Measurement of Oceanic Inelastic Scattering Using Solar Fraunhofer Lines

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ABSTRACT

It is demonstrated that Fraunhofer lines in the solar spectrum will be filled in by inelastic scattering in the ocean. The relative depth of a Fraunhofer line, η, defined as the ratio of the irradiance at the center of the Fraunhofer line to the background continuum, can then be used to measure the amount of inelastic scattering in the light field, i.e., by measuring η, the relative contributions of elastic and inelastic processes to the light field can be deduced. An oceanographic instrument was developed to measure *in-situ* inelastic scattering in the ocean. It utilizes a 1 m monochromater, a CCD camera, and two irradiance collectors with a fiber optic light guide. Results of preliminary field measurements are presented and discussed.

1. INTRODUCTION

Oceanic inelastic processes are increasingly being postulated as important sources in the underwater light field but until now no direct measurements of these processes in ambient light conditions have been reported.

It has been demonstrated, theoretically, that Raman scattering can play a significant role in radiative transfer in the upper layers of the water column.[1-3] It has also been suggested that Raman scattering contributes to the light field leaving the sea surface and thus may influence the signal available for remote sensing in the visible region.[4] While the Raman scattering cross section for water has been measured in the laboratory many times, the results differ by a factor of 5,[1,5-9] and direct measurement in the ocean has not been possible until now. Fluorescence, another inelastic process, has been known to contribute to the light field in the red by virtue of the chlorophyll a pigment contained in marine phytoplankton.[10,11]. The contribution of fluorescence of chlorophyll a is evident by virtue of the distinct 685 nm gaussian peak of 25 nm width. Dissolved organic matter (DOM) can also contribute to the radiance leaving the sea surface via fluorescence in the blue-green.[12] In contrast to Raman scattering and chlorophyll fluorescence, DOM fluorescence is a broad-band emission which varies with both the nature and the concentration of the fluorescent compounds, therefore its contribution to the light field cannot be determined by a distinct spectral signature or by radiative transfer modeling. It must be measured directly. The total effects by all these inelastic processes could have a significant impact on the light field in natural waters.

Features in the solar spectrum can be used to allow the direct measurement of inelastic processes in the ocean. The spectrum of solar irradiance is not a continuum but instead contains sharp absorption lines caused by solar constituents as first observed by Fraunhofer. The depth and width of these lines vary, with the deepest lines having a center irradiance that is approximately 20% of the background irradiance and approximately a 1 Å line width. When light is shifted into these absorption lines via inelastic processes, the depth of these lines change. By making high spectral resolution measurements of the Fraunhofer lines and comparing the depth of these lines to the continuum, broadband inelastic scattering or fluorescence can be detected. This technique has been used to measure lunar surface luminescence by Grainger and Ring[13] and Potter and Mendell.[14] Plascyk used an airborne Fraunhofer line discriminator to measure luminescence on the earth surface from sources such as rhodamine WT dye and plant chlorophyll.[15] Theoretical calculations demonstrate that in the ocean, Raman scattering is sufficient to fill in the Fraunhofer lines.[16,17] Thus inelastically scattered light can be measured separately from elastically scattered light.

An instrument has been developed to observe the "filling in" of Fraunhofer lines throughout the visible in the ocean. We are thus able to measure irradiances from inelastically scattered and elastically scattered (including directly transmitted) light fields separately. Here we report on some preliminary experimental results.

2. THEORY

A variable η is defined to indicate the relative depth of the Fraunhofer lines:

$$\eta = \frac{\text{Irradiance at center of Fraunhofer line}}{\text{Irradiance of the background continuum}}$$

With such a definition $\eta = 0.2$ implies that the Fraunhofer line is very deep, i.e., the irradiance at the center of the Fraunhofer line is only 20 percent of the background, while $\eta = 1$ means that the Fraunhofer line has completely disappeared.

