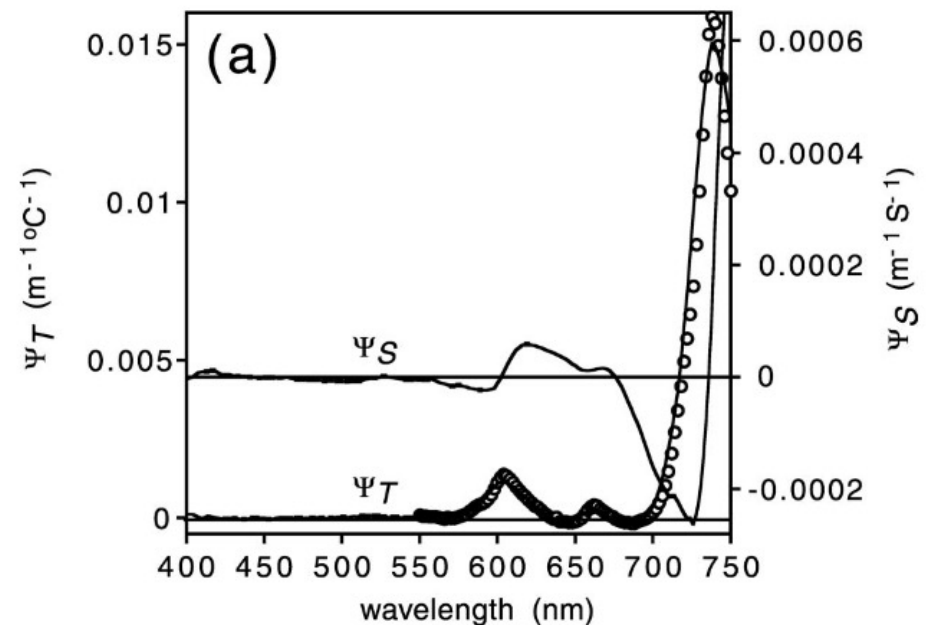


Figure: Sullivan et al., 2006. *Appl. Opt.* 45(21): 5294-5309.

“Colored dissolved organic matter” (CDOM)

- What is “dissolved”?

“Colored dissolved organic matter” (CDOM)

What is “dissolved”?

- Smaller than filter size
- Fully “solvated” (all parts of the molecule interact with solvent)
- Gel assembly?

• *tendency to stay suspended in still water*
 → Always state your assumptions...

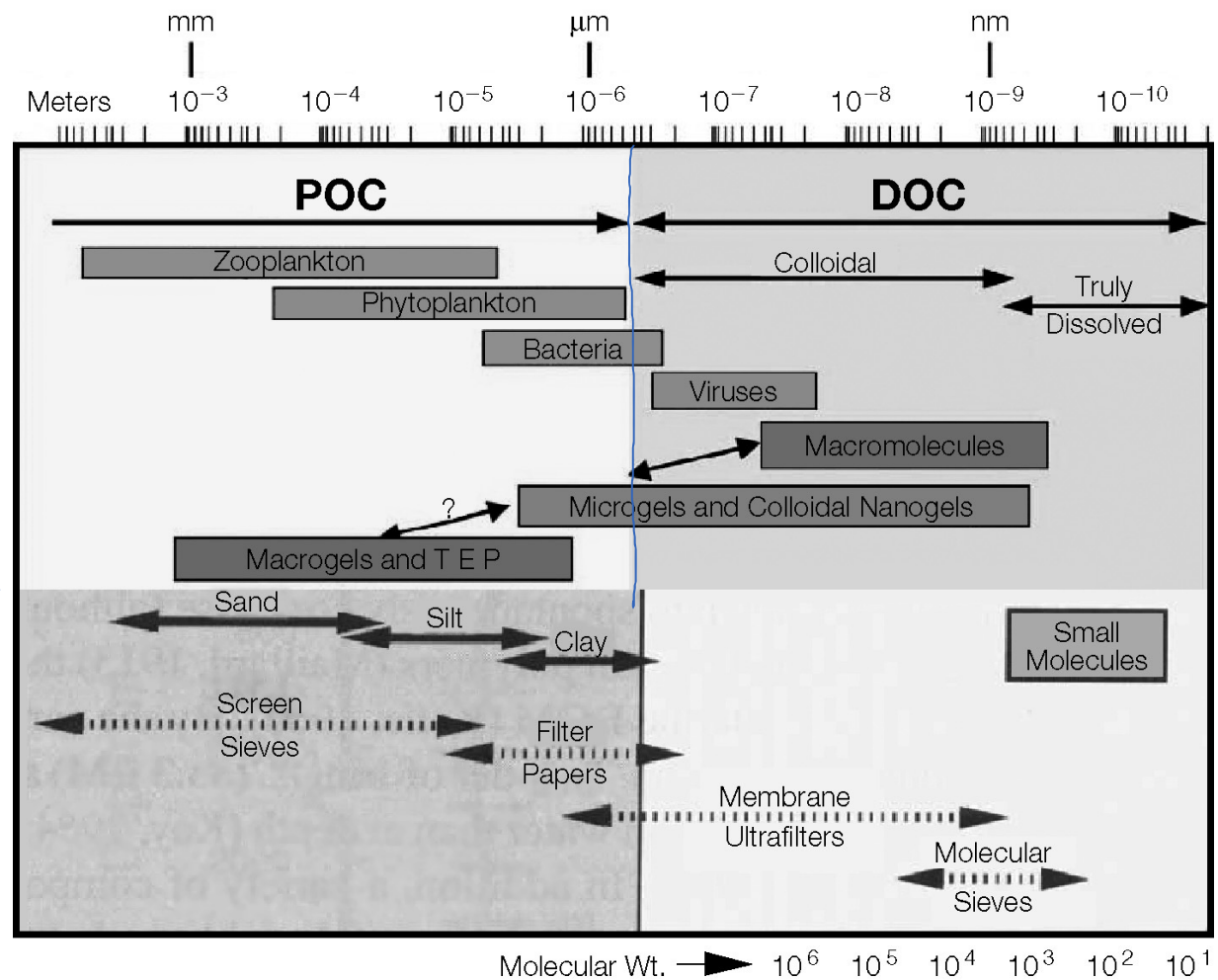


Figure: Libes, *Introduction to Marine Biogeochemistry*, 2009. Figure 22.1. ISBN 978-0-12-088530-5

“Colored dissolved organic matter” (CDOM)

- What is “dissolved”?
- What is “organic”?
 - Are all absorbing materials in the ocean (besides water) “organic”?

