



Inelastic Scattering

Ken Voss, Ocean Optics Summer class, 2017

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?

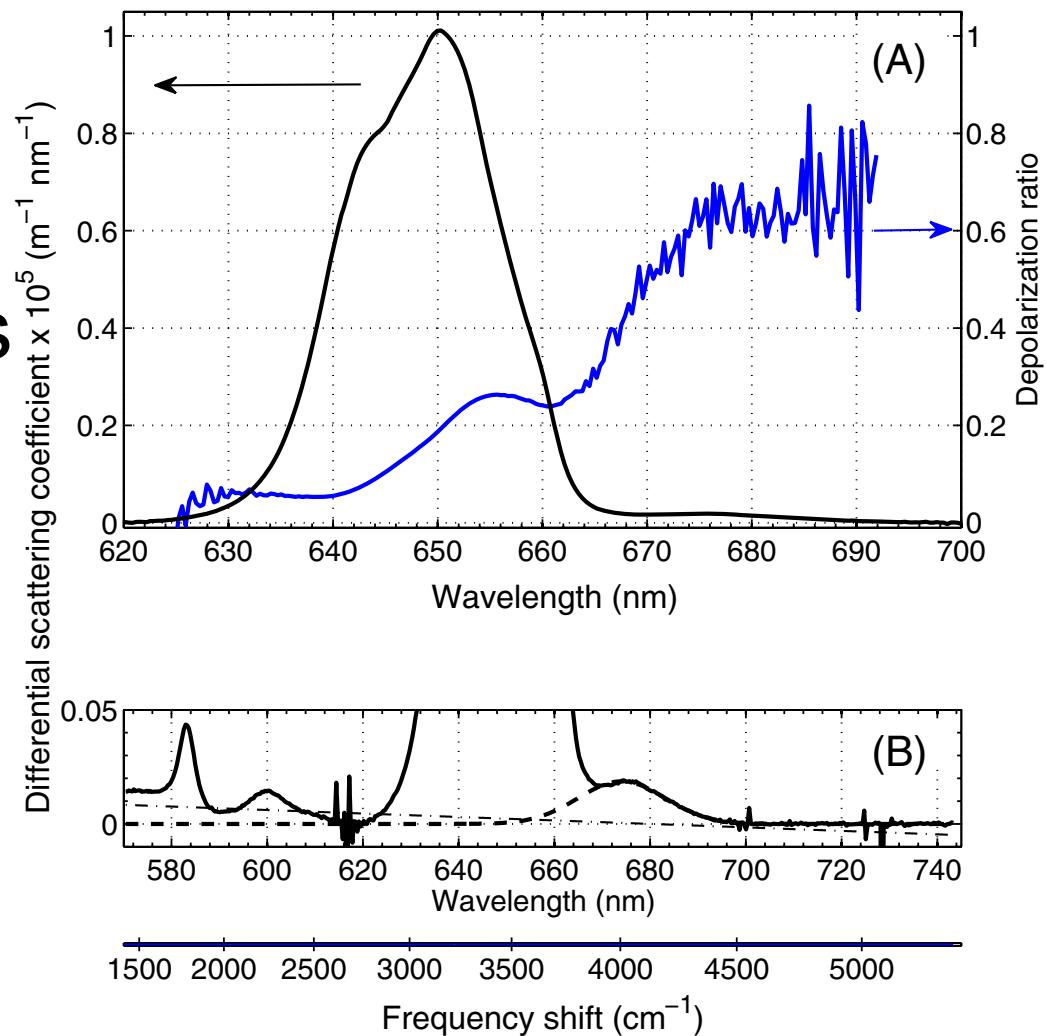
Remember your freshman physics class and all that time you spent learning about collisions? Two types of collisions: elastic and in-elastic. What was the difference?

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)

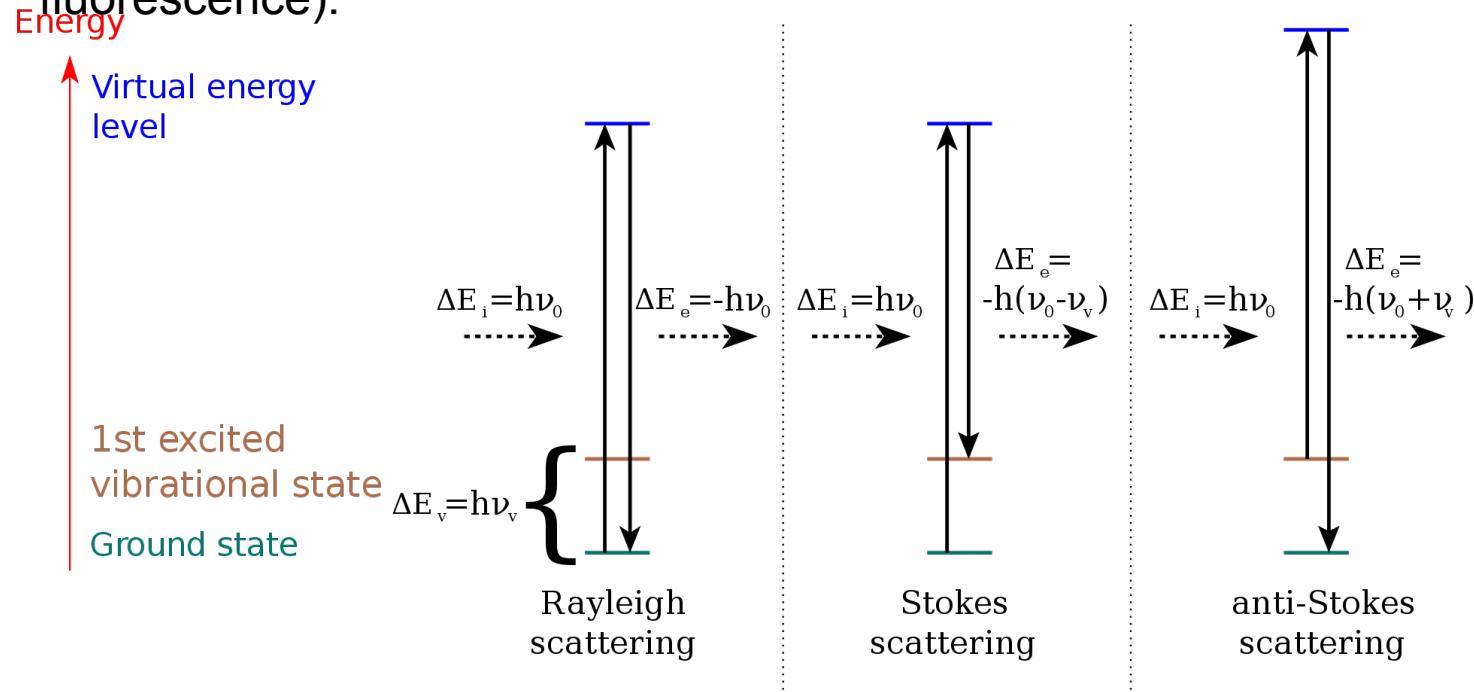
In-elastic scattering: photons come in with one wavelength and leave with another wavelength. (remember Compton scattering of photons?). Difference between this and fluorescence is basically a short intermediate time for the event (which leads to other effects).