In the ocean, all the inelastic processes (Raman scattering, DOM fluorescence and chlorophyll fluorescence) are broadband compared to the width of the Fraunhofer lines, which is typically 0.1 nm. Therefore, they will add irradiance to both the continuum and the Fraunhofer line equally. Thus, as the inelastically generated irradiance grows to be a more significant proportion of the total irradiance, the Fraunhofer lines will become shallower, i.e., η increases. The maximum η is unity and occurs when all the light is generated from inelastic processes. We expect this to happen in the spectral regions where absorption is large. By comparing η just above sea surface, η_s, and η at depth, $\eta(z)$, we can find the irradiance generated from inelastic processes (in) and elastic processes (el) separately. Simply,

$$E_d^{(in)}(z,\lambda) = \frac{\eta - \eta_s}{1 - \eta_s} E_d^{total}(z,\lambda) \tag{1}$$

and

$$E_d^{(el)}(z,\lambda) = \frac{1 - \eta}{1 - \eta_s} E_d^{total}(z,\lambda), \tag{2}$$

where $E_d^{total}(z,\lambda)$ is the irradiance in the background continuum, e.g., the average in a band 1 nm away from the Fraunhofer line. Similar relationships exists for upward irradiance. Thus, measurements of η, $E_d^{total}(z,\lambda)$ and $E_u^{total}(z,\lambda)$ yield information on inelastic processes as well as elastic processes. In clear water, where there is less chlorophyll a fluorescence and DOM fluorescence, Raman scattering is the major inelastic process. In contrast, DOM fluorescence is expected to make a large contribution in coastal waters.

3. EXPERIMENTAL PROCEDURE

The instrument developed to measure in situ inelastic scattering in the ocean is shown schematically in Fig. 1. Two fiber optic irradiance collectors, one above the sea surface (1) and one underwater (2), are constructed to collect either upward or downward irradiances according to their orientation. Light is transmitted through a 1 mm core all silica fiber to the fiber adapter (3). The adapter changes the solid angle of the light cone from the optic fiber to match the solid angle of the monochrometer (4) for maximum throughput. The monochrometer is a 1 m focal length Czerny-Turner with a 2400 groves/mm holographic grating (SPEX-1000M). A thermoelectrically cooled CCD array detector (EG&G OMA-IV) is placed at the position where normally the exit slit would be. This array monitors the Fraunhofer lines from the sky and underwater at the same time so filling in of these Fraunhofer lines can be seen immediately by comparison. While the basic design of both the sky and underwater collectors follow that of Smith and Tyler,[18] the design of both collectors was optimized for a cosine angular response by trial-and-error. The resultant response is shown in Fig. 2. The monochrometer provides a linear dispersion of 4 Å/mm, which results in a 1 Å line covering 0.25 mm at the exit slit. Under these circumstances, a 1 Å wide Fraunhofer line will span at least 13 of the 19 μm pixels on the CCD array. The resolution is measured to be 0.08 Å; sufficient for the experiment. Total length of the optical fiber is 122 m for the underwater light collector and 10 m for the surface light collector. The wavelength calibration is carried out using a low pressure mercury lamp. For the data presented here the entrance slit width used was 100 μm unless otherwise specified. The CCD detector was cooled to -54 C° and integration time was 5 seconds, long enough to provide large signal to noise ratio and reduce the effect of surface waves. With this arrangement, the noise level is about 640 counts while the signal is generally 10^4 counts.

The Fraunhofer lines measured are provided in Table 1.

Table 1. Fraunhofer Lines Studied

Fraunhofer Notation	λ (nm)	Element
C	656.28	H
D_1	589.59	Na
D_2	588.99	Na
F	486.13	H_β
G'	434.05	H_γ

They range from blue to red. Observations were made from a pier near the mouth of the Port of Miami, where the water is very turbid. Irradiances near each of the four lines were measured from just below the surface down to 6 m in 0.5 m increments. This is only a preliminary data set to test the performance of the instrument, further measurements will be obtained in clear coastal waters in late summer, 1992.

4. EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 3 shows the downwelling irradiance in the vicinity of the four Fraunhofer lines as a function of depth. In each panel, the upper curve is at the surface, and the actual depths for the other curves are labeled on the figure. Only selected depths are shown for clarity. The filling-in of the lines is obvious. In all four spectral regions, the absorption line structure at the surface is replaced by a featureless spectrum at 6.0 m.

The value of η derived for $E_d(z,\lambda)$ for the four regions is presented in Fig. 4 and shows a steady increase with depth. The inelastic contribution (fraction) to $E_d(z,\lambda)$ derived from Eq. (1) is presented in Fig. 5. It is seen that the inelastic scattered component increases with depth and can be as high as 100%.

