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Inelastic Scattering

Ken Voss, Ocean Optics Summer class, 2015

Remember your freshman physics class and all that time you spent learning about collisions? Two types of collisions: elastic and in-elastic. What was the difference?

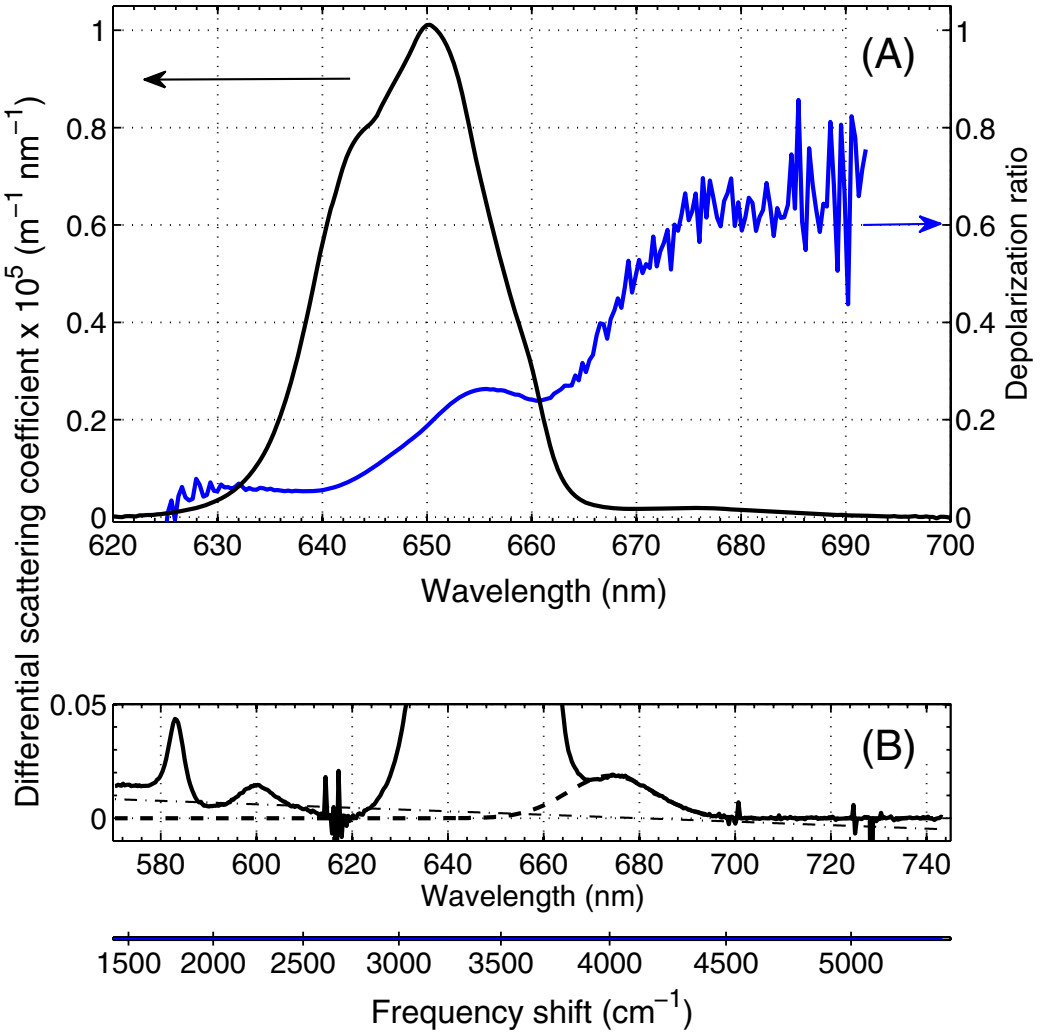
Remember your freshman physics class and all that time you spent learning about collisions? Two types of collisions: elastic and in-elastic. What was the difference?

Elastic collisions conserved Kinetic energy and momentum, inelastic just momentum….was energy lost?

So elastic scattering: photons come in and out of the process with the same energy (wavelength)

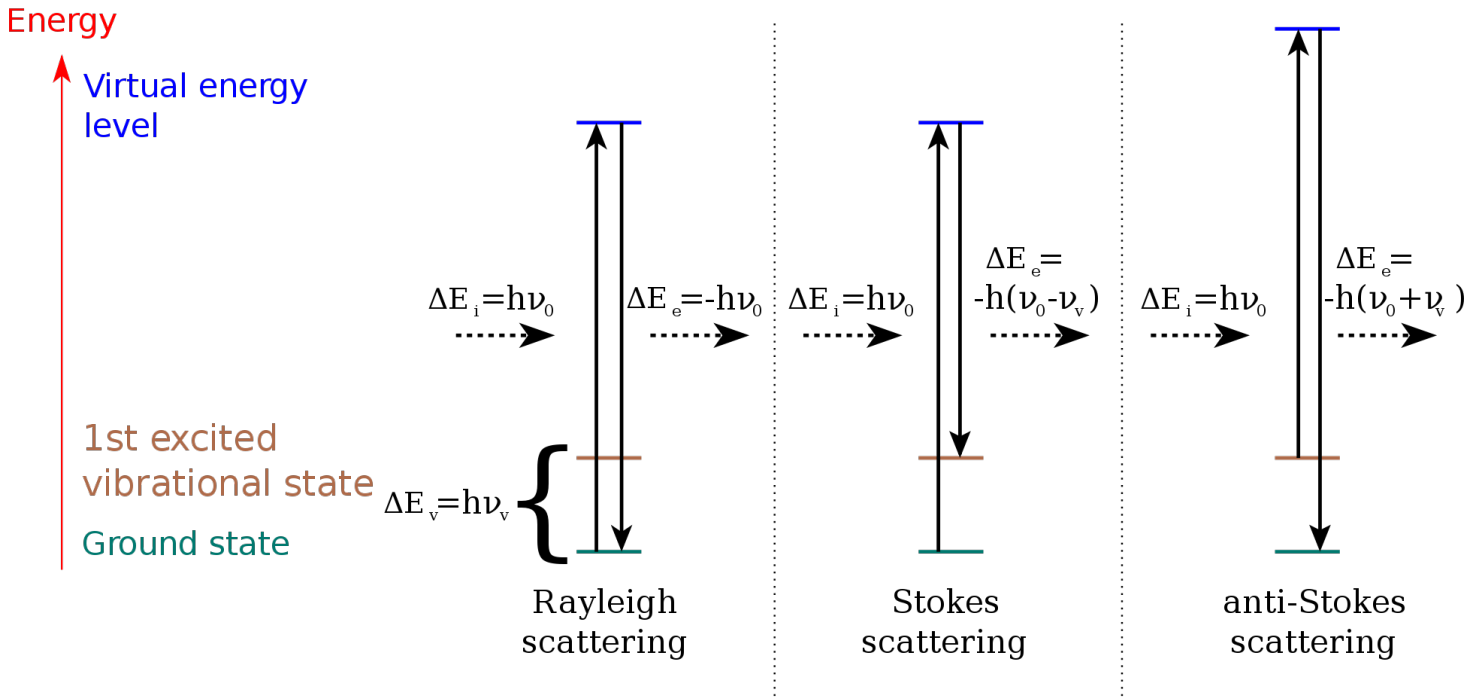
In-elastic scattering: photons come in with one wavelength and leave with another wavelength. (remember Compton scattering of photons?). Difference between this and fluorescence is basically a short intermediate time for the event (which leads to other effects).