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)

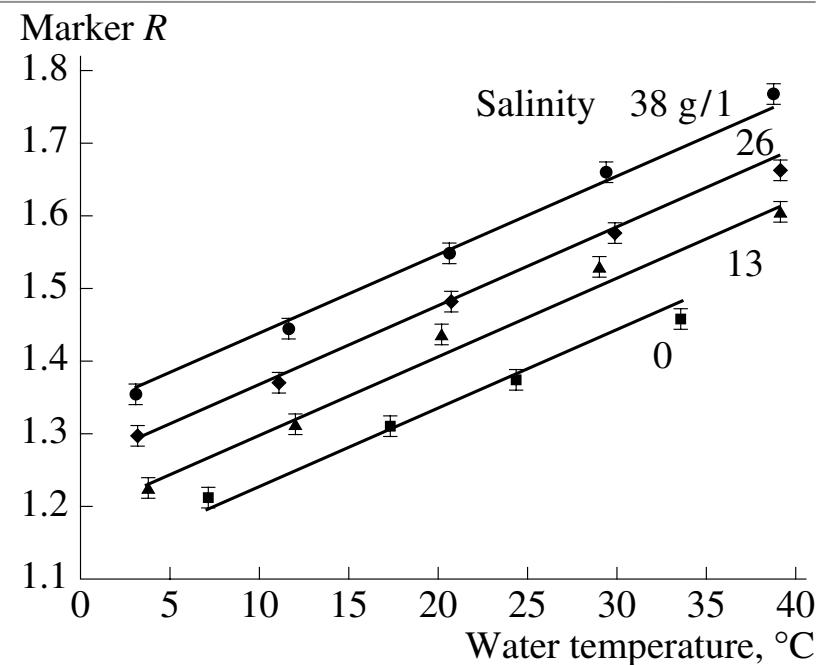
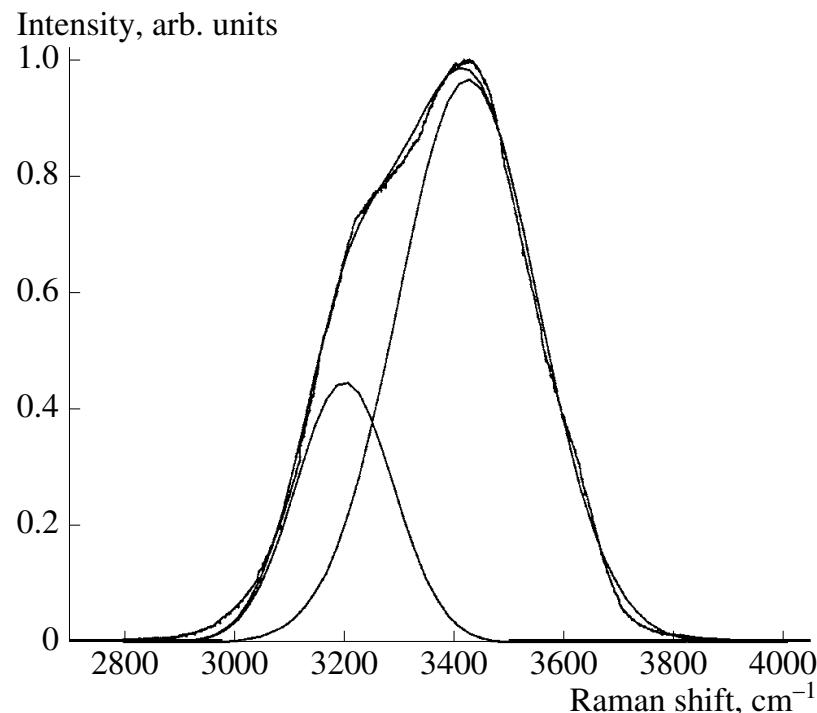


Introduction

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 probability of this happening is greatly enhanced if there is a nearby transition to the virtual energy level (but if too close can cause issues of confusion with fluorescence).



Raman Scattering



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: $1/\text{Final Lambda} = 1/\text{wavelength} - \text{shift}$ all in cm or cm⁻¹

Importance in the natural light field:

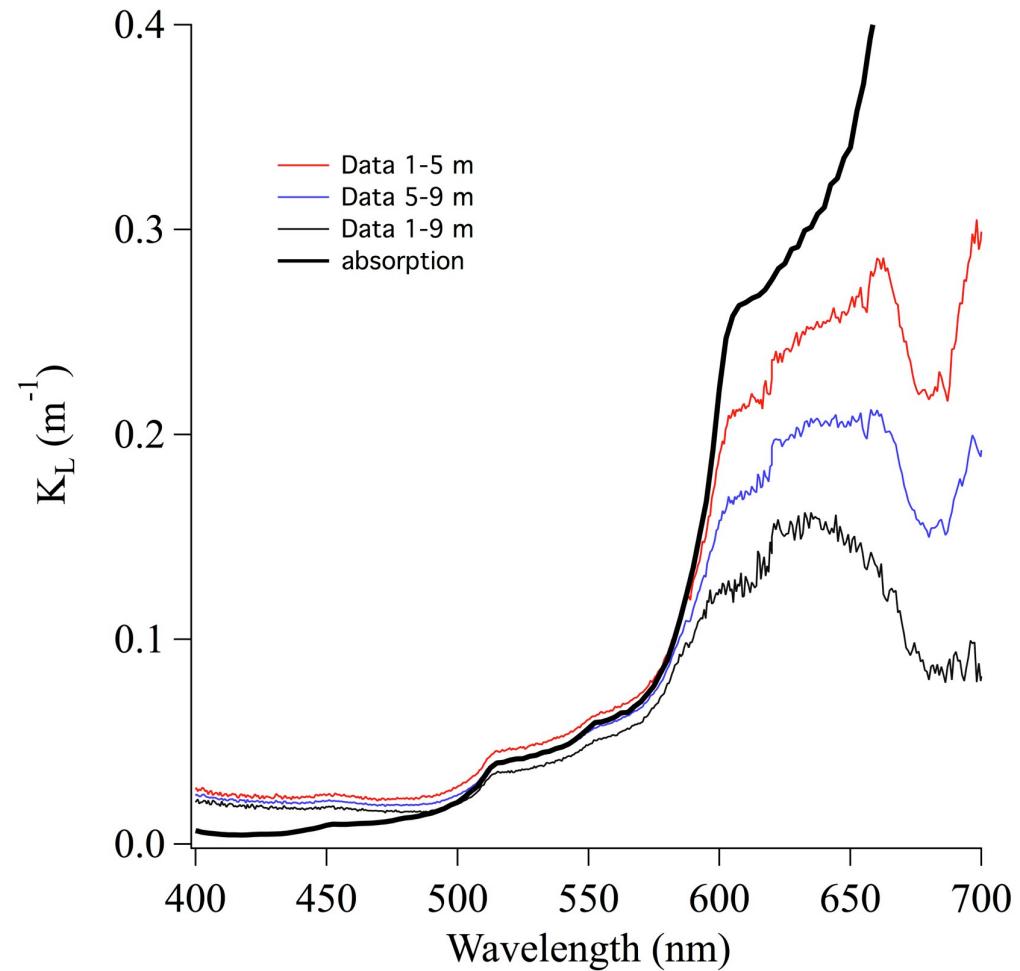
By the early 80's the ocean optics community were getting multispectral instruments, either full blown spectrometers (for example Ray Smith and John Tyler, Vislab) or multi channel radiometers, such as the MER-1032 made by Biospherical instruments.

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

Raman Scattering

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.