Considering the location of the measurements, we believe that most of the inelastically scattered light is the result of fluorescence. In the presence of fluorescence, radiative transfer equation will contain an additional source term

$$\int_{\lambda' < \lambda} a_f(z,\lambda')q_f(z,\lambda' \to \lambda)E_o(z,\lambda')d\lambda'$$

where $a_f(z,\lambda')$ is the absorption coefficient of the fluorescing compound at the exciting wavelength λ', $q_f(z,\lambda' \to \lambda)$ is the quantum efficiency for fluorescence at λ with excitation at λ', and $E_o(z,\lambda')$ is the scalar irradiance associated with the light field at λ'. Thus, the resulting source of the fluorescence depends on several wavelength-dependent factors. Since none of the factors were measured during this first test of the instrument, further discussion of the source of fluorescence is not warranted.

5. SUMMARY AND CONCLUSIONS

In this report we have described high spectral resolution instrumentation designed to measure the inelastic scattering contribution to the light field in the ocean. The instrument was tested in the turbid waters near the entrance of the Port of Miami and excellent spectra were obtained. These spectra clearly show the filling-in of the Fraunhofer lines by inelastic processes. In fact, the rich line structure in the spectrum near the surface was transformed into a featureless continuum at the depth of 6 m. The results suggested that the instrumentation has the capacity for similar performance in the open ocean.

