

# Modeling of elastic and inelastic scattering effects in oceanic optics

Vladimir I. Haltrin<sup>†</sup>, George W. Kattawar<sup>††</sup>, and Alan D. Weidemann<sup>†</sup>

<sup>†</sup> Naval Research Laboratory, Ocean Sciences Branch, Code 7331  
Stennis Space Center, MS 39529-5004, USA. e-mail: <haltrin@nrlssc.navy.mil>

<sup>††</sup> Center for Theoretical Physics, Department of Physics, Texas A&M University,  
College Station, Texas 77843-4242, USA. e-mail: <kattawar@silly.tamu.edu>

## ABSTRACT

The results of model calculations of apparent optical properties for realistic marine waters with inclusion of Raman scattering and fluorescence are presented. It is shown that the underwater light spectrum can be divided, by a threshold wavelength, into two regions with different behavior of apparent optical properties, and also that inelastic effects are significant and should be considered in ocean optics measurements.

**Keywords:** ocean optics, optical properties, light propagation, scattering, absorption, diffuse reflectance, sea water, Raman scattering, chlorophyll fluorescence, CDOM fluorescence.

## 1. INTRODUCTION

A rigorous derivation of all the equations needed to perform ocean model calculations involving both elastic and inelastic processes was presented by Haltrin and Kattawar [1]. In order to determine the importance of inelastic effects in the ocean, we need quantitative results for different realistic water types at different depths for wavelengths throughout the visible spectrum. On the basis of algorithms developed in Ref. [1], an ANSI FORTRAN-77 code was written and tested [2]. The compiled version runs in about 23 seconds on a 120MHz Apple Power Macintosh 9500 or 19 seconds on 150MHz SGI Indy and produces results for 31 depths between 0–200 *m*, and 109 wavelengths in the spectral range from 380 to 780 *nm*.

In order to make this paper convenient to readers who don't wish to involve themselves in the mathematics of Ref. [1], we present here a brief qualitative description of the approach used for deriving the equations which were coded to obtain the results.

As a basis for our calculations we chose the scalar equation of transfer for radiation with an inelastic source term. This approach is not new in optics and has been widely used in the physics of multi-speed neutron transport. All we do is to adjust the inelastic term to include both Raman scattering and fluorescence in marine water, which can easily be done on the basis of investigations by such authors as Walrafen [3] and Gordon [4].

The objectives of our approach are as follows: a) the solutions should be valid for the complete range of variability of inherent optical properties, *i. e.* equally applicable for both very clear and extremely turbid marine waters, in the complete range of the visible spectrum (380-780 *nm*); b) the precision of the results should be in the range of 6-8%, *i. e.* comparable with the precision of *in situ* marine optical measurements, and c) we should be able to calculate downward and upward irradiances and such apparent optical properties as diffuse reflectance, downward and upward irradiance attenuation coefficients, euphotic zone depth, *etc.* in the whole range of the visible spectrum, for a complete range of inherent optical properties and for any depth (when applicable).

On the basis of these criteria we have chosen a self-consistent two-flow approach [1] to simplify the original inelastic equation of transfer for radiance. This approach was originally used for elastic-scattering calculations [5], it is non-restrictive on values of optical parameters and gives the requisite precision for most ocean optics studies.

It is not clear from the description of this method how precise it is, and it is impossible to derive any proof of precision theoretically. The estimate of precision was made by comparison with Monte-Carlo calculations and the agreement in the results was sufficient to satisfy our objectives formulated above.

In the calculations, presented in Ref. [1], we reduced the complexity of the final computations by only considering a homogeneous, optically infinitely deep ocean illuminated by plane-parallel sun rays. The generalization to arbitrary illumination, finite depth and vertical inhomogeneity can easily be made, but it will increase the complexity of the final equations and significantly increase the computation time.