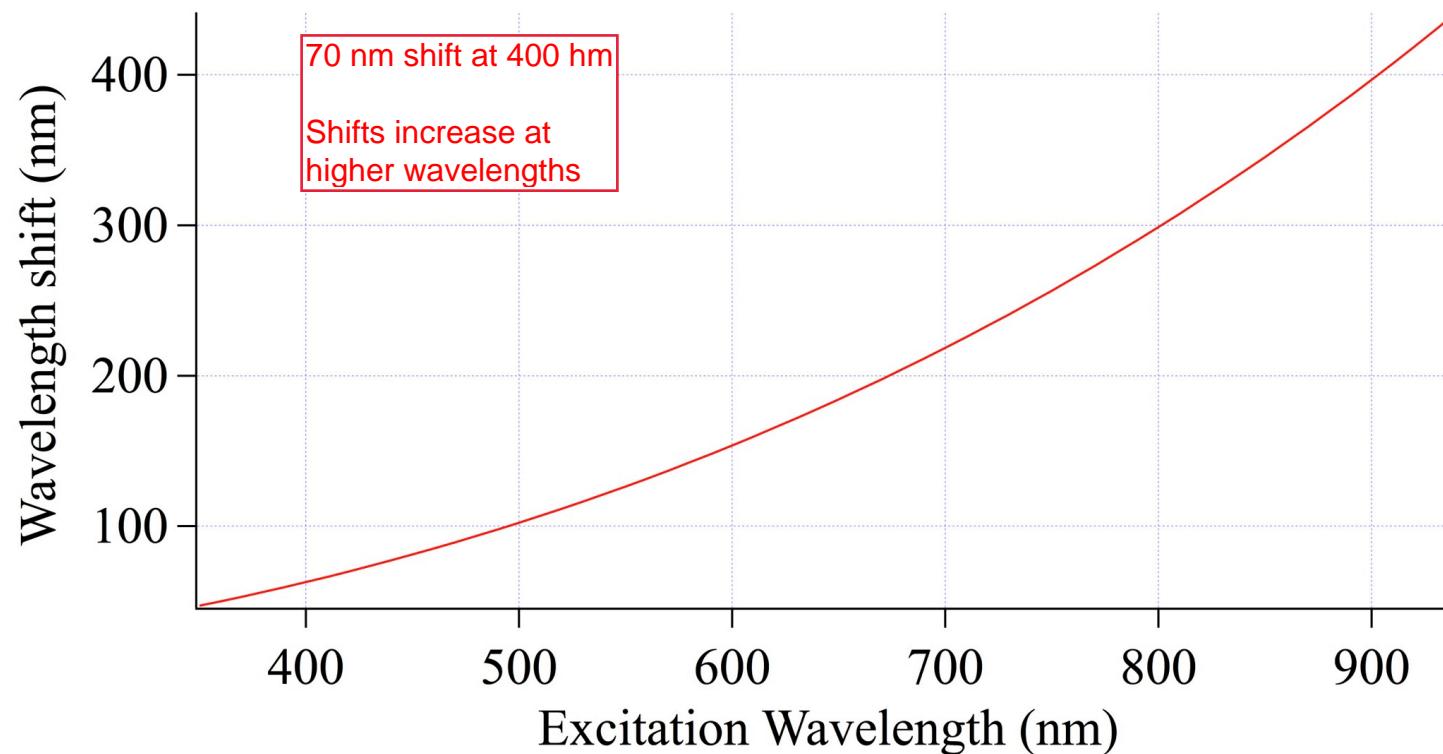
Stavn and Weidemann, Applied Optics, 1988.

Marshall and Smith, Applied Optics, 1990

Characteristics of Raman scattering:

- 1) relatively weak, $b_r = 1.84 \times 10^{-4} \text{ m}^{-1}$ at 532 nm, vs rayleigh scattering, $1.8 \times 10^{-3} \text{ m}^{-1}$.
- 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 wavelength and photon vs energy.

Raman Scattering



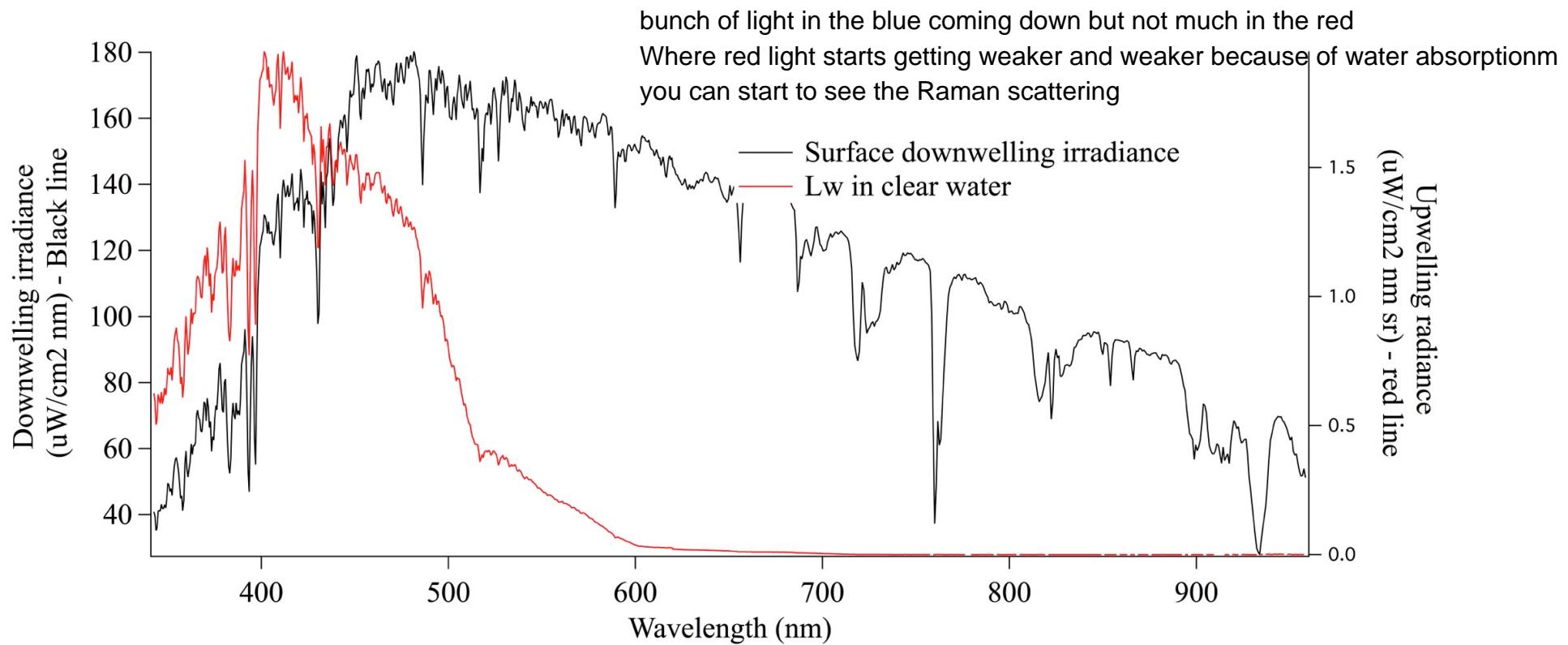
Energy shift is constant (3400 cm^{-1}), which causes a varying shift in wavelength, increasing towards red:

Note how to use this shift: $1/\text{Final Lambda} = 1/\text{wavelength} - \text{shift}$