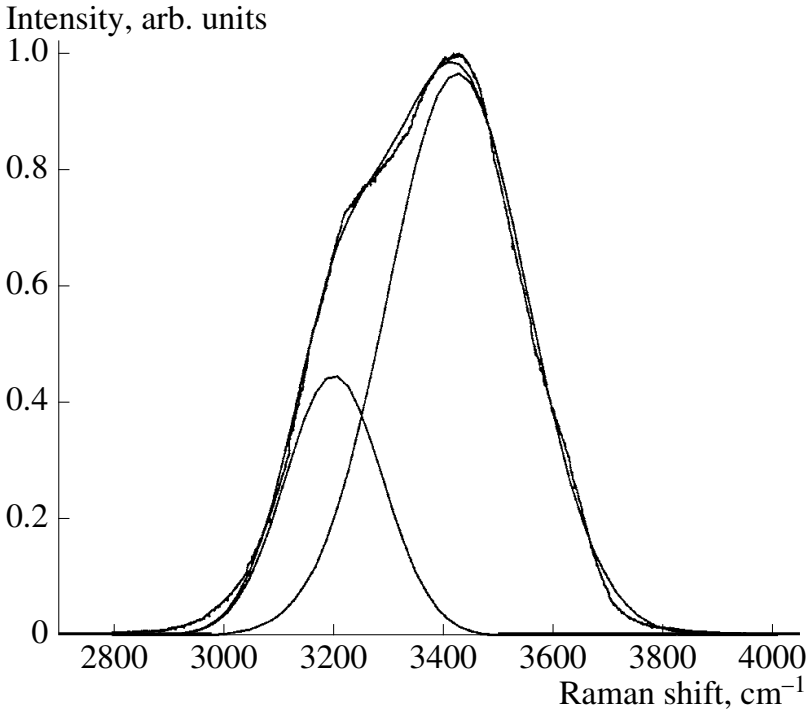
Strongest, most evident in natural seawater, in-elastic scattering process is Raman scattering, although by most accounts, water has a weak Raman cross section. (first seen 1920's)

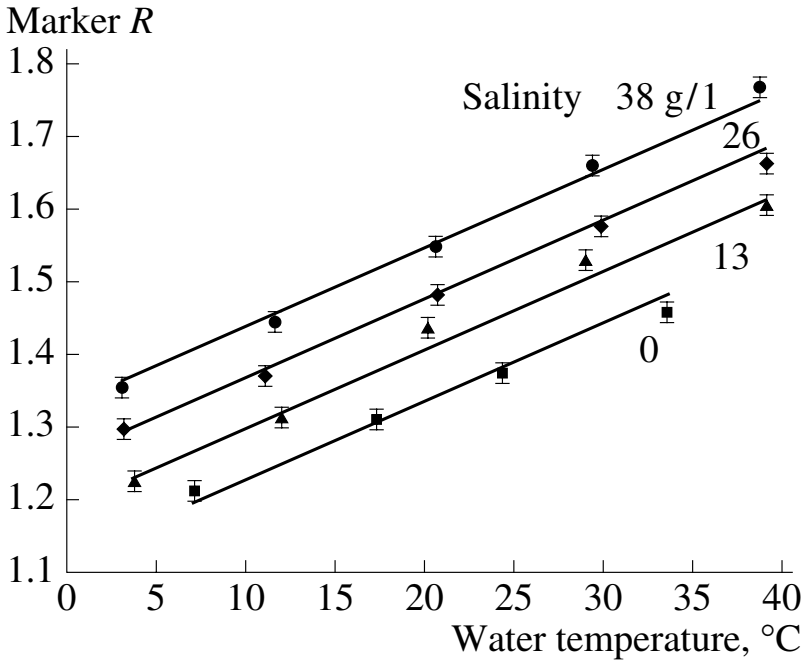


Excitation 532 nm, Applied Optics, Bray et al., 52,2503-2510, 2013

As opposed to the absorption process discussed earlier, the initial photon does not have to match an energy level to be absorbed, at least for a very short time, limited by the uncertainty principle ($\Delta E \Delta t < \hbar$). But the probablility of this happening is greatly enhanced if there is a nearby transistion (but if too close can cause issues of confusion with fluorescence).







Figures from Becucci et al., Laser Physics, 9, 422-425, 1999

For water two main peaks, around 3200 cm-1 and 3400 cm-1 (O-H stretch in water), ratio depends on temp and salinity. Proposed as early as the 70's to be used with lasers to remotely sense water temperature. (Leonard, Caputo and Hoge) Also used to calibrate a lidar return. Note how to use this shift: 1/Final Lambda= 1/wavelength - shift

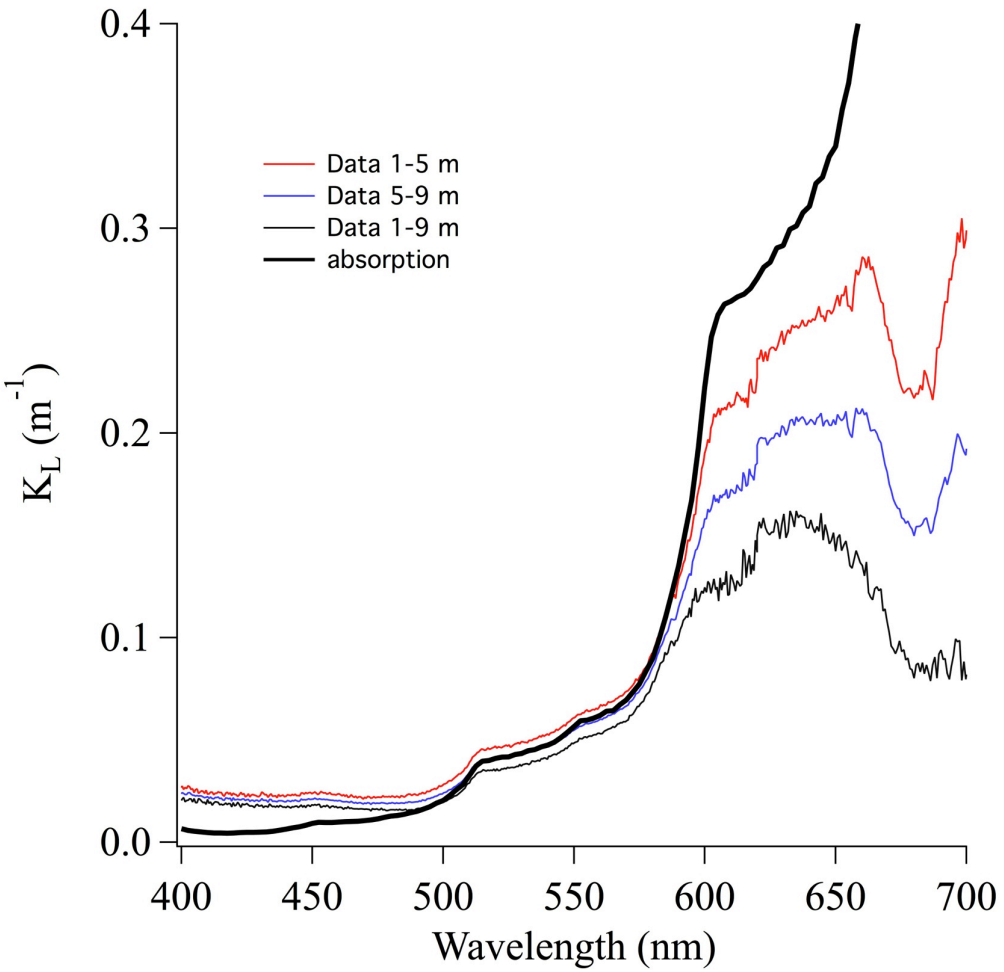
Importance in the natural light field:

By the early 80's the ocean optics community were getting multispectral instruments, either full blown spectrometers (for example Ray Smith and John Tyler, Vislab) or multi channel radiometers, such as the MER-1032 made by Biospherical instruments.

Seeing strange results: Diffuse attenuation coefficients less than water absorption.

K, which you expect has to be larger than absorption was being measured to be less than absorption when approaching red wavelengths.

Sought instrument problems: leaks in filters for example… hard problem in general where light is weak (red).