## 2. MODEL OF OPTICAL PROPERTIES

Recent studies [6] show that Raman scattering and fluorescence cause significant changes in the apparent optical properties of sea water. The magnitude and spectral shape of these effects depend not only on the inelastic components themselves but also, to a significant degree, on the spectral distributions and magnitudes of the elastic inherent optical properties. For that reason it is very important to model realistic ocean optics situations in order to estimate the significance of inelastic effects at different wavelengths and depths in the ocean.

We have adopted the following model [7-10] for the calculations presented: The absorption coefficient  $a(\lambda)$  ( $m^{-1}$ ) is taken to be:

$$a(\lambda) = \left. \begin{aligned} a_w(\lambda) + a_c(C_c, \lambda) + a_f(C_f, \lambda) + a_h(C_h, \lambda), \quad a_c(C_c, \lambda) = a_c^0(\lambda) C_c^{0.602} \\ a_f(C_f, \lambda) = a_f^0 C_f \exp(-k_f \lambda), \quad a_h(C_h, \lambda) = a_h^0 C_h \exp(-k_h \lambda) \end{aligned} \right\}, \quad (1)$$

where  $a_w(\lambda)$  is the pure water absorption coefficient [8],  $\lambda$  is the vacuum wavelength of light in  $nm$ ,  $a_c^0(\lambda)$  is the specific absorption coefficient of chlorophyll [9] ( $m^2/mg$ ),  $C_c$  is the total concentration of chlorophyll ( $mg/m^3$ ),  $a_f^0 = 35.959 m^2/mg$  is the specific absorption coefficient of fulvic acid (the first component of colored dissolved organic matter (CDOM) or yellow substance);  $k_f = 0.0189 nm^{-1}$ ;  $a_h^0 = 18.828 m^2/mg$  is the specific absorption coefficient of humic acid (the second component of CDOM);  $k_h = 0.01105 nm^{-1}$ ;  $C_f$  and  $C_h$  are, respectively, the concentrations of fulvic and humic acids ( $mg/m^3$ ). The values for  $a_w(\lambda)$ , and  $a_c^0(\lambda)$  are given in Ref. [9], and values for CDOM are taken from Refs. [10, 11].

The elastic scattering ( $b^E(\lambda)$ ) and backscattering ( $b_B(\lambda)$ ) coefficients are calculated according to Kopelevich [7]:

$$b^e(\lambda) = b_w(\lambda) + b_s^0(\lambda) C_s + b_l^0(\lambda) C_l, \quad (2)$$

$$b_B(\lambda) = 0.5 b_w(\lambda) + B_s b_s^0(\lambda) C_s + B_l b_l^0(\lambda) C_l, \quad (3)$$

$$B_s = 0.5 \int_{-1}^0 p_s(\mu) d\mu = 0.039, \quad B_l = 0.5 \int_{-1}^0 p_l(\mu) d\mu = 6.4 \cdot 10^{-4}, \quad (4)$$

where  $b_w(\lambda)$  is the scattering coefficient of pure water,  $b_s^0(\lambda)$  and  $b_l^0(\lambda)$  are the specific scattering coefficients for the small and large particulate matter respectively [7],  $B_s$  is the backscattering probability for the small particles,  $p_s(\mu)$  is the scattering phase function for the small particles,  $B_l$  is the backscattering probability for the large particles,  $p_l(\mu)$  is the scattering phase function for the large particles,  $C_s$  and  $C_l$  are the concentrations ( $g/m^3$ ) of small and large particles respectively. We derived the equation for  $b_w(\lambda)$  by interpolating the data given in Ref. [12]:

$$b_w(\lambda) = (5.826 \cdot 10^{-3} m^{-1}) (\lambda_0 / \lambda)^{4.322}, \quad \lambda_0 = 400 nm, \quad (5)$$

and adopted the scattering coefficients for small and large particulate matter from Ref. [7]:

$$b_s^0(\lambda) = (1.1513 m^2 / g) (\lambda_0 / \lambda)^{1.7}, \quad b_l^0(\lambda) = (0.3411 m^2 / g) (\lambda_0 / \lambda)^{0.3}. \quad (6)$$

For the inelastic part of the optical model we used the approach given in the paper by Haltrin and Kattawar [1].