Raman Scattering

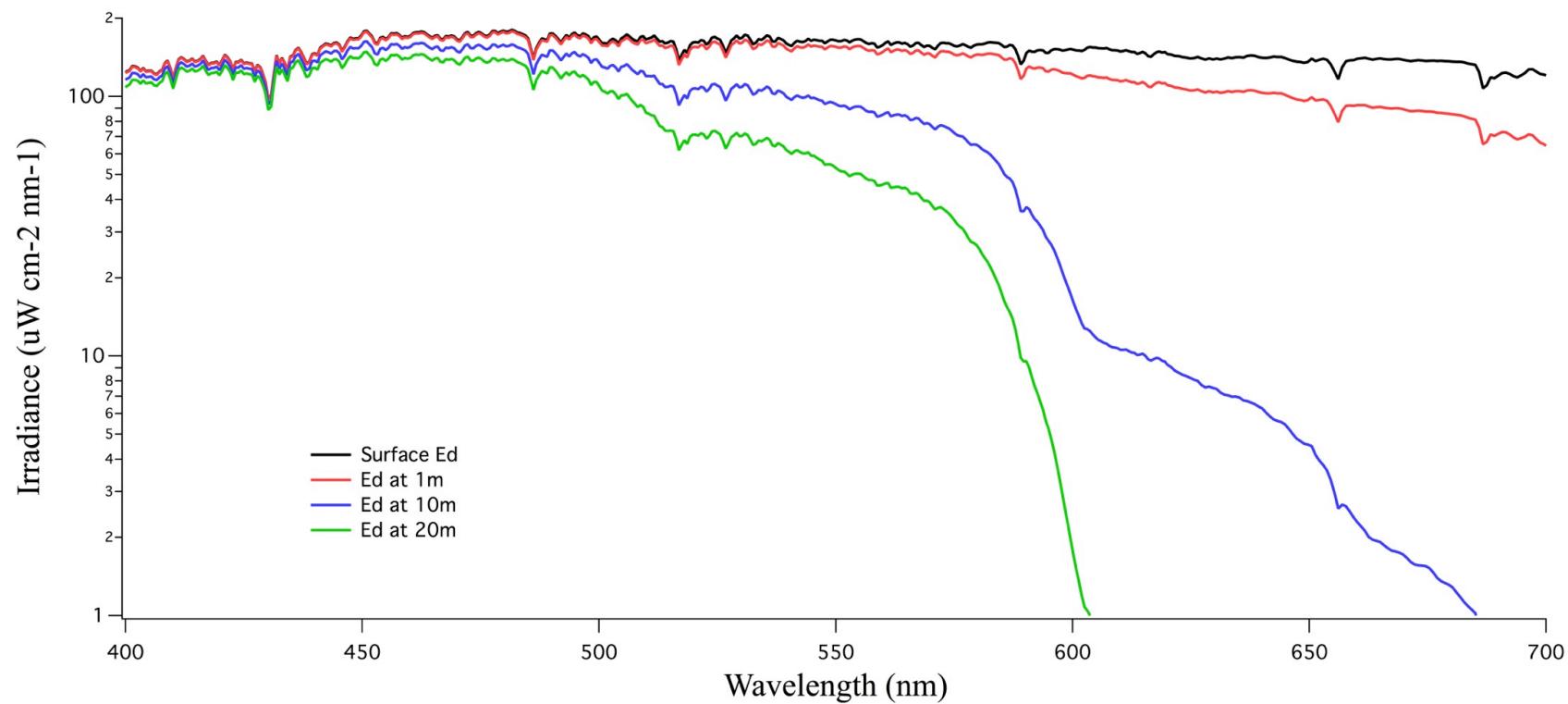
Look at natural light field

Water vapor, oxygen abs. lines along with fraunhofer lir



Raman Scattering

Raman becomes important when the amount of light at the emission wavelength is reduced in elastic processes relative to the excitation wavelength



Raman Scattering

- 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

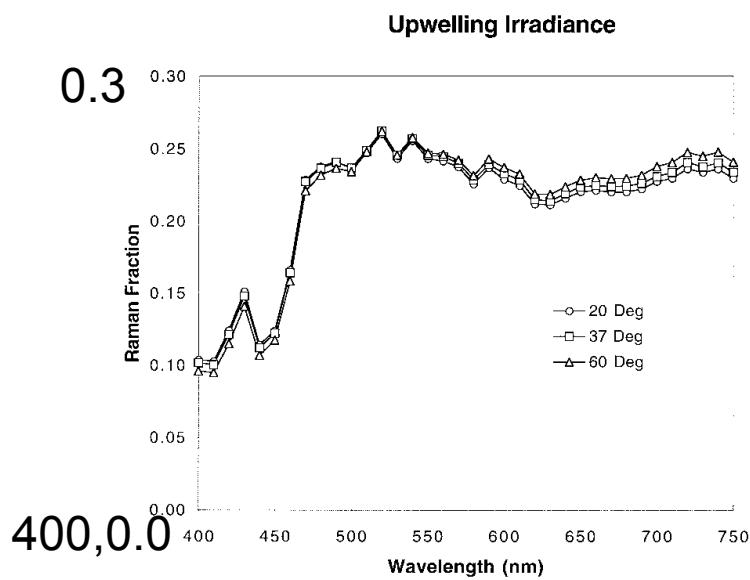


Fig. 4. Raman fraction of E_u for a water body consisting of pure seawater for $\theta_0 = 20^\circ, 37^\circ$, and 60° .

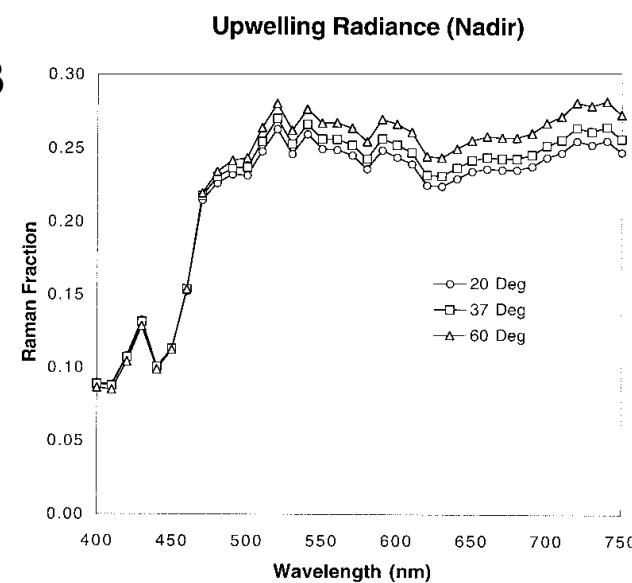


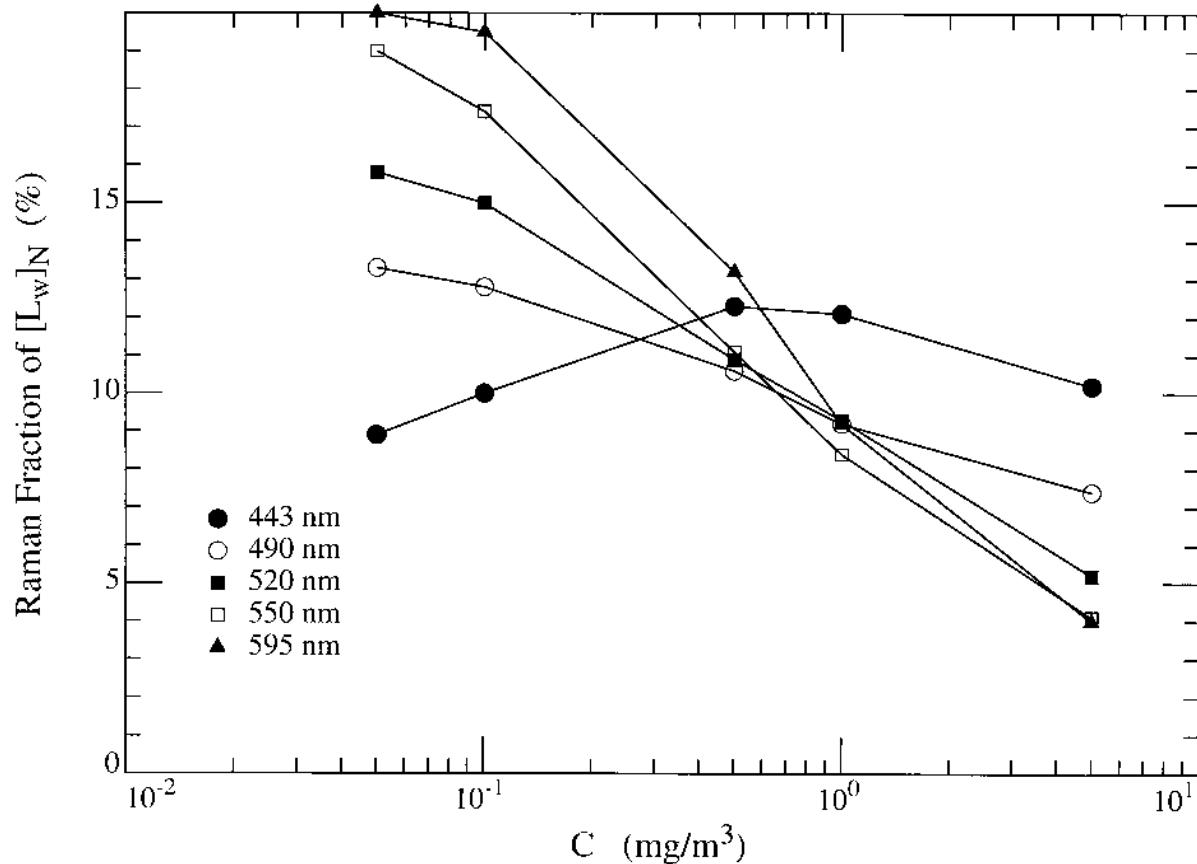
Fig. 3. Raman fraction of L_u for a water body consisting of pure seawater for $\theta_0 = 20^\circ, 37^\circ$, and 60° .