We knew Raman was there, particularly for laser excitation, most thought it was unimportant in Natural light. Series of people figured out that we were wrong:

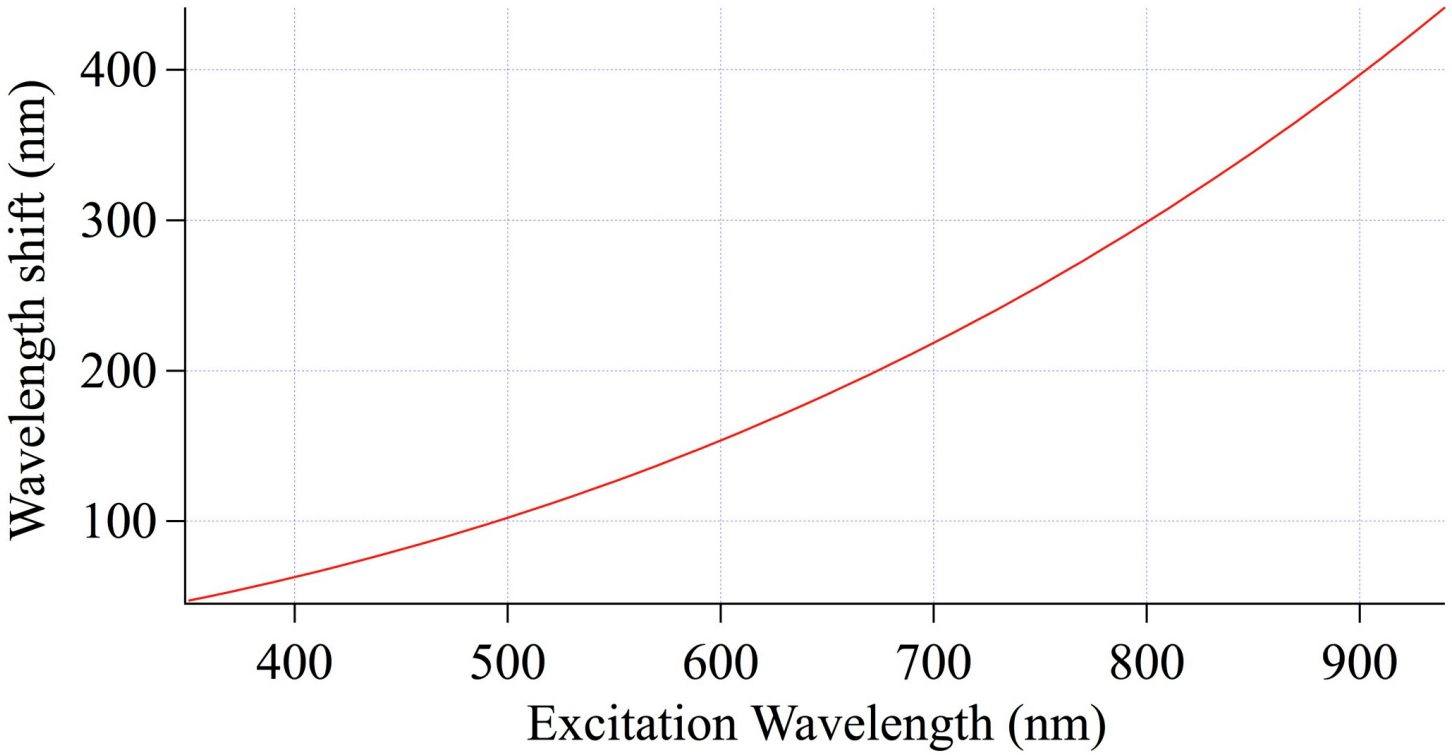
Sugihara, Kishino and Okami, J. Oceanogr. Soc. Japan, 1984.

Stavn and Weidemann, Applied Optics, 1988.

Marshall and Smith, Applied Optics, 1990

Characteristics of Raman scattering:

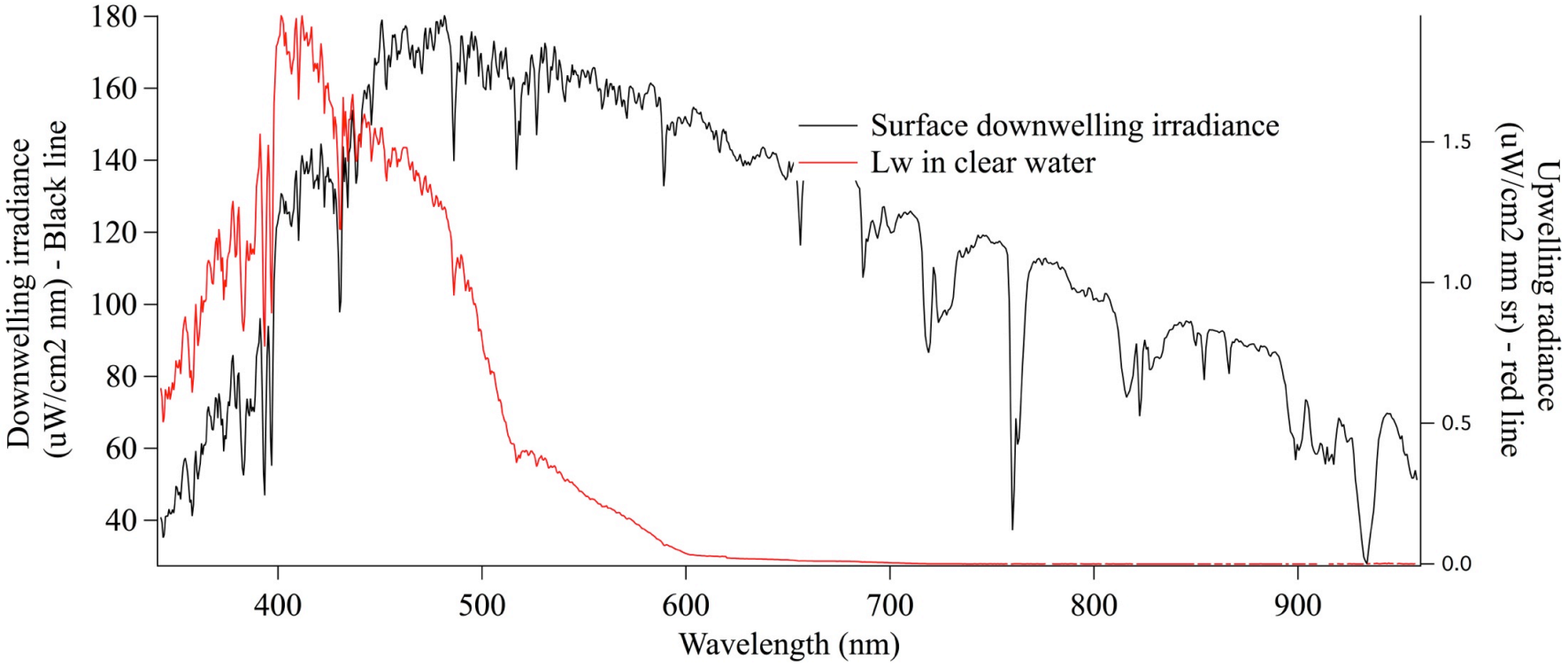
1) relatively weak, b_r =1.84 x 10^{-4} m^{-1} at 532 nm, vs rayleigh scattering, 1.8 x 10^{-3} m^{-1}.
2) scattering phase function like water Rayleigh, but higher depolarization factor.
3) wavelength shift approximately 3400 cm^{-1}.
4) strength varies with wavelength, around λ^{-5}, depending on whether you are talking excitation or emission and photon vs energy.