Optical nitrate sensor (ISUS, SUNA)

- Measurement principle: If concentration-specific UV absorption by NO_3^- is known, then measure absorption and calculate concentration (Beer's Law – more later).
- Sea salt interferences: bromide (Br^-), nitrite (NO_2^-), and bisulfide (HS^-)
- Non sea-salt interference: CDOM
- Nitrite has a similar absorption maximum to nitrate but $[\text{NO}_2^-]$ is usually small (except where oxygen is low...)

Johnson and Coletti, 2002. *Deep-Sea Res. I*, 49: 1291-1305.

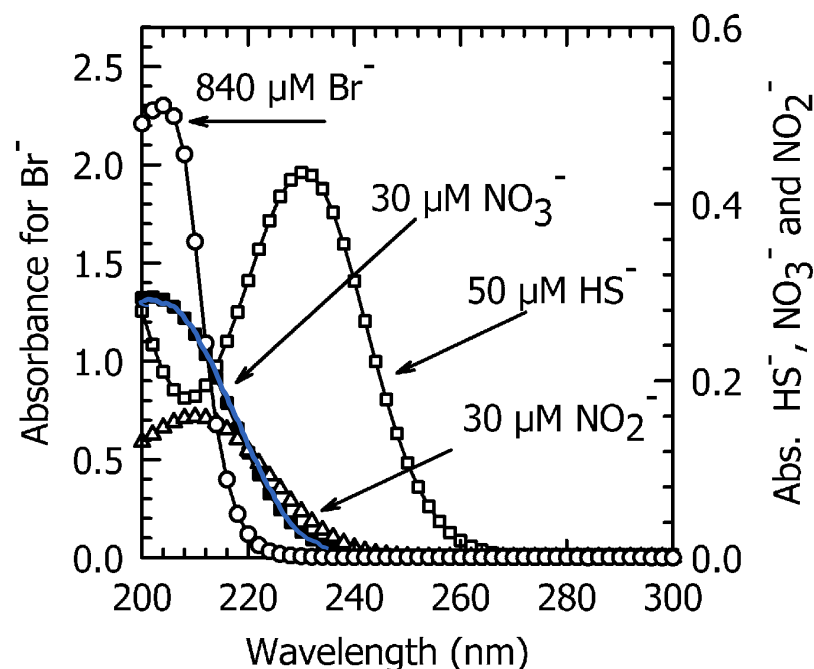
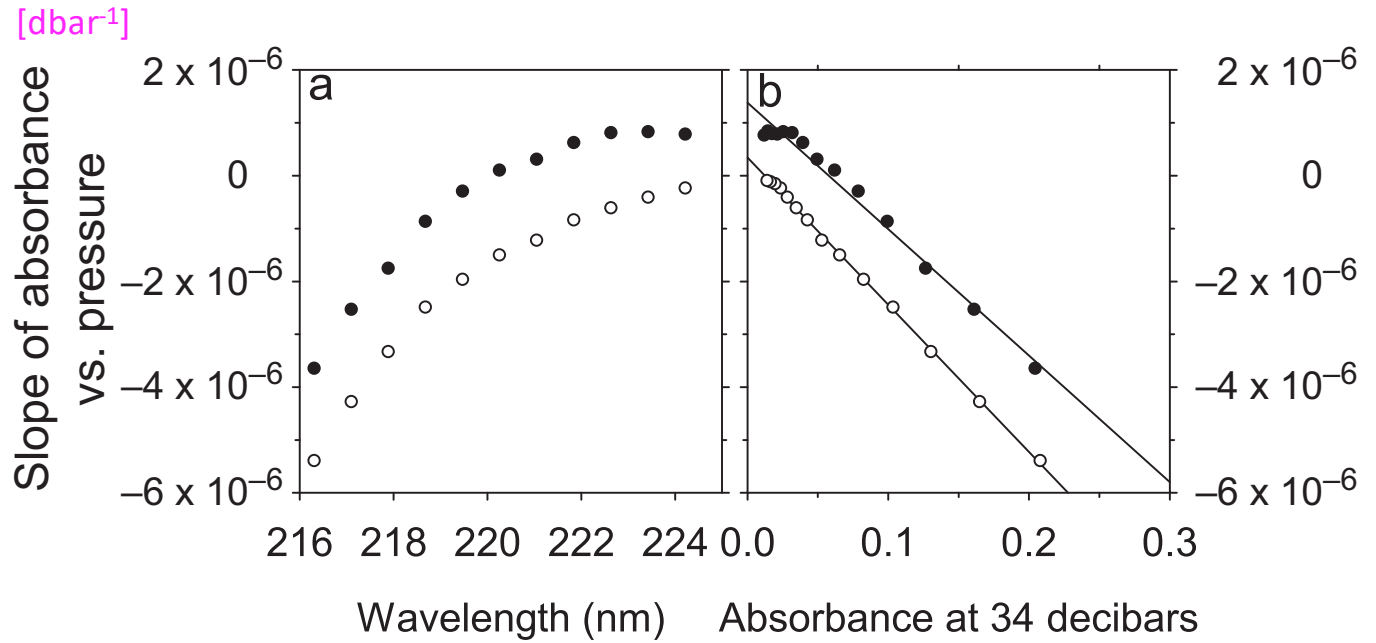
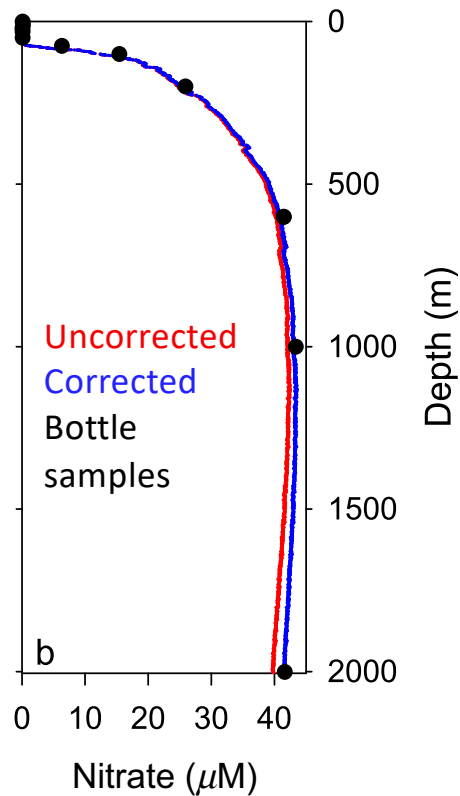