Gordon, AO, 3166-3174, 1999

UNIVERSITY Note...most important for clear (pure) water...why?
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Raman Scattering



Phytoplankton will absorb the emitted light from the Raman scattering

As chlorophyll goes up the Raman fraction goes down

The shift in blue is coming from excitation in UV

You are loosing your excitation as you increase in chlorophyll

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

Should say...this modeling done without current knowledge of the UV.

Gordon, AO, 3166-3174, 1999

Measuring Raman Scattering

How do you measure?

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

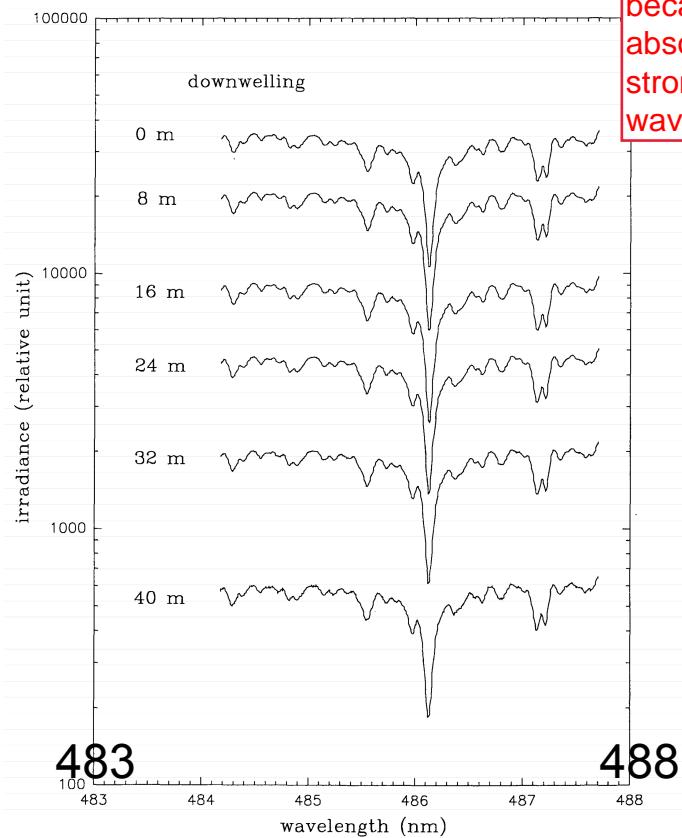
In the field:

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.

Measuring Raman Scattering



excitation at 480
always stays
stronger than the
light at 400 nm
because it is
absorbed as
strongly at that
wavelength

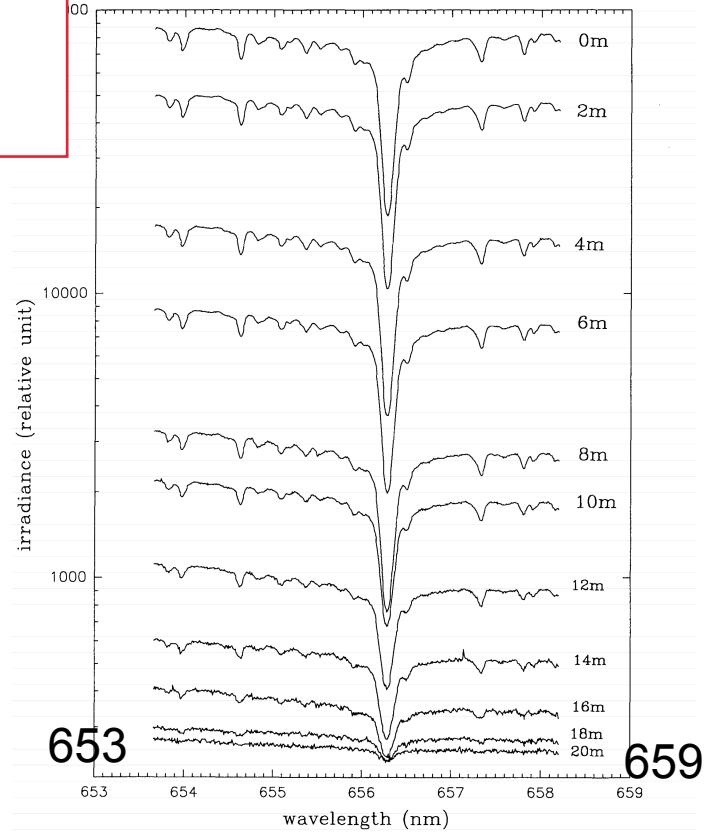


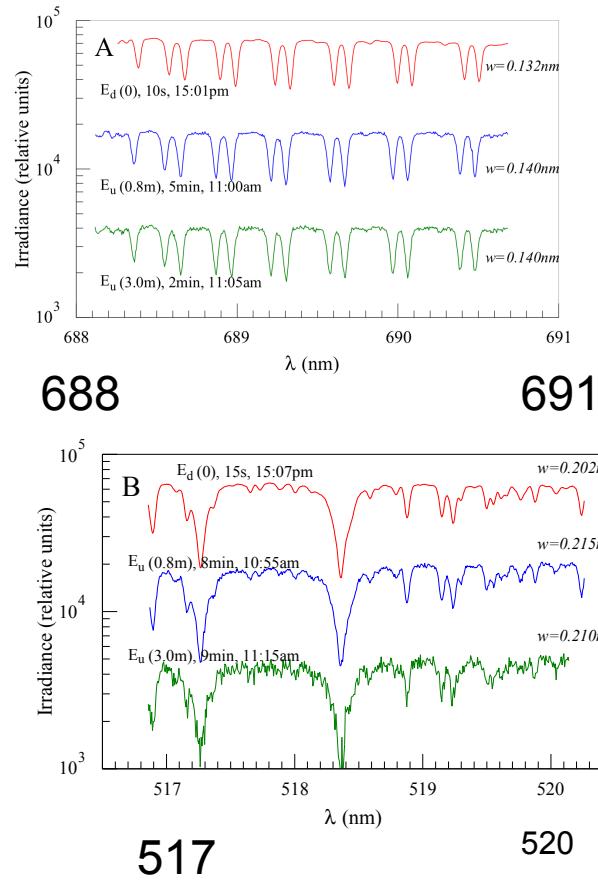
Figure 6. The spectrum near 656 nm measured at various depths. As can be seen, the Fraunhofer line is filled quickly.