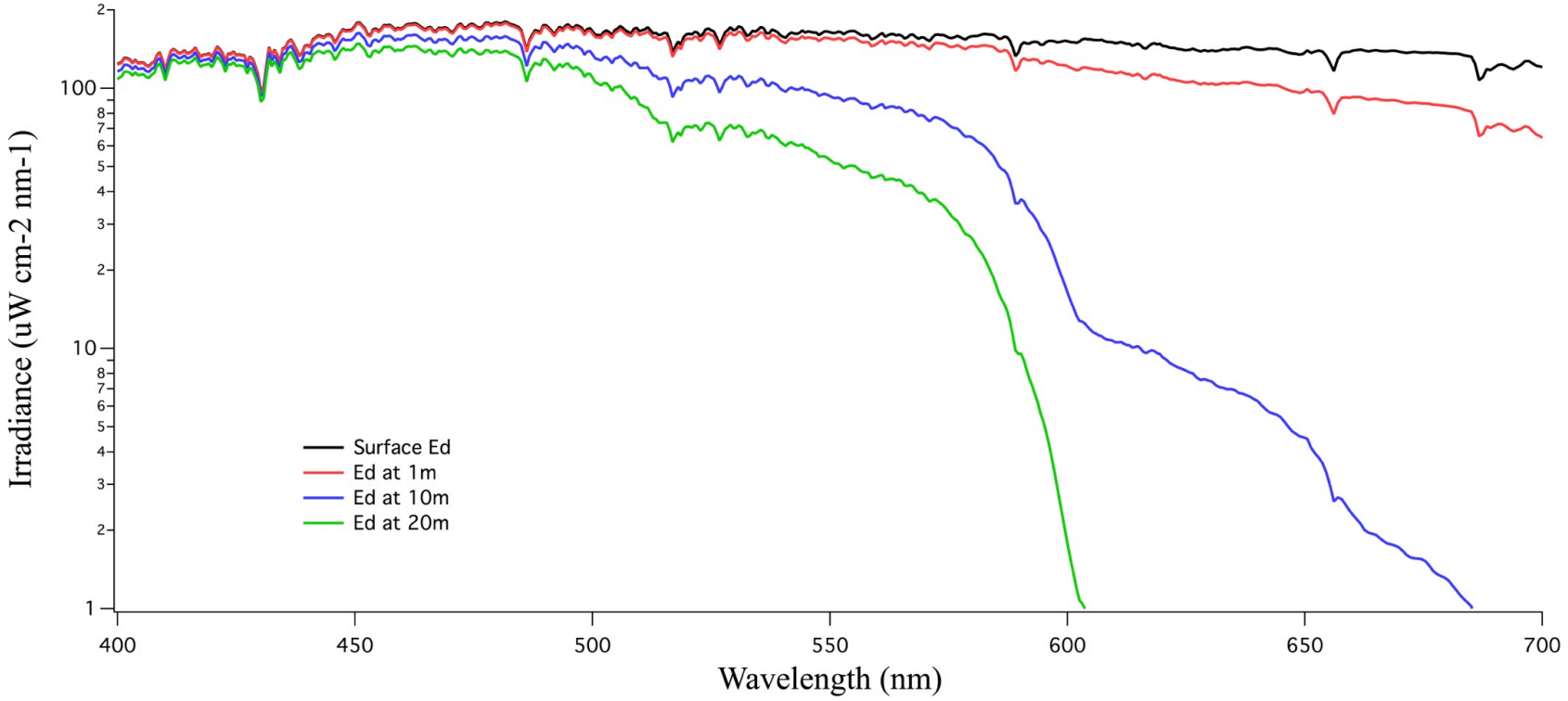
Energy shift is constant (3400 cm^{-1}), which causes a varying shift in wavelength, increasing towards red:
Note how to use this shift: 1/Final Lambda= 1/wavelength - shift

Look at natural light field

Water vapor, oxygen abs. lines along with fraunhofer lin



Raman becomes important as the amount of light at the emission wavelength is reduced relative to the excitation wavelength



1) Raman important because it shifts light from where it is abundant to where the “elastic” part is small.

2) Need to be careful when interpreting measurements at these wavelengths

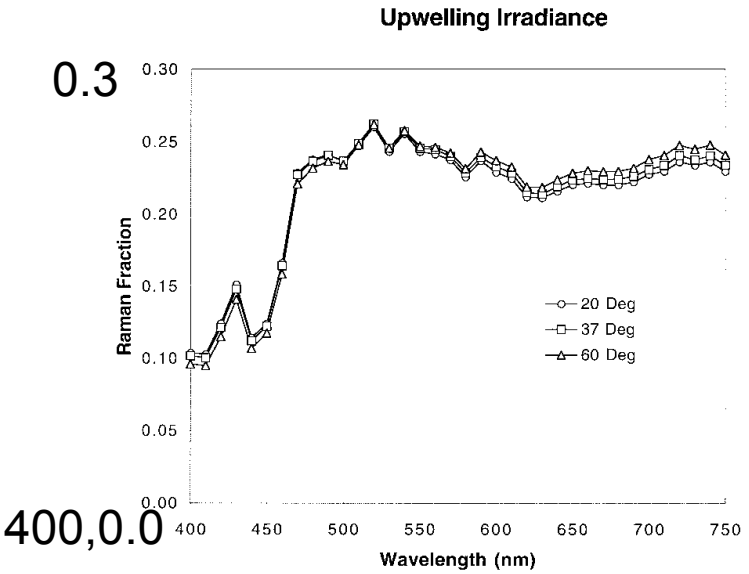


Fig. 4. Raman fraction of E_u for a water body consisting of pure seawater for $\theta_0 = 20°$, 37°, and 60°.

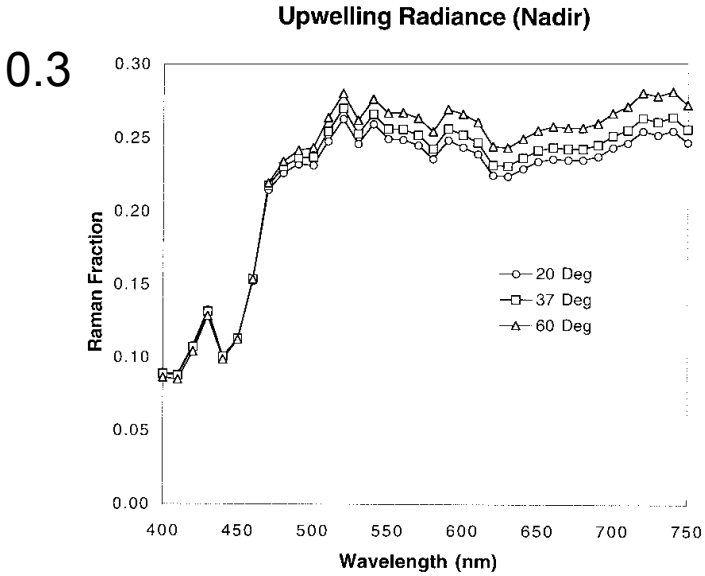


Fig. 3. Raman fraction of L_u for a water body consisting of pure seawater for $\theta_0 = 20°$, 37°, and 60°.