Fig. 1. Absorption spectra of bromide, bisulfide, nitrate and nitrite at concentrations typical of seawater. Each salt was dissolved in deionized water. Spectra were collected with a Hewlett-Packard HP 8452 spectrophotometer. Cell path length was 1 cm. Note that the left axis applies to bromide and the right axis to the other species.

Pressure dependence of bromide absorption



White circles = measured during decompression. Black circles = measured during compression (when a contaminant from the pump may have been present). Compression from 34-2068 dbar.

Why is bromide absorption pressure-dependent?
What other molecules could behave the same way?

Figures: Sakamoto et al., 2017. 10.1002/lom3.10209

“Colored dissolved organic matter” (CDOM)

- What is “dissolved”?
However you define it.
- Are all absorbing materials in the ocean* (besides water) “organic”? *No! Be aware of inorganic absorbers, in your spectral region of interest.*
- OK, now we can talk about CDOM.

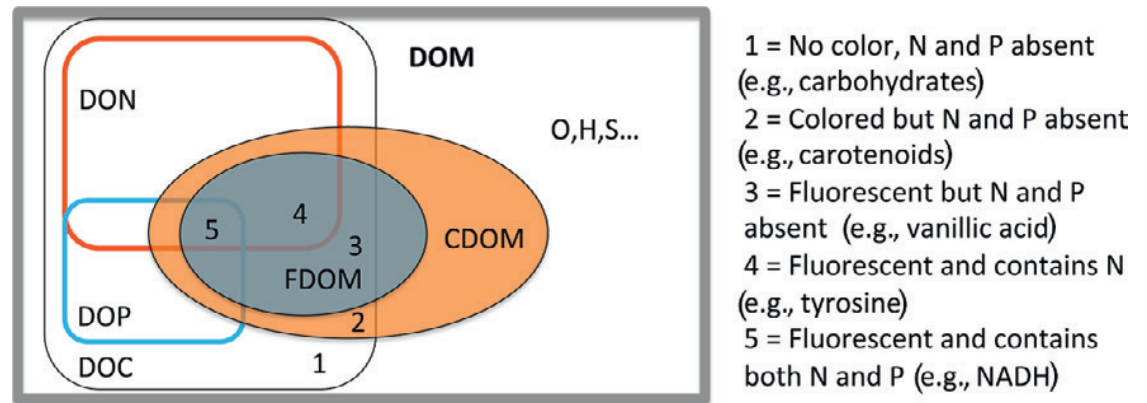


Figure: Stedmon and Nelson, 2015, *Biogeochemistry of Marine Dissolved Organic Matter*, 2nd ed.

* In some seasonally-anoxic lakes also consider *iron!*

Generic CDOM absorption spectrum

Why is the spectrum smooth? Two hypotheses have been proposed:

1. It is a superposition of many conjugated “pi” bonds with a range of energies (proposed by Shifrin, 1988)
2. It arises from intramolecular charge transfer along a series of coupled, excited chromophores (Blough and Del Vecchio, 2004)