6. ACKNOWLEDGMENTS

7. REFERENCES

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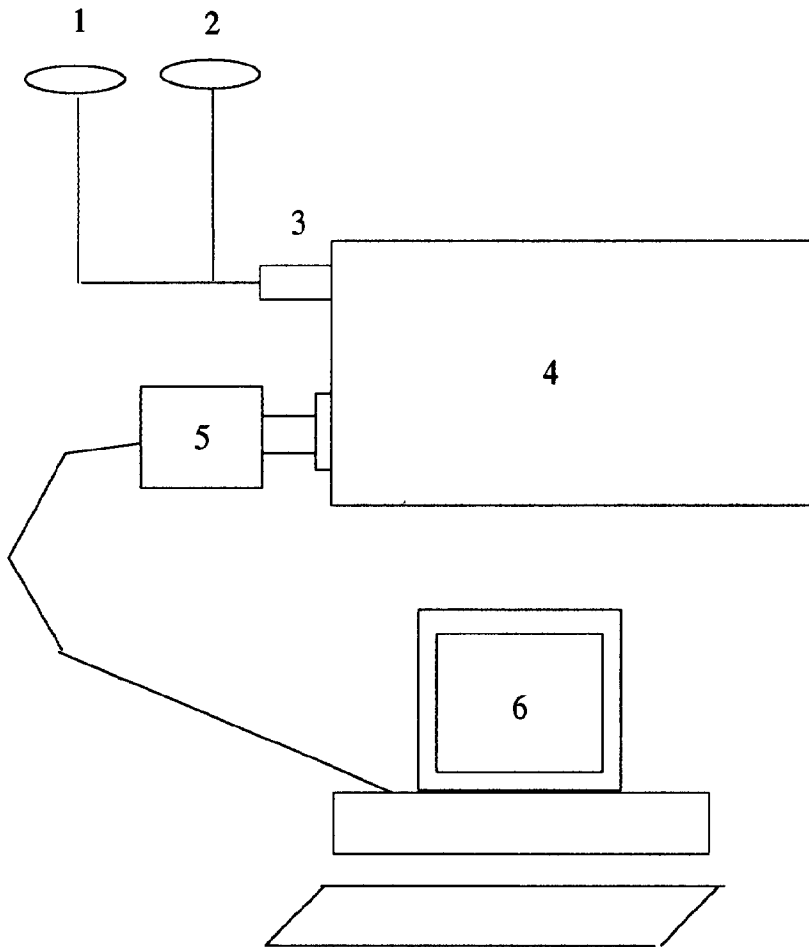
Fig. 1 Block diagram of instrumental design for measuring inelastic scattering using Fraunhofer lines. Numbers referenced in text.
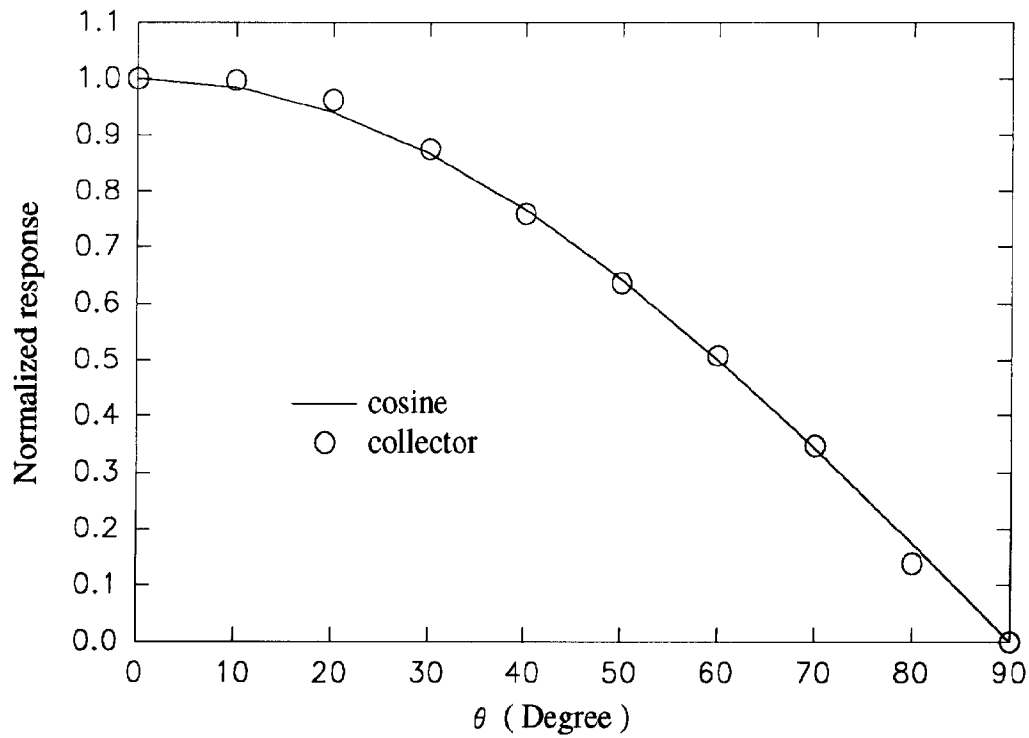
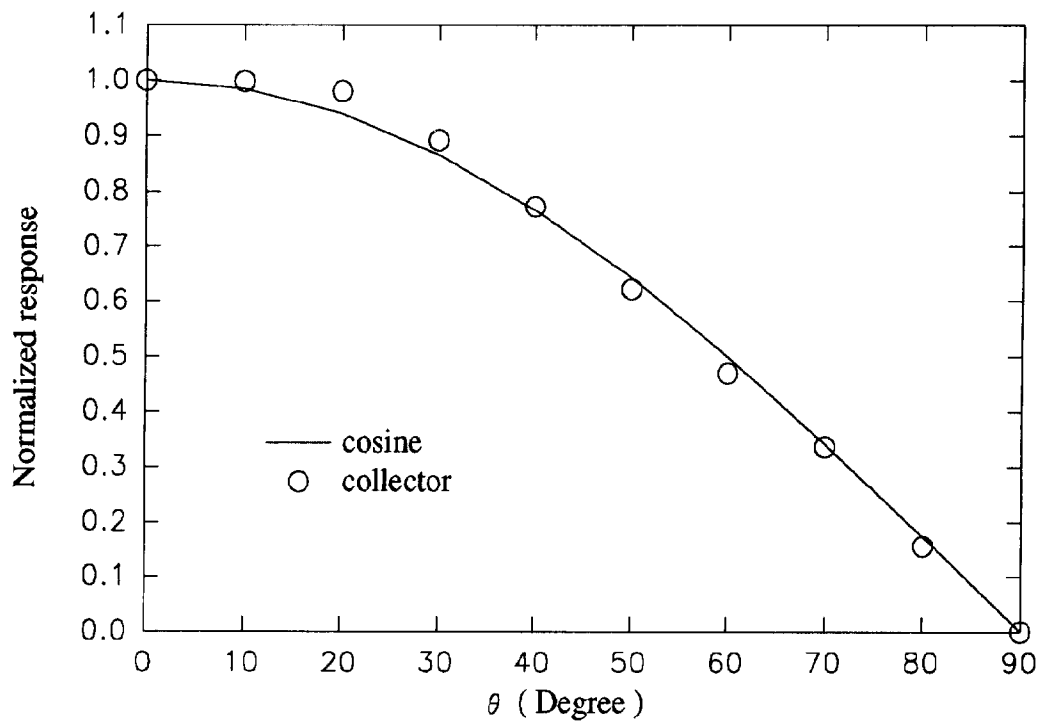Fig. 2a Angular response of airborne light collector.