Gordon, AO, 3166-3174, 1999

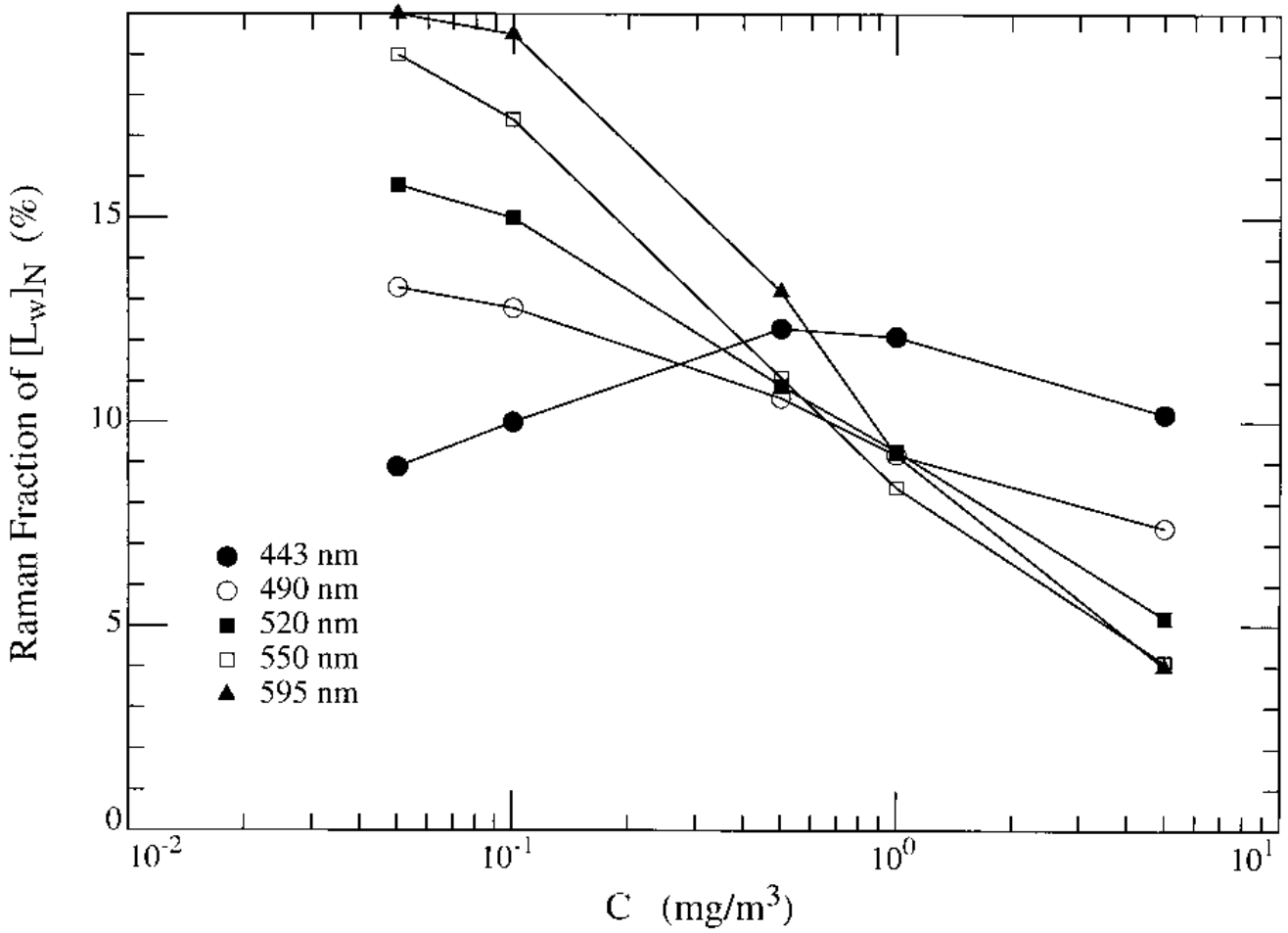


Fig. 6. Raman fraction of $(L_w)_N$ as a function of C for $\theta_0 = 37°$ and wavelengths of interest in ocean color remote sensing.

Gordon, AO, 3166-3174, 1999

How do you measure?

In lab, 90 degree scattering experiments…must be careful to exclude excitation. Also careful of polarization effects on instrumentation.

In the field:
1) indirectly….make measurements and model how much Raman should be there given the measured excitation field.

2) directly….Ring effect….3 groups, basically simultaneously, but independently worked along these lines in early 90's…..NOSC (now SPAWAR), TAMU, UM. TAMU only theory, NOSC specifically for a specific application, SLC, and UM both theory and experiment.

Key: Broad emission spectrum, sharp lines in the light field….Ring effect measures the filling of existing spectral lines by a broad emission source.

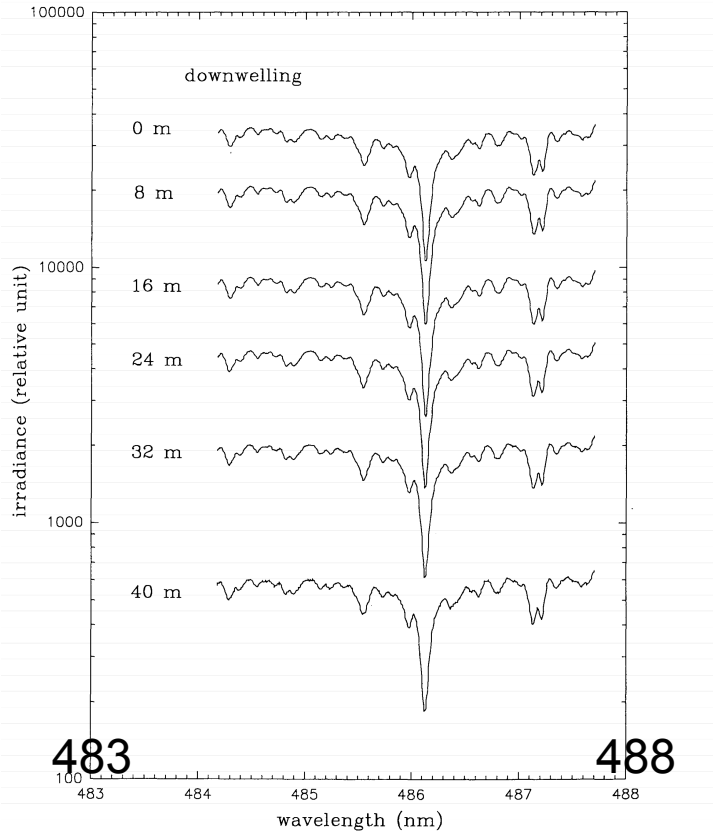


Figure 7. The spectrum near 486 nm measured at various depths. Virtually no change is observed in the Fraunhofer line.

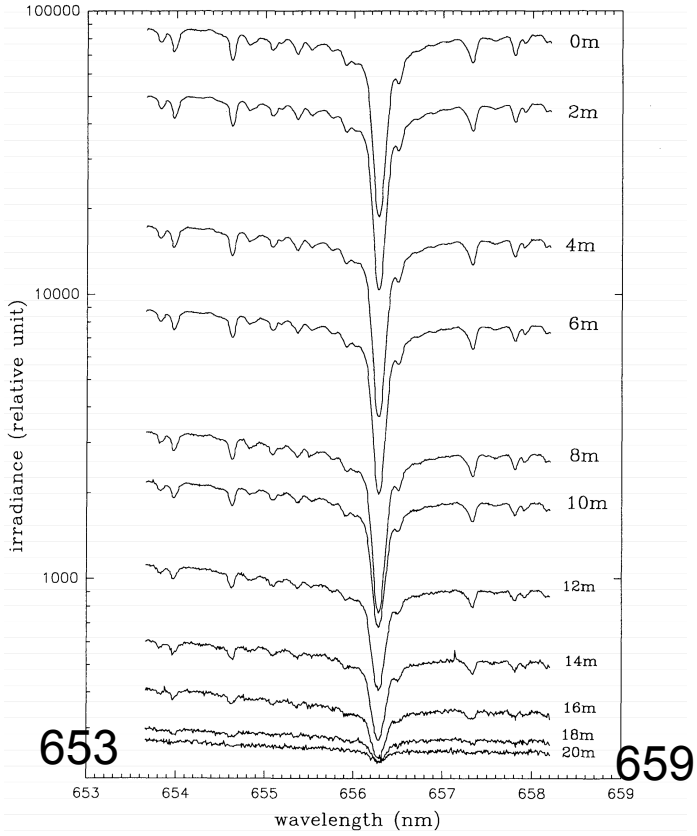
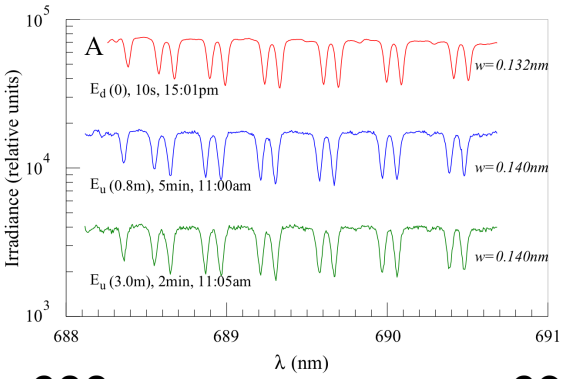


Figure 6. The spectrum near 656 nm measured at various depths. As can be seen, the Fraunhofer line is filled quickly.

Ge et al, JGR, 13227-13236, 1995

Can use this to also look at fluorescence.



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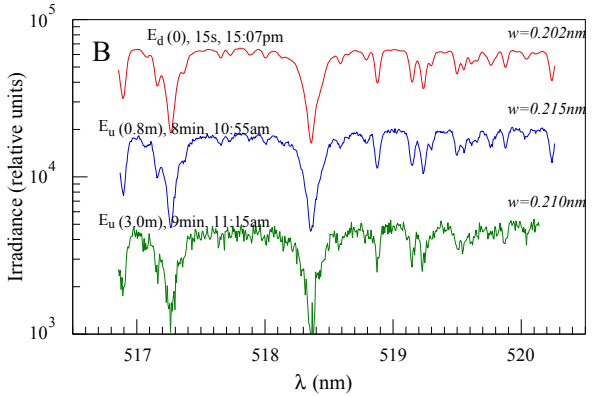

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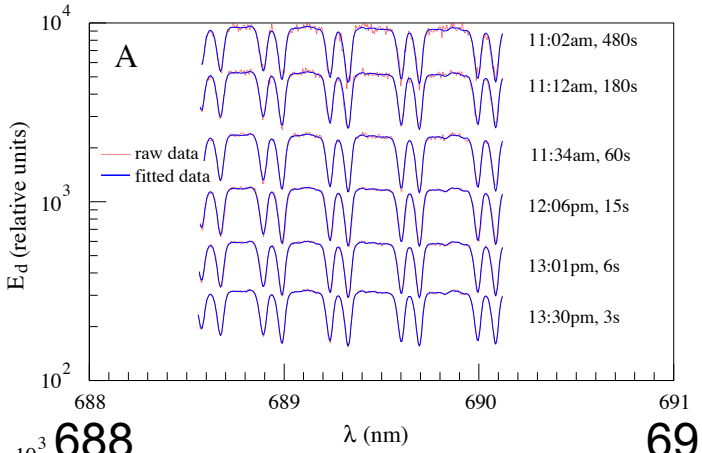