Ge et al, JGR, 13227-13236, 1995

Measure the depth
of fraunhofer lines
to get Raman
scattering

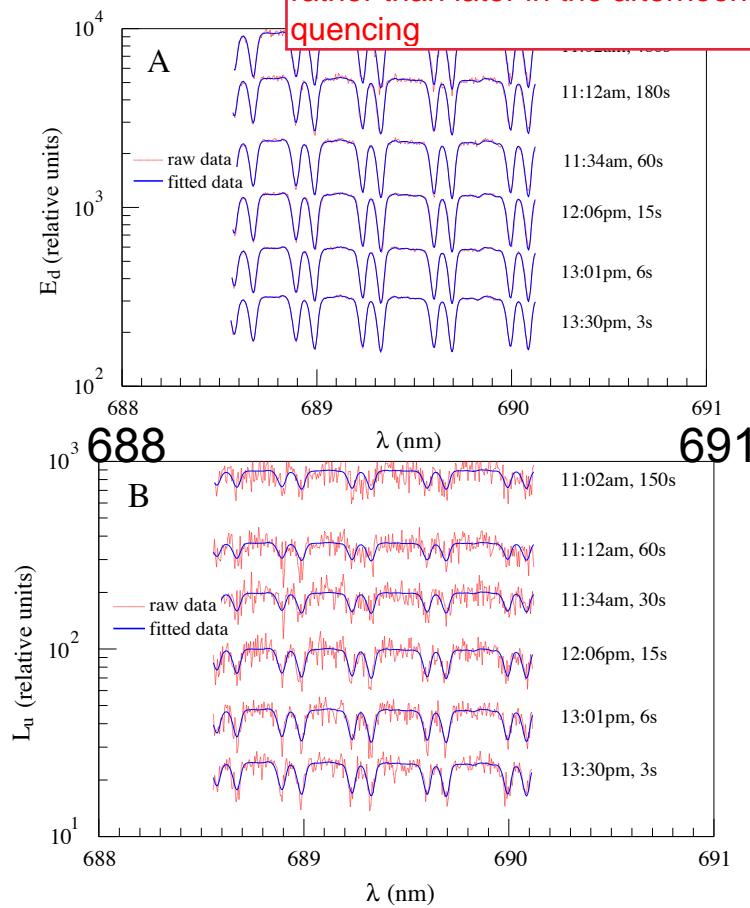
Using Ring effect

Can use this to also look at fluorescence.



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

This is showing you that the Raman scattering is much higher than the upwelling radiance. Because the upwelling radiance doesn't have those Fraunhofer lines - more fluorescence early in the morning rather than later in the afternoon - this is fluorescence quenching



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Brillouin Scattering

hard to distinguish this type of shift from elastic so you need high resolution hyperspectral

Other Inelastic scattering: Brillouin scattering

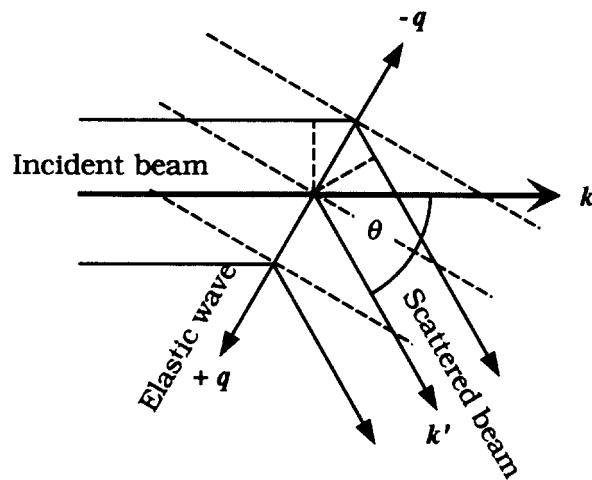


Figure 2. Schematic showing the scattering of an incident electromagnetic wave from an elastic wave.

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

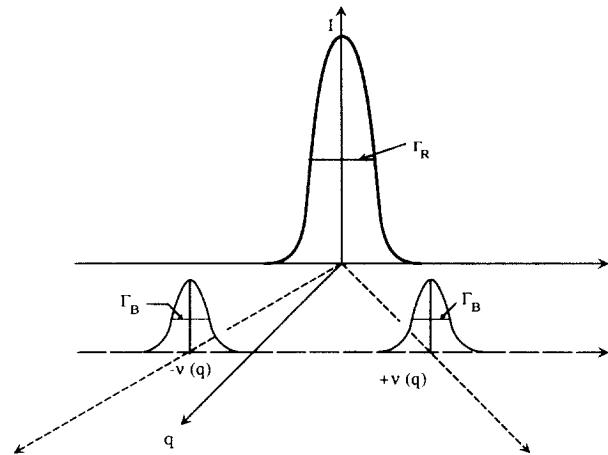


Figure 3. Spectrum of scattered light showing both the central or Rayleigh peak ($\text{FWHM} = \Gamma_R$) and the Brillouin doublets ($\text{FWHM} = \Gamma_B$) as a function of frequency ν .

Typical values (530nm, backscattering, $v_s=1500$ m/s, wavelength shift is 7×10^{-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.

Fluorescence

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) ,

CDOM fluorescence

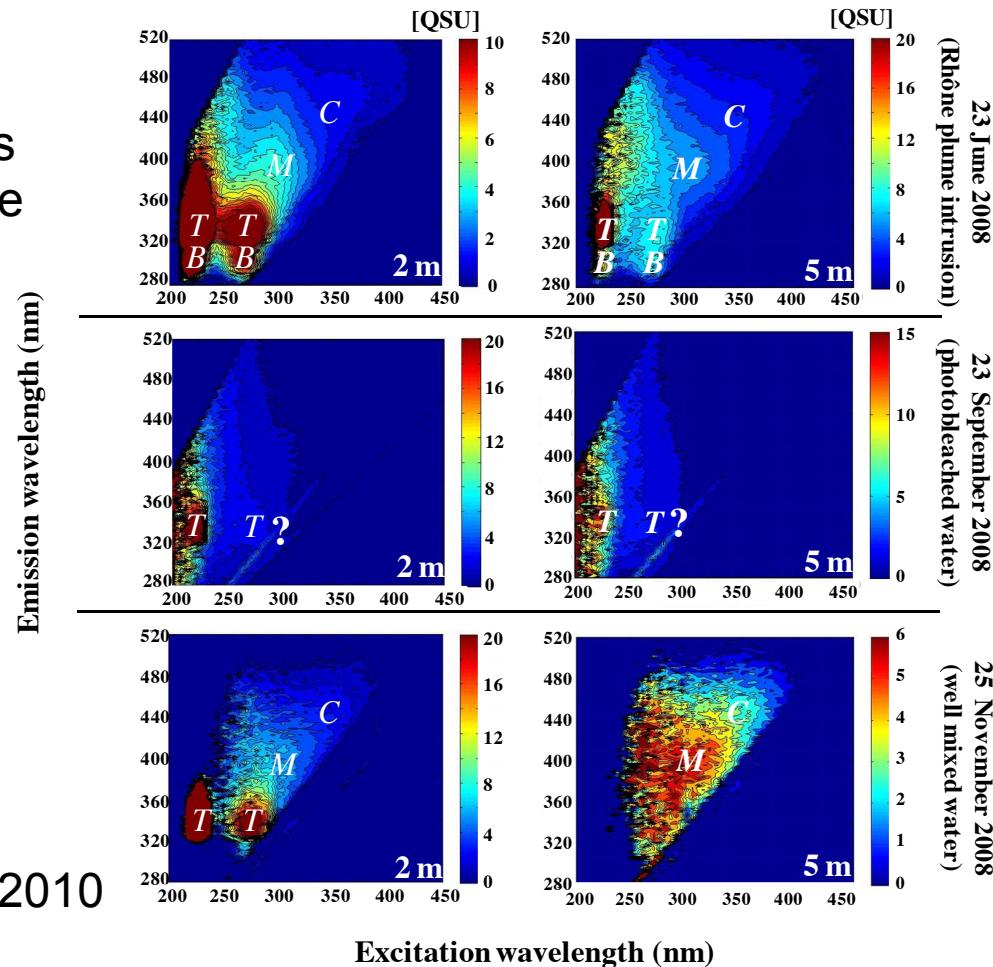
Other fluorescent properties (besides Chl and pigments described in next lecture)