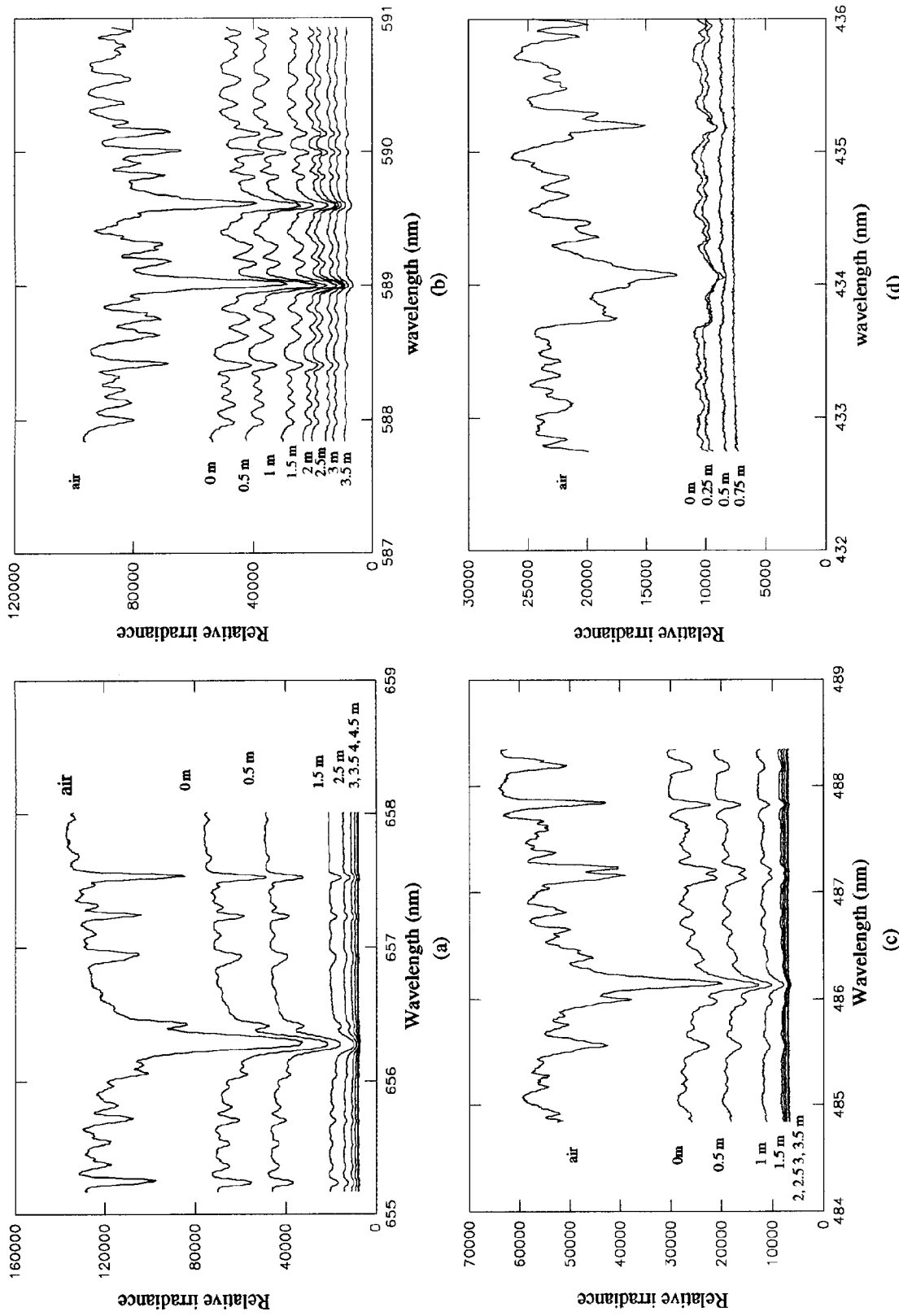Fig. 2b Angular response of underwater light collector.