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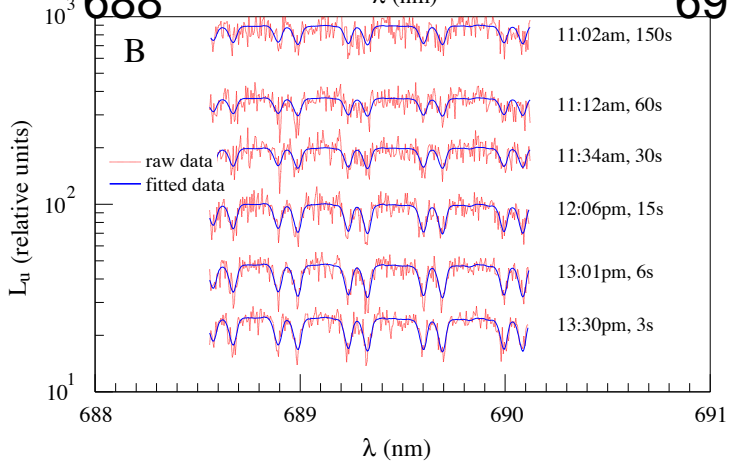

Top 689 nm, bottom 518 nm, in shark river Above Brain Coral in Dry Tortugas

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Other Inelastic scattering:
Brillouin scattering

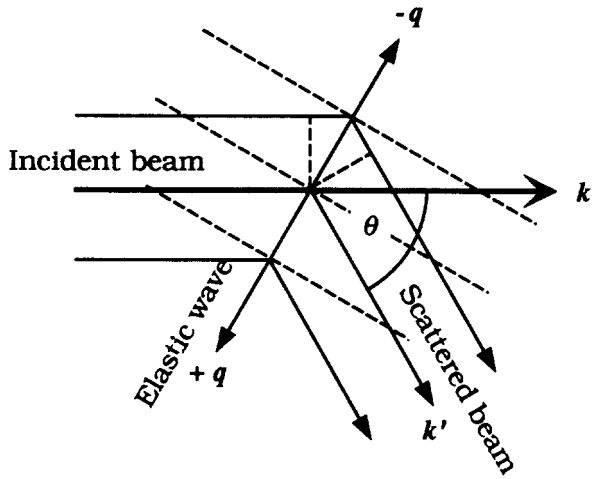


Figure 2. Schematic showing the scattering of an incident electromagnetic wave from an elastic wave.

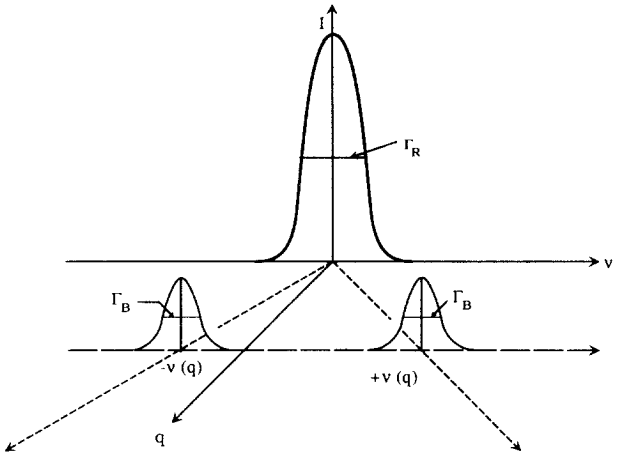


Figure 3. Spectrum of scattered light showing both the central or Rayleigh peak (FWHM = Γ_R) and the Brillouin doublets (FWHM = Γ_B) as a function of frequency ν.

$$\frac{\Delta\lambda_B}{\lambda} = \frac{\Delta\nu_B}{\nu} = \pm 2n\frac{v_s}{c}\sin\frac{\theta}{2}, \qquad (5)$$

Typical values (530nm, backscattering, v_s=1500 m/s, wavelength shift is 7 x10^{-3} nm.

Note shift depends on speed of sound and n, which depend on salinity and temperature, but sound speed changes more rapidly with temperature.

Now Fluorescence

Remember distinction is lifetime, longer intermediate state, more chance to "forget" information about incoming photon….

Phytoplankton fluorescence basically isotropically emitted (Gordon et al., L&O, 1993).

Probably also completely depolarizing for phytoplankton, has been used separate polarization from natural light. Found one article using techniques on extracted compounds from Red Tide organisms.

Polarization of Fluorescence generally used as an indication of the lifetime of the state and diffusion of the fluorophore.

" The impact of algal fluorescence on the underwater polarized light field ", A. Tonizzo, A. Ibrahim, J. Zhou, A. Gilerson, B. Gross, F. Moshary, S. Ahmed (2010), Proceedings of SPIE Ocean Sensing and Monitoring II (5-9 April, Orlando, FL) ,

Other fluorescent properties (besides Chl and pigments described in next lecture)

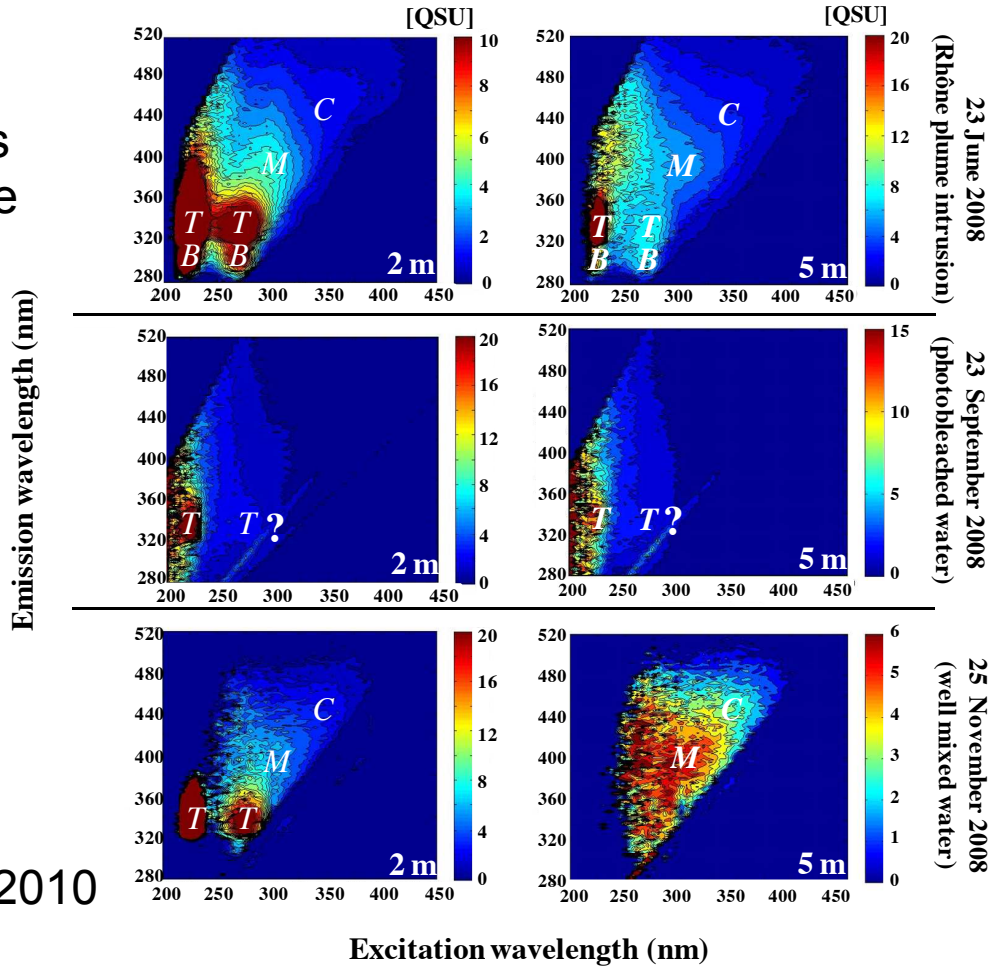
CDOM Fluorescence, EEMS techniques (Paula Coble, USF) :