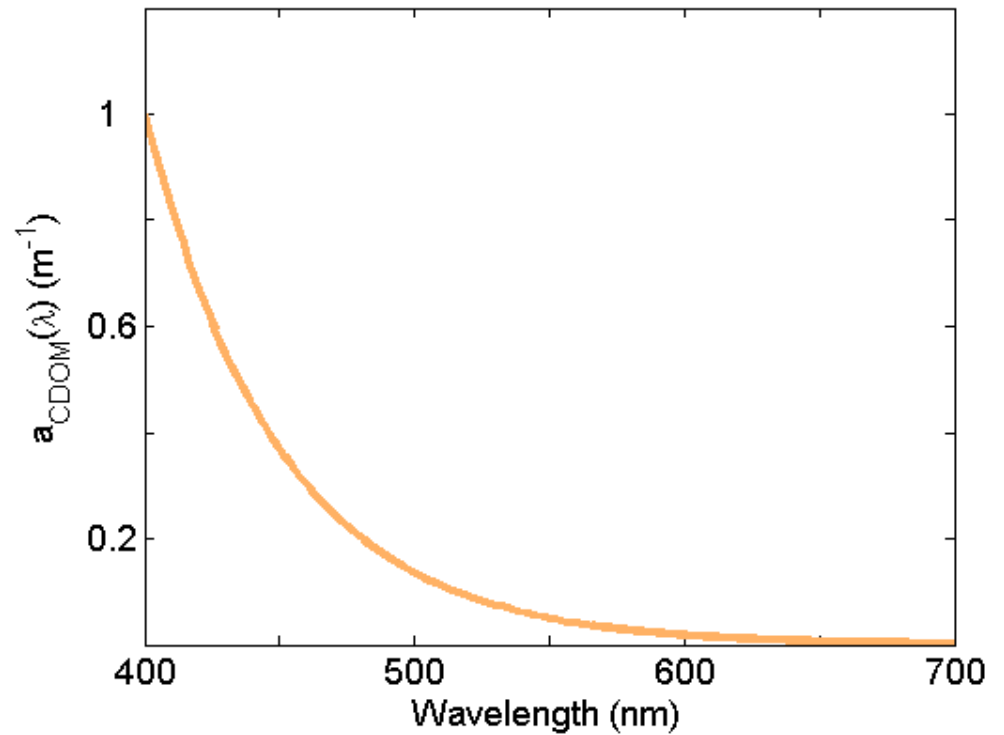
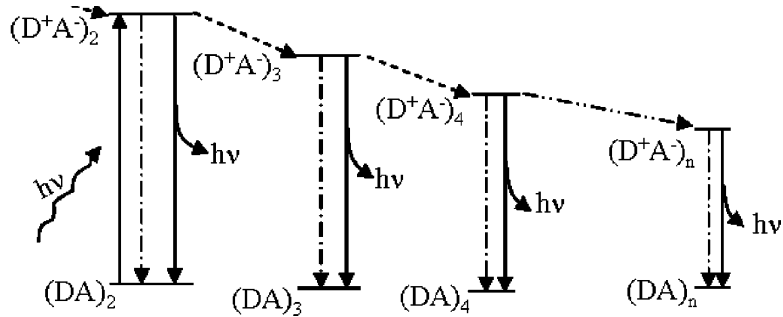


Figure 5.4. Mobley et al., 2022. *The Oceanic Optics Book*

Figure: Del Vecchio and Blough, 2004. doi: 10.1021/es049912h

Modeling “CDOM”

- Single-exponential function often describes the absorption magnitude and spectral dependence well, with two parameters:

$$a_{CDOM}(\lambda) = \underline{a_{CDOM}(\lambda_0)} e^{-\underline{S_{CDOM}}(\lambda-\lambda_0)}$$

\downarrow
 0.01 - 0.02 nm⁻¹

- Steeper spectral slope is often interpreted as CDOM that is
 - Lower molecular weight
 - More photobleached/degraded
 - More “fulvic” in character (as opposed to “humic”)
 - Operational definition from soil chemistry; based on solubility as a function of pH
- Does S_{CDOM} depend on the wavelength range of measurement?

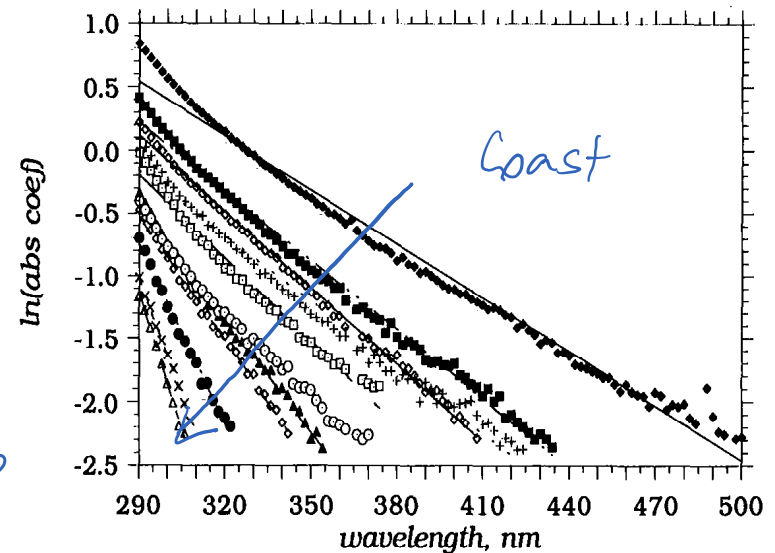


Fig. 2. Representative absorption spectra, plotted as the natural logarithm of the absorption coefficient (m^{-1}) vs. wavelength. These spectra were collected in August 1991 on the transect between the central Gulf of Mexico and Oyster Bay.

Figure, Green and Blough 1994, *Limnol. Ocean.*, 39(8):1903-1916.

Modeling “CDOM”

Spectra do not always follow a smooth or exponential functional shape!