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
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CDOM

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

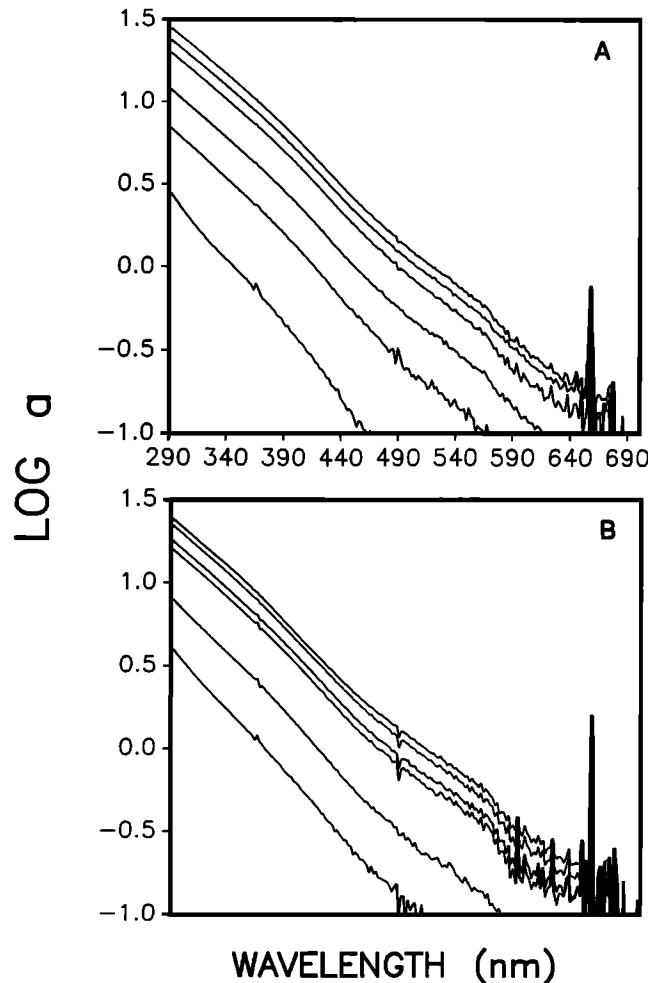
These samples from Orinoco Basin
Blough et al, JGR, 1993

Absorption spectra typically:

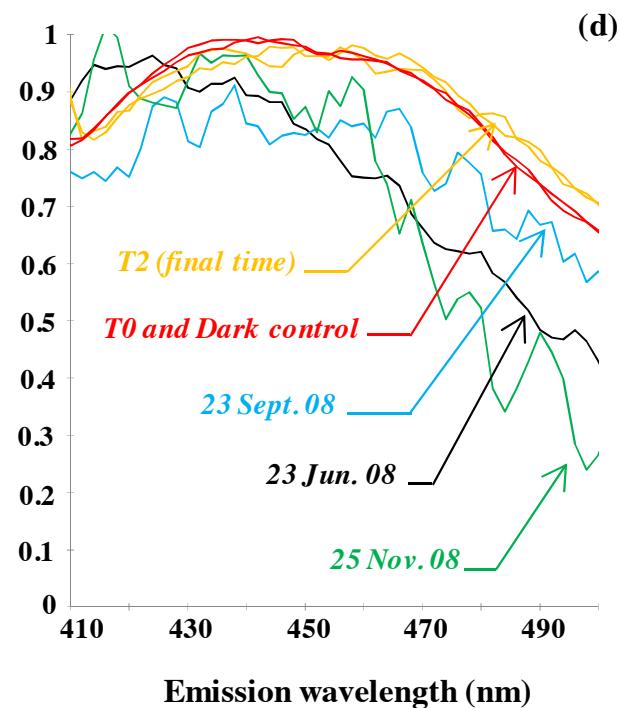
$$a_\lambda = a_{450\text{nm}} e^{S(450\text{nm}-\lambda)}$$

S in these cases on the order of 0.014

Typically 0.014-0.02.



Or measured with fluorescence:



Or single excitation and emission:

Wetlabs ECO/FL: 370nm/460 nm



Excitation at 350 nm

In most models of upwelling radiance, CDOM fluorescence is ignored, why?

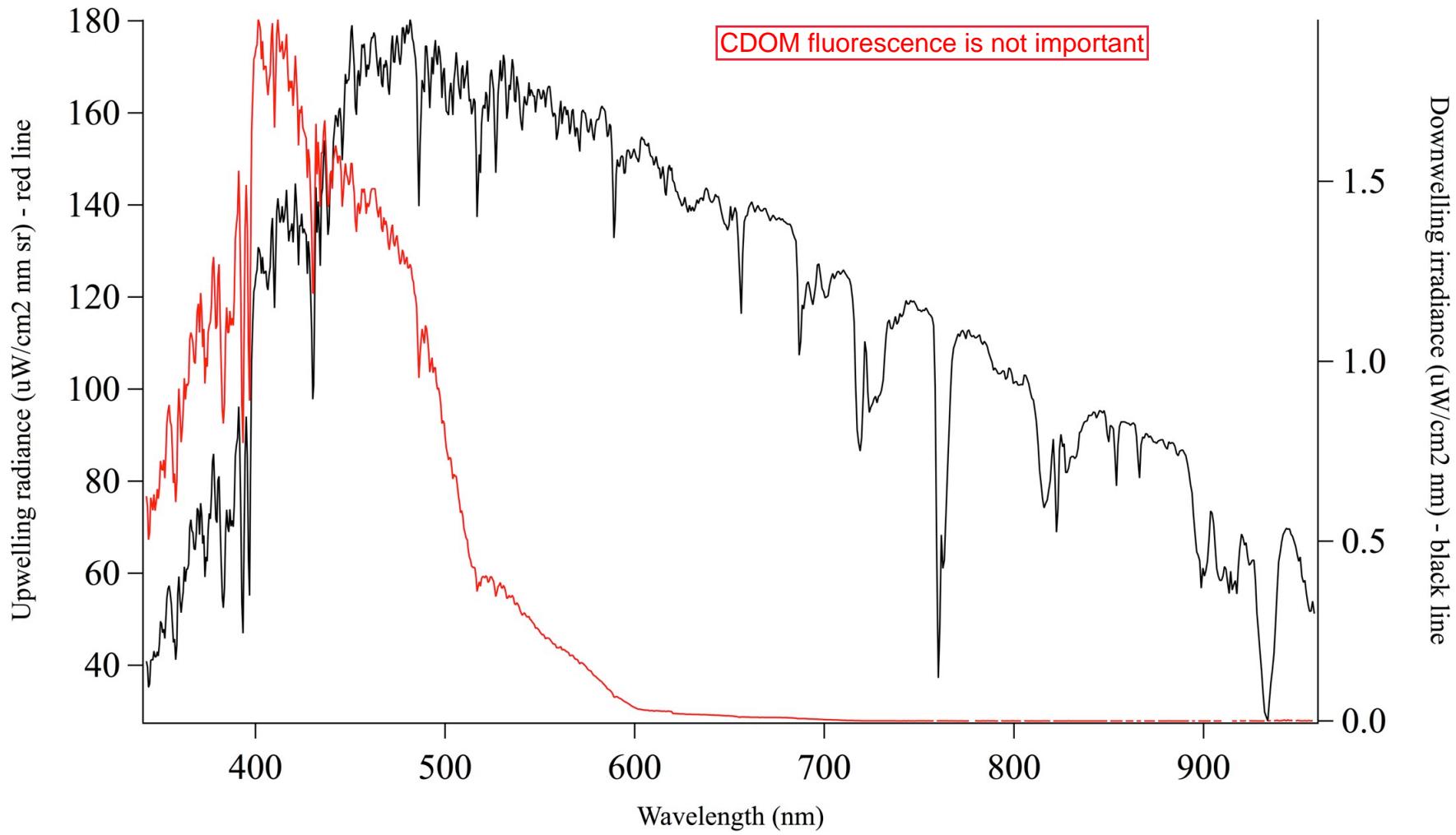
(hint on next slide?)