Fig. 3 downwelling irradiances in digital counts near four different Fraunhofer lines as a function of depth. Depth is marked on panels. At each wavelength, E_d was measured down to 6 m. Only selected depths are shown here.
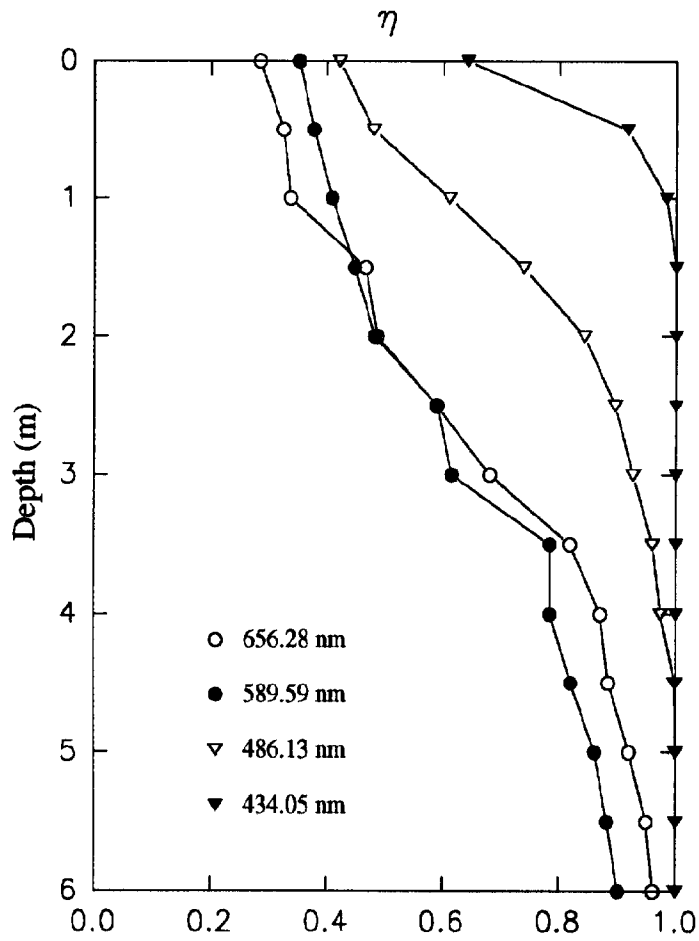
Fig. 4 η at different wavelengths
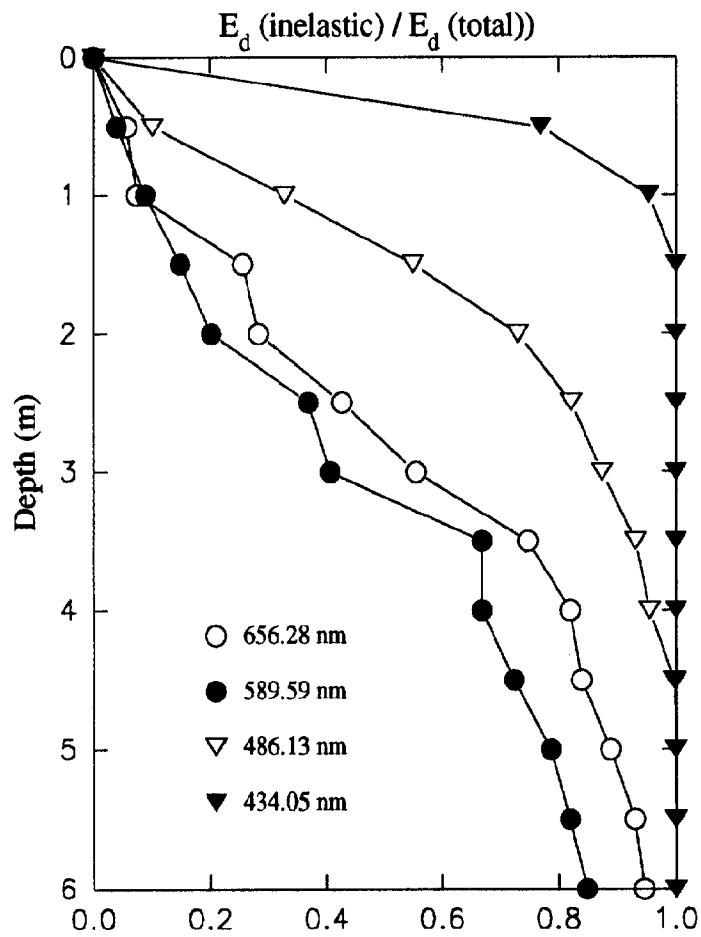
as a function of depth.

Fig. 5 Ratio of inelastically generated
irradiance and total downwelling
irradiance at different wavelengths as
a function of depth.