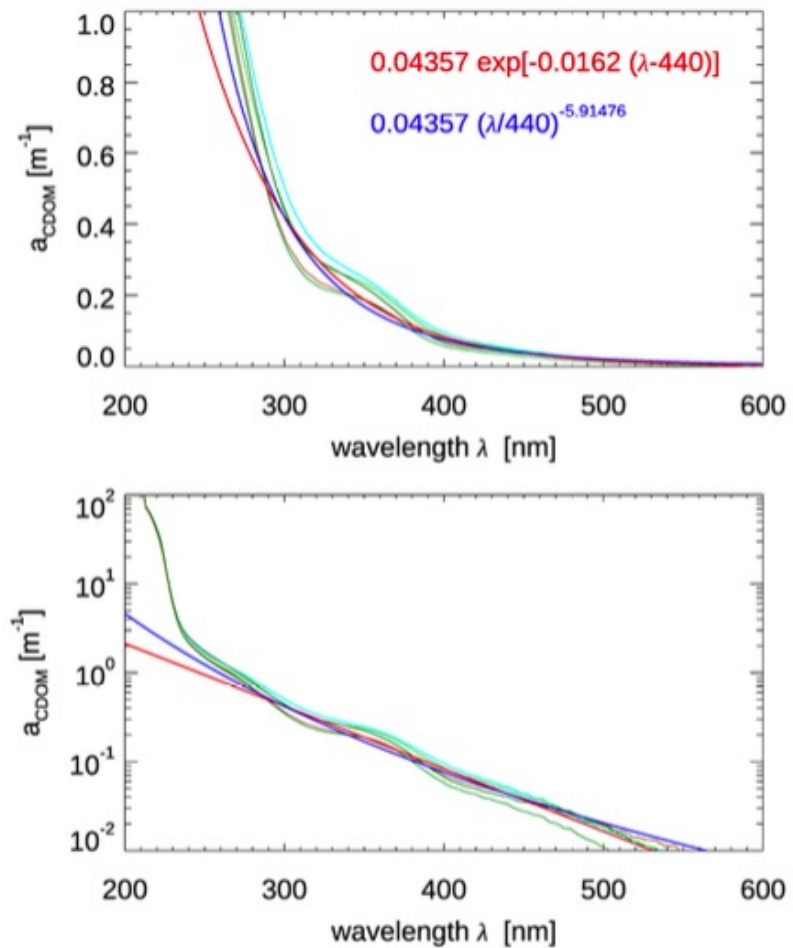


Figure 8.15, Mobley et al., *The Oceanic Optics Book*, 2022. Data courtesy of A. Lyoub.

Non-pigmented particle absorption aka “non-algal particles” (NAP)

- Absorption by operationally defined particles
- Excluding the contribution by phytoplankton pigments

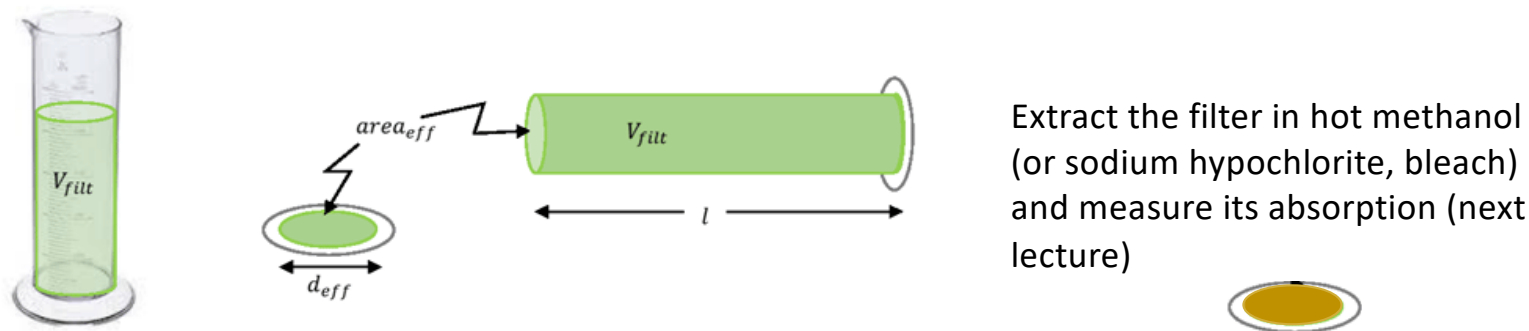


Figure 5.16: Diagrammatic representation of the geometric pathlength of the filtered sample. V_{filt} is the filtered volume, d_{eff} is the diameter of the circular distribution of particles on the filter, and is used to compute the effective area, area_{eff} . The volume filtered can be expressed as a cylinder of area area_{eff} and length, l . The geometric pathlength of the sample is l .

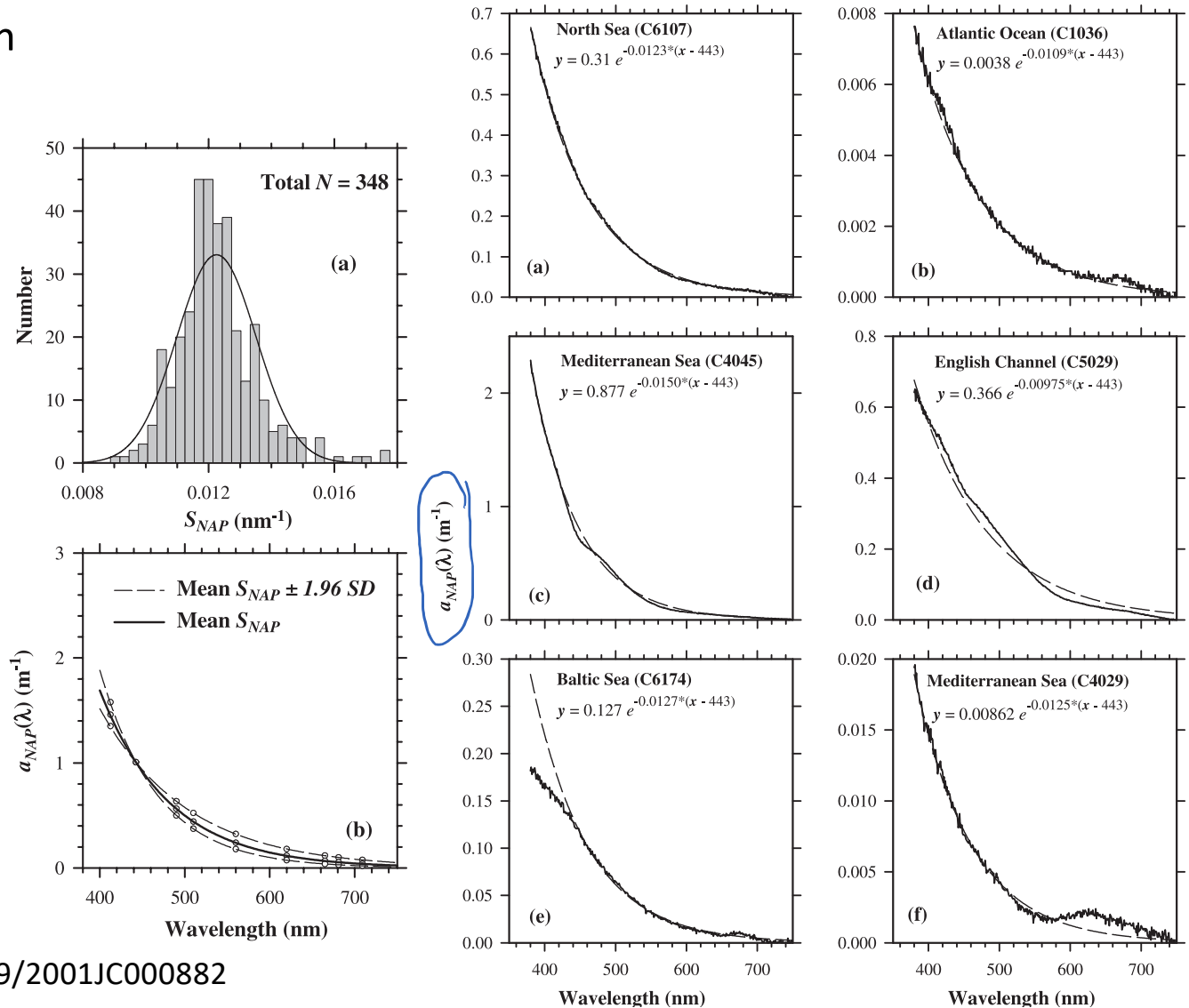
Figure, C. Roesler, in Mobley et al. 2022, *The Oceanic Optics Book*