## 3. ILLUSTRATIONS

Results from model calculations are presented in figures 1 to 4 for different optical water types. We present here only a few illustrations, but we use all available data to formulate the results and conclusions. For the purposes of convenience we have chosen the chlorophyll concentration  $C_c$  as our main parameter in the computations. The concentration of scattering particles  $C_p = C_s + C_l$  was estimated from the regression given in paper by Clark, Backer and Strong [13]:  $C_p = 0.5 C_c^{0.75}$ . Following Carder *et al.* [11], we adopted a fixed ratio of humic to fulvic acid:  $C_h / (C_h + C_f) = 0.1$ . All other concentrations were found by minimizing the difference between an actual and remotely estimated chlorophyll concentrations:  $C_c - 1.92 [R(550)/R(440)]^{1.8}$ .

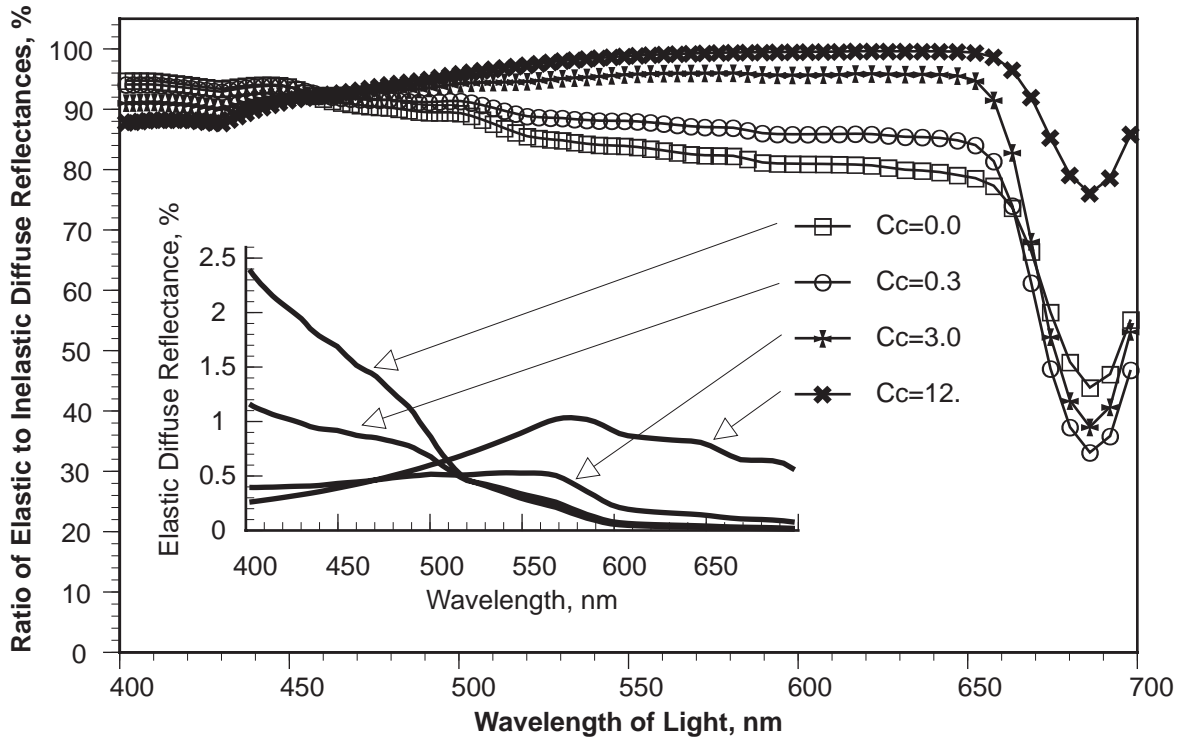


Fig.1. Ratio of elastic to inelastic diffuse reflectances as a function of wavelength for chlorophyll concentrations from 0.05 to 12 mg/m<sup>3</sup>.