Note how emission depends on excitation, and on sample

These samples
From Bay of Marseilles

Peaks:
M UVA marine humic
C UVA Humic like
B tyrosine like
T Tryptophine like
A UVC humic like

Para et al., Biogeoscience, 2010



CDOM typically measured in the field by either absorption, which is also its largest natural effect on the light field:

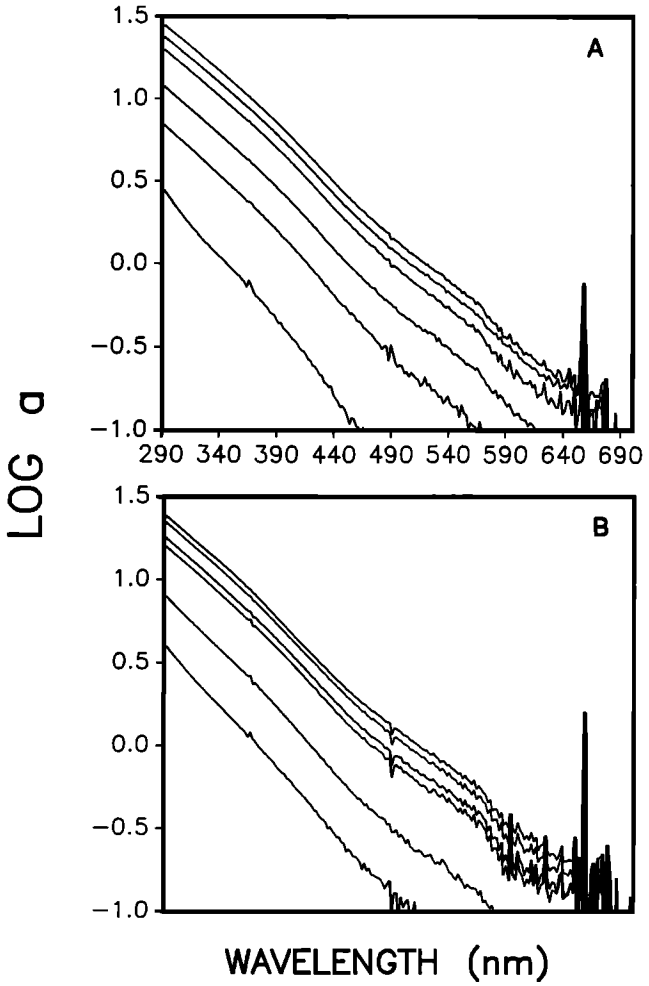
These samples from Orinoco Basin
Blough et al, JGR, 1993

Absorption spectra typically:

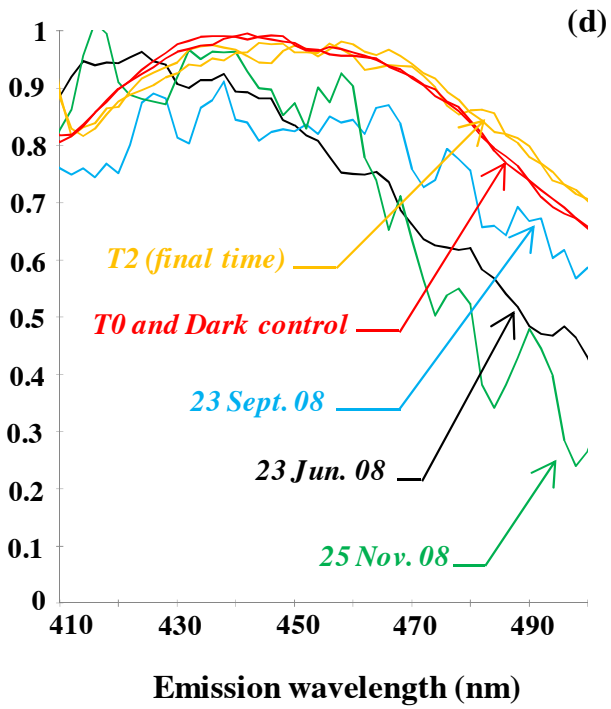
$$a_\lambda = a_{450\,nm} e^{S(450\,nm-\lambda)}$$

S in these cases on the order of 0.014

Typically 0.014-0.02.



Or measured with fluorescence:



Excitation at 350 nm

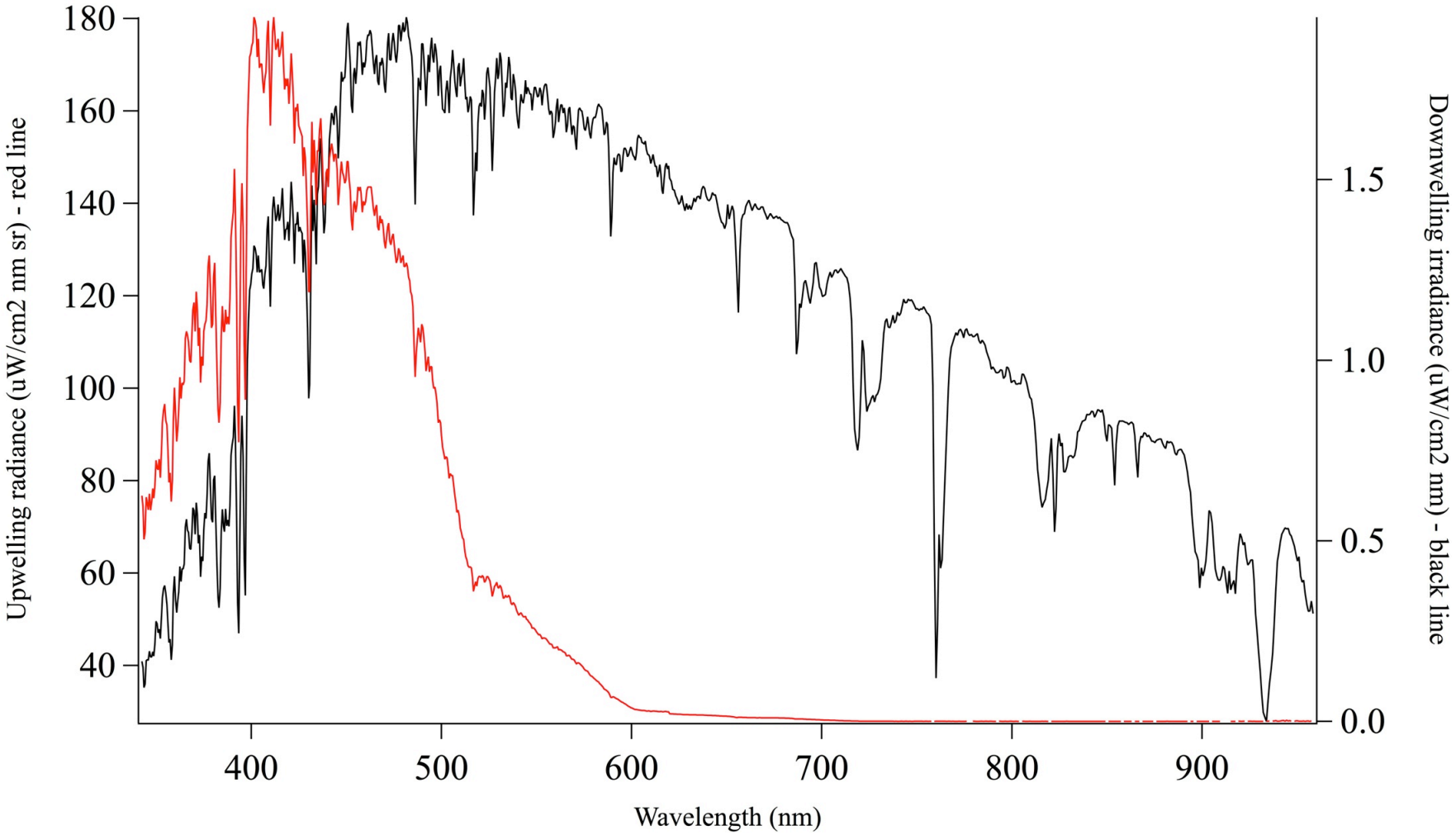
Or single excitation and emission:

Wetlabs ECO/FL: 370nm/460 nm

In most models of upwelling radiance, CDOM fluorescence is ignored, why?
(hint on next slide?)