Contributors to a_{NAP}

- All phytoplankton cellular components that weren't soluble in the methanol
- All non-phytoplankton cells and organisms
- All non-living particles of biological origin
- All non-living mineral particles

Non-algal particle absorption

- Similar to a_{CDOM} spectral shape... but some departures
- Babin et al. (2003) mean +/- SD:
 $S_{NAP} = 0.0123 \pm 0.0013 \text{ m}^{-1}$
- What causes the shoulders?



Figures: Babin et al., 2003. 10.1029/2001JC000882

Mineral contributions to $a_{\text{NAP}}(\lambda)$

$$\frac{a}{[C]} \frac{\text{m}^{-1}}{\text{g}/\text{m}^3} = \frac{\text{m}^2}{\text{g}}$$

- Mineral samples with high iron have higher $a(\lambda)$
- Loss of $a_{\text{NAP}}(\text{UV-blue})$ “shoulders” along freshwater-marine sample transect
- Spectral derivatives: quantify the shoulders, then relate to electronic transitions of a specific subfraction of iron oxides present in the particles

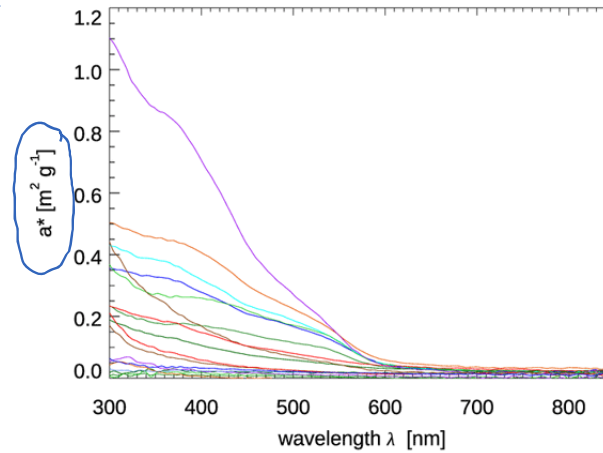
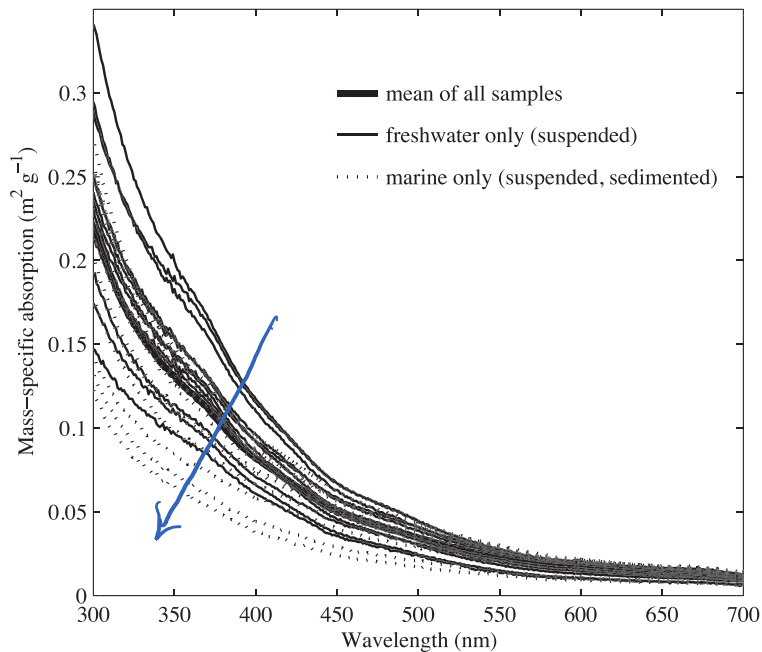
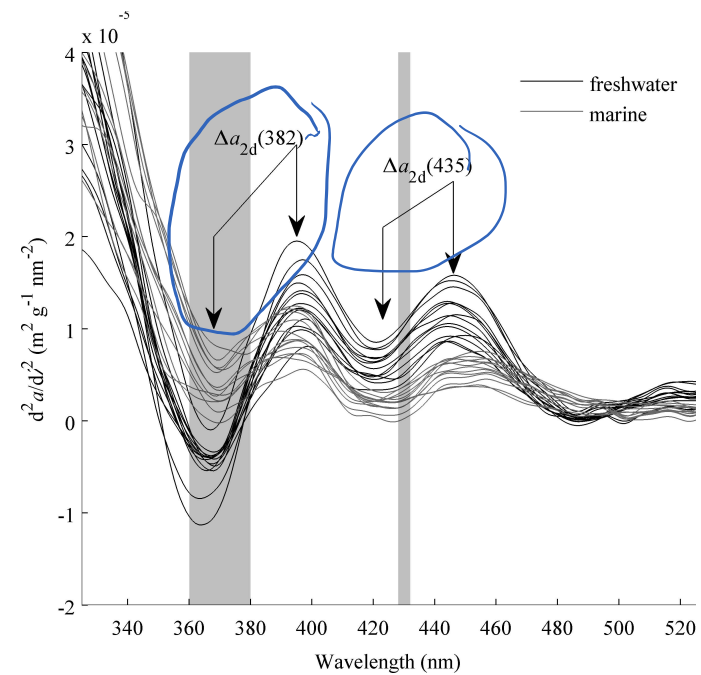