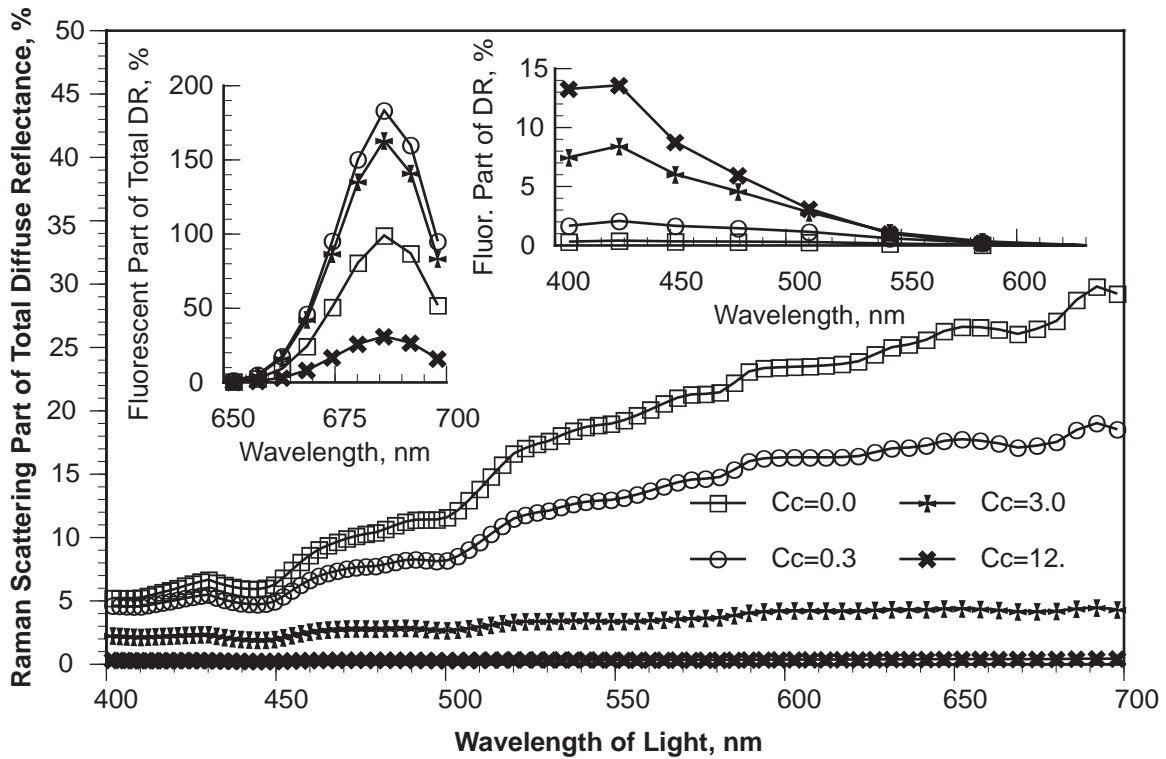


Fig.2. Raman scattering part of total diffuse reflectance as a function of wavelength for chlorophyll concentrations from 0.05 to 12 mg/m<sup>3</sup>.