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 absorbs in the UV and shifts it in the blue where there is already a lot of light so it doesn't really show up in the natural light field unlike Raman scattering

CDOM fluorescence



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Oils

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

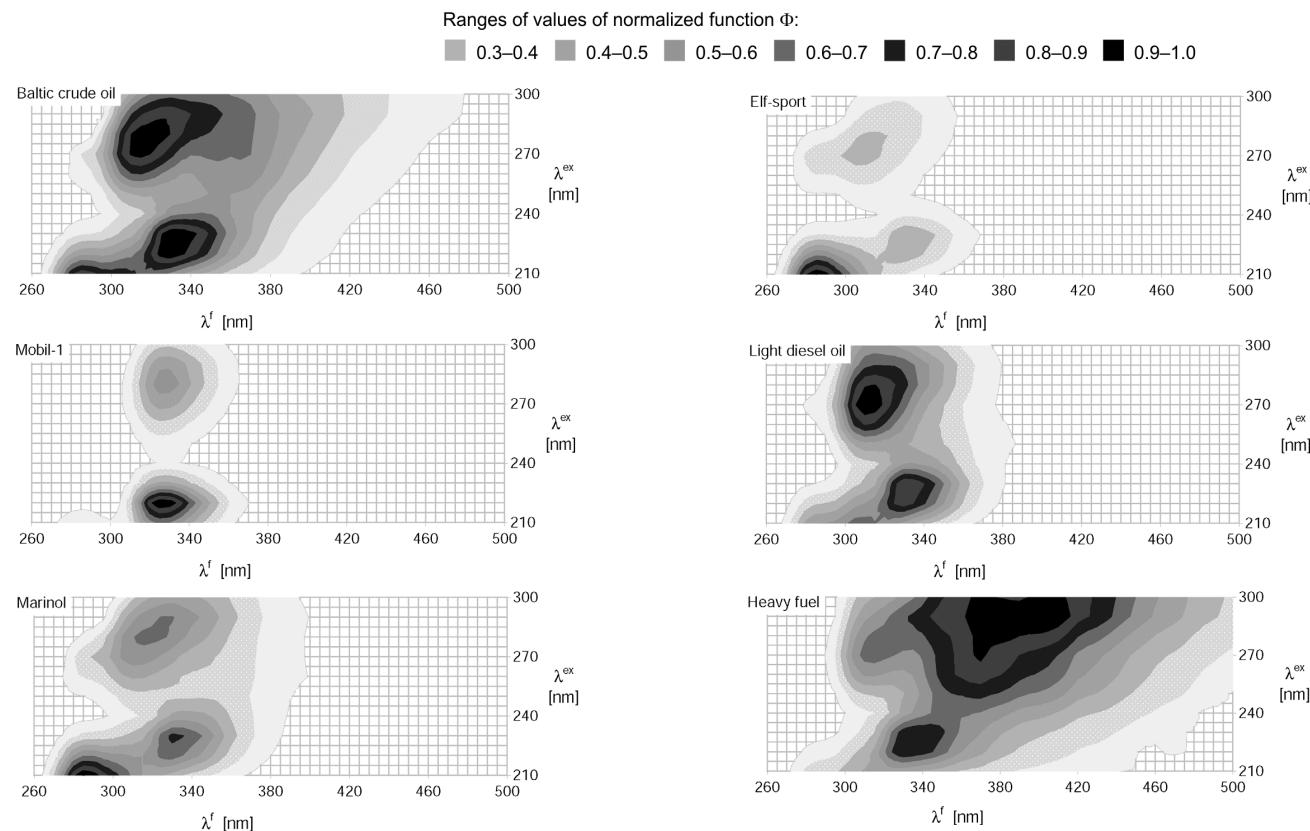
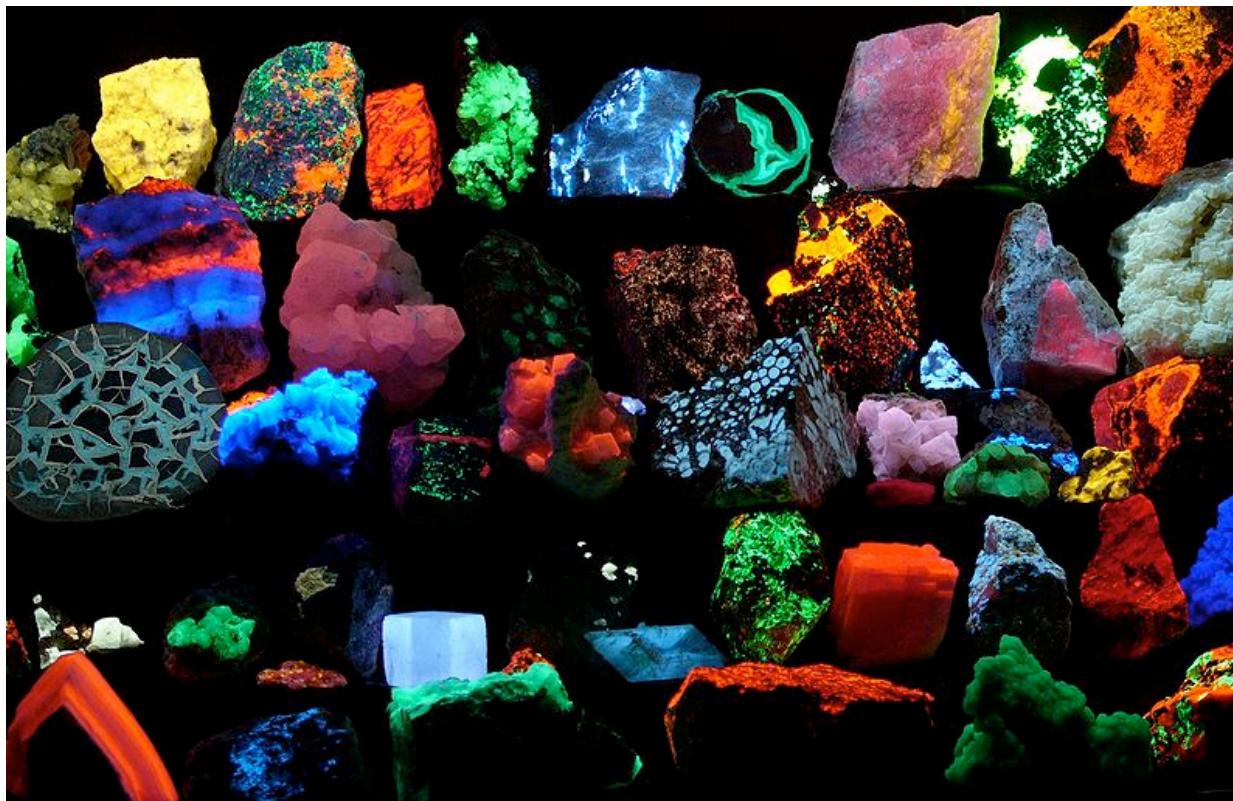


Fig. 1. Examples of the normalized total spectra Φ of hexane solutions of oils.

Minerals

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).



Conclusion

because it scatters
light in part of the
spectra where
there isn't much
light

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 (in my data and view...not necessarily everyone).

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.