Figure 8.21 Mobley et al. 2022, *The Oceanic Optics Book*. Data from Stramski et al., 2007, *Limnol. Ocean.* 52(6): 2418-2433.

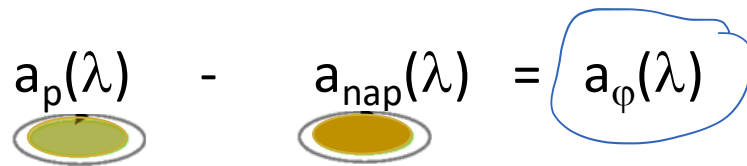


Figures: Estapa et al. 2012, *Limnol. Ocean.* 57(1): 97-112.



Phytoplankton pigment absorption: $a_{\phi}(\lambda)$

- Measured by difference:

$$a_p(\lambda) - a_{\text{nap}}(\lambda) = a_{\phi}(\lambda)$$


- Sum of all solvent-extractable pigments in the cell
- Pigments are “packaged” – bound in membranes inside chloroplasts
- Not all pigments are extractable in methanol (water-soluble phycobiliproteins)

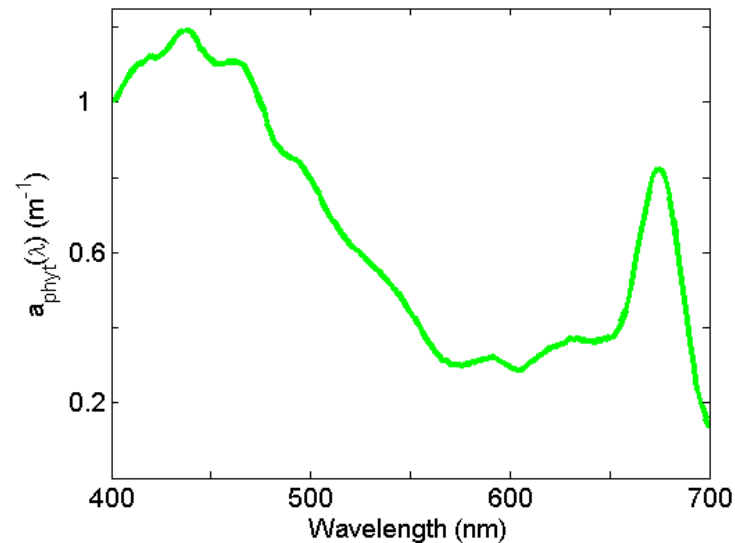


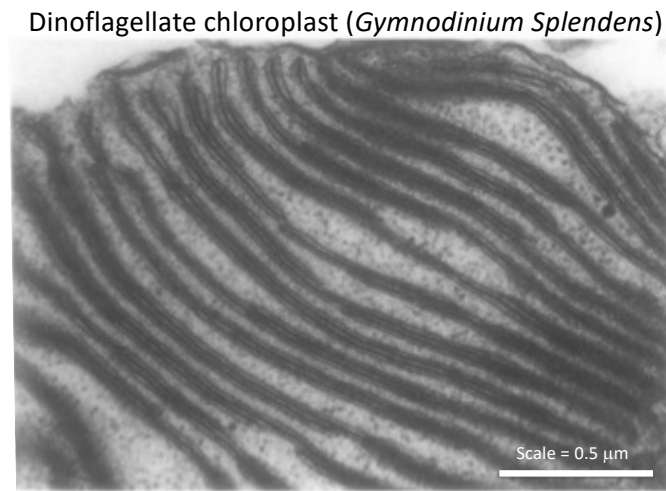
Figure 5.2: Generic phytoplankton absorption spectrum for mixed algal composition (modified from Roesler et al. (1989)).