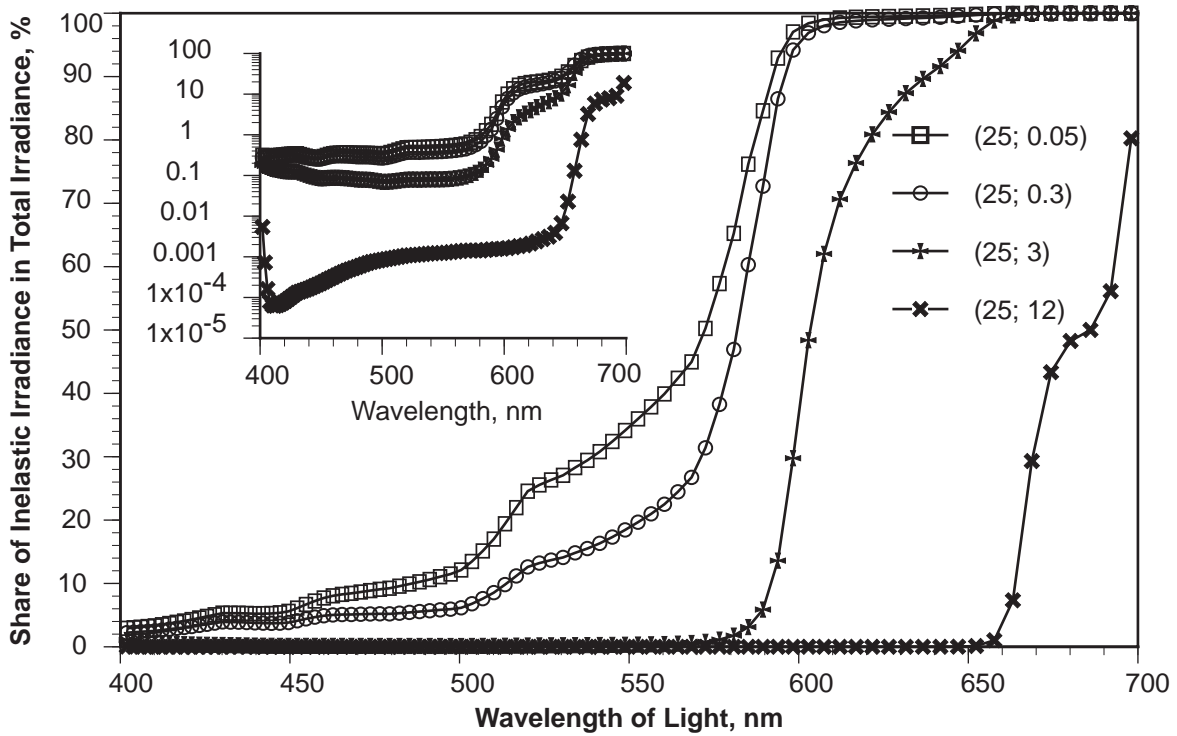


Fig.3. Share of inelastic irradiance in total irradiance as a function of wavelength for 25 m depth and chlorophyll concentrations from 0.05 to 12  $mg/m^3$ .