Would be useful to have the quantum fluorescence efficiencies, which are rarely measured (one exception Hawes et al, Ocean Optics XI, 1992, on concentrated samples.)
Most measurements are related to quinine sulfate or some other fluorescent material which makes it difficult to include in optical models

CDOM flurorescence



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Other materials: Oils fluoresce when illuminated by UV…can get fingerprints for these with EEMS systems. (Stelmaszewski, Optica Applicata, 405-418, 2004)

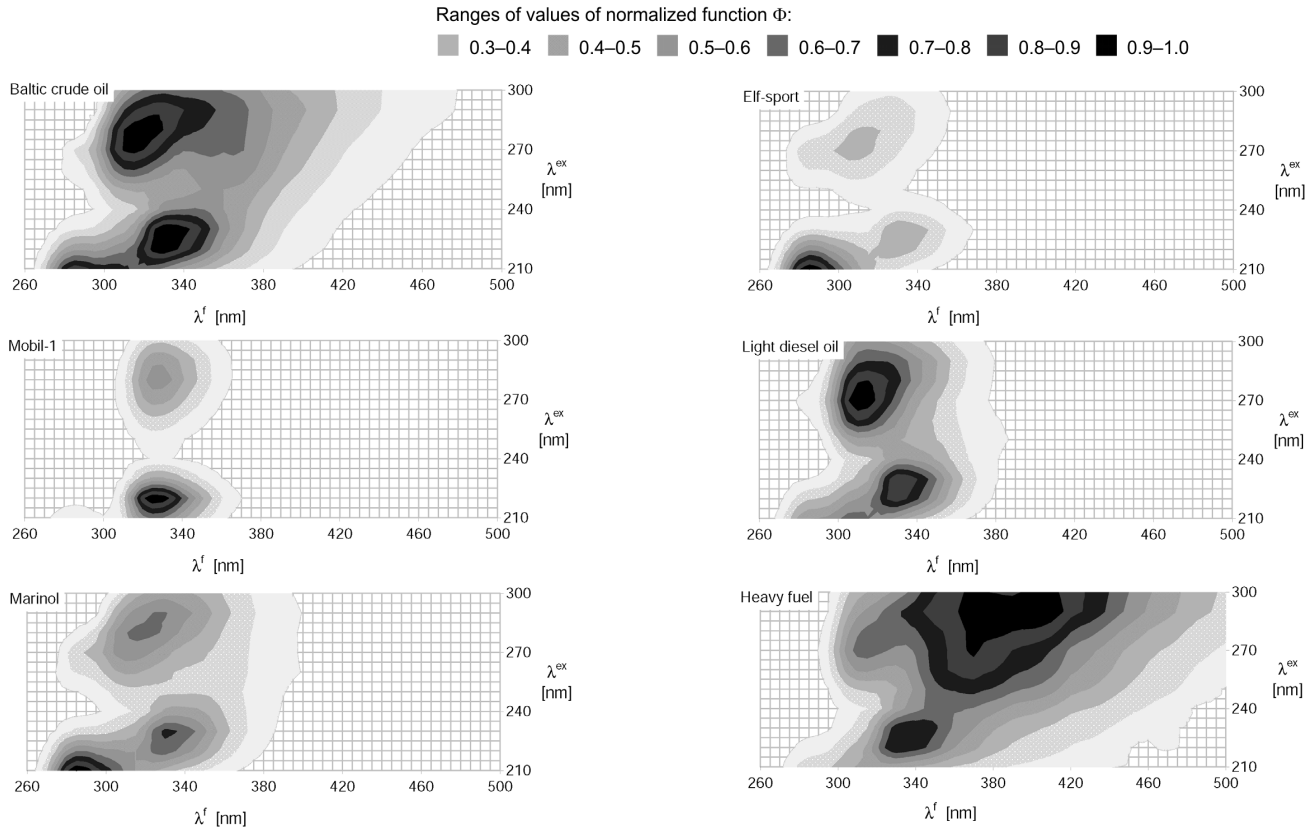
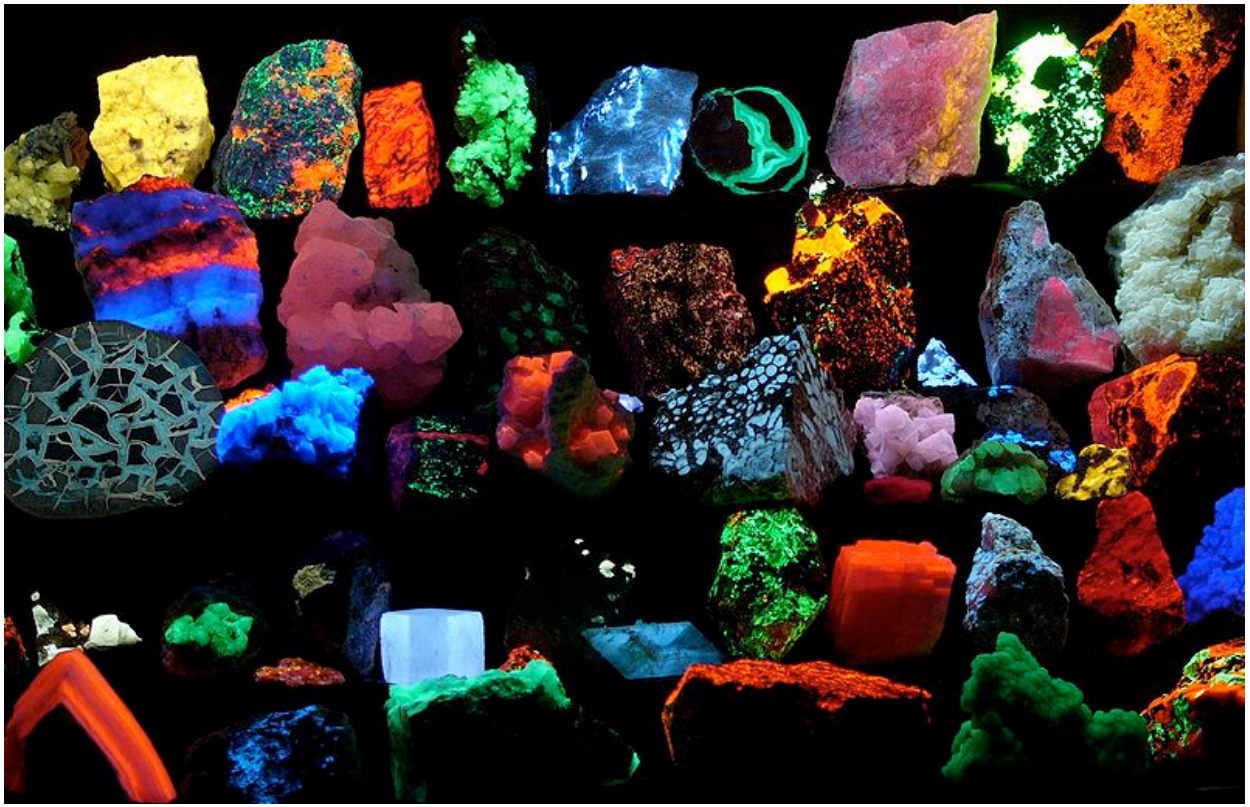


Fig. 1. Examples of the normalized total spectra Φ of hexane solutions of oils.

Minerals (such as calcite) fluoresce when illuminated by UV light.
365nm Ex looks pink, 320 nm looks red, 254 nm looks blue. Typically not enough UV to matter (except to geologists, and the Fluorescent Mineral Society).



http://en.wikipedia.org/wiki/File:Fluorescent_minerals_hg.jpg

Inelastic scattering:
Raman important to take into consideration when modeling light field and comparing models with data.

Brillouin scattering: could be an interesting technique for lidar remote sensing temperature. Being applied by Thomas Walther (Germany now after Fry's lab).

CDOM fluorescence important for measuring CDOM, not as big a deal in the natural light field.

Oil fluorescence important for detecting, fingerprinting oil, not as much in the natural light field

Mineral fluorescence important for identifying minerals…not in natural light field.