Where are the pigments found, in a phytoplankton (or other algal) cell?
 Inside chloroplasts (in eukaryotes, not prokaryotes)

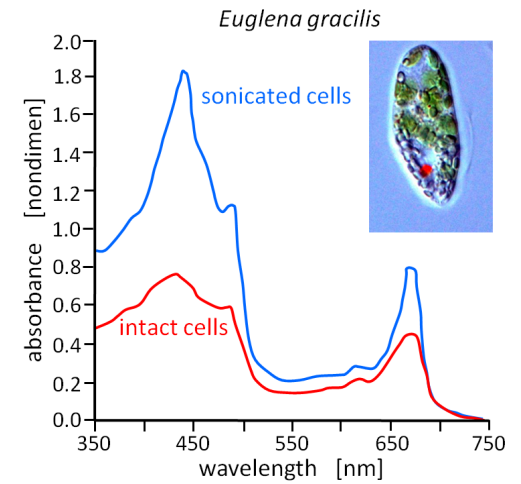
... which contain thylakoid membranes
 ... which contain photosystems I and II
 ... which contain pigments



Diatom (*Coccinodiscus centralis*)



Dinoflagellate chloroplast (*Gymnodinium Splendens*)



Schematic of thylakoid membrane

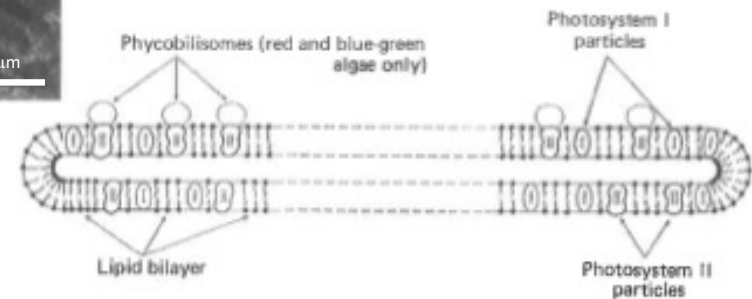
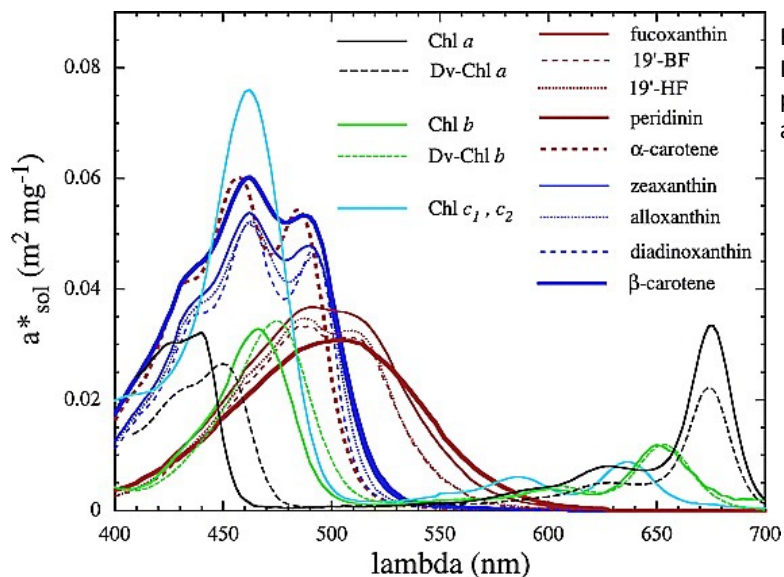


Figure 1: Phytopedia, https://www.eoas.ubc.ca/research/phytoplankton/diatoms/centric/coccinodiscus/c_centralis.html
 Figures 2-3: JTO Kirk, *Light and Photosynthesis in Aquatic Ecosystems*, Ch. 8. Cambridge University Press, 2011.
 Figure 4 (spectrum): Fig. 8.10, Mobley et al. 2022, *The Oceanic Optics Book*.



Bricaud et al, *JGR*, 2004.
In-vivo weight-specific
phytoplankton pigment
absorption spectra

Pigments have characteristic absorption spectra, and can be used to discriminate among phytoplankton taxa.

More on this (and also phytoplankton and pigment fluorescence!) by Sasha and Ivona, later this week!

Jeffrey, UNESCO 1997
Summary table of
chlorophyll marker
pigments for different
algal groups

Also: carotenoids,
biliproteins, many
degradation products!

TABLE 4.1. Summary of signature pigments useful as markers of algal groups and processes in the sea (see also Table 2.3, Chapter 2; and Chapter 13)^{a,b}

Pigment	Algal group or process	Key references
A. Chlorophylls (see Table 2.3, Chapter 2)		
Chl <i>a</i>	All photosynthetic microalgae (except prochlorophytes)	See Table 2.3, Chapter 2
Divinyl chl <i>a</i>	Prochlorophytes	Goericke & Repeta (1992)
Chl <i>b</i>	Green algae: chlorophytes, prasinophytes, euglenophytes	See Table 2.3, Chapter 2
Divinyl chl <i>b</i>	Prochlorophytes	Goericke & Repeta (1992)
Chl <i>c</i> family	Chromophyte algae	Jeffrey (1989)
Chl <i>c</i> ₁	Diatoms, some prymnesiophytes, some freshwater chrysophytes, raphidophytes	Jeffrey (1976b); Stauber & Jeffrey (1988); Jeffrey (1989); Andersen & Mulkey (1983)
Chl <i>c</i> ₂	Most diatoms, dinoflagellates, prymnesiophytes, raphidophytes, cryptophytes	Jeffrey <i>et al.</i> (1975); Stauber & Jeffrey (1988); Andersen & Mulkey (1983)
Chl <i>c</i> ₃	Some prymnesiophytes, one chrysophyte, several diatoms and dinoflagellates	Jeffrey & Wright (1987); Vesik & Jeffrey (1987); Jeffrey (1989); Johnsen and Sakshaug (1993)
Chl <i>c</i> ₃₅₋₇₀	One prasinophyte	Jeffrey (1989)
Phtylated chl <i>c</i> -like ^c	Some prymnesiophytes	Nelson & Wakeham (1989); Jeffrey & Wright (1994)
Mg3,S DVP	Some prasinophytes	Ricketts (1966); Jeffrey (1989)
Bacteriochlorophylls	Anoxic sediments	Repeta <i>et al.</i> (1989); Repeta and Simpson (1991)

Class context: Week 1 roadmap