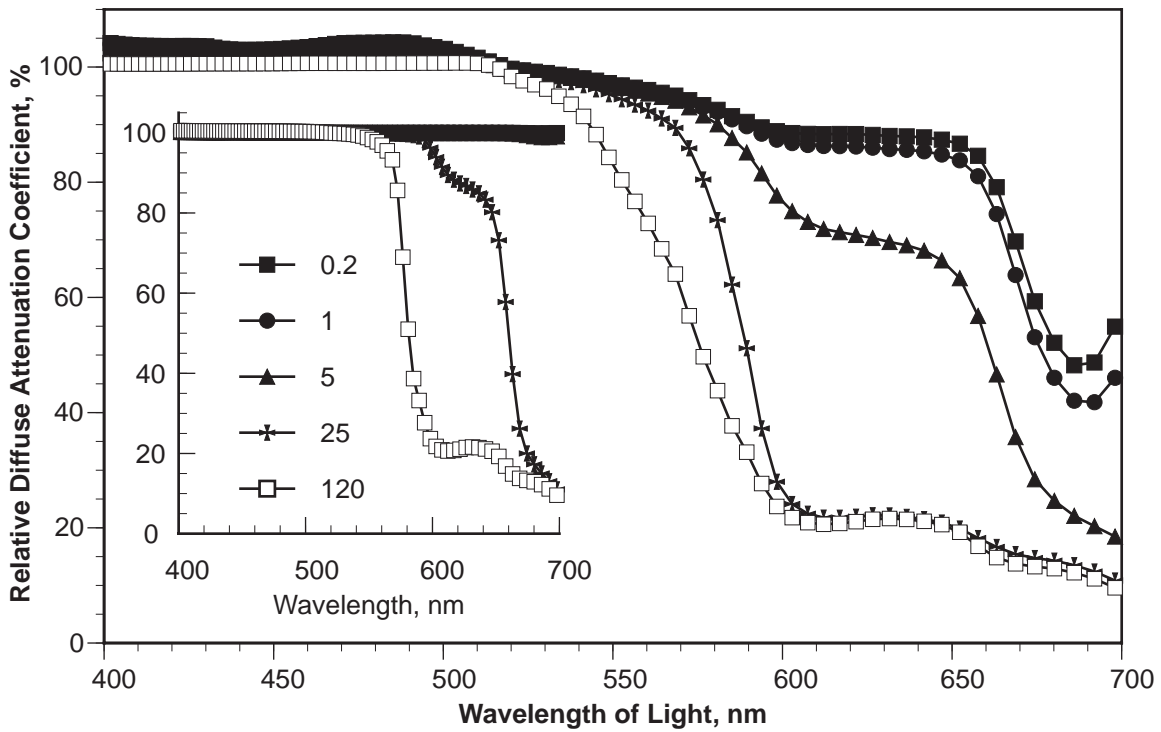


Fig.4. Relative to elastic inelastic diffuse attenuation coefficient as a function of wavelength for depths from 0.2 to 120 m and chlorophyll concentration 0.3  $mg/m^3$ .

We used the following sets of concentrations  $(C_c, C_f, C_h, C_s, C_l)$ : (0.05, 0.1385, 0.0154, 0.0019, 0.0114), (0.3, 0.8134, 0.0904, 0.0109, 0.0869), (3.0, 7.5339, 0.8371, 0.0713, 2.5287), and (12.0, 91.7042, 10,1942, 0.8207, 13.2652).

Fig. 1 shows the ratio of elastic diffuse reflectance (DR) to the inelastic DR for four types of marine water with different chlorophyll concentrations  $C_c$ . The insert of Fig. 1 shows the spectral dependence of the elastic total DR for waters with these concentrations of chlorophyll. Note the strong dependence of DR on  $C_c$  in the blue part of the spectrum  $400 \leq \lambda \leq 500 \text{ nm}$ . The general behavior of modeled dependencies correspond to the experimental curves including the pivotal point at  $\lambda \sim 520 \text{ nm}$ .

Fig. 2 shows the spectral dependence of the Raman scattering contribution to total DR as well as the fluorescent portion (insets) for four chosen concentrations of chlorophyll. Both figures demonstrate significance of inelastic scattering effects on the diffuse reflection coefficient. The Raman scattering correction to DR increases from 6% at 400 nm to about 30% at 700 nm. It is most significant at small concentrations of chlorophyll and decreases with increasing values of  $C_c$ .

Fig. 3 shows the share of upward and downward (the inset) inelastic (Raman scattering plus fluorescence) irradiances to the total irradiance at a depth of 25 m for four different concentrations of chlorophyll. Changes in the spectral shape of the curves for the cases considered here are determined not only by the spectral characteristics of the attenuation coefficient but also by the transfer of energy from the blue to the red end of the spectrum by Raman scattering and fluorescence. With increasing depth, it is clearly seen that the portion of inelastic scattering increases at wavelengths greater than 580 nm causing a predominance of the inelastic light at chosen depths ( $z > 25 \text{ m}$ ). At smaller depths ( $z \leq 25 \text{ m}$ ) the relative upward component is significantly higher than the corresponding downward component and with increasing depth experiences the same saturation phenomenon as the downward component.

Fig. 4 shows the relative to elastic upward and downward (the inset) diffuse attenuation coefficient (DAC) as a function of wavelength for five different depths and  $C_c = 0.3 \text{ mg/m}^3$ . The results of computations shown in Fig.4 reveal the remarkable effect that the upward and downward diffuse attenuation coefficients in the red-green part of the spectrum are far less than the corresponding elastic diffuse attenuation coefficients. This would imply of course that the measured DAC, under conditions of natural illumination, is actually smaller than the DAC computed using only elastic scattering. This effect has been observed *in situ* by Sugihara *et al.* [6].

## 4. CONCLUSIONS

Raman scattering corrections are higher for pure water and decline with increase in productivity or chlorophyll concentration. The highest value for the Raman scattering correction in terms of upward irradiances is about 30% at about 430 nm which constitutes about 5% of the total diffuse reflectance at this wavelength. The highest relative Raman correction to DR is about 25% at 700 nm. In eutrophic waters with chlorophyll concentration of  $3 \text{ mg/m}^3$ , the relative Raman correction to the diffuse reflectance is about 3% throughout the entire range of the visible spectrum.

Fluorescent corrections are proportional to the concentrations of chlorophyll (red fluorescence at 685 nm) and CDOM or yellow substance (blue fluorescence at 425 nm). In pure water there is no fluorescence. The relative values of fluorescent corrections to DR in eutrophic water ( $3.0 \text{ mg/m}^3$  of chlorophyll) are 8% and 150% for the blue and red fluorescence peaks of chlorophyll respectively.

### 4.1 Threshold wavelength

There is a threshold wavelength approximately equal to the minimum wavelength in the spectral distribution of the irradiance attenuation coefficient plus one half of the Raman shift wavelength ( $\sim 35 \text{ nm}$ ). This threshold wavelength divides the underwater light spectrum into two different parts. In the red part of the spectrum the inelastic part of the underwater light field increases with depth eventually reaching 100% of the total if the ocean is optically deep. In the blue part of the spectrum the inelastic part of the light exponentially decreases with depth. In optically deep oceans, at sufficient depths, the relative inelastic spectrum has the form of a step function with a zero value on the blue side of the threshold wavelength and a value of unity on the red side.

This phenomenon affects the behavior of the total irradiance attenuation coefficient. On the blue side of the threshold wavelength the total irradiance attenuation coefficients almost coincide with the elastic ones. To the red side of the threshold wavelength the total irradiance attenuation coefficients begin to decrease. Thus the apparent effect of water clarification in the red part of the spectrum is achieved.

#### 4.2 Importance of this work for ocean optics

The three components of inelastic light can be categorized by their relative importance as follows: Raman scattering, the most important component, is the major cause for dividing the spectrum into two different regions, a blue region dominated by elastic light, and a red region dominated by inelastic light.

Red fluorescence (caused by chlorophyll), the second in importance, plays a predominant role in the vicinity of its emittance peak near 685 nm, especially when the concentration of chlorophyll is large. Blue fluorescence (caused by CDOM), although the least important, should definitely be taken into account in the spectral region near its peak at 425 nm, especially when the concentration of yellow substance is large.

The importance of all these components depends primarily on the value and spectral shape of the elastic absorption coefficient of water. The existence of the threshold wavelength is a combined result of Raman scattering and the shape of the absorption curve which has a minimum in the blue part of the spectrum.

For optical remote sensing both the blue and red portions of the spectrum should be reconsidered. The 3-7% corrections to the diffuse reflectance in the blue part of the spectrum and 50% or more in the red part are very important to the effectiveness of the algorithms dealing with the inversion of concentrations of dissolved and suspended substances.

Analysis of underwater light fields given in this presentation show that it is no longer possible to ignore inelastic effects in the analysis of oceanographic measurements of apparent optical properties of marine water, especially in the part of the spectrum to the red of 500 nm and at depths exceeding several optical depths.

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